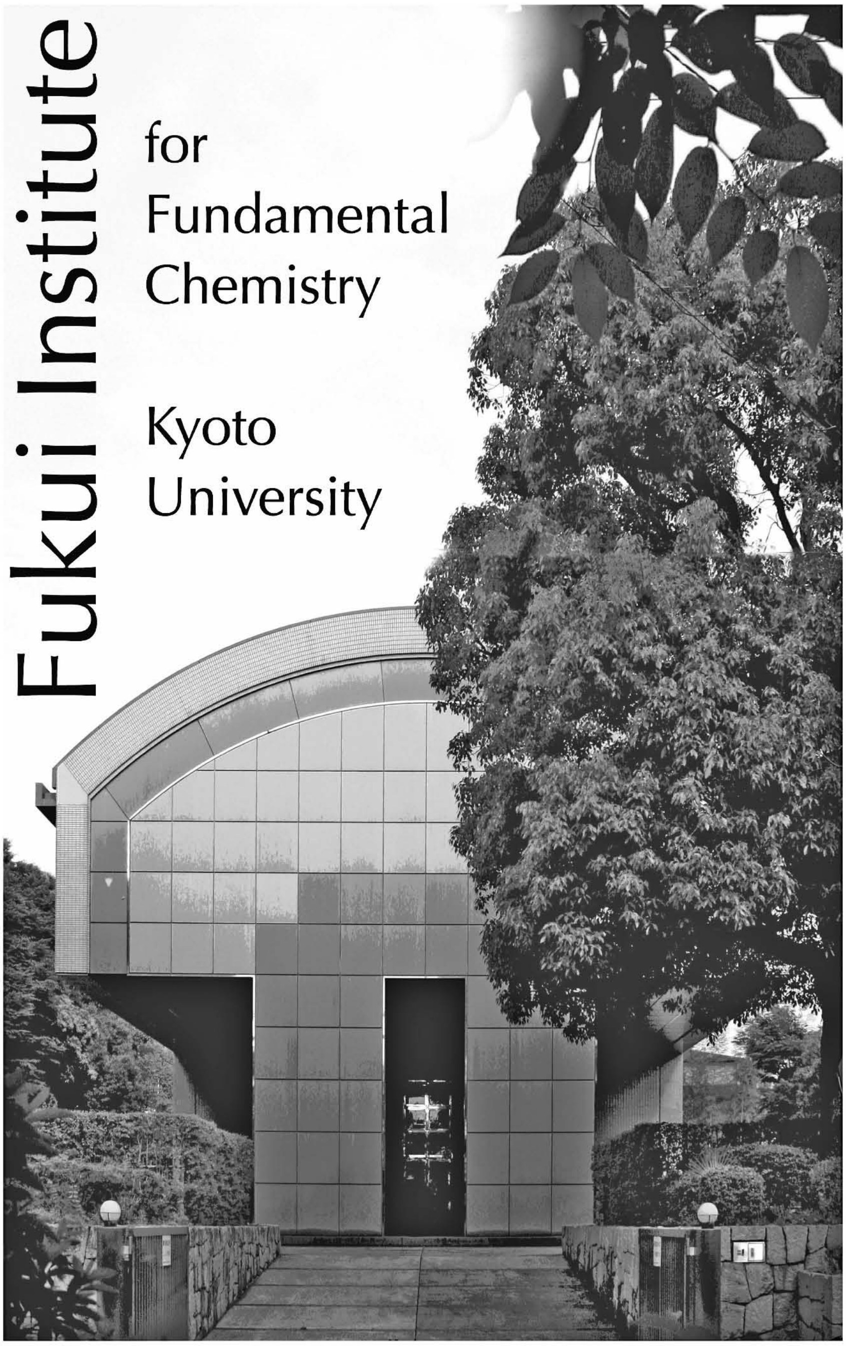
京都大学
福井謙一記念研究センター

Annual Report
2011

Fukui Institute for Fundamental Chemistry Kyoto University

年 報
2011



京都大学
福井謙一記念研究センター

はじめに

2011年度(平成23年度)の京都大学福井謙一記念研究センターの活動をまとめた年報をお届けします。本センターは、京都大学本部構内の北、約1キロの高野川沿いの静かな住宅街に独立して位置しております。専任教員は理論研究部門と総合研究部門に准教授各1名を持っているに過ぎませんが、センター長のほか2名の副センター長と10名のスーパーバイザーとして工学研究科、理学研究科、化学研究所所属の教員にご協力頂いており、このメンバーが運営委員会を構成しています。そして世界中から集めた優れた博士研究員に研究活動の機会を与える制度を持っており、若手研究者が国際的な雰囲気の中で日夜研究にいそしんでいます。この福井センターフェローと呼ばれる博士研究員は、センター雇用であることによって自分自身のアイディアで一定期間、自由闊達に研究できる身分を保証されています。

2006年(平成18年)9月に福井謙一記念研究部第一のリサーチリーダーとして世界的な理論化学者の諸熊奎治先生(分子科学研究所名誉教授)を米国エモリー大学から招聘し、研究面でのリーダーシップを発揮して頂いております。諸熊先生は，科学技術振興機構の戦略的創造研究推進事業の予算で博士研究員を採用され、全員がセンターで研究に励んでおられます。さらに2009年度(平成21年度)には福井謙一記念研究部第二も設置し、名古屋大学名誉教授（前副学長）の大峯巖先生をリサーチリーダーとして招聘し、研究体制を拡大しました。なお、大峯先生は2010年(平成22年)4月に分子科学研究所長に転出されました。その後任として、2011年(平成23年)4月に京都大学物質―細胞統合システム拠点(iCeMS)特任教授の榊　茂好先生を研究部第二のリサーチリーダーとして招聘しました。榊先生は、遷移金属化合物や類縁化合物に関する研究で顕著な業績を挙げておられ、現在は科学研究費補助金「d-電子複合系の理論化学：新しい高精度大規模計算法による微視的理解と予測」を推進しておられます。榊先生は、この予算で博士研究員を採用され、そのメンバーもセンターで研究に励んでいます。私達は、センターが若手研究者の登竜門となることを期待しています。実際に、センターの博士研究員であった多くの方々が、現在、国内外の大学、研究機関で活躍しておられます。

当センターの歴史を簡単にご紹介します。ご承知のように故福井謙一京都大学名誉教授はフロンティア軌道理論を提案したご功績により、1981年(昭和56年)にわが国で最初のノーベル化学賞を受賞されました。福井先生が京都大学ご退官後に研究を続けられるように、京都市と産業界などのご支援で1985年(昭和60年)に財団法人「基礎化学研究所」が設立されました。専任研究員数名の規模でしたが、研究のレベルは高く、当時の研究員は現在、東京大学、名古屋大学、分子科学研究所の教授になり、理論化学分野でトップクラスの研究者として活躍しています。この基礎化学研究所は1998年（平成10年）の福井先生のご逝去の後、2002年(平成14年)に本学に寄贈されて福井

謙一記念研究センターとなり、現在にいたっています。京都大学の部局となった後、森島 績、中辻 博、榊 茂好、田中 功の各先生にセンター長としてご指導を頂きました。

本センターは、国際活動も活発で、2005 年(平成 17 年)よりチェコおよびスロバキアと理論化学・計算化学シンポジウムを定期的に開催しております。2011 年(平成 23 年)には国内外(主にドイツ、東欧、中国、韓国)から第一線の研究者を招き、第 1 回福井センター理論化学・計算化学国際シンポジウムを開催しました。こうした国際連携活動をさらに活性化するという観点から、2011 年(平成 23 年)10 月に国際連携研究室を設置し、その運営上必要となるコーディネーター役として、特定准教授及び特定助教各 1 名を配置しました。本センターは、今後も、理論化学・計算化学分野におけるわが国の窓口の役割を果たし、国際連携活動を展開して行きたいと考えております。

例年晩秋に福井センターシンポジウムを開催しており、学外のトップクラスの研究者による特別講演、運営委員の講演、並びに京都大学内外からのポスター発表を行っております。研究発表のレベルは高く、特別講演に来られた講師からも毎年高い評価を得ております。

さらに社会貢献活動の一環として、2011 年(平成 23 年)が福井先生のノーベル化学賞受賞 30 周年にあたるため、これを節目として本センター玄関ロビーに先生ゆかりの文物の展示コーナーを設置しました。コーナーでは先生が使用された机、椅子、ノーベル賞メダル・賞状(複製)、研究ノート・メモ、写真などを展示し、常設展示として一般に公開しています。

本センターは、上述のように規模は大きくありませんが、研究活動は活発です。今後も、京都大学あるいは国内外との共同研究を積極的に進めて行きたいと考えております。とくに実験科学者との共同研究は重要であり、そのような連携研究をさらに活発化したいと考えております。

この年報により、本センターの活動に興味をお持ち頂ければ幸甚です。そして、それが共同研究の契機となり、時間をかけて大きな成果に結実していくことを念願しています。最後になりましたが、本センターの順調な活動はひとえに工学研究科、理学研究科、化学研究所のご協力、ご援助の賜物であり、ここに心から御礼申し上げる次第です。

平成 24 年 11 月

京都大学福井謙一記念研究センター長
田中　一義

目　　次

資料

（本冊子は下記アドレス(URL)にて、ウェブ上でも閲覧いただけます。
http://www.fukui.kyoto-u.ac.jp/publication/AnnualReport2011.pdf)

Ⅰ　専任教員・スーパーバイザー

１．教員組織

平成２３年度

職名		氏名	備考
センター長		田中 功	工学研究科材料工学専攻
総合研究部門	副センター長	田中 一義	工学研究科分子工学専攻
理論研究部門	副センター長	太田 隆夫	理学研究科物理学・宇宙物理学専攻
協議員	工学研究科長	小森 悟	工学研究科機械理工学専攻
	理学研究科長	山極 壽一	理学研究科生物科学専攻
	化学研究所長	時任 宣博	化学研究所物質創製化学研究系
総合研究部門 スーパーバイザー	教授	赤木 和夫	工学研究科高分子化学専攻
	教授	田中 勝久	工学研究科材料化学専攻
	教授	佐藤 直樹	化学研究所複合基盤化学研究系
	教授	北川 進	物質－細胞統合システム拠点 （工学研究科合成・生物化学専攻）
	教授	吉川 研一	理学研究科物理学・宇宙物理学専攻
理論研究部門 スーパーバイザー	教授	谷村 吉隆	理学研究科化学専攻
	教授	今堀 博	物質－細胞統合システム拠点 （工学研究科分子工学専攻）
	教授	山本 量一	工学研究科化学工学専攻
	准教授	高田 彰二	理学研究科生物科学専攻
	准教授	林 重彦	理学研究科化学専攻
総合研究部門	准教授	長谷川 淳也	専任 （工学研究科合成・生物化学専攻協力講座）
理論研究部門	准教授	中尾 嘉秀	専任 （工学研究科分子工学専攻協力講座）
国際連携研究室	特定准教授	石田 俊正	専任
国際連携研究室	特定助教	池野 豪一	専任
福井謙一 記念研究部第一	リサーチ リーダー	諸熊 奎治	研究員（学術研究奨励）
福井謙一 記念研究部第二	リサーチ リーダー	榊 茂好	研究員（学術研究奨励）
福井謙一 記念研究部第一	特定助教	前田 理	次世代研究者育成センター 特定助教（白眉）

２．教員プロフィール

(1) センター長

【氏名（ふりがな）】	田中　功（たなか　いさお）
【職名】	センター長、教授
【所属】	工学研究科　材料工学専攻
【研究室】	吉田キャンパス　工学部物理系校舎　量子材料学研究室
【直通電話】	075-753-5465
【FAX】	075-753-5447
【電子メールアドレス】	tanaka@cms.MTL.kyoto-u.ac.jp
【ホームページ】	http://cms.mtl.kyoto-u.ac.jp/tanaka.html
【研究分野】	材料科学
【現在の研究課題】	セラミックス基礎科学，計算材料科学
【研究内容キーワード】	量子材料設計，第一原理計算，電子エネルギー損失分光，X線吸収分光
【最終学歴】	1987年3月大阪大学大学院基礎工学研究科物理系専攻博士後期課程修了
【学位】	1987年3月大阪大学工学博士
【略歴】	1987年4月　日本学術振興会特別研究員 (PD)、1987年6月大阪大学産業科学研究所・助手、1993年4月京都大学工学部・助手、1996年5月京都大学大学院エネルギー科学研究科・助教授、2001年7月京都大学大学院工学研究科・助教授、2003年12月京都大学大学院工学研究科・教授
【在外研究歴】	1992年4月 -1993年3月　ドイツ マックスプランク金属研究所・客員研究員（アレキサンダー・フォン・フンボルト財団奨学研究員）
【所属学会】	日本金属学会、日本セラミックス協会、日本鉄鋼協会，応用物理学会、American Ceramic Society、Materials Research Society
【学会活動】	*Journal of American Ceramics Society* フェロー・編集委員、*World Academy of Ceramics* 会員、*Journal of Physics : Condensed Matter* 編集委員、日本金属学会評議員
【主な著書、学術論文】 （過去5年以内）	1. A. Seko, F. Oba, I. Tanaka, Classification of spinel structures based on first-principles cluster expansion analysis, *Phys. Rev. B* **81** (2010) 054114 2. A. Matsumoto, Y. Koyama, I. Tanaka, Structures and energetics of Bi_2O_3 polymorphs in a defective fluorite family derived by systematic first-principles lattice dynamics calculations, *Phys. Rev. B* **81** (2010) 094117 3. M. Choi, F. Oba, I. Tanaka, Role of Ti Antisitelike Defects in $SrTiO_3$, *Phys. Rev. Lett.* **103** (2009) 185502 4. First-principles investigation of atomic structures and stability of proton-exchanged layered sodium titanate M. Mori, Y. Kumagai, K. Matsunaga, and I. Tanaka, *Phys. Rev. B* ,**79** (2009) 144117 5. W. Olovsson, I. Tanaka, T. Mizoguchi, P. Puschnig, and C. Ambrosch-Draxl, All-electron Bethe-Salpeter calculations for shallow-core x-ray absorption near-edge structures, *Phys. Rev. B* **79**, (2009) 041102. 6. K. Yuge, A. Seko, Y. Koyama, F. Oba, and I. Tanaka,First-principles-based phase diagram of the cubic BNC ternary system, *Phys. Rev. B* **77**, (2008) 094121 7. I. Tanaka and F. Oba, First principles calculations for modern ceramic science and engineering, *J. Phys: Condens. Matter* **20**, (2008) 064215 8. A. Seko, A. Togo, F. Oba, and I. Tanaka, Structure and stability of a homologous series of tin oxides, *Phys. Rev. Lett.* **100**, (2008) 045702
【学術関係の受賞】	ドイツ政府　ﾌｨﾘｯﾌﾟ・ﾌﾗﾝﾂ・ﾌｫﾝ・ｼｰﾎﾞﾙﾄ賞 (2008年) ﾙｰﾏﾆｱ科学ｱｶﾃﾞﾐｰ ﾄﾞﾗｺﾞﾐｰﾙ・ﾌﾙﾑｾﾞｽｺ賞 (2006年) 米国ｾﾗﾐｯｸｽ学会　ﾘﾁｬｰﾄﾞ・ﾌﾙﾗｰｽ賞 (2004年)

⑵ 副センター長

【氏名（ふりがな）】	田中　一義（たなか　かずよし）
【職名】	教授
【所属】	工学研究科分子工学専攻
【研究室】	桂 A4 棟 205
【直通電話】	075-383-2549
【FAX】	075-383-2555
【電子メールアドレス】	ktanaka@moleng.kyoto-u.ac.jp
【ホームページ】	http://www.moleng.kyoto-u.ac.jp/~moleng_03/index_J.html
【研究分野】	物理化学・量子化学
【現在の研究課題】	分子ナノ工学、量子機能化学
【研究内容キーワード】	単一分子スピン、単一分子発光、元素化学の量子論
【学歴】	1978 年 3 月京都大学工学研究科石油化学専攻博士課程修了
【学位】	1978 年 3 月　工学博士（京都大学）
【略歴】	1979 年 6 月米国エナージー・コンバージョン・デバイシズ社リサーチケミスト、1981 年 12 月京都大学工学部助手、1988 年 12 月同助教授、1996 年 11 月京都大学大学院工学研究科教授
【所属学会】	日本化学会・日本物理学会・高分子学会
【学会活動】	フラーレン・ナノチューブ・グラフェン学会幹事
【主な著書、学術論文】 （過去 5 年以内）	1. 分子エレクトロニクスの基盤技術と将来展望（共監修および共著 , シーエムシー出版 , 2009） 2. 物理化学（化学マスター講座）（共著 , 丸善 , 2010） （以上著書） 1. A. Ito, Y. Nakano, M. Urabe, T. Kato, and K. Tanaka, “Triradical Cation of *p*-Phenylenediamine Having Two Nitroxide Radical Groups: Spin Alignment Mediated by Delocalized Spin”, *J. Am. Chem. Soc.*, **128**, 2948-2953 (2006). 2. Y. Hirao, M. Urabe, A. Ito, and K. Tanaka, “Intramolecular Spin Transfer in a Spiro-Fused Bis(triarylamine)”, *Angew. Chem., Int. Ed.*, **46**, 3300-3303 (2007). 3. A. Ito, Y. Yamagishi, K. Fukui, S. Inoue, Y. Hirao, K. Furukawa, T. Kato, and K. Tanaka, “Trimacrocyclic Arylamine and Its Polycationic States”, *Chem.Commun.*, **2008**, Issue 48 (December 28), 6573-6575 (2008). 4. A. Ito, D. Sakamaki, H. Ino, A. Taniguchi, Y. Hirao, K. Tanaka, K. Kanemoto, and T. Kato, “Polycationic States of Oligoanilines Based on Wurster's Blue”, *Eur. J. Org. Chem.*, **2009**, Issue 26 (September), 4441-4450 (2009). 5. A. Ito, Y. Yokoyama, R. Aihara, K. Fukui, S. Eguchi, K. Shizu, T. Sato, and K. Tanaka, “Preparation and Characterization of N-Anisyl-Substituted Hexaaza[1_6]paracyclophane”, *Angew. Chem. Int. Ed.*, **49**, 8205-8208 (2010). 6. K. Suzuki, T. Matsuo, D. Hashizume, H. Fueno, K. Tanaka, and K. Tamao, “A Planar Rhombic Charge-Separated Tetrasilacyclobutadiene”, *Science*, **331**, 1306-1309 (2011). （以上学術論文）

【氏名（ふりがな）】	太田　隆夫　（おおた　たかお）
【職名】	教授
【所属】	福井謙一記念研究センター　理論研究部門
【研究室】	理学部５号館４２２
【直通電話】	075-753-3740
【FAX】	075-753-3811
【電子メールアドレス】	takao@scphys.kyoto-u.ac.jp
【ホームページ】	http://www.ton.scphys.kyoto-u.ac.jp/nonlinear/
【研究分野】	相転移理論・非平衡系の統計物理学
【現在の研究課題】	非平衡ソフトマター物理学
【研究内容キーワード】	高分子共重合体・ミクロ相分離・共連結構造・パターン形成
【最終学歴】	1977年1月京都大学大学院理学研究科物理学第一専攻博士課程修了
【学位】	1977年1月理学博士（京都大学）
【略歴】	1979年7月　九州大学理学部助手、1987年8月お茶の水女子大学理学部助教授、1991年1月お茶の水女子大学理学部教授、1999年4月広島大学大学院理学研究科教授、2004年1月京都大学基礎物理学研究所教授、2006年7月京都大学大学院理学研究科教授
【在外研究歴】	1978年9月-1979年6月　米国Pittsburgh大学物理（David. Jansnow教授）（Mellon財団研究員）
【所属学会】	日本物理学会、中性子科学会、数理生物学会
【学会活動】	JPSJ Head Editor
【主な著書、学術論文】 （過去５年以内）	1. T. Ohkuma and T. Ohta, Deformable self-propelled particles with a global coupling, *Chaos* **20**, 023101(1-13) (2010) 2. T. Hiraiwa and T. Ohta, Viscoelasticity of a Single Semiflexible Polymer Chain, *Macromolecules* **42**, 7553-7562 (2009) 3. T. Ohta, T. Ohkuma and K. Shitara, Deformation of a self-propelled domain in an excitable reaction-diffusion system, *Phys. Rev.* **E 80**, 056203 (2009) 4. T. Sakaue and T. Ohta, Probing Nonequilibrium Fluctuations through Linear Response, *Phys. Rev.* **E 77**, 050102R (2008) 5. Y. Tonosaki, H. Tokuda, V. Zykov and T. Ohta, Phase Dynamics for Nonlinear Dissipative Waves under Symmetric Feedback, *Europhysics Letters* **83** 50011-1-6 (2008) 6. R. Tamate, K. Yamada, J. Vinals, and T. Ohta, Structural rheology of microphase separated diblock copolymers, *J. Phys. Soc. Jpn.*,**77** 034802 (2008) 7. M. Yanagisawa, M. Imai, T. Masui, S. Komura, Takao Ohta, Growth Dynamics of Domains in Ternary Fluid Vesicles, *Biophysical Journal* **92**, 115-125 (2007) 8. H. Shoji, K. Yamada, D. Ueyama and Takao Ohta, Turing patterns in three dimensions, *Phys. Rev.* **E 75**, 046212(13) (2007)
【学術関係の受賞】	アレキサンダー・フォン・フンボルト賞（２００８年）

⑶ スーパーバイザー

【氏名（ふりがな）】	赤木　和夫（あかぎ　かずお）
【職名】	教授
【所属】	工学研究科高分子化学専攻
【研究室】	赤木研究室
【直通電話】	075-383-2595
【FAX】	075-383-2760
【電子メールアドレス】	akagi@fps.polym.kyoto-u.ac.jp
【ホームページ】	http://www.fps.polym.kyoto-u.ac.jp
【研究分野】	高分子化学、液晶化学、物質化学
【現在の研究課題】	導電性、液晶性、発光性、階層らせん性の共役系高分子の合成と性質
【研究内容キーワード】	導電性高分子、液晶性共役高分子、不斉液晶反応場、階層構造制御
【最終学歴】	京都大工学研究科博士後期課程
【学位】	工学博士
【略歴】	福井大工助手、筑波大物質工講師、助教授、教授、同大学院数理物質科学研究科教授、学際物質科学研究センター長
【在外研究歴】	カリフォルニア大学サンタバーバラ校交換研究員、コーネル大学客員研究員
【所属学会】	日本化学会、高分子学会、日本液晶学会、アメリカ化学会
【学会活動】	文部科学省科研費（特定領域研究、2005-2008）「次世代共役ポリマーの超階層制御と革新機能」領域代表、Chair of 18th Iketani Conference, International Conference on Control of Super-Hierarchical Structures and Innovative Functions of Next-Generation Conjugated Polymers (2008)、Chair of International Conference on Science and Technolgy of Synthetic Metals (2010).
【主な著書、学術論文】（過去5年以内）	1. H. Hayasaka, T. Miyashita, K. Tamura, K. Akagi, “Helically π-Stacked Conjugated Polymers Bearing Photoresponsive and Chiral Moieties in Side Chains: Reversible Photoisomerization-Enforced Switching between Emission and Quenching of Circularly Polarized Fluorescence”, *Adv. Func. Mater.*, **20**, 1243 (2010). 2. M. Goh, G. Piao, M. Kyotani, K. Akagi, “Cis-Rich Helical Polyacetylene Synthesized in Low-Temperature Chiral Nematic Liquid Crystal”, *Macromolecules*, **42**, 8590 (2009). 3. K. Akagi, “Helical Polyacetylene - Asymmetric Polymerization in a Chiral Liquid Crystal Field”, *Chem. Rev.*, **109**, 5354 (2009). 4. T. Mori, T. Sato, M. Kyotani, K Akagi, “Macroscopically Aligned Helical Conjugated Polymers in Orientation-Controllable Chiral Nematic Liquid Crystal Field”, *Macromolecules*, **42**, 1817 (2009). 5. M. Kyotani, S. Matsushita, T. Nagai, Y. Matsui, M. Shimomura, A. Kaito. K. Akagi, “Helical Carbon and Graphitic Films Prepared from Iodine-Doped Helical Polyacetylene Film using Morphology-Retaining Carbonization”, *J. Am. Chem. Soc.*, **130**, 10880 (2008). 6. M. Goh, M. Kyotani, K. Akagi, “Highly Twisted Helical Polyacetylene with Morphology Free From Bundle of Fibrils Synthesized in Chiral Liquid Crystal Reaction Field”, *J. Am. Chem. Soc.*, **129**, 8519 (2007).
【学術関係の受賞】	日本化学会学術賞 (1999 年度)、日産科学賞 (2000 年度)、日本液晶学会賞論文賞 (2001 年度)、つくば賞 (2001 年度)、高分子学会賞 (2002 年度)、 文部科学大臣表彰科学技術賞 (2005 年度)、筑波大学名誉教授称号授与（2009 年度)、日本液晶学会賞業績賞（2010 年度）

【氏名（ふりがな）】	田中　勝久　（たなか　かつひさ）
【職名】	教授
【所属】	工学研究科 材料化学専攻
【研究室】	桂キャンパス A3 クラスター 018
【直通電話】	075-383-2801
【FAX】	075-383-2420
【電子メールアドレス】	tanaka@dipole7.kuic.kyoto-u.ac.jp
【ホームページ】	http://dipole7.kuic.kyoto-u.ac.jp/
【研究分野】	無機固体化学
【現在の研究課題】	酸化物薄膜および非晶質酸化物の磁気的性質・表面プラズモンを利用した光機能材料の作製
【研究内容キーワード】	酸化物、薄膜、非晶質、表面プラズモン、磁気的性質、光学的性質
【学歴】	1984 年 3 月 京都大学工学部工業化学科卒業 1986 年 3 月 京都大学大学院工学研究科工業化学専攻修士課程修了
【学位】	1986 年 3 月 京都大学大学院工学研究科工業化学専攻修士課程修了
【略歴】	1986 年 4 月 三重大学工学部助手 1989 年 4 月 京都大学工学部助手 1999 年 7 月 京都工芸繊維大学工芸学部助教授 2004 年 4 月 京都大学大学院工学研究科教授 2009 年 10 月 豊橋技術科学大学客員教授
【所属学会】	日本セラミックス協会、日本化学会、応用物理学会、日本物理学会、粉体粉末冶金協会、日本材料学会、Materials Research Society、Optical Society of America
【学会活動】	粉体粉末冶金協会 理事、日本材料学会 理事
【主な著書、学術論文】 （過去 5 年以内）	1. Y. Hasegawa, T. Adachi, A. Tanaka, M. Afzaal, P. O’Brien, T. Doi, Y. Hinatsu, K. Fujita, K. Tanaka, and T. Kawai, “Remarkable Magneto-Optical Properties of Europium Selenide Nanoparticles with Wide Energy Gaps”, *Journal of the American Chemical Society* **130** (2008) 5710-5715. 2. X. Meng, K. Fujita, S. Murai, and K. Tanaka, “Coherent Random Lasers in Weakly Scattering Polymer Films Containing Silver Nanoparticles”, *Physical Review A* **79** (2009) 053817-1-7. 3. H. Akamatsu, S. Oku, K. Fujita, S. Murai, and K. Tanaka, “Magnetic Properties of Mixed-Valence Iron Phosphate Glasses”, Physical Review B **80** (2009) 134408-1-9. 4. H. Akamatsu, K. Fujita, S. Murai, and K. Tanaka, “Ferromagnetic Eu^{2+}-Based Oxide Glasses with Reentrant Spin Glass Behavior”, *Physical Review B* **81** (2010) 014423-1-9. 5. X. Meng, K. Fujita, S. Murai, T. Matoba, and K. Tanaka, “Plasmonically Controlled Lasing Resonance with Metallic-Dielectric Core-Shell Nanoparticles”, *Nano Letters* **11** (2011) 1374-1378.
【学術関係の受賞】	The Australasian Ceramic Society/Ceramic Society of Japan (ACS/CJS) Joint Ceramic Award (1997 年)、日本セラミックス協会学術賞 (2005 年)

【氏名（ふりがな）】	佐藤　直樹　（さとう　なおき）
【職名】	教授
【所属】	化学研究所　複合基盤化学研究系　分子集合解析研究領域
【研究室】	宇治キャンパス化学研究所本館 N-324C 号室
【直通電話】	0774-38-3080
【FAX】	0774-38-3084
【電子メールアドレス】	naokis@e.kuicr.kyoto-u.ac.jp
【ホームページ】	http://www.kuicr.kyoto-u.ac.jp/labos/is2/scope_J.html
【研究分野】	有機物性化学
【現在の研究課題】	有機結晶・薄膜の構造・電子構造・電子物性の相関研究
【研究内容キーワード】	有機半導体・有機薄膜・分子集合体・電子分光・界面物性・分子系構築
【最終学歴】	1976年3月東京大学大学院理学系研究科化学専門課程修士課程修了
【学位】	1983年3月理学博士（東京大学）
【略歴】	1976年4月分子科学研究所分子集団研究系技官、1984年4月熊本大学理学部助手、1987年4月東京大学教養学部助教授、1992年5月京都大学化学研究所教授
【在外研究歴】	1989年5月－7月 スウェーデン Linköping 大学物理学科（William R. Salaneck 教授）（Visiting Scholar）
【所属学会】	日本化学会、日本物理学会、日本分光学会、分子科学会
【学会活動】	日本化学会有機結晶部会長、日本化学会有機結晶ディビジョン主査、分子科学会運営委員
【主な著書、学術論文】 （過去5年以内）	1. R. Murdey, N. Sato and M. Bouvet, Frontier electronic structures in fluorinated copper phthalocyanine thin films studied using ultraviolet and inverse photoemission spectroscopies, *Mol. Cryst. Liq. Cryst.* **455** (2006) 211-218. 2. H. Yoshida, K. Inaba and N. Sato, X-ray diffraction reciprocal space mapping study of the thin film phase of pentacene, *Appl. Phys. Lett.* **90** (2007) 181930. 3. H. Yoshida and N. Sato, The crystallographic and electronic structures of three different polymorphs of pentacene, *Phys. Rev. B* **77** (2008) 235205. 4. T. Hiramatsu, T. Sasamori, H. Yoshida, N. Tokitoh and N. Sato, Reversible polymorphic crystalline transition of a push–pull-type molecule: {4-[4,5-bis(methylsulfanyl)-1,3-dithiol-2-ylidene]cyclohexa-2,5-dien-1-ylidene} malononitrile (BMDCM), *J. Mol. Struct.* **922** (2009) 30-34. 5. R. Murdey, M. Bouvet, M. Sumimoto, S. Sakaki and N. Sato, Direct observation of the energy gap in lutetium bisphthalocyanine thin films, *Synth. Met.* **159** (2009) 1677-1681. 6. J. Tsutsumi, H. Yoshida, R. Murdey, S. Kato and N. Sato, An accurate calculation of electronic contribution to static permittivity tensor for organic molecular crystals on the basis of the charge response kernel theory, *J. Phys. Chem. A* **113** (2009) 9207-9212. 7. J. Tsutsumi, H. Yoshida, R. Murdey and N. Sato, Spontaneous buildup of surface potential with a thin film of a zwitterionic molecule giving non-centrosymmetric crystal structure, *Appl. Phys. Lett.* **95** (2009) 182901.
【学術関係の受賞】	1985年4月日本化学会（第34回）進歩賞受賞

【氏名（ふりがな）】	北川　進　（きたがわ　すすむ）
【職名】	副拠点長
【所属】	物質－細胞統合システム拠点
【研究室】	桂キャンパスA4棟319号室
【直通電話】	075-383-2733
【FAX】	075-383-2732
【電子メールアドレス】	kitagawa@icems.kyoto-u.ac.jp
【ホームページ】	http://www.sbchem.kyoto-u.ac.jp/kitagawa-lab/index.html
【研究分野】	錯体化学、無機化学
【現在の研究課題】	新規多孔性材料の開拓とその応用
【研究内容キーワード】	多孔性配位高分子、金属有機構造体、光機能、超分子構造
【最終学歴】	1979年3月京都大学大学院石油化学専攻博士課程修了
【学位】	1979年7月工学博士（京都大学）
【略歴】	1979年4月近畿大学理工学部助手、1983年4月近畿大学理工学部講師、1988年4月近畿大学理工学部助教授、1992年4月東京都立大学理学部化学教室無機化学第一講座教授、1998年6月京都大学大学院工学研究科合成・生物化学専攻教授、2007年10月京都大学物質 - 細胞統合システム拠点・副拠点長および京都大学大学院工学研究科合成・生物化学専攻（兼任）教授
【在外研究歴】	1986年-1987年Texas A&M大学Cotton研究室博士研究員
【所属学会】	日本化学会、錯体化学会、物理学会、高分子学会、米国学会
【主な著書、学術論文】 （過去5年以内）	1. “One-dimensional imidazole aggregate in aluminum porous coordination polymers with high proton conductivity”, S. Bureekaew, S. Horike, M. Higuchi, M. Mizuno, T. Kawamura, D. Tanaka, N. Yanai and S. Kitagawa, *Nature Materials*, **2009**, 8, 831-836. 2. “Selective sorption of oxygen and nitric oxide by an electron-donating flexible porous coordination polymer”, S. Shimomura, M. Higuchi, R. Matsuda, K. Yoneda, Y. Hijikata, Y. Kubota, Y. Mita, J. Kim, M. Takata and S. Kitagawa, *Nature Chemistry*, **2010**, 2, 633-637. 3. “Photoactivation of a nanoporous crystal for on-demand guest trapping and conversion”, H. Sato, R. Matsuda, K. Sugimoto, M. Takata and S. Kitagawa, *Nature Materials*, **2010**, 9, 661-666. (Highlighted in News & Views in the same issue.).
【学術関係の受賞】	1. 2002年第19回日本化学会学術賞 2. 2007年Earl L. Muetterties Memorial Lectureship (University of California, Berkeley) 3. 2007年平成19年度錯体化学会賞 4. 2008年Humboldt Research Award, Germany 5. 2009年第61回日本化学会賞 6. 2010年トムソン・ロイター引用栄誉賞受賞 7. 2011年平成23年度科学技術分野の文部科学大臣表彰研究部門

【氏名（ふりがな）】	吉川　研一　（よしかわ　けんいち）
【職名】	教授
【所属】	理学研究科　物理学・宇宙物理学専攻
【研究室】	理学研究科　吉川研究室
【直通電話】	075-753-3749
【FAX】	075-753-3779
【電子メールアドレス】	yoshikaw@scphys.kyoto-u.ac.jp
【ホームページ】	http://www.yklab.jp/
【研究分野】	非線形科学・生命物理学
【現在の研究課題】	１）非平衡開放系での時間的・空間的秩序の自発的生成に関する研究 ２）生命現象の物理学
【研究内容キーワード】	非平衡開放系・時空間的秩序の自己生成・自己組織化・高分子物理学
【最終学歴】	1976年5月京都大学大学院工学研究科博士課程修了
【学位】	1976年5月工学博士（京都大学）
【略歴】	1976年10月　徳島大学教養部講師、1979年4月　徳島大学教養部助教授、1988年4月　名古屋大学教養部助教授、1990年11月　名古屋大学教養部教授、1991年4月　名古屋大学大学院人間情報学研究科教授、1998年4月　京都大学大学院理学研究科教授、2002年9月　京都大学福井謙一記念研究センター兼任教授（現在に至る）、1998年10月 ~1999年6月 Universite Louis Pasteur　客員教授、2009年2月 ENS, Paris 客員教授
【在外研究歴】	長期のものはなし
【所属学会】	物理学会、日本化学会、生物物理学会など
【学会活動】	Vise Chair, Commission C-6, International Union of Pure and Applied Physics、など
【主な著書、学術論文】 （過去5年以内）	1. “Large-scale vortex lattice emerging from collectively moving microtubules”, Yutaka Sumino, Ken H. Nagai, Yuji Shitaka, Dan Tanaka, Kenichi Yoshikawa, Hugues Chaté and Kazuhiro Oiwa, *Nature*, **483**(7390), 448–452 (2012) 2. “In Vitro Murine Leukemia Retroviral Integration and Structure Fluctuation of Target DNA”, Tatsuaki Tsuruyama, Weizhi Liu and Kenichi Yoshikawa, *PLoS ONE*, **7**(2), e31533/1–8 (2012) 3. “Rigidity Matching between Cells and the Extracellular Matrix Leads to the Stabilization of Cardiac Conduction”, Marcel Hörning, Satoru Kidoaki, Takahito Kawano and Kenichi Yoshikawa, *Biophysical Journal*, **102**(3), 379–387 (2012) 4. “Enhancement of DNA compaction by negatively charged nanoparticles: Effect of nanoparticle size and surfactant chain length”, Sergii Rudiuk, Kenichi Yoshikawa and Damien Baigl, *Journal of Colloid and Interface Science*, **368**(1), 372–377 (2012) 5. “Cell-Sized confinement in microspheres accelerates the reaction of gene expression”, Ayako Kato, Miho Yanagisawa, Yuko Sato, Kei Fujiwara and Kenichi Yoshikawa, *Scientific Reports (Nature Publishing Group)*, **2**, 283/1–5 (2012)
【学術関係の受賞】	日本IBM科学賞 (1991)

【氏名】	Tanimura Yoshitaka
【職名】	Professor
【所属】	Department of Chemistry
【研究室】	Faculty of Science, 6th building #256
【直通電話】	075-753-4017
【FAX】	075-753-4018
【電子メールアドレス】	tanimura@kuchem.kyoto-u.ac.jp
【ホームページ】	http://theochem.kuchem.kyoto-u.ac.jp
【研究分野】	Chemical Physics
【現在の研究課題】	nonlinear optical response
【研究内容キーワード】	statistical physics
【学歴】	Keio University
【学位】	Ph. D
【所属学会】	Japanese Physical Soc
【主な著書、学術論文】 （過去5年以内）	1. A. G. Dijkstra and Y. Tanimura, Correlated fluctuations in the exciton dynamics and spectroscopy of DNA, *New J. of Phys.* **12**, 055005 (19pages) (2010). 2. M. Tanaka and Y. Tanimura, Multistate Electron Transfer Dynamics in the Condensed Phase: Exact Calculations from the Reduced Hierarchy Equations of Motion Approach, *J. Chem. Phys.* **132**, 214502 (11pages) (2010) 3. A. G. Dijkstra and Y. Tanimura, Non-Markovian entanglement dynamics in the presence of system-bath coherence, *Phys. Rev. Lett* **104**, 250401 (4 pages) (2010). 4. A. Sakurai and Y. Tanimura, Does hbar play a role in multidimensional spectroscopy? Reduced hierarchy equations of motion approach to molecular vibrations, *J. Phys. Chem. A* **115**, 4009-4022 (2011) 5. T. Hasegawa and Y. Tanimura, A polarizable water model for intramolecular and intermolecular vibrational spectroscopies, *J. Phys. Chem. B* **115**, 5545-5553(2011).
【学術関係の受賞】	Morino Foundation

【氏名（ふりがな）】	今堀　博　（いまほり　ひろし）
【職名】	教授
【所属】	物質－細胞総合システム拠点（工学研究科　分子工学専攻）
【研究室】	桂キャンパス　A4 棟　002 号室
【直通電話】	075-383-2566
【FAX】	075-383-2571
【電子メールアドレス】	imahori@scl.kyoto-u.ac.jp
【ホームページ】	http://www.moleng.kyoto-u.ac.jp/~moleng_05/
【研究分野】	有機化学・光化学
【現在の研究課題】	人工光合成・有機太陽電池・ドラッグデリバリー
【研究内容キーワード】	ポルフィリン・フラーレン・ナノチューブ・自己組織化・電子移動
【最終学歴】	1990 年 3 月京都大学大学院理学研究科博士後期課程修了
【学位】	1990 年 3 月理学博士（京都大学）
【略歴】	1990 年 4 月　米国ソーク生物学研究所博士研究員、1992 年 4 月大阪大学産業科学研究所助手、1999 年 11 月大阪大学大学院工学研究科助教授、2001 年 12 月科学技術振興機構さきがけ研究代表者（兼任）、2002 年 2 月京都大学大学院工学研究科教授、2002 年 9 月京都大学福井謙一記念研究センタースーパーバイザー（兼任）、2007 年 10 月京都大学物質―細胞統合システム拠点教授
【所属学会】	日本化学会、光化学協会、米国化学会、米国電気化学会
【主な著書、学術論文】 （過去 5 年以内）	1. T. Sagawa, S. Yoshikawa, and H. Imahori, “1-D Nanostructured Semiconducting Materials for Organic Photovoltaics,” *J. Phys. Chem. Lett.* (Perspective), **1**, 1020-1025 (2010). 2. H. Imahori, T. Umeyama, and S. Ito, “Large π Aromatic Molecules as Potential Sensitizers in Dye-Sensitized Solar Cells,” *Acc. Chem. Res.* **42**, 1809-1818 (2009). 3. Y. Matano and H. Imahori, “Phosphole-Containing Calixpyrroles, Calilxphyrins, and Porphyrins: Synthesis and Coordination Chemistry,” *Acc. Chem. Res.* **42**, 1193-1204 (2009). 4. H. Imahori, T. Umeyama, “Donor-Acceptor Nanoarchitecture on Semiconducting Electrodes for Solar Energy Conversion,” *J. Phys. Chem. C* (Feature Article), **113**, 9029-9039 (2009). 5. A. Kira, T. Umeyama, Y. Matano, K. Yoshida, S. Isoda, J.-K. Park, D. Kim, H. Imahori, “Supramolecular Donor-Acceptor Heterojunctions by Vectorial Stepwise Assembly of Porphyrins and Coordination-Bonded Fullerene Arrays for Photocurrent Generation,” *J. Am. Chem. Soc.*, **131**, 3198-3200 (2009).
【学術関係の受賞】	1. 2004 年光化学協会賞 2. 2006 年日本学術振興会賞 3. 2006 年日本化学会学術賞 4. 2007 年東京テクノ・フォーラム 21 ゴールド・メダル賞 5. 2007 年大阪科学賞 6. 2007 年ナイスステップ研究者

【氏名（ふりがな）】	山本　量一　（やまもと　りょういち）
【職名】	教授
【所属】	工学研究科　化学工学専攻
【研究室】	桂キャンパス　A4 棟 118 号室
【直通電話】	075-383-2661
【FAX】	075-383-2651
【電子メールアドレス】	ryoichi@cheme.kyoto-u.ac.jp
【ホームページ】	http://www-tph.cheme.kyoto-u.ac.jp/
【研究分野】	ソフトマターの計算化学
【現在の研究課題】	コロイド分散系の計算機シミュレーション
【研究内容キーワード】	ソフトマター、コロイド、計算機シミュレーション、ガラス転移
【最終学歴】	1992 年 3 月神戸大学大学院 工学研究科修士課程化学工学専攻修了
【学位】	1996 年 3 月博士（工学）京都大学
【略歴】	1994 年 9 月 神戸大学大学院自然科学研究科物質科学専攻助手、1996 年 3 月 京都大学大学院理学研究科物理学・宇宙物理学専攻助手、2000 年 1 月 同講師、2004 年 10 月 京都大学大学院工学研究科化学工学専攻助教授、2007 年 4 月 同准教授、2008 年 10 月 同教授
【在外研究歴】	2000 年 9 月 -2001 年 8 月　英国ケンブリッジ大学化学教室（J-P. Hansen 教授）（文部省在外研究員（若手））
【所属学会】	日本物理学会、化学工学会、分子シミュレーション研究会
【主な著書、学術論文】 （過去 5 年以内）	1. R. Tatsumi and R. Yamamoto, Direct numerical simulation of dispersed particles in a compressible fluid, *Phys. Rev. E* **85**, 066704 (2012). 2. H. Mizuno and R. Yamamoto, Mechanical responses and stress fluctuations of a strongly sheared supercooled liquid, *Eur. Phys. J. E*, **35**, 29 (2012). 3. H. Kobayashi and R. Yamamoto, Implementation of Lees-Edwards periodic boundary conditions for direct numerical simulations of particle dispersions under shear flow, *J. Chem. Phys.*, **134**, 064110 (2011). 4. S. Yasuda and R. Yamamoto, Rheological properties of polymer melt between rapidly oscillating plates: an application of multiscale modeling, *EPL*, **86**, 18002 (2009). 5. T. Iwashita and R. Yamamoto, Short-time motion of Brownian particles in a shear flow, *Phys. Rev. E*, **79**, 031401 (2009). 6. Y. Nakayama, K. Kim and R. Yamamoto, Simulating (electro) hydrodynamic effects in colloidal dispersions: smoothed profile method, *Eur. Phys. J. E*, **26**, 361-368 (2008).
【学術関係の受賞】	2007 年 1 月 ホソカワ研究奨励賞、2002 年 12 月 分子シミュレーション研究会学術賞

【氏名（ふりがな）】	高田　彰二（たかだ　しょうじ）
【職名】	准教授
【所属】	理学研究科　生物科学専攻　生物物理学教室
【研究室】	理学部1号館205号室
【直通電話】	075-753-4220
【FAX】	075-753-4222
【電子メールアドレス】	takada@biophys.kyoto-u.ac.jp
【ホームページ】	http://theory.biophys.kyoto-u.ac.jp
【研究分野】	理論生物物理学
【現在の研究課題】	生体分子の構造機能についての理論およびコンピュータシミュレーション研究
【研究内容キーワード】	タンパク質、分子モーター、分子動力学、生体分子モデリング
【最終学歴】	1991年9月総合研究大学院大学数物科学研究科機能分子科学専攻博士後期課程退学
【学位】	1994年3月理学博士（総合研究大学院大学）
【略歴】	1991年～1995年岡崎国立共同研究機構技官（分子科学研究所）、1995年～1998年日本学術振興会研究員（イリノイ大学化学科）、1998年～2001年神戸大学理学部化学科講師、2001年～2007年神戸大学理学部化学科助教授、2007年～京都大学理学研究科生物科学専攻生物物理教室准教授。
【在外研究歴】	1995年5月 -1998年3月　米国イリノイ大学化学科（日本学術振興会研究員）
【所属学会】	日本生物物理学会、日本物理学会
【学会活動】	日本生物物理学会運営委員
【主な著書、学術論文】（過去5年以内）	1. Wenfei Li and Shoji Takada, Self-learning multiscale simulation for achieving high accuracy and high efficiency simultaneously, *Journal of Chemical Physics*, **130**: 214108(6 pages), 2009 2. Naoto Hori, George Chikenji, R. Stephen Berry, and Shoji Takada, Folding energy landscape and network dynamics of small globular proteins, *Proceedings of the National Academy of Sciences USA*, **106**: 73-78, 2009 3. Kei-ichi Okazaki, and Shoji Takada, Dynamic energy landscape view of coupled binding and protein conformational change: Induced-fit versus population-shift mechanisms, *Proceedings of the National Academy of Sciences USA*, **105**: 11182-11187, 2008. 4. Kei-ichi Okazaki, Nobuyasu Koga, Shoji Takada, Jose N Onuchic, and Peter G Wolynes, Multiple-basin energy landscapes for large amplitude conformational motions of proteins: Structure-based molecular dynamics simulations, *Proceedings of the National Academy of Sciences USA*, **103**(No.32):11844-11849, 2006. 5. Nobuyasu Koga and Shoji Takada, Folding-based molecular simulations reveal mechanisms of the rotary motor F1-ATPase, *Proceedings of the National Academy of Sciences USA*, **103**(No.14):5367-5372, 2006.

【氏名（ふりがな）】	林　重彦　（はやし　しげひこ）
【職名】	准教授
【所属】	理学研究科　化学専攻
【研究室】	理学研究科6号館154号室
【直通電話】	075-753-4006
【FAX】	075-753-4000
【電子メールアドレス】	hayashig@kuchem.kyoto-u.ac.jp
【ホームページ】	http://kuchem.kyoto-u.ac.jp/riron/hayashig
【研究分野】	理論化学・生物物理学
【現在の研究課題】	タンパク質分子機能の理論的研究
【研究内容キーワード】	タンパク質機能・分子シミュレーション
【学歴】	1997年11月　京都大学大学院理学研究科化学専攻博士課程修了
【学位】	1997年11月　博士（理学）（京都大学）
【略歴】	1998年4月日本学術振興会特別研究員（名古屋大学）、2000年4月米国イリノイ大学ベックマン研究所博士研究員、2003年6月京都大学福井謙一記念研究センター博士研究員、2003年10月科学技術振興機構さきがけ研究員、2005年5月京都大学大学院理学研究科准教授
【所属学会】	生物物理学会
【主な著書、学術論文】 （過去5年以内）	1. Local entropy difference upon a substrate binding of a psychrophilic α-amylase and a mesophilic homologue. Takahiro Kosugi and Shigehiko Hayashi, *Chem. Phys. Lett.*, **501**, 517-522 (2011). 2. Protein collective motions coupled to ligand migration in myoglobin. Yasutaka Nishihara, Shigeki Kato, and Shigehiko Hayashi, *Biophys. J.*, **98**, 1649-1657 (2010). 3. Electronic coulombic coupling of excitation-energy transfer in xanthorhodopsin. Kazuhiro Fujimoto, and Shigehiko Hayashi, J. *Am. Chem. Soc.*, **131**, 14152-14153 (2009). 4. Proton transfer reactions in reaction center of photosynthetic bacteria, *Rhodobacter sphaeroides*. Yu Kaneko, Shigehiko Hayashi, and Iwao Ohmine, *J. Phys. Chem. B*, **113**, 8993-9003 (2009). 5. Photochemical reaction dynamics of the primary event of vision studied by a hybrid molecular simulation. Shigehiko Hayashi, Emad Tajkhoshid, and Klaus Schulten, *Biophys. J.*, **96**, 403-416 (2009).

⑷ 専任教員

【氏名（ふりがな）】	長谷川　淳也　（はせがわ　じゅんや）
【職名】	准教授
【所属】	福井謙一記念研究センター　総合研究部門
【研究室】	福井記念研究センター 206
【直通電話】	075-711-7867
【FAX】	075-781-4757
【電子メールアドレス】	hasegawa@fukui.kyoto-u.ac.jp
【ホームページ】	http://www.fukui.kyoto-u.ac.jp/~hasegawa
【研究分野】	理論化学・量子化学
【現在の研究課題】	光機能性蛋白質の発現メカニズムの解明、励起状態理論の開発
【研究内容キーワード】	光機能性蛋白質、励起状態理論、電子相関理論
【最終学歴】	1998年3月京都大学工学研究科合成・生物化学専攻博士後期課程修了
【学位】	1998年3月博士（工学）、京都大学
【略歴】	1999年11月京都大学工学研究科合成・生物化学専攻助手、2007年4月京都大学工学研究科合成・生物化学専攻助教、2008年12月京都大学工学研究科合成・生物化学専攻講師、2011年10月京都大学福井謙一記念研究センター准教授、2012年4月分子科学研究所客員准教授
【在外研究歴】	1998年4月 -1999年10月　Lund大学理論化学科（B. O. Roos教授、スウェーデン）
【所属学会】	日本化学会、分子科学会、理論化学研究会、米国化学会、生物物理学会
【学会活動】	量子化学研究協会　理事
【主な著書、学術論文】 （過去5年以内）	1. T. Kawatsu, K. Matsuda, and J. Hasegawa, “Bridge-Mediated Excitation Energy Transfer Pathways through Protein Media: a Slater Determinant-Based Electronic Coupling Calculation Combined with Localized Molecular Orbitals”, *J. Phys. Chem. A* **115**(39), 10814-10822 (2011). 2. K. Fujimoto, K. Asai, and J. Hasegawa, “Theoretical Study of the Opsin Shift of Deprotonated Retinal Schiff Base in the M state of Bacteriorhodopsin”, *Phys. Chem. Chem. Phys.* **12**(40), 13107-13116 (2010). 3. J. Hasegawa, T. Ise, K. Fujimoto, A. Kikuchi, E. Fukumura, A. Miyawaki, and Y. Shiro, “Excited States of Fluorescent Proteins, mKO and DsRed: Chromophore-protein Electrostatic Interaction Behind the Color Variations”, *J. Phys. Chem. B*, **114**(8), 2971-2979 (2010). 4. K. Fujimoto, J. Hasegawa, and H. Nakatsuji, “Color tuning mechanism in human red, green, and blue cone visual pigments: SAC-CI theoretical study”, *Bull. Chem. Soc. Jpn.* **82**(9), 1140-1148 (2009). 5. N. Nakatani, J. Hasegawa, and H. Nakatsuji, “Red Light in Chemiluminescence and Yellow-green Light in Bioluminescence: Color-tuning Mechanism of Firefly, Photinus pyralis, studied by the SAC-CI method”, *J. Am. Chem. Soc.* **129**, 8756-8765 (2007).
【学術関係の受賞】	平成9-11年 日本学術振興会特別研究員、平成21年9月 分子科学会奨励賞、平成23年9月 QSCP Promising Scientist Prize of CMOA

【氏名（ふりがな）】	中尾　嘉秀　（なかお　よしひで）
【職名】	准教授
【所属】	福井謙一記念研究センター　理論研究部門
【研究室】	京都大学桂キャンパス A4-024
【直通電話】	075-383-2546
【FAX】	075-383-2799
【電子メールアドレス】	nakao.yoshihide.5a@kyoto-u.ac.jp
【ホームページ】	http://www.moleng.kyoto-u.ac.jp/~moleng_10/index_J.html
【研究分野】	計算化学・理論化学
【現在の研究課題】	機能性分子の物性の理論的解明
【研究内容キーワード】	機能性金属錯体、スピン、発光
【学歴】	2003 年 3 月 東京大学大学院工学系研究科応用化学専攻博士課程修了
【学位】	2003 年 3 月 博士 (工学) (東京大学)
【略歴】	2003 年 4 月 京都大学大学院工学研究科助手、2007 年 4 月 京都大学大学院工学研究科助教、2011 年 1 月 京都大学福井謙一記念研究センター准教授
【所属学会】	日本化学会、分子科学会
【主な著書、学術論文】 （過去 5 年以内）	1. Y. Nakao, K. Saito, S. Sakaki, “Theoretical investigation of μ-O-bridged dinuclear Re complexes. Electronic structure, bonding nature, and absorption spectra”, *Int. J. Quant. Chem.* **109**, 2319-2327 (2009). 2. K. Umakoshi, K. Saito, Y. Arikawa, M. Onishi, S. Ishizaka, N. Kitamura, Y. Nakao, S. Sakaki, “Luminescent Heteropolynuclear Complexes of 3,5-Dimethylpyrazolate [Pt$_2$Au$_2$M$_2$(Me$_2$pz)$_8$] (M=Ag, Cu) Showing the Synergistic Effect of Three Transition Elements in the Excited State”, *Chem. Eur. J.* **15**, 4238-4242 (2009). 3. Y. I. Kurokawa, Y. Nakao, S. Sakaki, “Inverted Sandwich Type Dinuclear Chromium(I) Complex and Its Analogues of Scandium(I), Titanium(I), Vanadium(I), Manganese(I), and Iron(I): Theoretical Study of Electronic Structure and Bonding Nature”, *J. Phys. Chem. A*, **114**, 1191-1199 (2010). 4. H. Ando, Y. Nakao, H. Sato, S. Sakaki, “Comparison of Electronic Structures and Light-induced Excited Spin State Trapping between [Fe(2-picolylamine)$_3$]$^{2+}$ and Its Iron(III) Analogue”, *Dalton Trans.* **39**, 1836-1845 (2010). 5. Y. Nakajima, Y. Nakao, S. Sakaki, Y. Tamada, T. Ono, F. Ozawa, “Electronic structure of four-coordinate iron(I) complex supported by a bis(phosphaethenyl) pyridine ligand”, *J. Am. Chem. Soc.* **132**, 9934-9936 (2010).

【氏名（ふりがな）】	石田　俊正　（いしだ　としまさ）
【職名】	特定准教授
【所属】	福井謙一記念研究センター　国際連携研究室
【研究室】	福井記念研究センター 205
【直通電話】	075-711-7838
【FAX】	075-711-7838
【電子メールアドレス】	ishida@fukui.kyoto-u.ac.jp
【ホームページ】	http://www.fukui.kyoto-u.ac.jp/~ishida
【研究分野】	計算化学・理論化学
【現在の研究課題】	光機能分子・生体分子の反応・ポテンシャル面生成法
【研究内容キーワード】	光機能分子・生体分子・ポテンシャル面・非断熱遷移
【最終学歴】	1989年3月東京大学理学系大学院相関理化学専攻博士課程修了
【学位】	1989年3月理学博士（東京大学）
【略歴】	1989年4月　静岡大学教養部助手、1995年4月静岡大学教養部助教授、1995年10月静岡大学工学部助教授、2002年4月岡崎国立共同研究機構分子科学研究所助教授（流動部門）、2004年4月静岡大学工学部助教授、2004年10月京都大学福井謙一記念研究センター助教授、2007年4月同准教授、2011年10月同特定准教授
【在外研究歴】	1996年4月 -1997年3月　米国 Northwestern 大学化学（George C. Schatz 教授）（文部省在外研究員（若手））
【所属学会】	日本化学会、日本分子化学会、日本コンピュータ化学会、American Physical Society
【主な著書、学術論文】（過去5年以内）	1. Toshimasa Ishida, Shinkoh Nanbu, and Hiroki Nakamura, Non-adiabatic ab initio dynamics of two models of Schiff base retinal, *J. Phys. Chem. A*, **113**(16), 4356–4366 (2009). 2. Toshimasa Ishida and Jun-ichi Aihara, Aromaticity of neutral and doubly charged polyacenes, *Phys. Chem. Chem. Phys.* **11**, 7197 - 7201 (2009) 3. Wilfredo C. Chung, Shinkoh Nanbu, and Toshimasa Ishida, “Nonadiabatic ab Initio Dynamics of a Model Protonated Schiff Base of 9-cis Retinal”, *J. Phys. Chem. A*, **114** (32), 8190–8201 (2010). 4. Shinkoh Nanbu, Toshimasa Ishida and Hiroki Nakamura, “Future Perspectives of Nonadiabatic Chemical Dynamics”, C*hemical Science*, **1**, 663-674 (2010) 5. Wilfredo Credo Chung,* Shinkoh Nanbu, and Toshimasa Ishida, “A Nonadiabatic Ab Initio Dynamics Study on Rhodopsin and its Analog Isorhodopsin: Chemical Dynamics Reasons Behind Selection of Rhodopsin by Life”, *Chem. Lett.* **40**, 1395-1397(2011).

【氏名（ふりがな）】	池野　豪一　（いけの　ひでかず）
【職名】	特定助教
【所属】	福井謙一記念研究センター
【研究室】	福井謙一記念研究センター 204
【直通電話】	075-711-7863
【FAX】	075-781-4757
【電子メールアドレス】	ikeno@fukui.kyoto-u.ac.jp
【ホームページ】	http://www.fukui.kyoto-u.ac.jp/users/ikeno/index_ja.html
【研究分野】	計算材料化学・電子分光の理論
【現在の研究課題】	電子分光法の理論および第一原理計算による解析
【研究内容キーワード】	X 線分光・電子線エネルギー損失分光・多重項・強相関
【学歴】	京都大学大学院工学研究科材料工学専攻博士後期課程修了
【学位】	2007 年 3 月 京都大学 博士 (工学)
【略歴】	2007 年 4 月 – 2009 年 3 月 京都大学大学院工学研究科 博士研究員 2009 年 4 月 – 2010 年 3 月ユトレヒト大学 (オランダ) 博士研究員 2010 年 4 月 – 2011 年 10 月 福井謙一記念研究センター フェロー 2011 年 11 月 – 現在 福井謙一記念研究センター 特定助教
【所属学会】	日本物理学会，日本金属学会
【主な著書、学術論文】（過去 5 年以内）	1. Hidekazu Ikeno, Teruyasu Mizoguchi, Yukinori Koyama, Zenpachi Ogumi, YasuharuUchimoto, and Isao Tanaka, “Theoretical Fingerprints of Transition Metal $L_{2,3}$ XANES/ELNES for Lithium Transition Metal Oxides by *ab initio* Multiplet Calculations”, *J. Phys. Chem. C* **115**, 11871 (2011). 2. Hidekazu Ikeno, Teruyasu Mizoguchi and Isao Tanaka, “*Ab initio* charge transfer multiplet calculations on the $L_{2,3}$ XANES and ELNES of 3d transition metal oxides”, *Phys. Rev. B* **83**, 155107 (2011). 3. Teruyasu Mizoguchi, Weine Olovsson, Hidekazu Ikeno and Isao Tanaka, “Theoretical ELNES using one-particle an multi-particle calculations”, *Micron* **41**, 695-709, (2010). 4. Hidekazu Ikeno, Frank M.F. de Groot, Eli Stavitski and Isao Tanaka, “Multiplet calculations of $L_{2,3}$ x-ray absorption near-edge structures for 3d transition-metal compounds”, *J. Phys.: Condens. Matter* **21**, 104208 (2009). 5. Hidekazu Ikeno, Teruyasu Mizoguchi, Yukinori Koyama, Yu Kumagai and Isao Tanaka, “First-principles calculations for $L_{2,3}$ ELNES/XANES of 3d transition metal monooxides”, *Ultramicroscopy* **106**, 970-975 (2006).
【学術関係の受賞など】	日本学術振興会特別研究員 (DC2) 2005-2006

⑸ リサーチリーダー

【氏名（ふりがな）】	諸熊　奎治　（もろくま　けいじ）
【職名】	リサーチリーダー
【所属】	福井謙一記念研究センター　福井謙一記念研究部門第一
【研究室】	福井謙一記念研究センター 202
【直通電話】	075-711-7843
【FAX】	075-781-4757
【電子メールアドレス】	morokuma@fukui.kyoto-u.ac.jp
【ホームページ】	http://www.fukui.kyoto-u.ac.jp/~morokuma; http://kmweb.fukui.kyoto-u.ac.jp/
【研究分野】	理論化学・計算化学
【現在の研究課題】	複雑分子系の複合分子理論によるシミュレーション
【研究内容キーワード】	複合分子理論。複雑分子系、シミュレーション、ナノ構造、酵素反応
【最終学歴】	1962 年 3 月京都大学大学院工学研究科博士課程単位修得退学
【学位】	1963 年 3 月工学博士（京都大学）
【略歴】	1962 年 4 月京都大学工学部助手、1964 年 9 月 Columbia 大学客員助教授、1966 年 9 月 Harvard 大学博士研究員、1967 年 9 月 Rochester 大学助教授、1971 年 9 月同教授、1976 年 12 月分子科学研究所教授、1993 年 1 月 Emory 大学 William H. Emerson 教授、2006 年 9 月 Emory 大学名誉教授、2006 年 9 月京都大学福井謙一記念研究センターリサーチリーダー
【所属学会】	日本化学会、American Chemical Society、分子科学会
【主な著書、学術論文】 （過去 5 年以内）	過去５年間に約１３０報 1. H.-B. Li, A. J. Page, S. Irle, and K. Morokuma, Theoretical Insights into Chirality-Controlled SWCNT Growth from a Cycloparaphenylene Template. *ChemPhysChem* **13**, 1479-1485 (2012). 2. F. Liu, and K. Morokuma, A Computational Study on the Working Mechanism of Stilbene Light-Driven Molecular Rotary Motor: Sloped Minimal Energy Path and Unidirectional Nonadiabatic Isomerization. *J. Am. Chem. Soc.* **134**, 4864-4876 (2012). 3. M. P. Grubb, M. L. Warter, H.-Y. Xiao, S. Maeda, K. Morokuma, S. W. North, No Straight Path: Multistate Roaming as the Only Route for the NO3 → NO + O2 Reaction, *Science*, **335**, 1075-1078 (2012). 4. S. Maeda and K. Morokuma, Toward Predicting Full Catalytic Cycles Using Automatic Reaction Path Search Method: A Case Study on HCo(CO)3-Catalyzed Hydroformylation, *J. Chem. Theo. Comp.* **8**, 380-385 (2012). 5. J. Pang, X. Li, K. Morokuma, N. S. Scrutton, and M. J. Sutcliffe, Large-scale Domain Conformational Change Is Coupled to the Activation of the Co-C bond in the B12-Dependent Enzyme Ornithine 4,5-Aminomutase: A Computational Study. *J. Am. Chem. Soc.* **134**, 2367-2377 (2012). 6. Y. Nishimoto, Z. Wang, K. Morokuma, and S. Irle, Molecular and electronic structures of endohedral fullerenes, Sc2C2@C3v-C82 and Sc2@C3v-C82: Benchmark for SCC-DFTB and proposal of new inner cluster structures, *Phys. Status Solidi B*, **249**, 324-334 (2012). 7. Y. Matsuda, K. Hoki, S. Maeda, K. Hanaue, K. Ohta, K. Morokuma, N. Mikami, and A. Fujii, Experimental and theoretical investigations of isomerization reactions of ionized acetone and its dimer. *Phys. Chem. Chem. Phys.* **14**, 712-719 (2012).
【学術関係の受賞】	International Academy of Quantum Molecular Science (IAQMS) Medal, 1978; 日本化学会賞, 1992; The Schrödinger Medal, The World Association of Theoretical Organic Chemists (WATOC), 1993; The Fukui Medal, Asian Pacific Association of Theoretical & Computational Chemists, 2005; 恩賜賞、日本学士院賞、2008; 瑞宝中綬章、2010

【氏名（ふりがな）】	榊　茂好　（さかき　しげよし）
【職名】	リサーチリーダー
【所属】	福井謙一記念研究センター：福井謙一記念研究部第２
【研究室】	303
【直通電話】	075-711-7907
【FAX】	075-711-4757
【電子メールアドレス】	Sakaki.shigeyoshi.47e@st.kyoto-u.ac.jp
【ホームページ】	http://www.users.iimc.kyoto-u.ac.jp/~z59354/
【研究分野】	理論化学・計算化学
【現在の研究課題】	遷移金属元素を含む複合電子系の構造、電子状態、反応過程の理論化学
【研究内容キーワード】	電子状態理論・遷移金属錯体・反応解析・触媒作用・励起状態
【学歴】	1974年3月　京都大学工学研究科燃料化学専攻博士課程単位取得退学
【学位】	1974年11月　工学博士（京都大学）
【略歴】	1975年4月　熊本大学工学部助手、1982年1月 同助教授、1990年4月　同教授を経て、2002年4月より京都大学工学研究科教授、2010年3月定年、現在に至る。
【所属学会】	日本化学会、触媒学会、近畿化学協会、ケイ素化学協会、American Chemical Society
【主な著書、学術論文】 （過去5年以内）	1. Pd(II)-Promoted Direct Cross-Coupling Reaction of Arenes via Highly Regioselective Aromatic C-H Activation: A Theoretical Study, A. Ishikawa, Y. Nakao, H. Sato, S. Sakaki, *Dalton Trans*., **39**, 3279-3289 (2010). 2. Comparison of Electronic Structures and Light-induced Excited Spin State Trapping between [Fe(2-picolylamine)$_3$]$^{2+}$ and Its Iron(III) Analogue, H. Ando, Y. Nakao, H. Sato, S. Sakaki, *Dalton Trans*., **39**, 1836-1845 (2010). 3. Spin-orbit coupling in a model Hamiltonian for d-d excited states of Ni^{2+} ion aqueous solution, S. Iuchi, S. Sakaki, *Chem. Phys. Lett*., **485**, 114-118 (2010). 4. Inverted Sandwich Type Dinuclear Chromium(I) Complex and Its Analogues of Scandium(I), Titanium(I), Vanadium(I), Manganese(I), and Iron(I): Theoretical Study of Electronic Structure and Bonding Nature, Y.-I. Kurokawa, Y. Nakao, S. Sakaki, *J. Phys. Chem. A*, **114**, 1191–1199 (2010). 5. Theoretical Study of Excited States of Pyrazolate- and Pyridinethiolate- Bridged Dinuclear Platinum(II) Complexes: Relationship between Geometries of Excited States and Phosphorescence Spectra, K. Saito, Y. Nakao, K. Umakoshi, S.Sakaki, Inorg. *Chem*., **49**, 8977–8985 (2010). 6. Multi-State CASPT2 Study of Native Iron(III)-dependent Catechol Dioxygenase and Its Functional Models: Electronic Structure and Ligand-to-Metal Charge- Transfer Excitation, N. Nakatani, Y. Hitomi, S. Sakaki, *J. Phys. Chem. B*, **115**, 4781–4789 (2011). 7. Theoretical Study of Photoinduced Epoxidation of Olefins Catalyzed by Ruthenium Porphyrin, A. Ishikawa, S. Sakaki, *J. Phys. Chem. A*, **115**, 4774–4785 (2011). 8. Noble Reaction Features of Bromoborane in Oxidative Addition of B − Br σ − Bond to M(PMe$_3$)$_2$ (M= Pt or Pd): Theoretical Study, G. Zeng, S. Sakaki, *Inorg. Chem*., **50**, 5290-5297 (2011). 9. Theoretical Study of Pt(PR$_3$)$_2$(AlCl$_3$) (R=H, Me, Ph, or Cy) Including an Unsupported Bond between Transition Metal and Non-Transition Metal Elements; Geometry, Bond Strength, and Prediction, S. Tsukamoto, S. Sakaki, *J. Phys. Chem. A*, **115**, 8520-8527 (2011). 10.Theoretical study on aquation reaction of cis-platin complex: RISM-SCF-SEDD, a hybrid aproach of accurate quantum chemical method and statistical mechanics, D. Yokogawa, K. Ono, H. Sato, S. Sakaki, *Dalton Trans*, **40** (42), 11125-11130 (2011). 11.Theoretical Study on High-Spin to Low-Spin Transition of Fe(pyrazine) [Pt(CN)$_4$]}: Guest-Induced Entropy Decrease, A. Hideo, Y. Nakao, H. Sato, M. Ohba, S.Kitagawa, S. Sakaki, *Chem. Phys. Lett*. **511**(4-6), 399-404 (2011).
【学術関係の受賞など】	第1回分子科学会賞 (2009年9月)

⑹ 特定助教（白眉）

【氏名（ふりがな）】	前田　理（まえだ　さとし）
【職名】	特定助教
【所属】	京都大学次世代研究者育成センター・京都大学福井謙一記念研究センター
【研究室】	福井謙一記念研究センター・208 号室
【直通電話】	075-711-7894
【FAX】	075-781-4757
【電子メールアドレス】	smaeda@fukui.kyoto-u.ac.jp
【ホームページ】	https://sites.google.com/site/satoshimaedahokkaidouniv/
【研究分野】	理論化学・計算化学
【現在の研究課題】	化学反応経路自動探索法の開発と応用
【研究内容キーワード】	ポテンシャルエネルギー曲面・遷移状態・反応経路・非断熱反応経路
【学歴】	2004 年 3 月　東北大学大学院理学研究科修士課程　修了 2007 年 3 月　東北大学大学院理学研究科博士課程　修了
【学位】	2007 年 3 月　理学博士（東北大学）
【略歴】	2004 年 4 月　日本学術振興会特別研究員（DC1） 2007 年 4 月　日本学術振興会特別研究員（PD） 2010 年 4 月　京都大学次世代研究者育成センター（特定助教） 2012 年 2 月　北海道大学大学院理学研究院化学部門物理化学分野（助教）
【所属学会】	日本化学会・日本物理学会・分子科学学会
【主な著書、学術論文】（過去 5 年以内）	1. Maeda, S.; Morokuma, K. A Systematic Method for Locating Transition Structures of A + B → X Type Reactions. *J. Chem. Phys.* **2010**, *132*, 241102/1-4. 2. Maeda, S.; Komagawa, S.; Uchiyama, M.; Morokuma, K. Finding Reaction Pathways for Multicomponent Reactions: The Passerini Reaction Is a Four-Component Reaction. *Angew. Chem. Int. Ed.* **2011**, *50*, 644-649. 3. Maeda, S.; Saito, R.; Morokuma, K. Finding Minimum Structures on Seam of Crossing in Reactions of Type A + B → X: Exploration of Nonadiabatic Ignition Pathways of Unsaturated Hydrocarbons. *J. Phys. Chem. Lett.* **2011**, *2*, 852-857. 4. Maeda, S.; Morokuma, K. Finding Reaction Pathways of Type A + B → X: Toward Systematic Prediction of Reaction Mechanisms. *J. Chem. Theory Comput.* **2011**, *7*, 2335-2345. 5. Maeda, S.; Morokuma, K. Toward Predicting Full Catalytic Cycle Using Automatic Reaction Path Search Method: A Case Study on $HCo(CO)_3$-Catalyzed Hydroformylation. *J. Chem. Theory Comput.* **2012**, *8*, 380-385.
【学術関係の受賞など】	2004 年度－ 2006 年度　日本学術振興会特別研究員（DC1） 2007 年 3 月　青葉理学振興会賞 2007 年 3 月　東北大学総長賞 2004 年度－ 2006 年度　日本学術振興会特別研究員（PD） 2008 年 10 月　平成 20 年度分子科学討論会優秀講演賞 2010 年 4 月　京都大学白眉研究者 2012 年 3 月　The PCCP Prize for Outstanding Achievement of Young Scientists in Physical Chemistry and Chemical Physics

Ⅱ　博士研究員

１．博士研究員組織

平成２３年度

職　名		氏　名
福井謙一記念 研究部第一	福井センターフェロー	Zhuofeng Ke
		Joonghan Kim
		Alister Page
		畑中　美穂
	（JST）フェロー	Xin Li
		K.R.S. Chandrakumar
		Fengyi Liu
		Hong-yan Xiao
		Lina Ding
		Haibei Li
		Lung Wa Chung
		Galina Petrova
		Raman Kumar Singh
	JSPS 外国人特別研究員	Travis Harris
福井謙一記念 研究部第二	福井センターフェロー	土方　優
	特推研究フェロー	青野　信治
		塚本　晋也
		Milind Deshmukh
		會　桂香
		高木　望
		中垣　雅之
		吉澤　輝高
		中谷　直樹
	JSPS 特別研究員	松井　亨
福井センターフェロー		Wilfredo Credo Chung
		岩城　貴史
		義永　那津人
		嶺澤　範行
		Kunkun Guo
（受入れ研究者） 分子科学研究所　専門研究職員		河津　励

２．博士研究員プロフィール

【氏名】	Zhuofeng Ke
【職名】	FIFC Fellow
【所属】	Morokuma Group, Fukui Institute For Fundamental Chemistry
【研究室】	Room 207
【直通電話】	075-711-7893
【電子メールアドレス】	zhuofeng.ke@fukui.kyoto-u.ac.jp
【研究分野】	Computational Chemistry
【現在の研究課題】	DNA-based asymmetric catalysis, pMMO enzymatic catalysis.
【研究内容キーワード】	Computational study of catalysis processes in organometallic systems and bio-systems
【学歴】	2002 B.Sc. in Chemistry, Sun Yat-sen University, 2005 M.Sc. in Polymer Chemistry and Physics, Sun Yat-sen University 2007 Jointly Educating Ph.D. in computational organometallic chemistry, University of North Texas, 2009 Ph.D. in Physical Chemistry (Theoretical and Computational Chemistry), Sun Yat-sen University
【学位】	Ph.D. in Physical Chemistry (Theoretical and Computational Chemistry), Sun Yat-sen University
【所属学会】	American Chemical Society
【学会活動】	241st ACS National Meeting in Anaheim, CA.
【主な著書、学術論文】 （過去５年以内）	1. Ke, Zhuofeng, Abe, S., Ueno, T., & Morokuma, Keiji,*J. Am. Chem. Soc.* **133** *(20)*, 7926-7941 (2011) *(JACS beta Select issue 13: Current Applications of Computational Chemistry in JACS - Molecules, Mechanisms and Materials)* 2. Liu, Y., Ke, Zhuofeng, Liu, Shuwen, Chen, Wen-Hua, Jiang, Shibo; Jiang, Zhi-Hong. *ChemMedChem* **6** *(9)*, 1654- 1664 (2011).. 3. Gao, H., Ke, Zhuofeng, DeYonker N. J., Wang J., Xu H., Mao Z.-W., Phillips, D.L., & Zhao C. *J. Am. Chem. Soc.*, **2011**, *133 (9),* 2904–2915 4. Ke, Zhuofeng & Cundari, T.R. *Organometallics* **29** *(4)*, 821-834 (2010). (Top10 Most Accessed Articles of Organometallics in 2010) 5. Guo, Z.; Xue, Jiadan; Ke, Zhuofeng; Phillips, D. L.*; Zhao, C.Y. *J. Phys. Chem. B*, **2009**, *113*, 6528–6532. 6. Foley, N. A.; Lee, J. P.; Ke, Zhuofeng; Gunnoe, T. B.*; and Cundari, T. R. *Acc. Chem. Res.* **2009**, *42*, 585–597 7. Lee, J. P.; Ke, Zhuofeng; Ramrez M. A.; Gunnoe, T. B.*; Cundari T. R.*; Boyle, P. D.; Petersen, J. L. *Organometallics* **2009**, *28*, 175 8–1775 8. Liu, Yan; Ke, Zhuofeng; Cui, Jianfang; Chen, Wen-Hua; Ma, Lin; Wang Bo*. *Bioorg. Med. Chem.* **2008**, *16*, 7185–7192. 9. Foley, Nicholas A.; Ke, Zhuofeng; Gunnoe, T. Brent*; Cundari, Thomas R.*; and Petersen, Jeffrey L. *Organometallics* **2008**, *27*, 3007–3017. 10. Guo, Zhen; Ke, Zhuofeng; Phillips, David Lee*; Zhao, Cunyuan*. *Organometallics* **2008**, *27*, 181–188.
【学術関係の受賞など】	Sun Yat-sen University Fellow 2009 State Scholarship Funds, China Scholarship Council (CSC) 2007

【氏名】	Joonghan Kim
【職名】	FIFC Fellow
【所属】	Fukui Kenichi Memorial Research Group 1, Fukui Institute for Fundamental Chemistry
【研究室】	Room 203
【直通電話】	075-711-7708
【FAX】	075-781-4757
【電子メールアドレス】	joonghan@fukui.kyoto-u.ac.jp; quatum99@gmail.com
【研究分野】	Computational Chemistry
【現在の研究課題】	DFTB-MD simulation of chirality-controlled carbon nanotube growth and determination of local chirality of carbon nanotube
【研究内容キーワード】	Carbon nanotube, density-functional tight-binding, chirality
【学歴】	2004 B. Sc., Hanyang University, Seoul, Korea 2010 Ph. D., KAIST, Daejeon, Korea
【学位】	Doctor of Philosophy, KAIST, Daejeon, Korea
【略歴】	2010, Postdoctoral fellow, KAIST, Daejeon, Korea
【所属学会】	Korean Chemical Society
【主な著書、学術論文】（過去 5 年以内）	1. Joonghan Kim, Yoon Sup Lee, and Hyotcherl Ihee, "Density Functional and Ab Initio Studies on Structures and Energies of the Ground State of CrCO", *Int. J. Quantum Chem.* **107**, 458 (2007). 2. Joonghan Kim, Tae Kyu Kim, Jangbae Kim, Yoon Sup Lee, and Hyotcherl Ihee, "Density Functional and Ab Initio Study of $Cr(CO)_n$ (n = 1 − 6) Complexes", *J. Phys. Chem. A* **111**, 4697-4710 (2007). 3. Joonghan Kim, Sunhong Jun, Jeongho Kim, and Hyotcherl Ihee, "Density Functional and Ab Initio Investigation of CF_2ICF_2I and CF_2CF_2I Radicals in Gas and Solution Phases", *J. Phys. Chem. A* **113**, 11059-11066 (2009). 4. Joonghan Kim, Tae Kyu Kim, and Hyotcherl Ihee, "Theoretical Study on the Reaction of Ti+ with Acetone and the Role of Intersystem Crossing", *J. Phys. Chem. A* **113**, 11382-11389 (2009). 5. Jeewon Kang, Joonghan Kim, Hyotcherl Ihee, and Yoon Sup Lee, "Molecular Structures, Energetics and Electronic Properties of Neutral and Charged Hg_n Clusters (n= 2–8)", *J. Phys. Chem. A* **114**, 5630-5639 (2010). 6. Joonghan Kim, Hyotcherl Ihee, and Yoon Sup Lee, "Spin-Orbit Density Functional and Ab Initio Study of HgX_n (X=F, Cl, Br, and I; n=1, 2, and 4)", *J. Chem. Phys.* **133**, 144309 (2010). 7. Joonghan Kim, Tae Kyu Kim, and Hyotcherl Ihee, "Density Functional and Spin-Orbit Ab Initio Study of CF_3Br: Molecular Properties and Electronic Curve-Crossing", *J. Phys. Chem. A* **115**, 1264-1271 (2011). 8. Joonghan Kim, Hyotcherl Ihee, and Yoon Sup Lee, "Spin-orbit ab initio study of two low-lying states of chloroiodomethane cation", *Theor. Chem. Acc.* **129**, 343-347 (2011). 9. Joonghan Kim, Stephan Irle, and Keiji Morokuma, "Determination of Local Chirality in Irregular Single-Walled Carbon Nanotubes Based on Individual Hexagons", *Phys. Rev. Lett.* **107**, 175505 (2011) 10. Joonghan Kim and Hyotcherl Ihee, "Theoretical Study on the Reaction of Butadiynyl Radical (C_4H) with Ethylene (C_2H_4) to Form C_6H_4 and H", *Int. J. Quantum Chem.* **112**, 1913-1925 (2012).

【氏名】	Alister Page
【職名】	Fukui Fellow
【所属】	Fukui Kenichi Memorial Research Group 1, Fukui Institute for Fundamental Chemistry
【研究室】	Room 203
【直通電話】	075-711-7831
【FAX】	095-781-4757
【電子メールアドレス】	alisterpage@fukui.kyoto-u.ac.jp
【研究分野】	Computational Chemistry
【現在の研究課題】	Molecular Dynamics simulations and electronic structure calculations of nanoscale self-assembly processes (in particular, carbon nanotube & graphene nucleation and growth).
【研究内容キーワード】	Single-walled carbon nanotube, garphene self-assembly, nucleation, growth, healing, (n,m)chirality, functionalization density-functional tight-binding
【学歴】	2004, Bachelor of Mathematics (Honours Class I), The University of Newcastle, Australia 2004, Bachelor of Science (Honours Class I), The University of Newcastle, Australia 2008, Doctor of Philosophy, The University of Newcastle, Australia
【学位】	Doctor of Philosophy, The University of Newcastle, Australia
【略歴】	2008, Postdoctoral Research Associate, Priority Research Centre for Energy, Department of Chemical Engineering, The University of Newcastle, Australia 2009-2010, CREST Postdoctoral Research Fellow, Fukui Institute for Fundamental Chemistry, Kyoto University, Japan 2010-2012, Fukui Postdoctoral Research Fellow, Fukui Institute for Fundamental Chemistry, Kyoto University, Japan
【所属学会】	American Chemical Society, Royal Australian Chemistry Institute
【主な著書、学術論文】 （過去 5 年以内）	1. Y. Wang, A. J. Page, H.-J. Qian, Y. Nishomoto, S. Irle, K. Morokuma, “Template Effect in the Competition Between Haeckelite and Graphene Growth on Ni(111): Quantum Chemical Molecular Dynamics Simulations.”, *J. Am. Chem. Soc.*, **133**, 18837, (2011) 2. A. J. Page, K.R.S. Chandrakumar, S. Irle, K. Morokuma, “SWNT Nucleation from Carbon-Coated SiO_2 Nanoparticles *via* a Vapor-Solid-Solid Mechanism”. *J. Am. Chem. Soc.*, **132**, 15699, (2011) 3. A. J. Page, Y. Ohta, S. Irle, K. Morokuma, “Mechanisms of Single-Walled Carbon Nanotube Nucleation, Growth and Healing Determined using QM/MD Methods”, *Acc. Chem. Res.*, **43**, 1375, (2010) 4. A. J. Page, Y. Ohta, Y. Okamoto, S. Irle, K. Morokuma, “Defect Healing During Single-Walled Carbon Nanotube Growth: A Density-Functional Tight-Binding Molecular Dynamics Investigation”, *J. Phys. Chem. C*, **113**, 20198, (2009) 5. A. J. Page, E. I. von Nagy-Felsobuki, “Rovibrational Spectra of LiH_2^+, $LiHD^+$ and LiD_2^+ Determined using FCI Property Surfaces”, *J. Phys. Chem. A*, **111**, 4478, (2007)
【学術関係の受賞など】	Australian Post-Graduate Award (2005-2008) RACI Chemistry Honours Prize (2004) Deans Medal, Faculty of Science and IT, The University of Newcastle (2004)

【氏名（ふりがな）】	畑中　美穂　（はたなか　みほ）
【職名】	福井謙一記念研究センターフェロー
【所属】	福井記念研究センター　諸熊グループ
【研究室】	福井記念研究センター 212
【直通電話】	075-711-7647
【電子メールアドレス】	miho@fukui.kyoto-u.ac.jp
【研究分野】	計算化学・理論化学
【現在の研究課題】	一酸化窒素還元酵素の反応機構に関する理論的研究
【研究内容キーワード】	酵素反応・ONIOM 法
【学歴】	2011 年 3 月 慶應義塾大学大学院 理工学研究科 基礎理工学専攻 博士課程修了
【学位】	2011 年 3 月 博士（理学）（慶應義塾大学）
【略歴】	2009 年 4 月 － 2010 年 3 月　慶應義塾大学大学院理工学研究科助教（有期・研究助成） 2011 年 4 月　京都大学福井謙一記念研究センターフェロー
【所属学会】	日本化学会・分子科学学会
【主な著書、学術論文】（過去 5 年以内）	1. M. Hatanaka, S. Yabushita, “An *ab initio* study on the f-f hypersensitive transition intensities of lanthanide tribromide molecules”, *Chem. Phys. Lett.* **504**, pp 193-198 (2011). 2. M. Hatanaka, S. Yabushita, “Theoretical Study on the f–f Transition Intensities of Lanthanide Trihalide Systems”, *J. Phys. Chem. A* **113**, pp 12615-12625 (2009). 3. T. Ikeno, I. Iwakura, A. Shibahara, M. Hatanaka, A. Kokura, S. Tanaka, T. Nagata, T. Yamada, “Newly Designed Catalysts for the Enantioselective Borohydride Reduction: Prediction from the Theoretical Analysis”, *Chem. Lett.* **36**, pp 738-739 (2007). 4. I. Iwakura, M. Hatanaka, A. Kokura, H. Teraoka, T. Ikeno, T. Nagata, T. Yamada, “The Reactive Intermediate of Catalytic Borohydride Reduction by Schiff Base-Cobalt Complexes”, *Chem. Asian J.* **1**, pp 656-663 (2006).
【学術関係の受賞など】	2011 年 4 月　福井謙一記念研究センターフェロー 2010 年 4 月　公益信託　林女性自然科学者研究助成基金　林フェロー 2009 年 3 月　日本化学会第 89 春季年会　学生講演賞

【氏名】	Xin Li
【職名】	Associate professor
【所属】	Dalian Institute of Chemical Physics, Chinese Academy of Sciences
【研究室】	Room 104
【直通電話】	+86-411-84379376
【電子メールアドレス】	lixinbj@gmail.com
【研究分野】	Computational Biochemistry
【現在の研究課題】	Studies of biological systems
【研究内容キーワード】	Reaction mechanisms of metalloenzymes and photobiology
【学歴】	June 2005, Ph. D., College of Chemistry, Liaoning Normal University
【学位】	Ph. D. in Physical Chemistry from Liaoning Normal University
【略歴】	July 2005-May 2007, Postdoctoral Fellow, Peking University July 2007-December 2011, Postdoctoral Fellow, Fukui Institute for Fundamental Chemistry
【主な著書、学術論文】 （過去5年以内）	1. Xin Li, Lung Wa Chung, Piotr Paneth, and Keiji Morokuma, “DFT and ONIOM(DFT:MM) Studies on Co-C Bond Cleavage and Hydrogen Transfer in B_{12}-Dependent Methylmalonyl-CoA Mutase. Stepwise or Concerted Mechanism?” *J. Am. Chem. Soc.* **131**, 5115-5125 (2009). 2. Xin Li, Lung Wa Chung, Hideaki Mizuno, Atsushi Miyawaki, and Keiji Morokuma, “A Theoretical Study on the Nature of On- and Off-States of Reversibly Photoswitching Fluorescent Protein Dronpa: Absorption, Emission, Protonation and Raman”, *J. Phys. Chem. B* **114**, 1114-1126 (2010). 3. Xin Li, Lung Wa Chung, Hideaki Mizuno, Atsushi Miyawaki, and Keiji Morokuma, “Primary Events of Photodynamics in Reversible Photoswitching Fluorescent Protein Dronpa”, *J. Phys. Chem. Lett.* **1**, 3328-3333 (2010). 4. Xin Li, Lung Wa Chung, Hideaki Mizuno, Atsushi Miyawaki, and Keiji Morokuma, “Competitive Mechanistic Pathways for Green-to-Red Photoconversion in the Fluorescent Protein Kaede: A Computational Study”, *J. Phys. Chem. B* **114**, 16666-16675 (2010). 5. Xin Li, Lung Wa Chung, and Keiji Morokuma, “Modeling Photobiology Using Quantum Mechanics (QM) and Quantum Mechanics/Molecular Mechanics (QM/MM) Calculations,” In “Computational Methods for Large systems: Electronic Structure Approaches for Biotechnology and Nanotechnology” *Reimers, J. R. Eds. John Wiley & Sons, Inc., Hoboken*, **2011**, pp 397-433. 6. Xin Li, Lung Wa Chung, and Keiji Morokuma,“Photodynamics of All-trans Retinal Protonated Schiff Base in Bacteriorhodopsin and Methanol Solution”, *J. Chem. Theory Comput.* (Lett.) **7**, 2694–2698 (2011). 7. Lung Wa Chung, Xin Li, Hajime Hirao, and Keiji Morokuma, “Comparative Reactivity of Ferric-Superoxo and Ferryl-Oxo Species in Heme and Non-Heme Complexes”, *J. Am. Chem. Soc.* (Commun.) **133**, 20076-20079 (2011). 8. Jiayun Pang, Xin Li, Keiji Morokuma, Nigel S. Scrutton, and Michael J. Sutcliffe, “Large-Scale Domain Conformational Change Is Coupled to the Activation of the Co–C Bond in the B_{12}-Dependent Enzyme Ornithine 4,5-Aminomutase: A Computational Study” *J. Am. Chem. Soc.* **134**, 2367-2377 (2012). 9. Chung, L. W.; Hirao, H.; Li, X.; Morokuma, K. “The ONIOM Method: Its Foundation and Applications to Metalloenzymes and Photobiology”, *WIREs Comput. Mol. Sci.* **2**, 327-350 (2012).
【学術関係の受賞など】	Postdoctoral Science Fund of China in Peking University, 2006; WATOC2011 Poster Prize

【氏名】	K. R. S. Chandrakumar
【職名】	JST Fellow
【所属】	Fukui Kenichi Memorial Research Group 1, Fukui Institute for Fundamental Chemistry
【研究室】	Room 203
【直通電話】	075-711-7834
【FAX】	075-781-4757
【電子メールアドレス】	krsc@fukui.kyoto-u.ac.jp; krschandrakumar@gmail.com
【研究分野】	Computational Chemistry
【現在の研究課題】	DFTB-MD simulation of carbon nanotube growth from the metal decorated carbon nanocones
【研究内容キーワード】	carbon nanotube, nanocones, self-assembly, nanocapsules, density-functional tight-binding
【学歴】	B.Sc., with distinction, Madurai Kamaraj University, (General Chemistry with Physics and Mathematics as ancillary subjects) 1994 M.Sc., with first class, Madurai Kamaraj University, (specialization in Physical Chemistry) 1996 Ph.D., Pune University, National Chemical Laboratory, 2003 Thesis Title: Theoretical studies on some aspects of chemical reactivity using density based descriptors.
【学位】	Doctor of Philosophy, Pune University, National Chemical Laboratory
【略歴】	Since 2004, working as a Scientific Officer at Bhabha Atomic Research Centre, India
【所属学会】	Chemical Research Society of India.
【主な著書、学術論文】 （過去 5 年以内）	1. Jena, N. K. Tripathy, M. K., Samanta, A. K., Chandrakumar, K. R. S. and Ghosh, S. K. “Water molecule encapsulated in carbon nanotube model systems: effect of confinement and curvature” *Theo. Chem. Acc.* **2012**, 131, 1-12. 2. Jena, N.K., Chandrakumar, K.R.S; Ghosh, S.K. Beyond the gold-hydrogen analogy: Doping gold cluster with H-atom-O_2 activation and reduction of the reaction barrier for CO oxidation *Journal of Physical Chemistry Letters* **2011** 2 1476-1480. 3. Page, A.J., Chandrakumar, K.R.S., Irle, S., Morokuma, K. SWNT nucleation from carbon-coated SiO 2 nanoparticles via a vapor-solid-solid mechanism *J. Am. Chem. Soc.* **2011**, 133, 621-628. 4. Page, A.J., Chandrakumar, K.R.S., Irle, S., Morokuma, K. “Thermal annealing of SiC nanoparticles induces SWNT nucleation: Evidence for a catalyst-independent VSS mechanism” *Physical Chemistry Chemical Physics* **2011**, 13, 15673-15680 5. Jena, N.K., Chandrakumar, K.R.S. Ghosh, S.K. DNA Base-Gold Nano Cluster Complex as a Potential Catalyzing Agent: An Attractive Route for CO Oxidation Process. *J. Phys. Chem. C* **2012**, (In Press).
【学術関係の受賞など】	Indo-European Collaborative Project Grant (FP7); Project Title: Modeling of Nano-scaled Advanced Materials Intelligently (MONAMI) Young Scientist Award in 2008 from Department of Atomic Energy (DAE) Young Scientist Medal Award in 2005 from the Indian National Science Academy (INSA)

【氏名】	Fengyi Liu
【職名】	JST Fellow
【所属】	Fukui Institute for Fundamental Chemistry
【研究室】	Room 207
【直通電話】	075-711-7893
【電子メールアドレス】	fengyiliu@fukui.kyoto-u.ac.jp
【研究分野】	Computational Chemistry
【現在の研究課題】	Theoretical calculation of molecular motor and switch
【研究内容キーワード】	Artificial/biological molecular motor, molecular switch
【学歴】	Jun. 1998, B. Sc. in Chemistry, Hebei Normal University, China Jun. 2001, M. Sc. in Chemistry, Hebei Normal University, China Dec. 2005, Ph.D. in Chemistry, Beijing University of Chemical Technology, China
【学位】	Ph. D. in Applied Chemistry, Beijing University of Chemical Technology
【略歴】	Sep. 2007-Jun. 2009, Postdoctoral researcher, Lund University, Sweden
【主な著書、学術論文】 （過去5年以内）	1. Fengyi Liu and Keiji Morokuma, Computational Study on the Working Mechanism of a Stilbene Light-Driven Molecular Rotary Motor: Sloped Minimal Energy Path and Unidirectional Nonadiabatic Photoisomerization, *J. Am. Chem. Soc.*, **2012**, 134, 4864–4876. 2. Shu-Feng Chen, Ya-Jun. Liu, Fengyi Liu, Luca De Vico, Roland Lindh, Multireference calculations on the chemical origin and mechanism of firefly bioluminescence, *Luminescence*, **2010**, 25, 89-90. 3. Fengyi Liu, Yajun liu, Luca De Vico, Roland Lindh, A CASSCF/CASPT2 Approach to the Decomposition of Thiazole-Substituted Dioxetanone: Substitution Effects and Charge-Transfer Induced Electron Excitation, *Chem. Phys. Lett.* **2009**,484,69-75. 4. Fengyi Liu, Yajun Liu, Luca De Vico, Roland Lindh, Theoretical Study of the Chemiluminescent Decomposition of Dioxetanone, *J. Am. Chem. Soc.*, **2009**, 131, 6181-6188. 5. Shu-Feng Chen,Feng-Yi Liu, Ya-Jun Liu, An ab initio investigation of the mechanisms of photodissociation in bromobenzene and iodobenzene, *J. Chem. Phys.*, **2009**, 131, 124304. 6. Jie Ren, Fengyi Liu, Yatong Zhang, David Wei Zhang, Initial reaction of HfO_2 atomic layer deposition on silicon surfaces with different oxygen levels: A density functional theory study, *Thin Solid Film*, **2007**, 515, 4702-4708.
【学術関係の受賞など】	Poster Prize on 7th Congress of the International Society for Theoretical Chemical Physics, 2011, Tokyo, Japan.

【氏名】	Hong-Yan Xiao
【職名】	JST Fellow
【所属】	Fukui Institute for Fundamental Chemistry
【研究室】	Room 208
【直通電話】	075-711-7894
【電子メールアドレス】	hyxiao@fukui.kyoto-u.ac.jp
【研究分野】	Computational Chemistry
【現在の研究課題】	Exploring photodissociation mechanism of small molecules by GRRM and AFIR programs
【研究内容キーワード】	Photodissociation, excited state, conical intersection, nonadiabatic transition
【学歴】	Jun. 2002, B. Sc. in Chemistry, Liaoning Normal University, China Jun. 2005, M. Sc. in Physical Chemistry, Liaoning Normal University, China Jun. 2008, Ph.D. in Physical Chemistry, Beijing Normal University, China
【学位】	Ph. D. in Physical Chemistry, Beijing Normal University
【略歴】	Since July 2008, working as an assistant researcher at Technical Institute of Physics and Chemistry, Chinese Academy of Science
【主な著書、学術論文】 （過去 5 年以内）	1. Ya-Jun Liu, Hong-Yan Xiao, Meng-Tao Sun, Wei-Hai Fang. Spin-orbit ab initio investigation of the photodissociation of dibromomethane in the gas and solution phases. *J. Comput. Chem.* **29**, 2513-2519 (2008) 2. Isabelle Navizet, Ya-Jun Liu, Nicolas Ferré, Hong-Yan Xiao, Wei-Hai Fang and Roland Lindh. Color-tuning mechanism of firefly investigated by multi-configurational perturbation method. *J. Am. Chem. Soc.* **132**, 706-712 (2010) 3. Hong-Yan Xiao, Zhen Zhen, Huan-Quan Sun, Xu-Long Cao, Zhen-Quan Li, Xin-Wang Song, Xiao-Hong Cui and Xin-Hou Liu. Molecular dynamics simulation of anionic surfactant at the water/n-alkane interface. *Acta Phys. -Chim. Sin.* **26**, 422-428 (2010) 4. Huan-Quan Sun, Hong-Yan Xiao, and Xin-Hou Liu. Structural properties of hydroxyl-substituted alkyl benzenesulfonates at the water/vapor and water/decane interfaces. *Sci. China Chem.* **54**, 1078-1085 (2011) 5. Hong-Yan Xiao, Satoshi Maeda and Keiji Morokuma. Excited-state roaming dynamics in photolysis of a nitrate radical. *J. Phys. Chem. Lett.* **2**, 934-938 (2011) 6. Michael P. Grubb, Michelle L. Warter, Hong-Yan Xiao, Satoshi Maeda, Keiji Morokuma and Simon W. North. No straight path: roaming in both ground- and excited-state photolytic channels of $NO_3 \rightarrow NO + O_2$. *Science* **335**, 1075-1078 (2012)
【学術関係の受賞など】	Qiu Shi Graduate Student Scholarship in Beijing Normal University (2007) National Natural Science Foundation of China (2010)

【氏名】	Lina Ding （丁麗娜）
【職名】	JST Fellow
【所属】	Fukui Institute For Fundamental Chemistry
【研究室】	Room 212
【直通電話】	075-711-7631
【電子メールアドレス】	ding@fukui.kyoto-u.ac.jp
【現在の研究課題】	photobiology
【研究内容キーワード】	Photo reaction mechanism of biochemical and metal-complexes systems
【学歴】	Jun. 2004, B. Sc. in Chemistry, Zhengzhou University, China Jun. 2007, M. Sc. in Organic Chemistry, Zhengzhou University, China Jun. 2010, Ph.D. in Physical Chemistry, Beijing Normal University, China
【学位】	Ph.D. in Physical Chemistry, Beijing Normal University, China
【主な著書、学術論文】 （過去 5 年以内）	1. Lina Ding, Lung Wa Chung, Keiji Morokuma "Reaction Mechanism of Photo-induced Decarboxylation of the Photoactivatable Green Fluorescent Protein:An ONIOM(QM:MM) Study", *To be submitted*. 2. Lina Ding, Keiji Morokuma, "Mechanisic study on the Photoisomerization in Polypyridyl mononuclear ruthenium(II) aquo (PMRA) complexe", *In preparation*. 3. Lina Ding, Wei-Hai Fang, "Exploring Light-Induced Decarboxylation Mechanism of o-Acetylphenyl-Acetic Acid from the Combined CASSCF and DFT Studies", *J. Org. Chem.* **2010**, 75, 1630-1636. 4. Lina Ding, Lin Shen, Xue-Bo Chen, Wei-Hai Fang, "Solvent Effects on photoreactivity of Valerophenone: A Combined QM and MM Study", *J. Org. Chem. Featured Article* **2009**, 74, 8956-8962. 5. Lina Ding, Xue-Bo Chen, Wei-Hai Fang, "Ultrafast Asynchronous Concerted Excited-State Intramolecular Proton Transfer and Photodecarboxylation of o-Acetylphenylacetic Acid Explored by Combined CASPT2 and CASSCF Studies", *Org. Lett.* **2009**, 11(7), 1495-1498. 6. Ganglong Cui, Lina Ding, Feng Feng, Yajun Liu, and Weihai Fang, "Insights into Mechanistic Photochemistry of Urea", *J. Chem. Phys.* **2010**, 132, 194308;
【学術関係の受賞など】	Beijing Normal University, Academic Excellence Award, 2009. Beijing Normal University, Scientific Achievement Award, 2010.

【氏名】	Hai-Bei Li
【職名】	JST Fellow
【所属】	Fukui Institute for Fundamental Chemistry
【研究室】	Room 203
【直通電話】	075-711-7834
【電子メールアドレス】	hpli@fukui.kyoto-u.ac.jp
【研究分野】	Computational Chemistry
【現在の研究課題】	MD simulations of the formation and growth of carbon nanostructures: fullerenes, and nanotubes
【研究内容キーワード】	Fullerene, Hydrocarbon combustions, Self-assembly, Single-walled carbon nanotube, Chirality, Graphene growth, Density-functional tight-bingding
【学歴】	2004, Bachelor of Chemistry, Qufu Normal University, China 2007, Master of Chemical Physics, University of Science and Technology of China, China 2010, Doctor of Chemical Physics, University of Science and Technology of China, China
【学位】	Doctor of Philosophy, University of Science and Technology of China
【主な著書、学術論文】 （過去 5 年以内）	1. Hai-Bei Li, Aister. J. Page, Sthephan. Irle and K. Morokuma, “Theoretical Insights for Chirality-Controlled SWCNT Growth from a Cycloparaphenylene Template”, *ChemPhysChem*, **13**, 1479, 2012. 2. Hai-Bei Li, Aister. J. Page, Ying Wang, Sthephan. Irle and K. Morokuma, “Sub-Surface Nucleation of Graphene Precursors near a Ni(111) Step- Edge”, *ChemComm*, Accepted. DOI:10.1039/c2cc32995f. 3. Hai-Bei Li, Shanxi Tian, and Jinlong Yang. Propene oxidation on $V_4O_{11}^-$ cluster: reaction dynamics to acrolein, *J. Phys. Chem. A*, **114**, 6542, 2010 4. Hai-Bei Li, Shanxi Tian, and Jinlong Yang. Propene oxidation with anionic cluster $V_4O_{11}^-$: selective epoxidation, *Chem. Eur. J* (communications) **15**, 10747, 2009 5. Hai-Bei Li, Shanxi Tian, and Jinlong Yang. Theoretical study of the stepwise protonation of the dioxo Manganese (V) porphyrin, *J. Phys. Chem. B*, **112**, 15807, 2008
【学術関係の受賞など】	Qiu Shi Graduate Student Scholarship (2009) Supported by the Scientific Research Foundation of Graduate School of USTC (2008)

【氏名】	Lung Wa Chung
【職名】	JST Fellow
【所属】	Fukui Kennichi Memorial Research Group 1, Fukui Institute For Fundamental Chemistry
【研究室】	Room 212
【直通電話】	075-711-7631
【電子メールアドレス】	chung@fukui.kyoto-u.ac.jp
【ホームページ】	https://sites.google.com/site/oscarlwchung/home
【研究分野】	Computational Chemistry, Biochemistry and Biophysics
【現在の研究課題】	Metalloenzymes, photobiology, multi-scale simulations
【研究内容キーワード】	Reaction mechanism of metalloenzymes, photobiology, bio-inspired systems and catalysis; multi-scale simulations development
【学歴】	Aug. 2000, B.Sc. in Chemistry (1st Hon.), The Hong Kong University of Science & Technology; Aug. 2003, M. Phil. in Chemistry, The Hong Kong University of Science & Technology; Aug. 2006, Ph. D. in Chemistry, The Hong Kong University of Science & Technology
【学位】	Ph. D. in chemistry, The Hong Kong University of Science & Technology
【主な著書、学術論文】 （過去5年以内）	1. Chung, L. W.; Li, X.; Sugimoto, H.; Shiro, Y.; Morokuma, K. "A DFT Study on a Missing Piece in Understanding of Heme Chemistry: The Reaction Mechanism for Indoleamine 2,3-Dioxygenase (IDO) and Tryptophan 2,3-Dioxygenase (TDO)" *J. Am. Chem. Soc.* **2008**, *130*, 12298. 2. Chung, L. W.; Hayashi, S.; Lundberg, M.; Nakatsu, T.; Kato, H.; Morokuma, K. "Mechanism of Efficient Firefly Bioluminescence via Adiabatic Transition State and Seam of Sloped Conical Intersection" *J. Am. Chem. Soc.* **2008**, *130*, 12880. 3. Li. X.; Chung, L. W.; Paneth, P.; Morokuma, K. "DFT and ONIOM(DFT:MM) Studies on Co-C Bond Cleavage and Hydrogen Transfer in B12-Dependent Methylmalonyl-CoA Mutase. Stepwise or Concerted Mechanism?" *J. Am. Chem. Soc.* **2009**, *131*, 5115. 4. Li. X.; Chung, L. W.; Mizuno, H.; Miyawaki, A.; Morokuma, K. "A Theoretical Study on the Natures of On- and Off-States of Reversibly Photoswitching Fluorescent Protein Dronpa: Absorption, Emission, Protonation and Raman" *J. Phys. Chem. B* **2010**, *114*, 1114 5. Chung, L. W.; Li, X.; Sugimoto, H.; Shiro, Y.; Morokuma, K. "ONIOM Study on a Missing Piece in Our Understanding of Heme Chemistry: Bacterial Tryptophan 2,3-Dioxygenase with Dual Oxidants", *J. Am. Chem. Soc.* **2010**, *115*, 11993. 6. Li, X.; Chung, L. W.; Mizuno, H.; Miyawaki, A.; Morokuma, K. "Primary Events of Photodynamic in Reversibly Photoswitching Fluorescent Protein Dronpa" *J. Phys. Chem. Lett.* **2010**, *1*, 3328. 7. Nakamura, A.; Munakata, K.; Ito, S.; Kochi, T.; Chung, L. W.; Morokuma, K.; Nozaki, K. "Pd-Catalyzed Copolymerization of Methyl Acrylate with Carbon Monoxide: Structures, Properties and Mechanistic Aspects toward Ligand Design" *J. Am. Chem. Soc.* **2011**, *133*, 6761. 8. Li, X.; Chung, L. W.; Morokuma, K. "Primary Events of Photodynamics of All-trans Protonated Retinal Schiff Base in Bacteriorhodopsin, Methanol Solution and Gas Phase" *J. Chem. Theory Comput. (Lett.)* **2011**, *7*, 2694. 9. Chung, L. W.; Hirao, H.; Li, X.; Morokuma, K. "The ONIOM Method: Its Foundation and Applications to Metalloenzymes and Photobiology", *WIREs Comput. Mol. Sci.* **2012**, *2*, 327. 10. Chung, L. W.; Li, X.; Hirao, H.; Morokuma, K. "Comparative Reactivity of Ferric-Superoxo and Ferryl-Oxo Species in Heme and non-Heme Complexes" *J. Am. Chem. Soc. (Commun.)* **2011**, *133*, 20076. 11. Tanaka, R.; Yamashita, M.; Chung, L. W.; Morokuma, K.; Nozaki, K. "Hydrogenation of Carbon Dioxide Catalyzed by Ir-PNP Complex: Reversibility and Reaction Mechanism" *Organometallics* **2011**, *30*, 6742.

【氏名】	Galina Petrova
【職名】	JST fellow
【所属】	Fukui Institute for Fundamental Chemistry
【研究室】	Room 208
【直通電話】	075-711-7894
【FAX】	075-711-7838
【電子メールアドレス】	petrova@fukui.kyoto-u.ac.jp
【研究分野】	Computational Chemistry
【現在の研究課題】	Hetero- and homogeneous catalysis
【研究内容キーワード】	metalloenzymes, DNA based asymmetric catalysis, reaction mechanisms
【学歴】	2009, Ph.D. degree in Organic chemistry, University of Sofia, Bulgaria 2003, B.Sc. in Chemistry (Theoretical and physical chemistry), University of Sofia, Bulgaria
【学位】	Ph.D. in Organic chemistry, University of Sofia, Bulgaria
【略歴】	12/2010-04/2012, Postdoctoral Scholar at FIFC, Kyoto University, Kyoto, Japan 02-11/2010, Postdoctoral Scholar at the Faculty of Chemistry, University of Sofia 06/2009–01/2010, Postdoctoral Scholar at the Faculty of Chemistry, University of Sofia & Excellence Centre for Advanced Materials UNION 7/2008–5/2009, Research chemist at the Faculty of Chemistry, University of Sofia
【所属学会】	Bulgarian Catalytic Club, Bulgarian Zeolite Association
【主な著書、学術論文】 （過去 5 年以内）	1. G. N. Vayssilov, G. P. Petrova, E. A. I. Shor, V. A. Nasluzov, A. M. Shor, P. S. Petkov, N. Rösch, “Reverse hydrogen spillover on and hydrogenation of supported metal clusters: Insights from computational model studies” *Phys. Chem. Chem. Phys.* **14**, 5879-5890 (2012). 2. G. N. Vayssilov, Y. Lykhach, A. Migani, T. Staudt, G. P. Petrova, N. Tsud, Tomáš Skála, A. Bruix, F. Illas, K. C. Prince, V. Matolín, K. M. Neyman, J. Libuda, “Support nanostructure boosts oxygen transfer to catalytically active platinum nanoparticles”, *Nature Materials*, **10**, 310–315 (2011). 3. G. P. Petrova, G. N. Vayssilov, N. Rösch, “Interaction of ethene and ethyne with bare and hydrogenated Ir_4 clusters. A density functional study”, *Catalysis Science & Technology*, **1**, 958-970 (2011). 4. N. Rösch, G. P. Petrova, P. St. Petkov, A. Genest, S. Krüger, H. A. Aleksandrov, G. N. Vayssilov, “Impurity Atoms on Small Transition Metal Clusters. Insights from Density Functional Model Studies”, *Topics in Catalysis*, **54**, 363-377 (2011). 5. M. A. Rangelov, G. P. Petrova, V. M. Yomtova, G. N. Vayssilov, “Catalytic Role of Vicinal OH in Ester Aminolysis - Proton Shuttle versus Hydrogen-Bonds Stabilization”, *J. Org. Chem.*, **75**, 6782–6792 (2010).
【学術関係の受賞など】	Student award for high academic achievements of the Foundation for support of the Bulgarian Higher Education named after Prof. Michael Klett (2003)

【氏名】	Raman Kumar Singh
【職名】	Post doctoral Researcher
【所属】	Fuel Cell Nanomaterials Centre, University of Yamanashi, Japan
【研究室】	6-43 Miyamae-cho, Kofu 400-0021
【直通電話】	055-254-7161
【FAX】	055-254-7161
【電子メールアドレス】	singh@yamanashi.ac.jp
【研究分野】	Computational Chemistry
【現在の研究課題】	Electronic structure calculation, electron-molecule resonance, proton conductivity of fuel cell membranes, nonlinear optical properties of materials, polyyne nano-fusion reactions
【研究内容キーワード】	Dyson orbital, vibrational excitation cross-sections, Nafion, polyyne, single-wall carbon nano tube
【学歴】	Dec 2004, Master of Technology, Birla Institute of Technology Mesra, India Jan 2010, Ph.D. in Chemistry, Indian Institute of Technology Bombay, India
【学位】	Ph.D. in Chemistry, Indian Institute of Technology Bombay, India
【略歴】	Feb 2010, Postdoctoral Researcher, RIKEN Advanced Science Institute, Japan April 2011,Postdoctoral Fellow, FIFC, Kyoto University, Japan Sept 2011, Postdoctoral Researcher, Fuel Cell Nanomaterials Centre, University of Yamanashi, Japan
【主な著書、学術論文】 （過去 5 年以内）	1. Raman K. Singh, Takao Tsuneda, Kenji Miyatake and Masahiro Watanabe, "Theoretical Investigation of Proton Conductivity in Proton Exchange Membranes for Fuel cells", *J. Phys. Chem. B*, submitted (2012). 2. Raman K. Singh and Takao Tsuneda, "Reaction Energetics on Long-range Corrected Density Functional Theory: Diels-Alder Reactions", *J. Comput. Chem.*, revised submitted (2012). 3. Raman K. Singh and M. K. Mishra, "Investigation of Ethynylpyridines using the Electron Propagator Theory", *Int. J. Quant. Chem.* **112**(2), 426-439 (2012). 4. Raman K. Singh, Takao Tsuneda and Kimihiko Hirao, "An Examination of Density Functionals on Aldol, Mannich and α-Aminoxylation Reactions Enthalpy Calculations", *Theor. Chem. Acc.* **130** (2-3), 153-160 (2011). 5. Raman K. Singh, J. V. Ortiz and M. K. Mishra, "Tautomeric Forms of Adenine: Vertical Ionization Energies and Dyson Orbital", *Int. J. Quant. Chem.* **110**(10), 1901-1915 (2010). 6. Raman K. Singh and M. K. Mishra, Investigation of Ethynylfurans using the Electron Propagator Theory, *J. Phys. Chem. A*, **113**(51), 14150-14155 (2009). 7. Raman K. Singh and M. K. Mishra, "Electronic Structure Analysis and Vertical Ionization Energies of Thiophene and Ethynylthiophenes", *J. Chem. Sci.*, **121**(5), 867-872 (2009). 8. J. Melin, Raman K. Singh, M. K. Mishra and J. V. Ortiz, Tautomeric Forms of Azolide Anions: Vertical Electron Detachment Energies and Dyson Orbitals, *J. Phys. Chem. A*, **111**(50), 13069-13074 (2007). 9. Raman K. Singh, M Sarma, A Jain, S Adhikari and M K Mishra, "Calculation of Vibrational Excitation Cross-Sections in resonant e-molecule scattering using the time dependent wave packet(TDWP) approach with application to the 2Π CO-shape resonance", *J. Chem. Sci.*, **119**(5), 385-389 (2007). 10. Raman K. Singh, M. Sarma and M. K. Mishra, "Approximate construction of local complex potentials for a time dependent wave packet based treatment of vibrational excitation cross-sections in resonant e-N2, e-CO and e-H2 scattering", *Indian J. Phys.*, **81**(10), 983-1002 (2007). 11. M. Sarma, Raman K. Singh and M. K. Mishra, "Local complex potential based time dependent wave packet approach to calculation of vibrational excitation cross-sections in e-N2, e-H2 and e-CO scattering," *Computation in Modern Science and Engineering,* Volume 2, Part A (American Institute of Physics), 963,227-230 (2007).
【学術関係の受賞など】	Fellowship for SAARC / IAESTE- Japan Academic Internship Programme 2008

【氏名】	Travis Harris
【職名】	JSPS Foreign Researcher
【所属】	Fukui Kenichi Memorial Research Group 1, Fukui Institute for Fundamental Chemistry
【研究室】	212
【直通電話】	075-711-7631
【FAX】	075-781-4757
【電子メールアドレス】	tvharris@fukui.kyoto-u.ac.jp
【研究分野】	Computational Chemistry
【現在の研究課題】	Computational studies of metalloenzymatic reactions
【研究内容キーワード】	Ferritin, ferroxidase, di-iron, non-heme
【学歴】	2006, B.A. (summa cum laude), Willamette University, Salem, OR, USA 2011, Ph.D., Montana State University, Bozeman, MT, USA
【学位】	Doctor of Philosophy, Montana State University, Bozeman, MT, USA
【略歴】	2011, General Chemistry Lab TA, Montana State University 2007, Research Assistant, Montana State University 2006, Biochemistry Lab TA, Willamette University
【主な著書、学術論文】 （過去 5 年以内）	1. Harris, T. V.; Szilagyi, R. K. Comparative Assessment of the Composition and Charge State of Nitrogenase FeMo-Cofactor. *Inorg. Chem.*, **2011**, *50* (11), 4811. 2. Harris, T. V.; Szilagyi, R. K. Nitrogenase Structure and Function Relationships by Density Functional Theory. In *Nitrogen Fixation: Methods and Protocols*; Ribbe, M. W. Ed.; Humana Press: New York, 2011; pp 267-292. 3. Harris, T. V.; Szilagyi, R. K.; McFarlane Holman, K. L. Electronic Structural Investigations of Ruthenium Compounds and Anticancer Prodrugs. *J. Biol. Inorg. Chem.* **2009**, *14* (6), 891. 4. Pool, V. L.; Klem, M. T.; Holroyd, J.; Harris, T.; Arenholz, E.; Young, M.; Douglas, T.; Idzerda, Y. U. Site Determination of Zn Doping in Protein Encapsulated $Zn_xFe_{3-x}O_4$ Nanoparticles. *J. Appl. Phys.* **2009**, *105* (7), 07B515. 5. Pandey, A. S.; Harris, T. V.; Giles, L. J.; Peters, J. W.; Szilagyi, R. K. Dithiomethylether as a Ligand in the Hydrogenase H-Cluster. *J. Am. Chem. Soc.* **2008**, *130* (13), 4533.
【学術関係の受賞など】	NSF Materials Computation Center Travel Grant, 2011 Kopriva Graduate Student Fellowship, 2009 Molecular Biosciences Fellowship, 2007–2011 Mildred Livingston Grant, 2007–2008 ACS Montana Travel Grant, 2007

【氏名】	Yuh Hijikata
【職名】	FIFC Fellow
【所属】	Fukui Institute for Fundamental Chemistry
【研究室】	Room 303
【直通電話】	075-711-7907
【電子メールアドレス】	hijikata@fukui.kyoto-u.ac.jp
【ホームページ】	http://www.users.iimc.kyoto-u.ac.jp/~z59354/member_e/hijikata.html
【研究分野】	Quantum Chemistry, Coordination Chemistry
【現在の研究課題】	Gas Adsorption
【研究内容キーワード】	Porous Coordination Polymers
【学歴】	Mar 2008, Master of Eng., Graduate School of Engineering, Kyoto University May 2011, Ph.D. of Eng., Graduate School of Engineering, Kyoto University
【学位】	Ph.D. of Eng. from Kyoto University
【略歴】	Oct. 2011- FIFC Fellow (Kyoto University) Apr. 2011-Sep. 2011 Specially Promoted Research Fellow (Kyoto University) Apr. 2008-Mar. 2011 JSPS Research Fellow (DC1) (Kyoto University)
【所属学会】	Chemical Society of Japan, Japan Society of Coordination Chemistry, Japan Society for Molecular Science
【主な著書、学術論文】（過去 5 年以内）	1. Nobuhiro YANAI, Koji KITAYAMA, Yuh HIJIKATA, Hiroshi SATO, Ryotaro MATSUDA, Yoshiki KUBOTA, Masaki TAKATA, Motohiro MIZUNO, Takashi UEMURA, and Susumu KITAGAWA, “Reporting structural transformation of soft porous crystals for detection of CO_2”, *Nat. Mater.*, **10**, 787-793 (2011) 2. Yuh HIJIKATA, Satoshi HORIKE, Daisuke TANAKA, Juergen GROLL, Motohiro MIZUNO, Jungeun KIM, Masaki TAKATA, and Susumu KITAGAWA, Differences of crystal structure and dynamics between soft porous nanocrystal and bulk crystal”, *Chem. Commun.*, **47**, 7632-7634 (2011) 3. Yuh HIJIKATA, Satoshi HORIKE, Masayuki SUGIMOTO, Hiroshi SATO, Ryotaro MATSUDA, and Susumu KITAGAWA, “Relationship between Channel and Sorption Properties in Coordination Polymers with Interdigitated Structures”, *Chem. Eur. J.*, **17**, 5138-5144 (2011) 4. Satoru SHIMOMURA, Masakazu HIGUCHI, Ryotaro MATSUDA, Ko YONEDA, Yuh HIJIKATA, Yoshiki KUBOTA, Yoshimi MITA, Jugeun KIM, Masaki TAKATA, and Susumu KITAGAWA, “Selective Sorption of oxygen and nitric oxide by an electron-donating flexible porous coordination polymer”, *Nat. Chem.*, **2**, 633-637 (2010) 5. Yuh HIJIKATA, Hiroyuki NAKASHIMA, and Hiroshi NAKATSUJI, “Solving non-Born-Oppenheimer Schrödinger equation for hydrogen molecular ion and its isotopomers using the free complement method”, *J. Chem. Phys.*, **130**, 024102-1-11 (2009)
【学術関係の受賞など】	JSPS Research Fellowships for Young Scientists (DC1) 2008-2011

【氏名（ふりがな）】	青野　信治　（あおの　しんじ）
【職名】	特推研究フェロー
【所属】	京都大学 福井謙一記念研究センター
【研究室】	福井記念研究センター 303 号室
【直通電話】	075-711-7907
【電子メールアドレス】	saono@fukui.kyoto-u.ac.jp
【研究分野】	溶液化学・計算化学・理論化学
【現在の研究課題】	溶液中の遷移金属錯体の化学反応の理論的解析
【研究内容キーワード】	3D-RISM-SCF 法、平均場 QM/MM 法、自由エネルギー解析、溶媒和構造解析、周期的結晶解析
【学歴】	2010 年 3 月 京都大学大学院理学研究科化学専攻博士後期課程研究指導認定退学
【学位】	2010 年 9 月 理学博士（京都大学）
【略歴】	2010 年 4 月 京都大学大学院理学研究科化学専攻 研修員 2010 年 5 月 京都大学 物質 - 細胞統合システム拠点 教務補佐員 2010 年 10 月 京都大学 物質 - 細胞統合システム拠点 特定研究員 2011 年 4 月 京都大学 福井謙一記念研究センター 特定研究員
【主な著書、学術論文】 （過去 5 年以内）	1. Aono S., Sakaki S., “Proposal of new QM/MM approach for geometry optimization of periodic molecular crystal: Self-consistent point charge representation for crystalline effect on target QM molecule” *Chem. Phys. Lett.* (accepted 2012). 2. Aono S., Yamamoto T. and Kato S. “Solution reaction space Hamiltonian based on an electrostatic potential representation of solvent dynamics” *J. Chem. Phys.* **134** 144108 (2011). 3. Aono S., Kato S. “Proton Transfer in Phenol-Amine Complexes: Phenol Electronic Effect on Free Energy Profile in Solution” *J. Comput. Chem.* **31** 2924-2931 (2010). 4. Aono S., Minezawa N. and Kato S. “Electronic spectra of coumarin-151 in polar solvents: Linear response free energy approach” *Chem. Phys. Lett.* **492** 193-197 (2010).

【氏名（ふりがな）】	塚本　晋也　（つかもと　しんや）
【職名】	特推研究フェロー
【所属】	福井謙一記念研究センター　福井謙一研究部第二　榊グループ
【研究室】	福井謙一記念研究センター　301
【直通電話】	075-711-7907
【FAX】	075-711-4757
【電子メールアドレス】	stsukamoto@fukui.kyoto-u.ac.jp
【ホームページ】	http://www.users.iimc.kyoto-u.ac.jp/~z59354/
【研究分野】	計算化学・理論化学
【現在の研究課題】	遷移金属錯体の理論研究
【研究内容キーワード】	遷移金属
【学歴】	2010 年九州大学大学院総合理工学府量子プロセス理工学専攻博士後期課程修了
【学位】	2010 年 3 月博士（理学）（九州大学）
【所属学会】	分子科学会、American Chemical Society
【主な著書、学術論文】（過去 5 年以内）	1. “Experimental and Theoretical Approaches Toward Anion-responsive Tripode-Lanthanide Complexes: Mixed Donor Ligand Effects on Highly Coordinated Complexation and Luminescence Sensing Profiles” Y. Kataoka, D. Paul, H. Miyoka, T. Yaita, E. Miyoshi, H. Mori, S. Tsukamoto, H. Tatewaki, S. Shinoda, and H. Tsukube, *Chem. A Eur. J.* **2008**, 14, 5258 2. “CASSCF and CASPT2 calculations for lanthanide trihalides LnX3 using model core potentials” S. Tsukamoto, H. Mori, H. Tatewaki, and E. Miyoshi, *Chem. Phys. Lett.* **2009**, 474, 28 3. “Theoretical Study of Pt(PR3)2(AlCl3)(R-H, Me, Ph, or Cy) Including an Unsupported Bond between Transition Metal and Non-Transition Metal Elements; Geometry, Bond Strength, and Prediction” S. Tsukamoto and S. Sakaki, *J. Phys. Chem. A*, **2011**, 115, 8520 4. “Theoretical Study of Metallasilatranes; Bonding Nature and Prediction of New Metallasilatrane” S. Sakaki, D. Kawai, and S. Tsukamoto, *Collect. Czech. Chem. Comm*, **2011**, 76, 619

【氏名】	Milind Madhusudan Deshmukh
【職名】	SPR Fellow
【所属】	Fukui Institute for Fundamental Chemistry
【研究室】	Room 304
【直通電話】	075-711-7907
【電子メールアドレス】	milind@fukui.kyoto-u.ac.jp
【ホームページ】	http://www.users.iimc.kyoto-u.ac.jp/~z59354/member_j/milind.html
【研究分野】	Theoretical and Computational Chemistry
【現在の研究課題】	Trapping gas molecules in Metal Organic Framework, Non covalent Interactions
【研究内容キーワード】	Metal-Organic Framework, Binding Energy, Potential Energy Surface
【学歴】	March 2001, Master of Sci., University of Pune, India October 2008, Doctor of Philosophy, Department of Chemistry, University of Pune, India
【学位】	Doctor of Philosophy from Department of Chemistry, University of Pune, India
【略歴】	August 2008 to April 2010: Postdoctoral Research Fellow, Tata Institute of Fundamental Research, Mumbai, India June 2010 to present: Postdoctoral Research Fellow, Kyoto University, Japan
【主な著書、学術論文】（過去 5 年以内）	1. Milind M. Deshmukh, and Shigeyoshi Sakaki, “Two-step Evaluation of Potential Energy Surface and Binding Energy of van der Waals Complexes” *J. Comput. Chem.* **33** 617 (2012). 2. Jayasree K. Kedkar, Milind M. Deshmukh, Shridhar R. Gadre. Shridhar P. Gejji, “Intramolecular Hydrogen Bonding and cooperative interactions in Calix[n]arenes (n = 4, 5)” *J. Phys. Chem. A.* **116**, 3739 (2012). 3. Milind M. Deshmukh and Shigeyoshi Sakaki, “Binding Energy of Gas Molecule with Two Pyrazine Molecules as Organic Linker in Metal-Organic Framework: Its Theoretical Evaluation and Understanding of Determining Factors” *Theo. Chem. Acc.* **130**, 475 (2011). 4. Milind M. Deshmukh, Bartolotti Libero Jr., and Shridhar R. Gadre, “Intramolecular Hydrogen Bond Energy and Cooperative Interactions in α-, β-, and γ-Cyclodextrin Conformers”, *J. Comput. Chem.* **32**, 2996 (2011). 5. Milind M. Deshmukh and Shridhar R. Gadre, “Estimation of N-H···O=C Intramolecular Hydrogen Bond Energy in Polypeptides”, *J. Phys. Chem. A.* **113**, 7927 (2009).
【学術関係の受賞など】	Senior Research Fellowship of Council of Scientific and Industrial Research (CSIR) 2005-2008. Senior Research Fellowship of Centre for Developing Advanced Computing (CDAC), Pune, 2004-2005.

【氏名】	Guixiang Zeng
【職名】	SPR Fellow
【所属】	Fukui Institute for Fundamental Chemistry
【研究室】	Room 303
【直通電話】	075-711-7907
【電子メールアドレス】	guixang.zeng@fukui.kyoto-u.ac.jp
【研究分野】	Computational Chemistry
【現在の研究課題】	Unusual Electronic Process of the H－H bond activation across a Ni－B unit
【研究内容キーワード】	H－H bond activation, metal-ligand cooperation mode, first-row transition metals
【学歴】	June 2010, Ph. D., School of Chemistry & Chemical Engineering, Nanjing University
【学位】	Ph. D. in Physical Chemistry from Nanjing University
【略歴】	Sep. 2010~, Postdoctoral Fellow, Kyoto University
【主な著書、学術論文】 （過去 5 年以内）	1. Guixiang Zeng, Yong Guo, Shuhua Li, “H_2 activation by a (PNP)Ir(C_6H_5)complex via the dearomatization/aromatization process of the PNP ligand: A computational study” *Inorg. Chem.* **48**, 10257 (2009). 2. Guixiang Zeng, Shuhua Li, “Mechanistic insight on the hydrogenation of conjugated alkenes with H_2 catalyzed by early main-group metal catalysts” *Inorg. Chem.* **49**, 3361 (2010). 3. Guixiang Zeng, Shuhua Li, “Insights on Dehydrogenative Coupling of Alcohols and Amines catalyzed by a (PNN)−Ru(II) Hydride Complex: Unusual Metal−Ligand Cooperation” *Inorg. Chem.* **50**, 10572 (2011). 4. Guixiang Zeng, Shigeyoshi Sakaki, “Noble Reaction Features of Bromoborane in Oxidative Addition of B−Br σ−Bond to $[M(PMe_3)_2]$ (M= Pt or Pd): Theoretical Study” *Inorg. Chem.* **50**, 5290 (2011). 5. Guixiang Zeng, Shigeyoshi Sakaki, “Theoretical Study on the Transition-Metal Oxoboryl Complex: M−BO Bonding Nature, Mechanism of the Formation Reaction, and Prediction of a New Oxoboryl Complex” *Inorg. Chem.* **51**, 4597 (2012)

【氏名（ふりがな）】	高木　望（たかぎ　のぞみ）
【職名】	特推研究フェロー
【所属】	福井謙一記念研究センター
【研究室】	福井謙一記念研究センター　榊研究室
【直通電話】	075-711-7907
【電子メールアドレス】	takagi@fukui.kyoto-u.ac.jp
【研究分野】	計算化学・理論化学
【現在の研究課題】	d- 電子複合系の理論化学、新規な化学結合を有する分子の設計と結合解析
【研究内容キーワード】	遷移金属元素、高周期典型元素、分子軌道計算
【学歴】	1997 年 3 月　立教大学理学部化学科　卒業 1999 年 3 月　東京都立大学大学院理学研究科化学専攻修士士課程　修了 2002 年 3 月　東京都立大学大学院理学研究科化学専攻博士課程　修了
【学位】	2002 年 3 月　理学博士（東京都立大学）
【略歴】	2002 年 4 月　日本学術振興会　特別研究員 (PD) 2005 年 4 月　自然科学研究機構・分子科学研究所　専門研究職員 2007 年 5 月　ドイツ・フィリップス = マールブルク大学　博士研究員 2011 年 1 月　自然科学研究機構・分子科学研究所　専門研究職員 2011 年 4 月　京都大学・福井謙一記念研究センター　特定研究員
【在外研究歴】	2007 年 5 月 -2010 年 12 月　ドイツ・フィリップス = マールブルク大学　博士研究員（Gernot Frenking 教授）
【所属学会】	日本化学会
【主な著書、学術論文】（過去 5 年以内）	1. “A Theoretical Study of Unusual Y-Shaped Three-coordinate Pt Complex: Pt(0) σ-Disilane Complex or Pt(II) Disilyl Complex?” N. Takagi, S. Sakaki, *J. Am. Chem. Soc., in press*. 2. “Carbodiphosphorane-Analogues $E(PPh_3)_2$ with E = C - Pb. A Theoretical Study with implications for ligand design” N. Takagi, R. Tonner, G. Frenking, *Chem. Eur. J.*, **18**, 1772-1780 (2012). 3. “Bonding Situation in “Early-Late” Transition Metal Complexes $Cl_3M-M'(PCl_3)_4$ (M = Ti, Zr, Hf; M’= Co, Rh, Ir) - Theoretical Study for a Ligand Fine Tuning of M-M’ Bonds -” N. Takagi, A. Krapp, G. Frenking, Z. *Anorg. Alleg. Chem.* **637**, 1728-1735 (2011). 4. “Divalent Pb(0) Compounds” N. Takagi, G. Frenking, *Theor. Chem. Acc.*, **129**, 615-623 (2011). 5. “Bonding Analysis for Metal-Metal Multiple bonds in $R_3M-M'R_3$ (M, M’ = Cr, Mo, W; R = Cl, NMe_2)” N. Takagi, A. Krapp, G. Frenking, *Inorg. Chem.*, **50**, 819-826 (2010). 6. “On the nature of homo- and heterodinuclear metal-metal quadruple bonds – Analysis of the bonding situation and benchmarking DFT against wavefunction methods” N. Takagi, A. Krapp, G. Frenking, *Can. J. Chem.*, **88**, 1079-1093 (2010). 7. “Divalent E(0) Compounds (E = Si - Sn)” N Takagi, T. Shimizu, G. Frenking, *Chem. Eur. J.*, **15**, 8593-8604 (2009). 8. “Divalent Si(0) Compounds” N Takagi, T. Shimizu, G. Frenking, *Chem. Eur. J.*, **15**, 3448-3456 (2009). 9. “Do Lead Analogues of Alkynes Take a Multiply Bonded Structure?” N. Takagi, S. Nagase, *Organometallics*, **26**, 3627-3629 (2007). 10. “Tin Analogues of Alkynes. Multiply Bonded Structures vs Singly Bonded Structures” N. Takagi, S. Nagase, *Organometallics*, **26**, 469-471 (2007). 11. “Effects of Bulky Substituent Groups on the Si-Si Triple Bonding in $RSi\equiv SiR$ and the Short Ga-Ga Distance in $Na_2[RGaGaR]$. A Theoretical Study” N. Takagi, and S. Nagase, *J. Organomet. Chem.* **692**, 217-224 (2007).
【学術関係の受賞など】	2002 年 -2005 年　日本学術振興会　特別研究員 (PD)

【氏名】	Masayuki Nakagaki
【職名】	SPR Fellow
【所属】	Fukui Institute for Fundamental Chemistry
【研究室】	Room 303
【直通電話】	075-711-7907
【電子メールアドレス】	nakagaki@fukui.kyoto-u.ac.jp
【ホームページ】	http://www.fukui.kyoto-u.ac.jp/
【研究分野】	Computational Chemistry
【現在の研究課題】	Electronic Structure of Inverted Sandwich Type Complexes
【研究内容キーワード】	Electronic Structure of Metal Complex, Multireference Theory
【学歴】	March 2005, Master of Sci., Graduate School of Science, Kyushu University March 2009, Doctor of Sci., Graduate School of Science, Kyushu University
【学位】	Doctor of Science from Kyushu University
【略歴】	Apr. 2009, Postdoctoral Fellow, Kyushu University
【所属学会】	Japan Society for Molecular Science
【主な著書、学術論文】 （過去 5 年以内）	1. M. Nakagaki, E. Nishi, K. Sakota, H. Nakano, H. Sekiya, “A model two-dimensional potential for internal rotation of 9-methylanthracene studied by electronic spectroscopy and DFT calculations” *Chem. Phys.* **328**, 190-196 (2006) 2. K. Sakota, Y. Komoto, M. Nakagaki, W. Ishikawa, H. Sekiya “Observ- ation of a catalytic proton/hydrogen atom relay in microsolvated 7-azaindole-methanol cluster enhanced by a cooperative motion of the hydrogen-bonded network” *Chem. Phys. Lett.* **435**, 1-4 (2007) 3. X. Zhang, Y. Komoto, K. Sakota, M. Nakagaki, H. Nakano, T. Shinmyozu, H. Sekiya “Heavy mass effect on excited-state double-proton transfer in 7-azaindole dimer by Cl substitution” *Chem. Phys. Lett.* **441**, 176-180 (2007) 4. X. Zhang, Y. Komoto, K. Sakota, N. Masayuki, T. Shinmyozu, S. Nanbu, H. Nakano, H. Sekiya “Remarkable suppression of the excited-state double-proton transfer in the 7-azaindole dimer due to substitution of the dimethylamino group studied by electronic spectroscopy in the gas phase” *Chem. Phys. Lett.* **443**, 194-198 (2007)

【氏名】	Terutaka Yoshizawa
【職名】	SPR Fellow
【所属】	Fukui Institute for Fundamental Chemistry
【研究室】	Room 303
【直通電話】	075-711-7907
【FAX】	075-711-4757
【電子メールアドレス】	yoshizawa@fukui.kyoto-u.ac.jp
【ホームページ】	http://www.users.iimc.kyoto-u.ac.jp/~z59354/
【研究分野】	Theoretical chemistry
【現在の研究課題】	Relativistic quantum chemical calculations of NMR shielding constants
【研究内容キーワード】	NMR, DFT, Douglas–Kroll–Hess method, Transition metal complexes
【学歴】	March 2006, Master of Sci., Graduate School of Science, Tokyo Metropolitan University March 2009, Doctor of Sci., Graduate School of Science and Engineering, Tokyo Metropolitan University
【学位】	Doctor of Science from Tokyo Metropolitan University
【略歴】	Apr. 2009, Postdoctoral Fellow, Kyushu University Jan. 2010, Postdoctoral Fellow, RIKEN Apr. 2011, (SPR) Fellow, Kyoto University
【主な著書、学術論文】 （過去 5 年以内）	1. T. Yoshizawa and M. Hada, "Calculations of Frequency-Dependent Molecular Magnetizabilities with Quasi-Relativistic Time-Dependent Generalized Unrestricted Hartree-Fock Method", *J. Comput. Chem.* **28**, 740–747, (2007) 2. T. Yoshizawa and M. Hada, "Relativistic quantum-chemical calculations of magnetizabilities of noble gas atoms using the Douglas–Kroll–Hess method", *Chem. Phys. Lett.* **458**, 223–226, (2008) 3. T. Yoshizawa and M. Hada, "Relativistic and Electron–Correlation Effects on Magnetizabilities Investigated by the Douglas–Kroll–Hess Method and the Second-Order Møller–Plesset Perturbation Theory", *J. Comput. Chem.* **30**, 2550–2566, (2009) 4. T. Yoshizawa and T. Nakajima, "Second-order generalized unrestricted Moller–Plesset perturbation theory for the spin–orbit part of zero-field splitting tensors", *Chem. Phys. Lett.* **515**, 296–301, (2011)
【学術関係の受賞など】	JSPS Research Fellowships for Young Scientists(DC) 2007-2009

【氏名（ふりがな）】	中谷　直輝　（なかたに　なおき）
【職名】	Postdoctral Associate
【所属】	Department of Chemistry, Princeton University
【研究室】	Frick Chemistry Laboratory, #355
【直通電話】	+1-609-258-9369
【電子メールアドレス】	naokin@princeton.edu
【研究分野】	理論・計算化学
【現在の研究課題】	テンソルネットワークアルゴリズムによるDMRGの多次元化
【研究内容キーワード】	DMRG, テンソルネットワーク、デンドリマー、遷移金属錯体
【学歴】	2010年3月　京都大学大学院工学研究科分子工学専攻博士課程修了
【学位】	2010年3月　工学博士（京都大学）
【略歴】	2009年4月　学術振興会特別研究員（DC2） 2011年4月　福井謙一記念研究センター研究フェロー
【主な著書、学術論文】 （過去5年以内）	1. Naoki Nakatani, Jun-ya Hasegawa, and Hiroshi Nakatsuji, “Red Light in Chemiluminescence and Yellow-Green Light in Bioluminescence: Color-Tuning Mechanism of Firefly, *Photinus Pyralis*, Studied by the Symmetry-Adapted Cluster-Configuration Interaction Method” *J. Am. Chem. Soc.* **129**(28), 8756-8765 (2007) 2. Naoki Nakatani, Jun-ya Hasegawa, and Hiroshi Nakatsuji, “Artificial color tuning of firefly luminescence: Theoretical mutation by tuning electronic interactions between protein and luciferin” *Chem. Phys. Lett.* **469**, 191-194 (2009) 3. Naoki Nakatani, Yoshihide Nakao, Hirofumi Sato, and Shigeyoshi Sakaki, “Theoretical Study of the Iron Sulfur Cluster-free Hydrogenase (Hmd): What is the Active Center of Hmd?” *Chem. Lett.* **38**(10), 958-959 (2009) 4. Naoki Nakatani, Yoshihide Nakao, Hirofumi Sato, and Shigeyoshi Sakaki, “Theoretical Study of Dioxygen Binding Process in Iron(III) Catechol Dioxygenase: “Oxygen Activation” vs. “Substrate Activation”” *J. Phys. Chem. B* **113**, 4826-4836 (2009) 5. Naoki Nakatani, Yutaka Hitomi, and Shigeyoshi Sakaki, “Multistate CASPT2 Study of Native Iron(III)-Dependent Catechol Dioxygenase and Its Functional Models: Electronic Structure and Ligand-to-Metal Charge-Transfer Excitation” *J. Phys. Chem. B* **115**, 4781-4789 (2011)
【学術関係の受賞など】	Poster Award on the 48th Sanibel Symposium (2008)

【氏名（ふりがな）】	松井　亨　（まつい　とおる）
【職名】	日本学術振興会 特別研究員 (PD)
【所属】	大阪大学大学院 理学研究科 化学専攻
【研究室】	奥村研究室
【直通電話】	06-6850-5405
【FAX】	06-6850-5550
【電子メールアドレス】	tmatsui@fukui.kyoto-u.ac.jp
【ホームページ】	http://www.users.iimc.kyoto-u.ac.jp/~z59354/member_j/matsui.html
【研究分野】	生物無機化学 , 生物物理化学
【現在の研究課題】	酸化還元電位の算出法
【研究内容キーワード】	酸化還元電位 , 酸解離定数 , pKa
【学歴】	2009 年 3 月 東京大学大学院工学系研究科応用化学専攻 博士課程修了
【学位】	2009 年 3 月 工学博士 (東京大学)
【略歴】	2008 年 4 月 日本学術振興会特別研究員 (DC2, 東京大学), 2009 年 4 月 日本学術振興会特別研究員 (DC2, 大阪大学), 2010 年 4 月 兵庫県立大学大学院生命理学研究科 特任助教 , 2011 年 4 月 日本学術振興会特別研究員 (PD), 福井謙一記念研究センター 客員研究員
【所属学会】	日本化学会 , 日本分子科学会
【主な著書、学術論文】 （過去 5 年以内）	1. T. Matsui, T. Sato and Y. Shigeta, “Sequence dependent proton-transfer reaction in stacked GC pair II: The origin of stabilities of proton-transfer products”, *Chemical Physics Letters*, **478**, pp.238-242 (2009). 2. T. Matsui, H. Miyachi, Y. Nakanishi, Y. Shigeta, T. Sato, Y. Kitagawa, M. Okumura and K. Hirao, “Theoretical Studies on Sulfur and Metal Cation (Cu(II), Ni(II), Pd(II), and Pt(II))-Containing Artificial DNA”, *Journal of Physical Chemistry B*, **113**, pp.12790-12795 (2008). 3. H. Miyachi, T. Matsui, Y. Shigeta and K. Hirao, “Effects of mercury(II) on structural properties, electronic structure and UV absorption spectra of a duplex containing thymine-mercury(II)-thymine nucleobase pairs”, *Physical Chemistry Chemical Physics*, pp. 909-917 (2010). 4. T. Matsui, A. Oshiyama and Y. Shigeta, “A Simple Scheme for pKa of 5-substituted Uracils” *Chemical Physics Letters*, **502**, pp.238-242 (2011). 5. Y. Nakanishi, T. Matsui, Y. Kitagawa, Y. Shigeta, T. Saito, Y. Kataoka, T. Kawakami, M. Okumura and K. Yamaguchi, “Electron Conductivity in Modified Models of Artificial Metal-DNA Using Green's Function-Based Scattering Theory”, *Bulletin of Chemical Society of Japan*, **84**, pp.366-375 (2011). 6. T. Matsui, H. Miyachi, T. Baba and Y. Shigeta, “A Theoretical Study on Reaction Scheme of Silver (I) Containing 5-Substituted Uracils Bridge Formation”, *the Journal of Physical Chemistry A*,.**115**, pp.8524-8531 (2011). 7. K. Kamiya, T. Matsui, T. Sugimura and Y. Shigeta, “Theoretical Insight into Stereoselective Reaction Mechanisms of 2,4-Pentanediol-Tethered Ketene-Olefin [2+2] Cycloaddition”, *The Journal of Physical Chemistry A*,**116**, pp. 1168-1175 (2012). 8. T. Matsui, T. Baba, K. Kamiya and Y. Shigeta, “'An accurate density functional theory based estimation of pKa value of polar residues combined with experimental data: from amino acids to minimal proteins”, *Physical Chemistry Chemical Physics*,**14**, pp. 4181-4187 (2012). 9. T. Matsui, H. Miyachi, Y. Shigeta and K. Hirao (2012) “Metal-Assisted Proton Transfer in Guanine-Cytosine Pair: An Approach from Quantum Chemistry”, in Some Applications of Quantum Mechanics, ISBN 978-953-51-0059-1, edited by Mohammad Reza Pahlavani , *InTech*, pp. 167-188.

【氏名】	Wilfredo Credo Chung
【職名】	Associate Professor 5
【所属】	Department of Chemistry, De La Salle University – Manila, Philippines
【研究室】	Room 312, St. Joseph Hall
【直通電話】	+63 2 536 0230
【FAX】	+63 2 524 0451
【電子メールアドレス】	wilfredo.chung@dlsu.edu.ph
【研究分野】	Computational Chemistry
【現在の研究課題】	Theoretical elucidation of reaction mechanisms and dynamics of important molecules in the electronic ground and excited states
【研究内容キーワード】	potential energy surface, wave packet dynamics, conical intersection, diabatic representation, QM/MM
【学歴】	March 1991, Bachelor of Science in Chemical Engineering, University of San Carlos, Cebu City, Philippines October 1999, Master of Science in Chemistry, Mindanao State University − Iligan Institute of Technology, Iligan City, Philippines March 2007, Doctor of Science, Graduate School of Science, Tohoku University
【学位】	Doctor of Science, Tohoku University
【略歴】	March 1992 − June 1993 Research and Development Chemist, Treasure Island Industrial Corporation, Cebu City, Philippines June 1994 − October 1996 Lecturer, Colleges of Arts, Sciences and Engineering, Saint Joseph Institute of Technology, Butuan City, Philippines November 1996 − March 2003 Lecturer, Department of Chemistry, Northern Mindanao State Institute of Science and Technology, Butuan City, Philippines August 2007 − September 2007 Postdoctoral Fellow, Laboratory of Theoretical Chemistry, Tohoku University October 2007 – September 2011 Center Fellow, Fukui Institute for Fundamental Chemistry, Kyoto University May 2012 – present Associate Professor 5, Department of Chemistry, De La Salle University – Manila, Philippines
【所属学会】	Chemical Society of Japan, Japan Society for Molecular Science, Chemical Society of the Philipines, Samahang Pisika ng Visayas at Mindanao
【主な著書、学術論文】 （過去 5 年以内）	1. W. C. Chung, S. Nanbu and T. Ishida, QM/MM Trajectory Surface Hopping Approach to Photoisomerization of Rhodopsin and Isorhodopsin: The Origin of Faster and More Efficient Isomerization for Rhodopsin, *J. Phys. Chem. B*, **116** (28), 8009–8023 (2012). 2. W. C. Chung, S. Nanbu and T. Ishida, A Nonadiabatic Ab Initio Dynamics Study on Rhodopsin and Its Analog Isorhodopsin: Chemical Dynamics Reasons behind Selection of Rhodopsin by Life, *Chemistry Letters* **40**, 1395-1397 (2011). 3. W. C. Chung and T. Ishida, An MD simulation of the decoy action of Epstein–Barr virus LMP1 protein mimicking the CD40 interaction with TRAF3, *Theoretical Chemistry Accounts* **130**, 401-410 (2011). 4. W. C. Chung, S. Nanbu and T. Ishida, Nonadiabatic ab initio dynamics of a model protonated Schiff base of 9-cis retinal, *J. Phys. Chem. A* **114**, 8190–8201 (2010). 5. W. M. I. Hassan, W. C. Chung, N. Shimakura, S. Koseki, H. Kono and Y. Fujimura Ultrafast radiationless transition pathways through conical intersections in photo-excited 9H-adenine, *Phys. Chem. Chem. Phys.*, **12**, 5317–5328 (2010).

【氏名（ふりがな）】	岩城　貴史　（いわき　たかふみ）
【職名】	FIFC Fellow
【所属】	京都大学福井謙一記念研究センター
【研究室】	Room 209
【直通電話】	075-711-7902
【電子メールアドレス】	iwaki@fukui.kyoto-u.ac.jp
【ホームページ】	http://www.fukui.kyoto-u.ac.jp/users/iwaki/topj.htm
【研究分野】	Soft Matter, Biological Physics
【現在の研究課題】	Interfacial Phenomena, PEMS of coarse-grained model polymer folding
【研究内容キーワード】	Polyelectrolyte, DNA folding transition, Thermofluid, Photophoresis
【学歴】	March 2001, Master of Sci., Graduate School of Science, Kyoto University March 2004, Doctor of Sci., Graduate School of Science, Kyoto University
【学位】	Doctor of Science from Kyoto University
【略歴】	Apr. 2004, Postdoctoral Fellow at The City University of New York, USA Apr. 2005, Okayama Institute for Quantum Physics
【所属学会】	The Physical Society of Japan
【主な著書、学術論文】 （過去 5 年以内）	1. T. Iwaki, N. Makita and K. Yoshikawa, “Folding transition of a single semiflexible polyelectrolyte chain through toroidal bundling of loop structures”, *The Journal of Chemical Physics* **129**(6), 065103 (13 pages) (2008) 2. T. Saito, T. Iwaki, and K. Yoshikawa, “DNA compaction induced by neutral polymer is retarded more effectively by divalent anion than monovalent anion”, *Chemical Physics Letters* **465**(1-3), 40-44(2008) 3. T. Iwaki, “Effect of internal flow on the photophoresis of a micron-sized liquid droplet”, *Physical Review E* **81**, 066315 (13 pages) (2010) 4. 吉川研一、岩城貴史、“細胞の自己組織化”に物理の視点から迫る”, パリティ　2011年5月号 pp. 13-21 5. Y. Higuchi, K. Yoshikawa, T. Iwaki, “Stiffness causes opposite trend on the folding transition of a single polymer chain in a confined space”, *Physical Review E* **84**, 021924 (5 pages)

【氏名（ふりがな）】	義永　那津人　（よしなが　なつひこ）
【職名】	助教
【所属】	東北大学　原子分子材料科学高等研究機構
【直通電話】	022-217-6333
【FAX】	022-217-6335
【電子メールアドレス】	yoshinaga@wpi-aimr.tohoku.ac.jp
【ホームページ】	http://www.wpi-aimr.tohoku.ac.jp/~yoshinaga/
【研究分野】	ソフトマター物理、生物物理
【現在の研究課題】	Self-propulsion and deformation of reactive droplet, Contraction of active gels
【学歴】	2007年3月　京都大学理学研究科　物理学・宇宙物理学専攻　博士課程修了
【学位】	2007年3月　理学博士（京都大学）
【略歴】	2007年4月　東京大学理学系研究科　日本学術振興会特別研究員PD、 2010年4月　京都大学福井謙一記念研究センター特定研究員
【所属学会】	日本物理学会
【主な著書、学術論文】（過去5年以内）	1. Hiroyuki Kitahata, Natsuhiko Yoshinaga, Ken H. Nagai, and Yutaka Sumino, “Spontaneous motion of a droplet coupled with a chemical wave” *Phys. Rev. E. Rapid Communications* **84**, 015101 (2011). 2. Philippe Marcq, Natsuhiko Yoshinaga, and Jacques Prost, “Rigidity sensing explained by active matter theory” *Biophys. J.* **101**, L33-L35 (2011). 3. Hong-Ren JIANG, Natsuhiko YOSHINAGA, and Masaki SANO, “Active Motion of Janus Particle by Self-thermophoresis in Defocused Laser Beam”, *Physical Review Letters*, **105**, 268302 (2010) Editor's suggestion and Viewpoint in Physics, 3, 108 (2010) Debut of a hot “fantastic voyager” 4. Natsuhiko YOSHINAGA, Jean-Francois JOANNY, Jacques PROST and Pilippe MARCQ, “Polarity patterns of stress fibers”, *Physical Review Letters*, **105**, 238103 (2010) 5. Takahiro SAKAUE and Natsuhiko YOSHINAGA, “Dynamics of Polymer Decompression: Expansion, Unfolding and Ejection”, *Physical Review Letters*, **102**, 148302 (2009). 6. Hong-Ren JIANG, Hirofumi WADA, Natsuhiko YOSHINAGA, and Masaki SANO, “Manipulation of Colloids by Nonequilibrium Depletion Force in Temperature Gradient”, *Physical Review Letters*, **102**, 208301 (2009).

【氏名（ふりがな）】	嶺澤　範行（みねざわ　のりゆき）
【職名】	福井センターフェロー
【所属】	京都大学福井謙一記念研究センター
【研究室】	京都大学福井謙一記念研究センター 209 号室
【直通電話】	075-711-7902
【FAX】	075-781-4757
【電子メールアドレス】	minezawa@fukui.kyoto-u.ac.jp
【研究分野】	理論化学・計算化学
【現在の研究課題】	時間依存密度汎関数法による非断熱遷移の解析
【研究内容キーワード】	時間依存密度汎関数法・円錐交差・非断熱分子動力学
【学歴】	2008 年 3 月京都大学大学院理学研究科化学専攻博士課程修了
【学位】	2008 年 3 月京都大学理学博士
【略歴】	2008 年 5 月米国アイオワ州立大学 (Mark S. Gordon 教授) 2011 年 10 月京都大学福井謙一記念研究センター・センターフェロー
【所属学会】	アメリカ化学会
【主な著書、学術論文】（過去 5 年以内）	1. A. Defusco, N. Minezawa, L. V. Slipchenko, F. Zahariev, and M. S. Gordon, “Modeling solvent effects on electronic excited states”, *J. Phys. Chem. Lett.* **2**, 2184-2192 (2011). 2. N. Minezawa and M. S. Gordon, “Photoisomerization of stilbene: A spin-flip density functional theory approach”, *J. Phys. Chem. A* **115**, 7901-7911 (2011). 3. N. Minezawa, N. De Silva, F. Zahariev, and M. S. Gordon, “Implementation of the analytic energy gradient for the combined time-dependent density functional theory/effective fragment potential method: Application to excited-state molecular dynamics simulations”, *J. Chem. Phys.* **134**, article No. 054111 [12 pages] (2011). 4. S. Aono, N. Minezawa, and S. Kato, “Electronic spectra of coumarin-151 in polar solvents: Linear response free energy approach”, *Chem. Phys. Lett.* **492**, 193-197 (2010). 5. N. Minezawa and M. S. Gordon, “Optimizing conical intersections by spin-flip density functional theory: Application to ethylene”, *J. Phys. Chem. A* **113**, 12749-12753 (2009).

【氏名】	Kunkun Guo
【職名】	FIFC Fellow
【所属】	Fukui Institute for Fundamental Chemistry
【研究室】	Room 204
【直通電話】	075-711-7838
【FAX】	075-711-7838
【電子メールアドレス】	guo@fukui.kyoto-u.ac.jp
【ホームページ】	http://www.fukui.kyoto-u.ac.jp/
【研究分野】	Soft matter physics
【現在の研究課題】	Phase separation of aqeuos two polymer system encapsulated by vesicle
【研究内容キーワード】	Photo-functional molecules, Potential surfaces, non-adiatbatic transition
【学歴】	June 2002, Master of Sci., ICCAS, China June 2005, Doctor of Sci., Fudan University, China
【学位】	Doctor of Science from Fudan University, China
【略歴】	August. 2005, Postdoctoral Fellow, Max-Planck Institute for Colloid and Interface, Germany
【所属学会】	Chemical Society of China, American Physics Society
【主な著書、学術論文】 （過去 5 年以内）	1. Kunkun Guo, Wenjia Xiao, Dong Qiu, “Polymerization of actin filaments coupled with adenosine triphosphate hydrolysis: Brownian dynamics and theoretical analysis”, *J. Chem. Phys.* **135**(10):105101 (2011). 2. Kunkun Guo, Jianfeng Li, “Exploration of the Shapes of double-walled vesicles with a confined inner membrane” *J. Phys.: Condens. Matter.* **23**:285103 (2011). 3. Kunkun Guo, Wenchi Han, “Growth of Dynamic Actin Filament via Brownian Dynamics Simulations,” *Acta Chimica Sinica*, **V69**(02):145-152 (2011). 4. Kunkun Guo, JC Shillcock, R Lipowsky, “Treadmilling of Actin Filaments via Brownian Dynamics Simulations”, *J. Chem. Phys.* **133**(15)155105(20100 5. Jiafang Wang, Kunkun Guo, Lijia An, M. Mueller, ZG Wang, “Micelles of Coil-Comb Block Copolymers in Selective Solvents: Competition of Length Scales,” *Macromolecules*, **43**, 2037(2010) 6. Kunkun Guo, Jiafang Wang, Feng Qiu, Hongdong Zhang, Yuliang Yang, “Shapes of fluid vesicles anchored by polymer chains”, *Soft matter*, **5**:1646(2009).

【氏名（ふりがな）】	河津　励　（かわつ　つとむ）
【職名】	分子科学研究所 専門研究職員
【所属】	総合研究部門
【研究室】	福井謙一記念研究センター 206
【直通電話】	075-711-7867
【FAX】	075-781-4757
【電子メールアドレス】	kawatsu@fukui.kyoto-u.ac.jp
【ホームページ】	http://www.fukui.kyoto-u.ac.jp/ users/kawatsu/index.html
【研究分野】	生物物理化学
【現在の研究課題】	革命的ハイパフォーマンス・コンピューティング・インフラ (HPCI) の構築
【研究内容キーワード】	電子移動、励起エネルギー移動、蛋白質科学、自由エネルギー計算
【学歴】	1999年3月　名古屋大学理学研究科物質理学専攻博士前期課程修了 2002年2月　名古屋大学理学研究科物質理学専攻博士後期課程修了
【学位】	2002年2月　理学博士（名古屋大学）
【略歴】	2002年3月 デューク大学化学科 ポスドク 2005年9月 ジョージア工科大学化学生化学科 ポスドク 2006年11月 京都大学福井謙一記念研究センター JST フェロー 2010年4月京都大学工学研究科合成・生物専攻 特定研究員 2011年10月自然科学研究機構分子科学研究所 専門研究職員
【所属学会】	American Physical Society、日本生物物理学会
【主な著書、学術論文】（過去5年以内）	1. T. Kawatsu, J. Hasegawa, “Excitation energy transfer in GFP-X-CFP model peptides (X = amino acids): Direct Versus through-bridge energy transfers,” *Int. J. Quantum Chem.* published online: 23 FEB 2012. 2. T. Kawatsu, J. Hasegawa, K. Matsuda, “Bridge-mediated excitation energy transfer pathways through protein media: a Slater determinant-based electronic coupling calculation combined with localized molecular orbitals,” *J. Phys. Chem. A* **2011**, *115*, 10814-10822. 3. J. Hasegawa, T. Kawatsu, K. Toyota, K. Matsuda, “Chemical-intuition based LMO transformation simplifies excited-state wave functions of peptides,” *Chem. Phys. Lett.* **2011**, *508*, 171-176. 4. T. Kawatsu, M. Lundberg, K. Morokuma, “Protein free energy corrections in ONIOM QM:MM modeling: A case study for isopenicillin N synthesis (IPNS),” *J. Chem. Theory Comput.* **2011**, *7*, 390-401. 5. M. Lundberg, T. Kawatsu, T. Vreven, M. J. Frisch and K. Morokuma, “Transition states in the protein environment – ONIOM QM:MM modeling of isopenicillin N synthesis,” *J. Chem. Theory Comput.* **2009**, *5*, 222-234.

Ⅲ　研究広報活動

１．若い人に贈る福井謙一先生ノーベル化学賞受賞 30 周年記念公開講座
― 最近の基礎化学の進展 ―

日時：平成２３年７月３０日（土）　13:00-16:00

場所：京都大学福井謙一記念研究センター　３Ｆ大会議室

プログラム

13:00-13:10　開会の挨拶

センター長 田中　功（京都大学工学研究科教授）

13:10-13:55　福井謙一博士の生い立ちとノーベル化学賞までの軌跡：

副センター長　田中　一義（京都大学工学研究科教授）

14:10-14:55　コンピュータで化学反応の世界を探る

センター リサーチリーダー　諸熊　奎治

15:10-15:55　基礎化学から応用への展開

センター運営委員　今堀　博（京都大学工学研究科教授）

・休憩時間や講座終了後に，福井先生記念の展示物を見学。

（この公開講座は、京都大学ジュニアキャンパス 2011
の特別協賛ゼミとしても提供した）

２．京都大学ジュニアキャンパス 2011　中学生向けゼミ
「化学―フロンティア軌道理論と電子計算機で化学が分かる？」

日時：平成２３年９月１７日（土）　14:30-16:00

14 時 30 分　榊　茂好（福井謙一記念研究センター リサーチリーダー）
「原子、分子、電子の軌道、フロンテイア軌道理論」

14 時 55 分　長岡正隆（名古屋大学情報科学研究科教授）
「福井謙一先生の思い出」

15 時 25 分　諸熊奎治（福井謙一記念研究センター リサーチリーダー）
「コンピュータで化学反応の世界を探る」

15 時 40 分　センター内見学

３．Fukui International Symposium for Theoretical Chemistry (FISTC)

Place:　Fukui Institute for Fundamental Chemistry, Kyoto University
Schedule:　Wednesday, August 31, 1300:opening, lectures and banquet
Thursday, September, 1, 2011, 9:00: lectures; 1700: closing
banquet: Aug. 31 PM 7:00-9:00
Organizers:　Keiji Morokuma, Shigeyoshi Sakaki

（詳細は資料編 3. Fukui International Symposium for Theoretical Chemistry (FISTC)参照）

４．福井謙一記念研究センターシンポジウム

第９回京都大学福井謙一記念研究センターシンポジウム

日　時　2012年（平成24年）1月6日

場　所　京都大学福井謙一記念研究センター（3F　大会議室）

講　演　玉尾　皓平(理化学研究所 基幹研究所 所長)
「深化･拡大を続ける有機元素化学:実験と理論の連携の舞台」　11:00—12:00

諸熊　奎治（福井謙一記念研究センター リサーチリーダー）
「化学反応の理論研究：フロンティア理論から現在、未来へ」　13:30—14:15

平尾　公彦（理化学研究所 計算科学研究機構 機構長）
「コンピュータと福井先生」　14:15—15:00

ポスターセッション　15:30—17:20

— コーヒーブレイク —

懇親会（１Ｆ多目的ルーム）　17:30—19:00

５．センターセミナー

第 9 回福井センターセミナー

日　　時　2012 年（平成 24 年）３月１６日　14:00－17:00

場　　所　京都大学福井謙一記念研究センター（3F　大会議室）

14：00－15：00　Shinkoh Nanbu (Sophia Univ., Tokyo)
“Nonadiabatic dynamics in photochemical processes”

15：00－15：30　Yoshihide Nakao (FIFC)
“Theoretical Study of Physical Properties in First-Row Transition Metal Complexes”

16：00－17：00　Shoji Takada (kyoto Univ.)
“Coarse-grained molecular simulasions of Large biomolecules：From theory to applications”

６．アウトリーチ活動

(1) 科学技術フェスタ in Kyoto 2011　　2011 年（平成 23 年）12 月１7-18 日

榊　茂好リサーチリーダが国立京都国際会館にて開催された「科学技術フェスタ in Kyoto 2011」に出展した。コンピュータを使う化学の研究について、特に、金属などに現れる d 電子、d 軌道の面白さを伝えた。

(2) ウォークイン　サイエンス　　2012 年（平成 24 年）２月 25-27 日

研究部第一のオフィスアシスタントの三木さん、堀さん、延山さんが理学研究科・社会交流室が主催する「ウォークイン　サイエンス」に出展し、Zest 御池河原町広場にて理論化学のデモンストレーションを行った。

(3) 京都大学アカデミックデイ　　2012 年（平成 24 年）３月 10 日

諸熊　奎治リサーチリーダーが「京都大学アカデミックデイ」に出展し、理論化学の面白さを伝えた。

７．福井謙一博士記念展示コーナー

2011 年(平成 23 年)が福井謙一博士のノーベル化学賞受賞 30 周年にあたるため、これを節目として本センター玄関ロビーに博士ゆかりの文物の展示コーナーを設置した。コーナーでは先生が使用された机、椅子、ノーベル賞メダル・賞状(複製)、研究ノート・

メモ、写真などを展示し、常設展示として一般に公開している。

2012年(平成24年) 1月6日に同コーナーの序幕式を行った。

福井謙一博士記念展示コーナー除幕式

日　　時　2012年(平成24年) 1月6日（10:00－10:45)
場　　所　京都大学福井謙一記念研究センター（1F　展示コーナー）
・開会の辞　　田中　功（福井謙一記念研究センター長）
・挨　拶　　江﨑　信芳（京都大学理事・副学長）
・挨　拶　　小森　悟（京都大学 工学研究科長）
・テープカット
・ご見学

Ⅳ　研究業績

１．専任教員

長谷川　淳也

総合研究部門　准教授
（平成 23 年 10 月 1 日から）

1. 今年度の研究の要約

生体関連分子の励起状態と機能に関する理論的研究

【始めに】 これまで、周辺の分子環境に応じて光吸収・発光エネルギーを大きく変化させる光機能性蛋白質について、理論化学計算によりメカニズムを解析してきた。その結果、色素の電子励起に伴う電荷分布の変化と、蛋白質の偏った静電ポテンシャル分布の協同効果により励起エネルギー準位が変化することを明らかにした。他方で、いくつかのレチナール蛋白質では、周辺アミノ酸の電子状態が励起エネルギーに寄与することを見出している。周辺環境との協同効果による化学現象の制御は、化学における重要なテーマであり、これを記述する理論化学を発展させる必要がある。今年度は、蛋白質の電子的効果を解析するために、新たに分子軌道の局在化法を開発した。これにより、意図した形状や領域に局在化した分子軌道を得ることが可能になった。今後、色素の励起に対して、蛋白質や溶液における分子環境がどのように応答するかを局在化軌道を用いて解析を進める予定である。また、この方法を応用し、励起エネルギー移動における super-exchange 機構について移動経路の解析を行なった。

ポルフィリン化合物の励起状態に関しても研究を継続的に進めている。今年度は、光化学系Ⅱの光合成反応中心に存在するクロロフィル集合体が示す特異的な光吸収特性に関して、大規模な励起状態計算に基づき解析を行ない、光合成細菌との比較を行なった。また、ポルフィリンの異性体であるポルフィセン化合物について、置換基の導入による光吸収エネルギーと酸化・還元ポテンシャルの特異的変化の起源について解析を行なった。

【参照軌道を用いる局在化法の開発：励起状態への応用】

これまで局在化分子軌道（LMO）の開発やその応用研究が多く報告されているが、意図した領域に意図した形状の LMO を与える方法はあまり知られていない。本研究では、minimum orbital deformation (MOD)法と Pipek-Mezey(PM)法を組み合わせた分子軌道の局在化法を提案し、ペプチド分子の LMO を求め、励起状態の計算に応用した。

図１a のように領域を分割し、フラグメント 1-3 については参照軌道を使用して MOD 法により、その他の部分は PM 法により局在化した。図１cd に示すように、四角枠内に示した参照軌道によく一致した局在化軌道が得られた。また、PM 法を用いて局在化した部分についても、ペプチド結合に局在した非共有電子対やπ軌道が得られた(図 1be)。

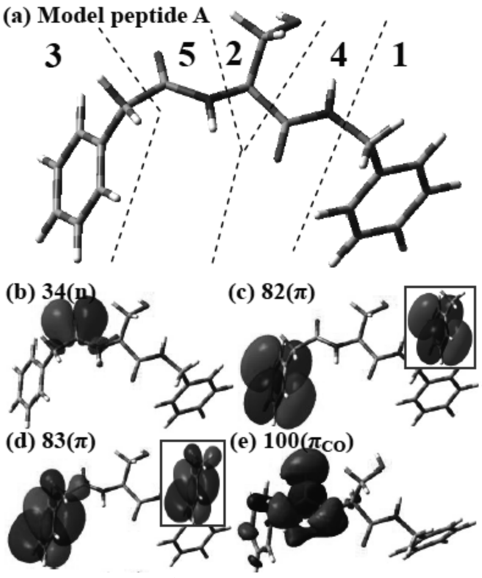


Fig. 1(a)モデルペプチドの構造と fragment への分割。(b-e)本方法による局在化軌道。四角枠内は各 fragment において用いられた参照軌道。

次に、この局在化軌道を用いて、励起状態の計算を行った。計算にはCIS法を用いた。図2aには、非局在化したCMOを用いて得られた励起状態の波動関数について示す。局所励起や電荷分離状態などの励起配置が混合し、複雑な電子構造が得られる。図2bには、本方法の局在化軌道を用いて得られた波動関数を示す。その結果、同状態が一つのアミノ酸残基の局所励起であることが明らかになる。非局在化したCMOを用いると、局所励起を記述するための軌道回転に相当する電子励起が混合し、波動関数を複雑化する原因になることがわかる。

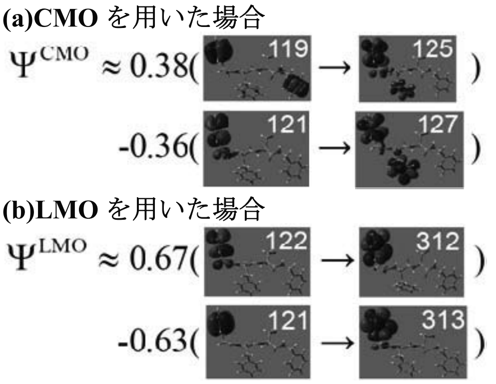


Fig. 2 モデルペプチドの第一励起状態における CIS 波動関数の主配置。(a)CMOと(b)LMOを用いた場合。

【局在化軌道を用いた励起エネルギー移動経路の解析】

励起エネルギー移動(EET)速度定数は、ドナーとアクセプターの励起状態間の electronic coupling, T_{IF}の大きさの自乗に比例する。従って、T_{IF}を計算・解析 することでEETのメカニズムを理解できる。本研究では、局在化した分子軌道を用いて、T_{IF}を計算する手法を開発した。また、EET経路を解析するためのtunneling configuration fluxに基づく手法を開発した。これにより、励起エネルギーの伝播経路に関する詳細な解析が可能となり、励起移動に用いられる軌道ペアの実空間的、エネルギー空間的な分布を理解することが可能である。

方法論の確認のために行った計算では、図 3 に示したペプチド化合物を用いた。Fragment 1-4から二つを選択し、ドナー・アクセプター対として T_{IF} を計算した。今回のモデルペプチド分子では、計算された T_{IF} におけるブリッジを介する間接項の寄与は、ドナー―アクセプター間の直接項と比べて小さかった。直接項の値は、クーロン相互作用の多極子展開における最低次でよく近似でき、双極子―双極子相互作用に駆動されるForster機構によることが分かった。他方でドナーとアクセプターの配向によっては間接項が支配的になる場合も確認できた。また、間接項においてEET経路を解析したところ、ブリッジのエキシトン状態を介した経路が主要であった。具体的には、図4に示したように、ペプチド結合部のπ−π^*遷移などの寄与が明らかになった。今回開発した局在化法では、参照軌道によく一致するように軌道を変換するので、対象となる系の軌道を化学的直観によく合致するものに変換でき、EET経路を直観的に理解することが可能となった。

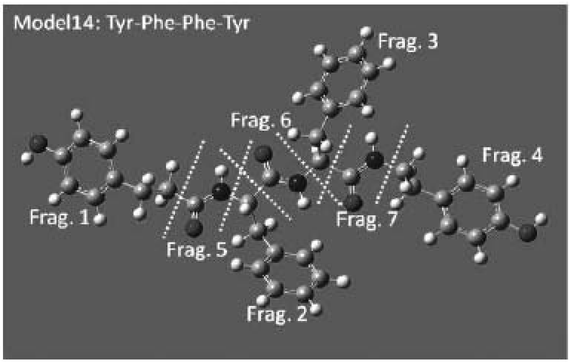


Fig. 3 モデルペプチド化合物の構造と領域分割のために設定した境界。

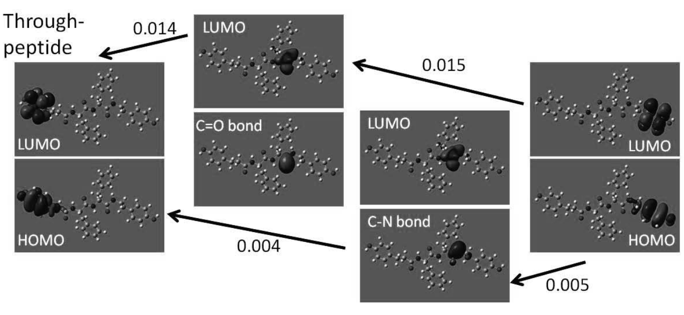
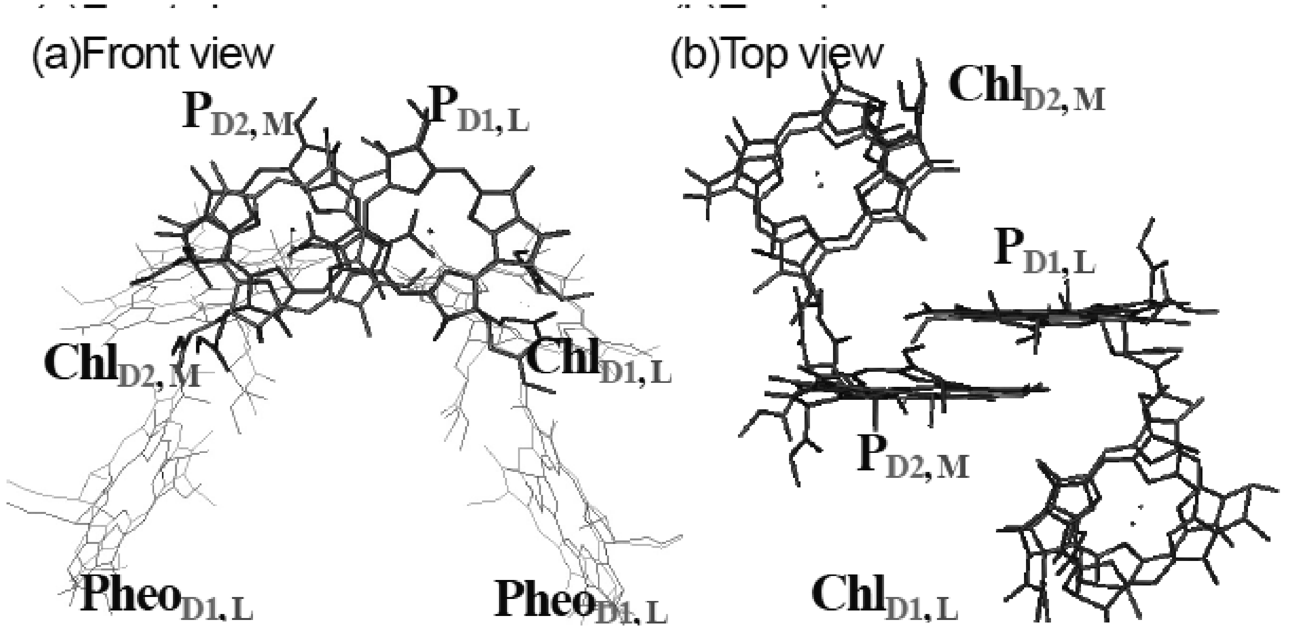


Fig. 4 局在化分子軌道を用いて計算した、ペプチド結合を介在した励起移動経路。数値は全体の流束に対する比率。

【PSII 反応中心の励起スペクトルと分子間相互作用の変化の起源に関する理論的研究】

光合成色素蛋白質複合体である PSII の反応中心(RC, 図 5 赤線)と紅色細菌反応中心(bRC, 図 5 青線)は、進化的に同一の起源を持ち、構造が類似するにもかかわらず、光吸収スペクトルの形状や励起電子移動メカニズムが大きく異なる(図 6ab)。本研究ではシアノバクテリア *T. elongatus* の RC におけるクロロフィル六量体（図 5）に関する量子化学計算を行い、励起状態の電子構造を解析し、観測される光吸収スペクトルを帰属した。

図 6 に示したように、PSII RC と bRC の計算スペクトルは、実験的に観測される光吸収スペクトルを定性的に再現できている。PSII の励起スペクトルにおいて最も振動子強度が大きい励起状態は、Chl_{D1} と P_{D2} の第一励起状態のエキシトンカップリングによるものであり、Chl_{D1}, P_{D2} の遷移双極子モーメントが互いに強め合うような相互作用がみられた。従来からスペシャルペアと呼ばれる P_{D1}, P_{D2} からなる二量体は、bRC のような強い相互作用は無く、この点において植物と細菌の反応中心の電子構造の違いが明らかになった。また、強い二量体形成が失われたことにより、PSII では P のイオ



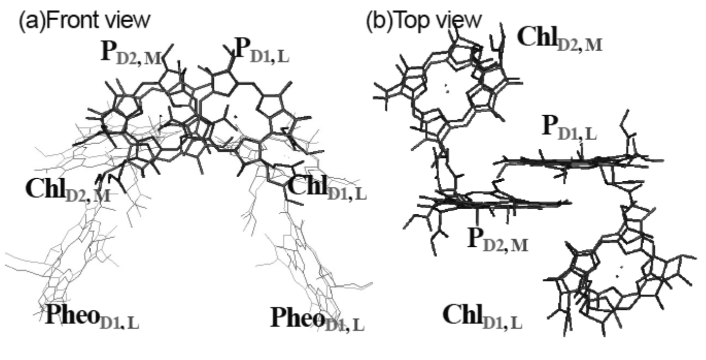


Fig. 5 PSII(緑)と紅色細菌(赤)の色素六量体.

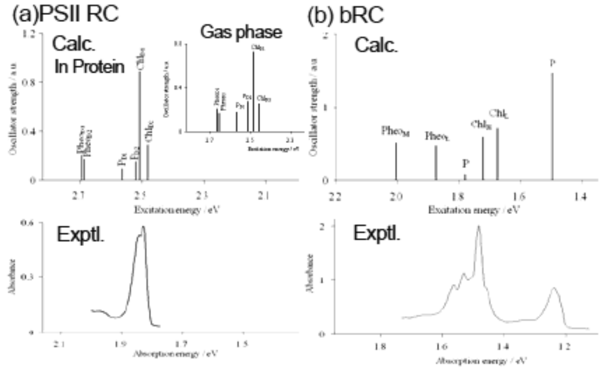


Fig. 6 (a)PSII RC (b)bRC の光吸収スペクトルについて、実験結果と計算結果。励起状態間の分子間相互作用を考慮するため、クロロフィル六量体を超分子として計算し、蛋白質は静電ポテンシャルとして考慮した。計算は CIS/6-31G*レベル。

【トリフルオロメチルポルフィセン化合物における特異的スペクトルシフトの解析】

近年合成された CF_3 基置換ポルフィセン化合物は、無置換ポルフィセン化合物と比較して、第一励起状態のエネルギー準位が約 0.25 eV もの赤方シフトを示すことが知られている。高波長側にシフトしたポルフィリン化合物は光力学療法への応用が期待されているため、励起エネルギーを制御する手法として CF_3 置換効果の解明が必要とされた。

このシフトの原因として、CF_3 基による電子的効果と構造歪み効果が考えられた。SAC-CI 計算を行いった結果、0.30 eV の赤方シフトが得られ、定量的に実験結果を再現できた。次に、この結果を解析するため、テトラフルオロポルフィセンにおける構造歪みを無置換ポルフィセンに導入したところ、0.23 eV の赤方シフトが得られた。従って、全シフトにおいて、構造歪みが 0.23 eV、電子的効果が 0.07 eV の寄与があることが明らかになった。このような構造歪みの導入がポルフィセン化合物の光吸収スペクトルのみでなく、参加還元特性にも変化が現れることが理解できた。

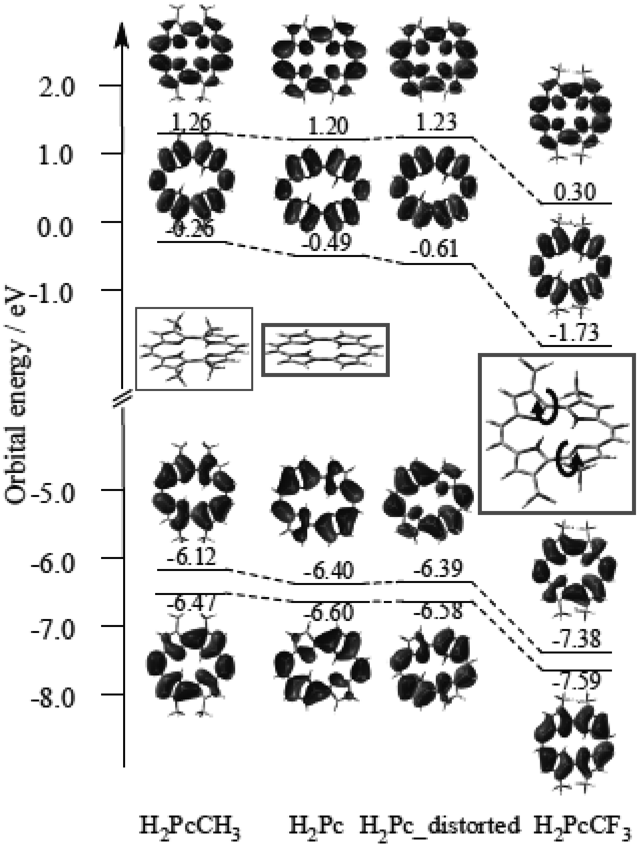


Fig. 7 励起に関与する軌道エネルギ―の構造依存性。ポルフィセン(H_2Pc), テトラメチルポルフィセン (H_2PcCH_3), テトラフルオロポルフィセン (H_2PcCF_3), H_2PcCF_3 の構造歪を導入した H_2Pc.。

2. 論文

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3. 総説

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4. 学会発表

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(2) J. Hasegawa
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BioInformatics in Torun - BIT11, N. Copernicus University, Torun, Poland, 2011.6.2-4.

(3) J. Hasegawa

“Excited states of photo-functional proteins” (Invited talk)
Fukui International Symposium for Theoretical Chemistry, Kyoto, 2011.8.1-9.1.

(4) J. Hasegawa
“Theoretical study on the excited states and molecular interactions of photo-functional proteins” (Invited talk)
The 14-th Asian Chemical Congress, Bangkok, Thailand, 2011.9.2-4.

(5) J. Hasegawa
“Excited states of photo-functional proteins: SAC-CI study” (Invited talk)
The 16-th Quantum Systems in Chemistry and Physics, Kanazawa, 2011.9.12-17.

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日本化学会第92春季年会（第２次先端ウオッチング）、慶應義塾大学、平成24年3月25-28日.

(7) 長谷川淳也
「光機能性蛋白質における励起状態と分子間相互作用」(招待講演)
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大阪大学蛋白質研究所セミナー“タンパク質科学の未来を語る　―実験・理論研究者の対話ー”, 大阪大学, 2011年11月21,22日.

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第5回分子科学討論会、札幌、9月20-23日, 2011.

(10) 長谷川　淳也、河津　励、松田　建児
参照軌道を用いる局在化法：励起状態への応用(Poster)
第14回理論化学討論会、岡山大学、5月12-14日, 2011.

中尾 嘉秀

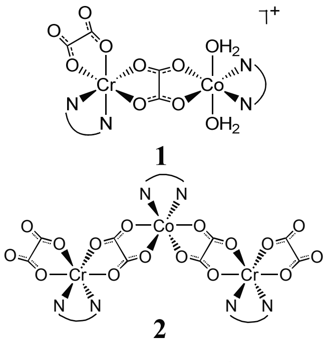
准教授

1. 今年度の研究の要約

今年度は遷移金属元素を含んだ機能性金属錯体の物性と梯子型π共役分子の固体中の光物性について研究を行った。

【始めに】遷移金属元素を含んだ金属錯体は様々な配位子との組み合わせで、多様な構造や電子状態をとることができ、様々な機能が発現することがある。発光性錯体は発光素子に、高スピン状態を保つ錯体は記憶素子などに応用できる可能性がある。これらの機能が発現する仕組みを理解することは機能性金属錯体の制御や設計に繋がるため、機能の発現機構の理論的解明が求められている。今年度はオキサラト架橋した多核金属錯体の磁気異方性とピラゾラト架橋した多核金属錯体の固体中の発光を量子化学計算により明らかにした。また、梯子型π共役化合物の固体中の発光について、周期的境界条件を用いた量子化学計算により明らかにした。

【オキサラト架橋多核金属錯体の磁気異方性に関する研究】金属間に強磁性相互作用を持つ多核金属錯体は、高密度磁気記憶媒体として応用が期待されている。Scheme 1に示したオキサラト架橋したCr(III)-Co(II)二核錯体(**1**)とCr(III)-Co(II)-Cr(III)三核錯体(**2**)はそれぞれの金属中心にS = 3/2のスピンが立ち、各金属中心の局所スピン間にも相互作用がある。また、**2**は低温で大きな磁気異方性が存在することが分かっている[1]。本研究では、金属間のスピン相互作用を理論計算により解明して、磁気異方性の本質を明らかにした。



1

2

Scheme 1. オキサラト架橋多核金属錯体

B3LYP法で高スピン状態の構造最適化を行い、高スピン状態と低スピン状態の相対エネルギーをBroken Symmetry(BS)法で計算した。局所スピンの組み合わせから考えられる全てのスピン多重度の1点計算にState-averaged CASSCF法とMCQDPT法を用いた。基底関数はCr, CoにStuttgart-DresdenのECPと基底関数を、その他の原子にcc-pVDZを使用した。磁気異方性を明らかにするために、Spin-Orbit Coupling(SOC)ハミルトニアンに外部磁場によって誘起される項を加えて各状態の計算を行い、誘起磁場の大きさを評価した。B3LYP計算ではGaussian 09を、その他の計算ではGAMESSを用いた。

計算により得られた*J*値をTable 1に示した。**1**と**2**は共に高スピン状態が最も安定で、金属間の局在スピンには非常に弱い強磁性相互作用が存在する。B3LYP計算の結果から山口らの方法[2]で*J*値を評価すると、**1**では2.18 $\mathrm{cm^{-1}}$となり、実験値の2.16 $\mathrm{cm^{-1}}$と良く一致した。CASSCF計算を用いて計算した結果は0.25 $\mathrm{cm^{-1}}$と実験値やB3LYP法と比べて非常に小さい値となった。次に、低温

Table 1. *J* value ($\mathrm{cm^{-1}}$)

Method	**1**	**2**
B3LYP	2.18	2.56
CASSCF	0.25	0.23
MCQDPT	0.74	
Expt.[1]	2.16	1.81

部の磁気異方性を解明するために、外部磁場による項を加えた SOC 計算を行い、ボルツマン分布を用いて温度と磁化率(χ_M)を調べた。温度-磁化率曲線は CASSCF 計算で得られた *J* 値では実験を再現せず、Figure 1 に示したように B3LYP 計算で得られた *J* 値の場合によく再現した。Figure 2 に **2** に対して *x*, *y*, *z* 軸方向から外部磁場をかけた場合の温度-磁化率曲線を示した。10 K 以下の低温では金属間で強磁性相互作用したスピンが *x* 軸方向に向いていることが明らかとなった。

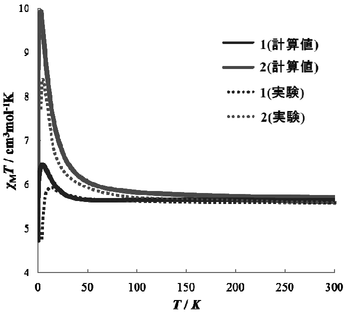


Figure 1. 温度-磁化率曲線

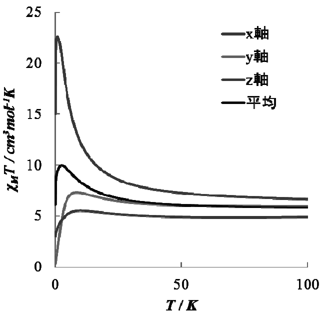


Figure 2. **2** の磁気異方性

【ピラゾラト架橋多核金属錯体の固体中の発光に関する研究】 リン光性の錯体は量子収率が高いことが知られており、発光デバイスへの応用が期待されている。$[Pt_2M_2(Bpym)_2(Bupz)_4](PF_6)_2$ (M = Au(**3**), Ag(**4**)) (Bpym = 2,2'-Bipyrimidine, Bupz = 3-tert- butylpyrazole)は特徴的なリン光を示す[3]。**3** のリン光スペクトルは π 共役系の振動準位に由来する微細構造を持ち、**4** のスペクトルも 150 K 以下で同様の微細構造を持つ。本研究では隣接するカウンターイオンと錯体の影響を考慮した量子化学計算を行い、固体中で発光する機構を理論的に解明した。

Pt, Au, Ag には Christiansen の有効内殻ポテンシャルと基底関数を、配位子には cc-pVDZ を用いた。構造最適化とエネルギーの評価には B3LYP 法を用いた。固体中の環境を再現するように隣接イオンや錯体の影響を点電荷で表現したモデル(固体モデル)を用いて構造最適化を行い、固体中の発光スペクトルを評価した。点電荷は NAO(Natural Atomic Orbital)法で決定し、固体モデルでの構造最適化では Buckingham Potential を用いた。全ての計算は Gaussian 09 で行った。

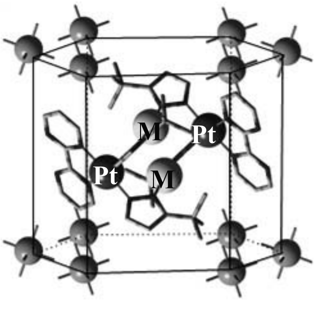


Figure 1. 固体モデル

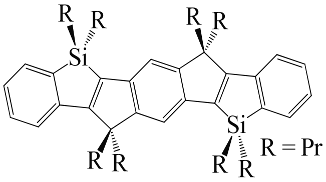
カウンターイオン無しで錯体のみの理論計算から、**3** と **4** の発光は LLCT (π^*(Bpym) → π(Bupz))であり、発光エネルギーはそれぞれ 2.33 eV, 2.23 eV となった。しかし、LLCT では振動準位に由来する微細構造が見られることは考えられず、実験の発光スペクトルと矛盾する。**3** と **4** の基底状態の最適化構造での M-M 間距離は、X 線構造のものと比べそれぞれ 0.39 Å, 0. 30 Å 長くなり、Bupz の向きは最適化構造と X 線構造とでは異なっていた。従って、固体中での錯体の電子状態を評価するには、隣接するカウンターイオン PF_6^- や錯体の効果を考慮した固体モデルで電子状態を考える必要がある。始めに、錯体に隣接する 12 個の PF_6^- の P 中心のみ点電荷を置いたモデル(Figure 1)で、点電荷を 0 から −1 まで変化させた計算を行った。点電荷を強くするに従い、1 重項と 3 重項の全エネルギーは共に上昇し、**3** と **4** の 2 状態間のエネルギー差も 0.07 eV, 0.10 eV とそれぞれ上昇した。**3** と **4** の T_1 状態では LLCT と MLCT の励起状態をとり、カウンターイオンに近い Bpym(π^*)に電荷が移動するため、電荷移動型の励起状態は不安定になる。また、錯体の NAO 電荷は点電荷の変化に伴い大きく変化したので、更に外側の錯体の電荷を考慮したモデルを考えた。錯体に隣接する PF_6^- を NAO 電荷で表現し、点電荷を隣接する錯体の中心に置いたモデルで、点電

Table 2. Emission Energies (eV)

	錯体のみ			固体モデル			
	MLCT	LLCT	π-π*	MLCT	LLCT	π-π*	Exp.[3]
1	2.44	2.33	2.37	2.44	—	2.32	2.52
2	—	2.23	2.20	—	2.62	2.29	2.40

荷を 0 から 2 まで変化させた計算を行ったところ、錯体の NAO 電荷の変化は小さかった。この電荷を隣接する錯体の電荷として用いて、固体モデル中で S_0, T_1 状態の構造最適化を行って、発光エネルギーを評価した。Table 2 に示したように、固体中では **3** と **4** は LLCT や MLCT よりも π−π*遷移の励起状態がエネルギー的に安定となった。固体モデルを導入することで、**3** と **4** のリン光は π*−π 遷移由来の発光であることが明らかになった。

【梯子型π共役化合物の固体中の発光に関する研究】多環式骨格を含む Scheme 2 に示すような梯子型 π 共役系分子は平坦で硬い分子構造を持ち、非常に安定で秩序だった結晶構造をとることが知られている[4]。また、π 共役系にヘテロ元素を導入して電子状態を制御できるため、新しい有機エレクトロニクス材料として非常に注目されている。しかしながら、固体中の π 共役化合物の発光に関して理論計算はほとんど行われておらず、設計の面からも電子状態の解明が求められている。本研究では梯子型 π 共役分子について、ヘテロ元素の寄与を明らかにし、気相中と固体中の安定構造を求めることで、吸収・発光エネルギーを明らかにした。



Scheme 2

気相中の計算では cc-pVDZ を基底関数として用いた。B3LYP 法及び TD-B3LYP 法で構造最適化を行い、励起エネルギーは TD-BLYP 法と TD-B3LYP 法、GMCPT 法で求めた。計算パッケージとして GMCPT 法のみ GAMESS を用い、他は全て Gaussian 09 で行った。固体中の構造最適化は CPMD パッケージで平面波基底、擬ポテンシャル及び周期的境界条件を用いて行った。ただし、固体中の励起エネルギーは気相中と同様に Gaussian 09 によって TD-B3LYP 法で評価した。

気相中における吸収・発光エネルギーについて TD-BLYP 法、TD-B3LYP 法、GMCPT 法で求めた結果を Table 3 に示した。この吸収・発光には HOMO-LUMO 間の遷移が大きく寄与しているため、S_1 状態の最適化構造はキノイド型となり、発光エネルギーは約 0.4 eV と大きくストークスシフトする。THF 中の吸収エネルギーの実験値は 2.94 eV であるが、TD-BLYP 法は吸収エネルギーを小さく見積もり、GMCPT 法は計算コストを抑えるため励起配置の制限を課したので吸収エネルギーを大きく見積もった。従って、吸収・発光エネルギーの評価には THF 中の実験値と比較的よく一致した TD-B3LYP 法を用いることにした。

ケイ素原子が π 共役系に与える影響を調べたところ、LUMO で σ*(Si-H)の反結合性相互作用が π 共役系に寄与するため、吸収・発光エネルギーを約 0.2 eV 低下させることが示された。また、ケイ素同士の位置が近い方が吸収・発光エネルギー共に小さくなることが明らかになった。固体中における S_0 状態の構造は気相中とほぼ同じであり、吸収エネルギーもほとんど変わらなかった。結晶構造が三斜晶をとるため、CPMD パッケージでは S_1 状態の構造最適化が不可能であり、振動子強度が得られない。側鎖を水素に置換した分子について、T_1 状態の最適化構造がそれぞれ Gaussian 09 と CPMD パッケージでほぼ同

Table 3. 気相中の吸収・発光エネルギー(eV)

	TD-BLYP	TD-B3LYP	GMCPT	Exp. in THF
Absorption	2.60	2.96	3.40	2.94
Emission	2.26	2.53	2.96	2.81

Table 4 吸収・発光エネルギー(eV)

	in solid	Exp. in solid
Absorption	2.90	—
Emission	2.41	2.61

じであること、気相中の S_1 状態及び T_1 状態の構造が大きく変わらず、吸収・発光エネルギーも近い値をとることを確認した。よって、固体中の S_1 状態の構造は T_1 状態の構造を代用することにして、固体中の吸収・発光エネルギーを Table 4 にまとめた。固体中の励起状態の構造は気相中と同様にキノイド型をとり、固体中の発光エネルギーは約 0.5 eV と大きくストークスシフトすることが明らかになった。今後、励起状態の構造緩和を明らかにするために、CPMD 法により解析する予定である。

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国際連携研究室　International Relationship Office

特定准教授　石田　俊正　**Program-specific Associate Professor　Toshimasa ISHIDA**

1. Summary of the research of the year

(1) A Nonadiabatic Ab Initio Dynamics Study on Rhodopsin and its Analog Isorhodopsin

Rhodopsin (Rh) has 11-cis retinal as chromophore and is the photosensitive chemical found on the outer segment of rod-like cells in the retina, the light-sensing structure of the eye. Isorhodopsin (isoRh) is an Rh analogue that contains 9-cis retinal embedded in the same opsin environment. Both are known to yield bathorhodopsin (bathoRh), a photoisomer that contains all-trans retinal, via cis-trans isomerization of the 11 or 9 position upon absorption of a photon. Despite their similarity, the photoisomerization period and quantum yield is largely different. Rhodopsin photoisomerization is experimentally known to be faster (t_{Rh} = 200 fs, t_{isoRh} = 600 fs) and more efficient (quantum yield: Φ_{Rh} = 0.65, Φ_{isoRh} = 0.22). We carried out non-adiabatic ab initio dynamics calculations on the two molecules.

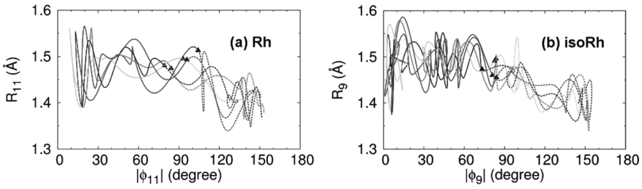

Figure 1. Change in length of the active bond $-C_n-C_{n+1}-$ against the absolute value of the dihedral angle $C_{n-1}-C_n-C_{n+1}-C_{n+2}$ for typical (a) Rh (n = 11) and (b) isoRh (n = 9) trajectories leading to the all-trans form. The solid and dashed lines show that trajectories are in the excited and ground states and the black triangles correspond to transition from the excitated state to the ground state.

The experimental photoisomerization period and bathoRh quantum yield were reproduced reasonably. One of slight differences between the simulation and experiments are due to the failure of the chosen QM/MM treatment to reproduce a ~0.2 kcal mol^{-1} barrier at the isoRh excited state reported in experiments. In our previous calculation, we found a 10 kcal mol^{-1} barrier at the excited-state potential energy surface of an isoRh model system that caused trapping of trajectories. Even a tiny barrier in the present case would have slowed down the photoisomerization by trapping the trajectories in the excited state and yield a quantitatively accurate timescale and quantum yield. Figure 1 shows the diagram of the active twist angle and the length of the active bond for five typical trajectories for Rh and isoRh. Fast and straightforward dynamics in Rh is shown in Figure 1a whereas complicated excited-state dynamics is evident in the isoRh case in Figure 1b. Why is the isoRh photoisomerization more difficult compared to that of Rh? One reason is the atomic displacements required by the chromophore at the excited state potential energy surface to reach the conical intersection region. Shown in Figure 2 is a superimposed image of the S_0 optimized geometry and the geometry adapted by the chromophore at the crossing region. The pocket that contains the retinal chromophore is similar in shape for both the Rh and isoRh case. Opsin residues Thr118 and Tyr268 create a narrow gap near the -C_9=C_{10}-C_{11}= region of the retinal chain with the two residues coming as close as 7 Å to each other. The isoRh photoisomerization is more difficult compared to that of Rh because of at least two reasons: (1) the isoRh isomerization requires more space than that of Rh and (2) the dihedral that needs to be twisted in the isoRh case (-C_9=C_{10}-) is situated within the narrow gap between Thr118 and Tyr268.

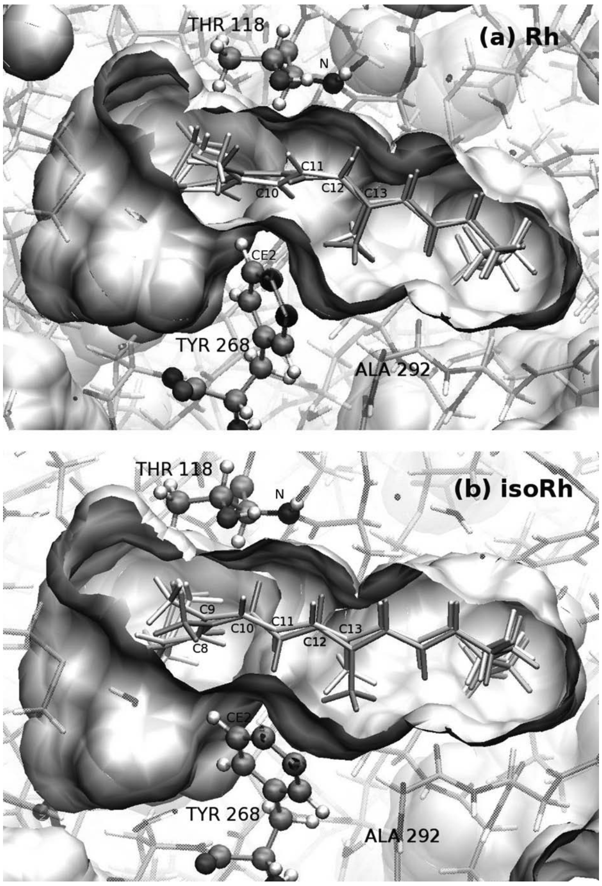

Figure 2. Superimposed structures of the S_0 optimized geometry (gray) and geometry at the MECI (pink) for the (a) Rh and (b) isoRh case. Also shown is the opsin pocket that contains the chromophore. The pocket surface is the overlapped envelope of amino residues surrounding the retinal chromophore, which is generated using the S_0 optimized geometry wherein the retinal chromophore is artificially removed.

Another reason would be the initial acceleration of retinal atoms induced by surrounding residues. The initial force between two atoms for a few retinal-opsin atom pairs is listed in Table 2. Cys187 and Tyr268 are close enough to the chromophore to significantly influence the isomerization. For example, for the atomic distance between the C_{12} hydrogen in retinal and the oxygen in Cys187, the projected inter-atomic force for Rh is about 15 times larger than the counterpart for isoRh. Also, a five-fold difference is found for the force between retinal C_{10} and Tyr268. Such differences partially explain the discrepancy in the rate and efficiency of the cis-trans isomerization between the Rh and isoRh chromophores.

Comparison with the previous gas-phase simulations reveals three other consequences shown below.

The protein causes (almost) one-way twist of the active angle. As shown in Figure 3(a), all of the Rh trajectories go through only one MECI region with clockwise-twisted ϕ_9 and counterclockwise-twisted ϕ_{11}. This MECI branches towards the formation of bathoRh (and the regeneration of the reactant). The relaxation of the excited state of isoRh, on the other hand, goes through two MECI regions, shown in Figure 3(b). Most of trajectories from isoRh go through

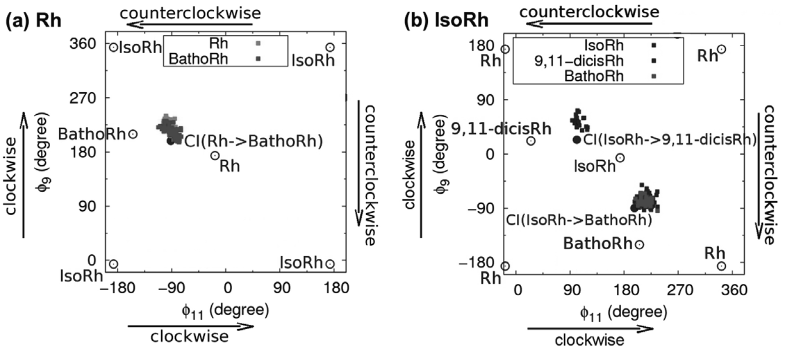

Figure 3. Diagram of the twist angles of -C_{11}=C_{12}- (ϕ_{11}) and -C_9=C_{10}- (ϕ_9) at the transition points. The minima in the ground state (open blue circles) and conical intersections (filled blue circles) obtained in the present calculations are plotted in the diagram. Rh = rhodopsin, isoRh = isorhodopsin, bathoRh = bathorhodopsin, 9,11-dicisRh = 9,11-dicis rhodopsin, CI=minimum energy conical intersection.

the MECI region with ϕ_9 ~ -90° and clockwise-twisted ϕ_{11}, which is shown as CI(isoRh->BathoRh). This MECI is responsible for all of bathoRh generation. A few trajectories go through another MECI region (CI(isoRh->9,11-dicisRh)), which is responsible for 9,11-dicisRh. Thus, photoexcitation of Rh only gives bathoRh as a product whereas isoRh yields 9,11-dicisRh in addition to bathoRh. Note that the reaction time is longer through CI(isoRh->BathoRh) (τ_{ave}=233 fs) than that through CI(isoRh->9,11-dicisRh) (τ_{ave}=188 fs). Secondly, the protein environment enhances the production of bathoRh. When the opsin environment was totally ignored, the calculated bathoRh (all-trans PSB) quantum yield was only 0.27 and 0.13, respectively. Explicit consideration of the opsin residues significantly improves the theoretical quantum yield to 0.51 and 0.31, respectively. This would be mainly due to the unidirectional rotation in opsin environment. The third effect of the opsin on the dynamics is to cause transitions to take place near MECIs. Comparison of transition points in Figure 3 with those in the calculations in vacuo reveals that the present transition points with the opsin environment are nearer the MECI points than the points without the opsin. The opsin would prevent inefficient, premature hops especially in the isoRh case.

(2) Changes in the Electronic Structures of a Single Sheet of Sashlike Polydiacetylene Atomic Sash upon Structural Transformations

Atomic sash (AS) is a single sheet of a sashlike macromolecule comprising a column of alkyl chains bridged by a polydiacetylene (PD) chain. The AS is produced by the intramonolayer polymerization of 17,19-hexatriacontadiyne molecules laid flat on a graphite (0001) surface under ultrahigh vacuum. In an AS conformer initially formed at low temperature (AS-I), the PD chain and the R carbon atoms of the alkyl chains are raised higher than other carbons of methylenes in contact with the substrate; with rising temperature, the AS-I is transformed to another conformer AS-II, in which all the carbon atoms are placed in a common plane. A simplified model is constructed in this study to obtain an optimized geometric structure of the AS-I, and its electronic structures are compared with those of the AS-II. The first-principles calculations for the model under periodic boundary conditions reveal that their energies are almost the same. The optimization also tells us the existence of the third stable conformer AS-III that has been suggested on the basis of STM images. In addition, it is found that the HOMO-LUMO energy gap of the AS-I is larger than that of the AS-II, and the orbital shapes dependent on the conformation successfully explain the result. This means that the AS-I → AS-II transformation of the ideal infinite polymer is not related to the chromatic transition of bulk PDs

(3) An MD simulation of the decoy action of Epstein–Barr virus LMP1 protein mimicking the CD40 interaction with TRAF3

The Epstein–Barr virus (EBV) is associated with a variety of malignancies and chronic active EBV infection is a severe systemic disease associated with high rates of mortality and morbidity. In this paper, the dynamics of the interaction of EBV-expressed latent membrane protein 1 (LMP1) with cellular signaling intermediate tumor necrosis factor receptor (TNFR)-associated factor 3 (TRAF3) is simulated using standard classical molecular dynamics (MD) protocols. For comparison, the dynamics of the interaction of TRAF3 with CD40, a TNFR mimicked by LMP1 to effect EBV infection is also calculated under similar conditions. Essential dynamics (ED) analysis is carried out to identify important degrees of vibrational freedom that relate to protein function and virus infection. Both the MD simulation and ED analysis reveal novel interactions that help explain the structural decoy action of LMP1 over CD40. These interactions involve the consensus sequence PXQXTXX shared by CD40 and LMP1. In LMP1, we have found novel interaction of Asp 209 with TRAF3 and the interaction is crucial although the adjacent Asp 210 was suggested to be essential by the X-ray analysis. In CD40, it is found that the hairpin formation is not indispensable for the interaction with TRAF3.

(4) Electronic and Magnetic Characteristics of Polycyclic Aromatic Hydrocarbons with Factorizable Kekul_e Structure Counts

The Kekulé structure count (*K*) for some types of polycyclic aromatic hydrocarbons (PAHs), such as fluoranthene and perylene, can be factorized into the product of those for two or more aromatic subunits. The ring-current map for these PAHs placed in a perpendicular magnetic field exhibits a substantial localization on aromatic subunits. We found that such localization of π circulation is a characteristic of fairly small *K*-factorizable species in the neutral electronic state. Even in such a case, no single π molecular orbital (πMO) is associated with localized π circulation.

Apparent localization of π circulation is caused by the superposition of currents induced by all occupied πMOs. π circulation is less localized in larger K-factorizable species.

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"Changes in the Electronic Structures of a Single Sheet of Sashlike Polydiacetylene *Atomic Sash* upon Structural Transformations"
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J. Phys. Chem. A. **115**(33), 9314-9321 (2011)

(4) Wilfredo Credo Chung,* Shinkoh Nanbu, and Toshimasa Ishida
“A Nonadiabatic Ab Initio Dynamics Study on Rhodopsin and its Analog Isorhodopsin: Chemical Dynamics Reasons Behind Selection of Rhodopsin by Life”,
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Comparison of the 9-cis retinal photoisomeriation with the 11-cis counterpart
文部科学省「最先端・高性能汎用スーパーコンピュータの開発利用」プロジェクト次世代ナノ統合シミュレーションソフトウェアの研究開発　第５回　公開シンポジウム
P102　2011/2/23　神戸

(2) 南部伸孝，石田俊正，徳江郁雄、関谷 博，中園 博
非断熱遷移を利用した分子設計
文部科学省「最先端・高性能汎用スーパーコンピュータの開発利用」プロジェクト次世代ナノ統合シミュレーションソフトウェアの研究開発　第５回　公開シンポジウム
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(3) Ishida, Toshimasa; Aono, Shigetoshi
“A QM/MM study on reactions of the axial ligand exchange in CooA protein”

第27回化学反応討論会 1P20　2011/6/8　東京工業大学（東京）

(4) Chung, Wilfredo Credo; Nanbu, Shinkoh; Ishida, Toshimasa
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Non-adiabatic ab initio dynamics of 11- and 9-cis retinal photoisomerizationNon-adiabatic ab initio dynamics of 11-cis retinal photoisomerization
Excited states and non-adiabatic processes in complex systems. Theoretical approaches(WATOC2011 Satellite Meeting), July 25, 2011 Sant Feliu de Guíxols, Spain

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Fukui International Symposium for Theoretical Chemistry, Aug. 31, 2011, Kyoto, Japan

(10) Wilfredo C. Chung、南部 伸孝、石田 俊正
A Nonadiabatic Ab Initio Dynamics Study on Rhodopsin and its Analog Isorhodopsin
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日本化学会第92春季年会　(4A4-01)　2012年3月28日　日吉

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静岡大学理学部化学科講演会　2011/6/3　静岡

(2) 石田俊正
「ロドプシンとイソロドプシンの動力学の理論的研究 ― なぜ生物はロドプシンを選んだか」
2011 年度 上智大学理工学部物質生命理工学科コロキウム　2011 年 10 月 24 日　上智大学（東京）

Hidekazu IKENO

Assistant Professor

1. Summary of the research of the year

Theoretical Fingerprints of Transition Metal $L_{2,3}$ XANES/ELNES for Lithium Transition Metal Oxides

Transition metal oxide crystals with topotactic and reversible lithium insertion/extraction capability, such as $LiCoO_2$, $LiNiO_2$, $LiMn_2O_4$, and their alloys, have been used as cathodes of a lithium ion battery. Although they have already been used commercially, many studies for improving their electrochemical performance, such as lifetime and rate capability, are still ongoing. Characterization of the transition metal ions in the cathodes during the charge/discharge cycles is one of the essential points for such studies. Among the many techniques, spectroscopic methods to measure X-ray absorption near-edge structures (XANES) and electron energy loss near-edge structures (ELNES) at transition metal $L_{2,3}$-edges (M $L_{2,3}$-edges) are very powerful to selectively observe the electronic states and local environment of transition metal ions.

It is known that M-$L_{2,3}$ XANES/ELNES show widely spread multiplet structure because of the strong electronic correlation among $2p$ core-hole and $3d$ electrons. For simulating these spectra, the present authors have developed an *ab initio* multiplet method based on the relativistic configuration interaction theory. Experimental M-$L_{2,3}$ XANES/ELNES with different d-electron numbers, coordination numbers, and symmetries have been successfully reproduced without any adjustable parameters[1,2].

In this work, we aim at providing theoretical fingerprints of M-$L_{2,3}$ XANES/ELNES for for $LiMO_2$ (M = Mn, Fe, Co, Ni) and Li-extracted MO_2 that should be useful for the analysis of experimental spectra. Theoretical spectra obtained by the *ab initio* multiplet method are given for six set of oxides with several different crystal structures. The effects of oxidation states, spin states, and crystal structures including that of the Jahn-Teller (JT) distortion on the M-$L_{2,3}$ XANES/ELNES are discussed[3].

First, the variations of M-$L_{2,3}$ spectra with M in the layered structures were studied. The results are summarized in Fig. 1. It is clearly seen that the spin state and oxidation state can be unambiguously determined using these theoretical fingerprints.

The variations of M-$L_{2,3}$ spectra of $LiMO_2$ and Li-extracted MO_2 with the crystal structures were examined for M = Mn and Fe. The dependence of spectral shapes on crystal structure was very small in the case of $LiMO_2$. The spectral difference became larger in the case of Li-extracted MO_2, which originated from the stronger covalent bonding between M-3d and O-2p orbitals in MO_2 than in $LiMO_2$.

The $L_3/(L_3+L_2)$ branching ratio was also calculated. The branching ratio changes with the atomic number, oxidation state, and spin state. The results imply that the branching ratio can be used to identify the oxidation and spin states, except for the case of Fe^{4+}. However, the branching ratio was insensitive to the crystalline structure.

The effects of the JT distortion on M-$L_{2,3}$ spectra for two compounds with d^4 high-spin state, namely, $\mathrm{LiMnO_2}$ and $\mathrm{FeO_2}$ with layered structures, were examined. The presence and orientation of the distortion can be easily and clearly detected by measuring the orientation dependence of the spectra, although the orientationally averaged spectra do not change so much with the JT distortion.

The ab initio multiplet calculations can well reproduce experimental spectra. It therefore has the predictive performance of theoretical fingerprints of M-$L_{2,3}$ XANES/ELNES for transition metal compounds with arbitrary atomic arrangement and symmetry. High-quality XANES/ELNES measurements and reliable theoretical fingerprint calculations should be a powerful and unique combination for the characterization of M ions during the charge/discharge cycles in the cathodes of lithium ion batteries.

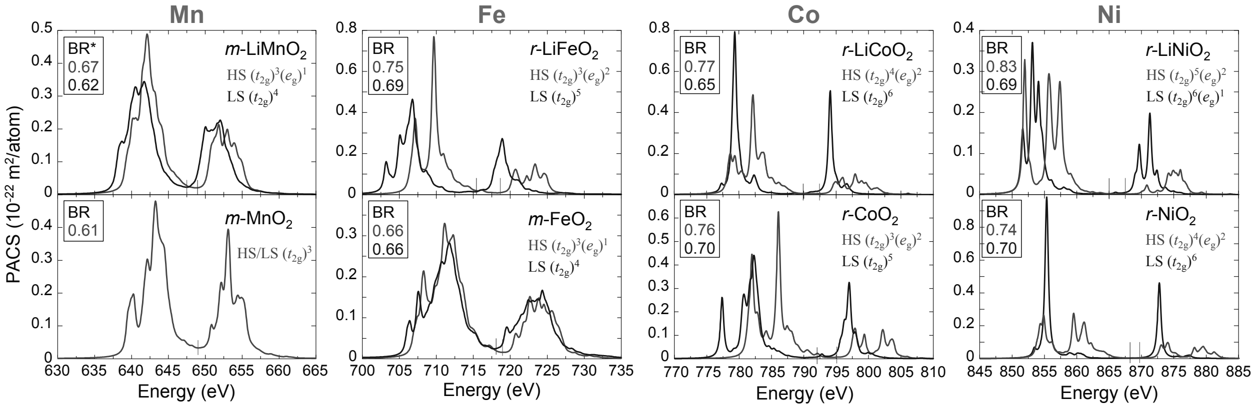

Fig. 1 Theoretical M-$L_{2,3}$ XANES/ELNES of $\mathrm{Li}M\mathrm{O_2}$ and Li-extracted $M\mathrm{O_2}$ (M=Co, Ni) with layered structures. Theoretical spectra from the high-spin (HS) and low-spin (LS) states are drawn in the black and red lines, respectively, for each compound.

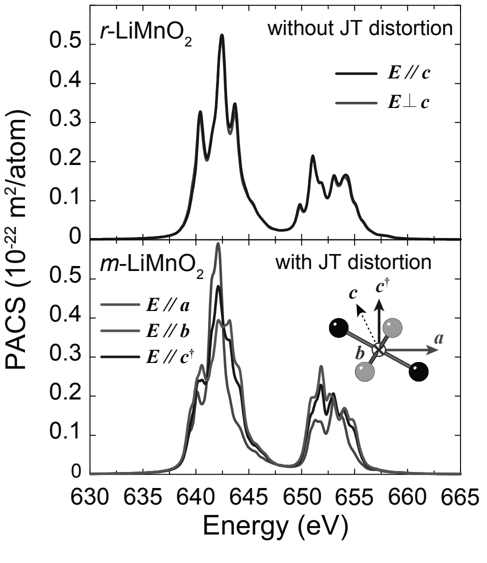

Fig. 2 Jahn-Teller effect on the theoretical Mn-$L_{2,3}$ XANES/ELNES of $\mathrm{LiMnO_2}$ with layered structures. Theoretical spectra are averaged over all directions.

Relativistic Configuration Interaction Calculations of X-ray Magnetic Circular Dichroism (XMCD)

Soft x-ray absorption spectroscopy (XAS) and its magnetic circular dichroism (XMCD) are widely used to investigate the electronic and magnetic structures of the selected element in materials. The XMCD is a difference of two XAS spectra taken in the magnetic field: the one is taken with left circularly polarized (LCP) light, and the other is taken with right circularly polarized (RCP) light. By using circularly polarized light, we can utilize not only the selection rule for angular momentu ($\Delta L = \pm 1$), but also that for magnetic momentum number: when LCP (RCP) light is irradiated, only electric dipole transitions with $\Delta M = +1$ ($\Delta M = -1$) are allowed. XMCD is usually interpreted using the sum-rules introduced by Thole and Carra[4,5] which enable us to determine the expectation values of orbital moment $<L_z>$ and spin moment $<S_z>$ at the ground state by just integrating observed spectra. However, it is known that the effective moment obtained by these sum-rules have large errors up to 30% in the real systems. The detailed analysis of XMCD by the first principle calculations is thus strongly desired.

In this study, we have extended the relativistic configuration interaction (CI) method to compute the electronic structure under the external magnetic field, and applied to the calculation of transition metal $L_{2,3}$ XMCD spectra. In order to include the effect of external magnetic field in the CI, the Zeeman term,

$$H_{\text{Zeeman}} = \sum_k \mu_B (\boldsymbol{l}_k + 2\boldsymbol{s}_k) \cdot \boldsymbol{B},$$

is added to the many-electron Hamiltonian. Here $\boldsymbol{B}$ is the external magnetic field, and μ_B is the Bohr magneton. After digonalizing the Hamiltonian matrix, the oscillator strengths of electric dipole transition are calculated for left and right-circularly polarized light, respectively, to obtain the XMCD spectra.

Fig. 3 shows $L_{2,3}$ XAS and XMCD of isolated Fe^{3+} ion (d^5, $^6S_{5/2}$ ground state) with various magnetic field. As the magnetic field stronger, the absolute amplitude of XMCD signal becomes larger because the Zeeman splitting at the initial state is larger. Inside the magnetic compounds, the exchange interaction among transition metals further split the multiplet levels. This effect can be mimicked by add the molecular field, $\boldsymbol{B}_\text{m}$, into $\boldsymbol{B}$. The spin and orbital contribution to the magnetic moment can also be obtained numerically from the eigenfunctions.

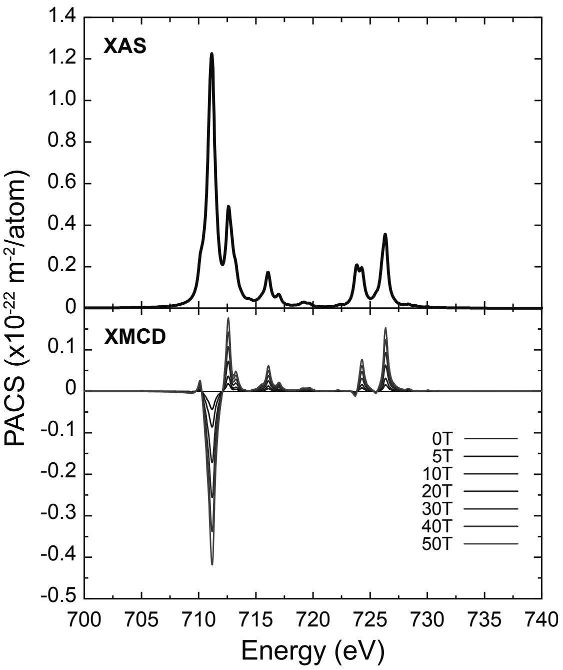

Fig 3. Theoretical $L_{2,3}$ XAS and XMCD spectra of the isolated Fe^{3+} ion with various magnetic field.

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(2) S. Ootsuki, H. Ikeno, Y. Umeda, H. Moriwake, A. Kuwabara, O. Kido, S. Ueda, I. Tanaka, Y. Fujikawa, and T. Mizoguch
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"*Ab Initio* Multiplet Method for $L_{2,3}$ XANES and ELNES of 3*d* Transition Metal Compounds"
The 15th International Conference on Thin Films (ICTF-15), (Nov. 8-11, 2011, Kyoto, Japan)

(2) Piter S. Miedema, Hidekazu Ikeno, Frank M.F. de Groot
"First principles multiplet calculations of the calcium 2p XAS spectra of CaO and CaF_2"
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3. Others

(1) 池野豪一
「遷移金属酸化物における
X線磁気円二色性の第一原理計算」
第9回 福井謙一記念研究センターシンポジウム (2012年1月6日，京都)

(2) 池野豪一
「強相関計におけるXASおよびXMCDの第一原理計算」
強磁場X線・中性子線実験の発展 (2012年3月23日，神戸)

２．リサーチリーダー

Keiji MOROKUMA

Research Leader, Kenichi Fukui Memorial Research Group 1

1. Summary of the research of the year

Multi-level Simulation of Complex Molecular Systems

The goals of the research of this group are 1. to develop further the hybrid theoretical methods (such as ONIOM) already proposed by us, 2. to demonstrate that such hybrid methods can be used for simulations of structures, reactions and dynamics and 3. to solve some of the important problems in each field. Our research is supported in part by the Institute and in large fraction by a 5-year grant in the area of High Performance Computing for Multi-Scale and Multi-Physics Phenomena from CREST (Core Research for Evolutional Science and Technology) program of JST (Japan Science and Technology Agency) until March 2012. With ten to twelve postdoctoral fellows (both Fukui fellows and JST fellows), a few visiting graduate students and several research assistants in the group, as well as in collaboration with my group at Emory University, the group of Prof. Stephan Irle (a CREST collaborator) of Nagoya University as well as Prof. Satoshi Maeda, Assistant Professor at Hakubi Center, Kyoto University and from November 2011 at Hokkaido University, we have a strong team of theoretical/computational chemists working together toward a common goal. Since detailed description on individual projects can be found in the reports of postdoctoral fellows, here the areas of studies and titles of individual projects are summarized.

I. Simulation of Reactions and Dynamics of Complex and Biomolecular Systems

In the area of **multi-level simulation of complex and biomolecular systems**, in recent years we have studied structures and reactions of metalloenzyme systems mainly using the active site models in which only the active site atoms are explicitly included in the QM calculations. In the last few years we have explicitly included the effects of protein employing the ONIOM QM/MM scheme. We optimized the structures of intermediates and transition states of enzymatic reactions, and in some cases included the statistical effects of protein by QM/MM molecular dynamics. In a few examples we have found that the protein effects completely changed the mechanism of reaction, compared to the active-site models. We also perform direct dynamics calculations using QM and QM/MM methods to study the primary events of photochemical processes of organic and biomolecular chromophores. We recently expanded our theoretical studies of catalytic reactions that take place in the nano cavity created by the protein and nucleic acids.

a) **Reaction Mechanism of Biosynthesis of Antibiotic Fosfomycin in HppE (**See research activities of Dr. Chung and Dr. Petrova)
b) **DFT study of the mechanism of NO reduction in bacterial nitric oxide reductase** (See research activities of Dr. Hatanaka)
c) **Effect of protein environment on the NO reduction: An ONIOM study reductase** (See research activities of Dr. Hatanaka)
d) **Comparative Reactivity of Hydrogen Atom Transfer (HAT) with Important Metal-Oxo and Ferric-Superoxo Species** (See research activities of Dr. Chung)
e) **Theoretical modeling of stereochemistry control of copper catalysts based on the chirality of DNA** (See research activities of Dr. Ptrova)
f) **Theoretical Study of Asymmetric Hydration Catalyzed by DNA-based Artificial Enzyme Metalloenzymes** (See research activities of Dr. Ke)
g) **Theoretical Study of Polymerization Catalyzed by Artificial Metalloenzymes** (See research activities of Dr. Ke)
h) **ONIOM Investigation of Iron Uptake by Ferritin** (See research activities of Dr. Harris)
i) **Ring-Opening and Ring-Closure Mechanism of Spiropyran-Merocyanine Photochromic Reaction** (See research activities of Dr. Liu)

j) **Photodynamics and Isomerization Mechanisms of All-trans and 13-cis, 15-syn Retinal Protonated Schiff Base in the light-adapted and dark-adapted Bacteriorhodopsin** (See research activities of Dr. Xin Li)
k) **Reaction Mechanism of Photo-induced Decarboxylation of the Photoactivatable Green Fluorescent Protein:An ONIOM(QM:MM) Study** (See research activities of Dr. Ding)
l) **Mechanistic study on the Photoisomerization in Polypyridyl mononuclear ruthenium(II) aquo (PMRA) complex** (See research activities of Dr. Ding)
m) **Reaction Mechanism of Hydrogenation of Carbon Dioxide Catalyzed by Ir-PNP Complex** (See research activities of Dr. Chung)

II. Simulation of Nanomaterials

In the area of **simulation of nanomaterials,** we continued our research efforts on quantum chemical molecular dynamics (QM/MD) computations of carbon and other nanostructure formation based on density functional tight binding (DFTB). Single-walled carbon nanotubes (SWNTs) have been one of representative nanotechnology materials and their various potential applications. Although SWNTs are known to be efficiently synthesized using metal catalyst, its growth mechanism is still not well understood. In order to understand interplay among feedstock carbon, nanotube, and metal, we have implemented growth simulations of metal-catalyzed SWNT using DFTB MD simulations. This year we invented a theoretical method to define the local chirality of irregular carbon nanotubes and used this definition to analyze mechanism of retention and loss of chirality during the growth of carbon nanotubes.

a) **Effects of Molecular Dynamics Thermostats on Descriptions of Chemical Non-Equilibrium** (See research activities of Dr. Page)
b) **Functionalization of Fullerenes Using a Genetic Algorithm** (See research activities of Dr. Page)
c) **The Reaction Pathway for C_4H_2 Polyyne Fusion Reactions: A Theoretical Investigation** (See research activities of Dr. Signh)
d) **Determination of Local Chirality in Irregular Single-Walled Carbon Nanotube Based on Individual Hexagons** (See research activities of Dr. Kim)
e) **Chirality-Controlled Carbon Nanotube Growth from Organic Templates** (See research activities of Dr. Page)
f) **SWCNT Growth from Chiral Carbon Nanorings: Prediction of Chirality and Diameter Influence on Growth Rates** (See research activities of Dr. Haibei Li)
g) **Sub-Surface Nucleation of Graphene Precursors near a Ni(111) Step-Edge** (See research activities of Dr. Haibei Li)

III. Method Developments and Applications

Previously we have extended the Global Reaction Route Mapping (GRRM) method developed previously by Ohno and Maeda to automatic search of the minimum of seam of crossing (MSX) including the conical intersection. This year we applied this method for elucidation of the mechanism of photodissociation reactions. In photodissociation of NO3, we found a totally new kind of reaction mechanism, in which the molecule in an excited state roam around a roaming transition state and branches into the direct excited state dissociation and the ground state dissociation after nonadiabatic transition to the ground state. This mechanism since has been unequivocally proved by an experimental study.

A new method, artificial force-induced reaction (AFIR) method, suitable to determining the transition and intermediates of reactions of two or more molecules $A + B (+C\ldots) \rightarrow X$, has been developed based on imposing an artificial attractive force between the reactant molecules. The application of this method to the Passerini and other multicomponent organic reactions has shown that textbook mechanisms of some of the multicomponent reactions are wrong, and actually additional molecules are involved as a catalyst. The method has also been used to determine the best reaction pathway for the full catalytic cycle for the reaction of $C_2H_4 + CO + H_2$ catalyzed by $HCo(CO)_3$.

(Work in collaboration with Prof. Maeda, who was Assistant Professor at Hakubi Center of Kyoto University and Visiting Assistant Professor at FIFC. See also his Research Activities)

a) **Finding Reaction Pathways of Type A + B → X: Toward Systematic Prediction of Reaction Mechanisms**
b) **No Straight Path: Roaming in Both Ground- and Excited-State Photolytic Channels of NO_3 → NO + O_2**
c) **Fitting Global *Ab Initio* Potential Energy Surfaces for Low-lying Doublet States of NO_3** (See research activities of Dr. Xiao)
d) **Exploring Multiple Potential Energy Surfaces: Photochemistry of Small Carbonyl Compounds Experimental and Theoretical Investigations of Isomerization Reactions of Ionized Acetone and Its Dimer**
e) **Theoretical Study of the Photodissociation Dynamic of Ketene**
f) **Toward Predicting Full Catalytic Cycle Using Automatic Reaction Path Search Method: A Case Study on $HCo(CO)_3$-Catalyzed Hydroformylation**

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4. Presentation at academic conferences and universities

1. Exciting World of Theoretical Studies of Chemical Reactions – From Gas Phase Reactions to Nano Structures, Catalysts, and Enzymatic Reactions Division of Chemistry and Biological Chemistry. Nanyang Technological University. March 26, 2012

2. How much can complex chemical reactions be understood by the use of theoretical and computational chemistry? Hiratsuka Symposium at Kanagawa University, March 9, 2012
3. Theoretical Studies of Chemical Reactions and Dynamics -- Mainly ONIOM Applications, The workshop "Introduction to Gaussian: Theory and Practice" February 23, 2012. Global Scientific Information and Computing Center (GSIC) ＆Computational Chemistry Collegium, Tokyo Institute of Technology (TITECH)
4. Two Stories of Chemical Reactions. 1. Exploring Reaction Pathways Using Automated Reaction Route Finders. 2. Nucleation, Growth and Healing Processes of Single-Walled Carbon Nanotubes. Quantum Molecular Dynamics: A Conference in Honor of William H. Miller, University of California, January 9-12, 2012
5. Application of molecular simulations to bionaoscience, Supercomputing Workshop, Institute for Molecular Science, Okazaki, Japan, January 24-25, 2012
6. Theoretical studies of chemical reactions. From the frontier theory to present and future. Fukui Center Symposium, January 6, 2012
7. Theoretical Studies of Chemical Reactions – From Simple Molecules to Complex Systems. Molecular Science Symposium, Sapporo, Japan, September 21, 2011.
8. Nucleation, Growth and Healing Processes of Single-Walled Carbon Nanotubes from Metal Clusters and SiO_2 and SiC Surfaces: Density Functional Tight-Binding Molecular Dynamics Simulation, Sixteenth International Workshop on Quantum Systems in Chemistry and Physics, Kanazawa, Japan, September 11, 2011
9. Theoretical Studies of Chemical Reactions and Dynamics of Biomolecular Systems in Protein, 14th Asian Chemical Congress (14ACC), Bangkok, Thailand, September 8, 2011
10. Theoretical Studies of Chemical Reactions – Gas Phase Reactions to Nano Structures, Catalyses, and Enzymatic Reactions in Ground and Excited Electronic States, 7th Congress of the International Society for Theoretical Chemical Physics, Waseda University, Tokyo, Japan, September 2, 2011
11. Exciting World of Theoretical Studies of Chemical Reactions ‐ From Gas Phase Reactions to Nano Structures, Catalysts, and Enzymatic Reactions, Dalian Institute of Chemical Physics, Chinese Academy of Science, Dalian, China,
12. Exploring Reaction Pathways Using Automated Reaction Route Finders. International Conference on Theoretical and High Performance Computational Chemistry, Xi'an, China, August 11-14, 2011
13. Computational Studies of Chemical Reactions of Molecular Systems: Overview of Our Recent Activities. 2011 Congress of World Association of Theoretical and Computational Chemistry (WATOC), Santiago de Compostela, Spain, July 16-22, 2011
14. ONIOM QM/MM studies of reactions of transition metal complexes in biological and biomimetic environment. 3rd Quantum Bioinorganic Chemistry Conference, Český Krumlov, Czech Republic; June 25-28, 2011
15. Exciting World of Theoretical Studies of Chemical Reactions ‐ From Gas Phase Reactions to Nano Structures, Catalysts, and Enzymatic Reactions. Heyrowsky Institute, Czech Academy of Science, Prague, Czech Republic, June 24, 2011

5. Public talks

1. Let's Explore the World of Chemical Reactions Using Computer (in Japanese), Open Lectures for High School Students, in Commemoration of the 30th Anniversary of Prof. Fukui's Nobel Prize, Fukui Institute for Fundamental Chemistry, Kyoto University, July 30, 2011.
2. Let's Explore the World of Chemical Reactions Using Computer (in Japanese), Kyoto University Junior Campus 2011, Fukui Institute for Fundamental Chemistry, Kyoto University, September 19, 2011.
3. Let's Explore the World of Chemical Reactions Using Computer (in Japanese), Academic Day, Kyoto University, March 10, 2012.
3. Let's Explore the World of Chemical Reactions Using Computer (in Japanese), Moriyama High School, Shiga Prefecture, March 19, 2012.
4. Let's Explore the World of Chemical Reactions Using Computer, Nanyang Technical University, Singapore, March 26, 2012.

Shigeyoshi SAKAKI

Research Leader, Kenichi Fukui Memorial Research Groups II

1. Summary of the research of 2011

Molecules and molecular systems which consist of transition metal element, organic moiety, non-transition metal element, and hypervalent element are attractive research targets in wide areas of chemistry. Actually, those molecules and complexes play important roles as metal enzymes, molecular catalysts, and molecular devices such as photosensitizer, molecular switch, luminescence material etc. Their functions deeply relate to their those electronic structures. In this regard, it is worthy elucidating the electronic structure of the complex system including transition metal element. Moreover, their electronic structures are interesting from the point of view of theoretical/computational chemistry, because their electronic structures are not simple but complicated in many cases. In particular, transition metgal complexes bearing large correlation effects are challenging research target even nowadays.

This year, we theoretically investigated (i) Noble Reaction Features in Oxidative Addition of B−Br σ−Bond of Bromoborane to $M(PMe_3)_2$ (M= Pt or Pd), (ii) Reaction Mechanism and Reaction Features of Epoxidation of alkenes by Ru-porphyrin (iii) MS-CASPT2 study of iron(III) complexes of catechol dioxygenase, (iv) HS→LS Transition of the Hoffmann type MOF, $\{Fe^{II}(pz)[Pt^{II}(CN)_4]\}$, by CS_2 absorption. We wish to report summary of them.

(i) Noble Reaction Features in Oxidative Addition of B−Br σ−Bond of Bromoborane to $M(PMe_3)_2$ (M= Pt or Pd)

Formation processes of *cis*−boryl complex~~es~~ via oxidative additions of B−H, B−B, and B−E (E═Si, Ge, or Sn) bonds to low−valent transition−metal complexes have been clarified theoretically.[1] However, the mechanism for *trans*-boryl complex produced by the oxidative addition of B−X (X═Cl, Br, or I) bond to Pd(0) and Pt(0) complexes remains unclear yet, in which the cis−trans isomerization is proposed to be involved. However, the cis-trans isomerization occurs via spin conversion process in general, [2] but the cis-trans isomerization taking place on single potential surface has not been investigated well. Here, we theoretically investigated the oxidative addition of the B−Br bond of bromoborane $Br_2B(OSiMe_3)$ to $M(PMe_3)_2$ (M = Pt or Pd) to explore possible reaction pathways and to clarify the process of the thermal cis−trans isomerization in this reaction.

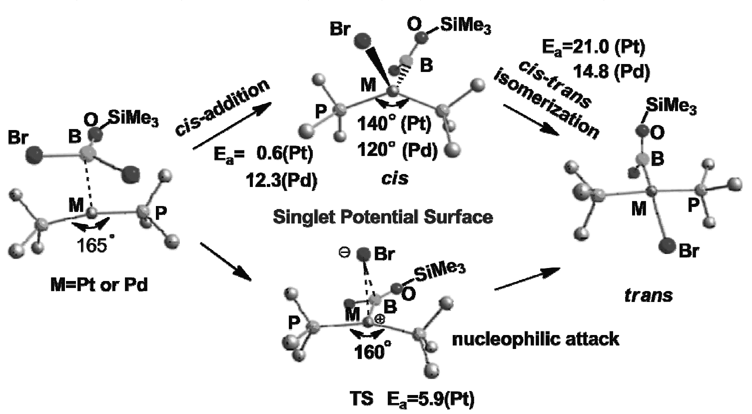


Fig. 1 Schematical geometry changes and energy changes in B-Br s-bond activation by Pt(0)

E_a (kcal/mol) is Gibbs energy barrier in solvent (toluene),

The first step is the coordination of $Br_2B(OSiMe_3)$ with $M(PMe_3)_2$ (M = Pt or Pd) to form a precursor complex. The next is the B−Br bond cleavage. In the Pt system, two reaction courses are possible (Scheme 1); one is the nucleophilic attack pathway which directly affords the *trans*−product. The other one is the stepwise reaction pathway which includes the *cis*−oxidative addition followed by the cis−trans isomerization. The former reaction course is more favorable. In the Pd system, only the stepwise pathway was found.

Interestingly, the thermal cis–trans isomerization was found to occur on the singlet potential energy surface due to the strong donation ability of the boryl group. The reason is interpreted in terms of the very strongly donating boryl ligand, as follows: Because the boryl ligand is very strongly donating, it destabilizes one d_σ orbital, the other four d orbitals become doubly occupied and hence the closed-shell singlet is the ground state.

(ii) Reaction Mechanism and Reaction Features of Epoxidation of alkenes by Ru-porphyrin

Epoxidation of olefine by $[Ru(TMP)(CO)(O)]^{-}$ (TMP = tetramesitylporphine), which is a key step of the photocatalyzed epoxidation of olefin by [Ru(TMP)(CO)], is studied mainly with the density functional theory (DFT) method, where [Ru(Por)(CO)] is employed as a model complex (Por = unsubstituted porphyrin). This reaction is of considerable interest because dioxygen molecule is not the oxygen source but water is the oxygen source; in other words, the water is employed as reactant. The CASSCF method was also used to investigate the electronic structure of important species in the catalytic cycle. In all of the ruthenium porphyrin species involved in the catalytic cycle, the weight of the main configuration of the CASSCF wave function is larger than 85%, suggesting that the static correlation is not very large. Also, unrestricted-DFT-calculated natural orbitals are essentially the same as CASSCF-calculated ones, here. On the basis of these results, we employed the DFT method in this work. Present computational results show characteristic features of this reaction, as follows: (I) The epoxidation reaction occurs via carboradical-type transition state. Neither carbocation-type nor concerted oxene-insertion-type character is observed in the transition state. (ii) Electron and spin populations transfer from the olefine moiety to the porphyrin ring in the step of the C_Obond formation. (iii) Electron and spin populations of the olefin and porphyrin moieties considerably change around the transition state. (iv) The atomic and spin populations of Ru change little in the reaction, indicating that the Ru center keeps the +II oxidation state in the whole catalytic cycle. (v) The stability of the olefiene adduct [Ru(Por)(CO)(O)(olefiene) considerably depends on the kind of olefin, such as ethylene, n-hexene, and styrene. In particular, styrene forms a stable olefin adduct. And, (vi) interestingly, the difference in the activation barrier among these olefin is small in the quantitative level (within 5 kcal/mol), indicating that this catalyst can be applied to various substrates. This is because the stabilities and

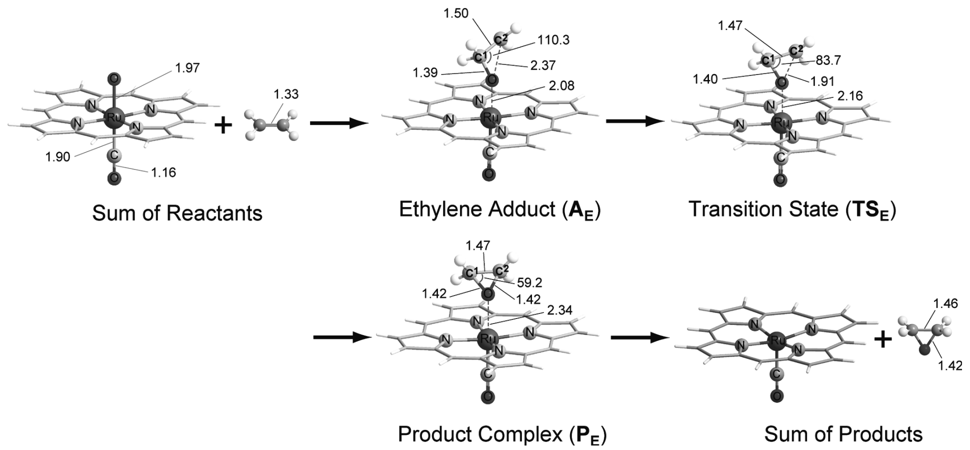


Fig.2 Geometry changes of ethylene epoxidation by Ru-porphyrin

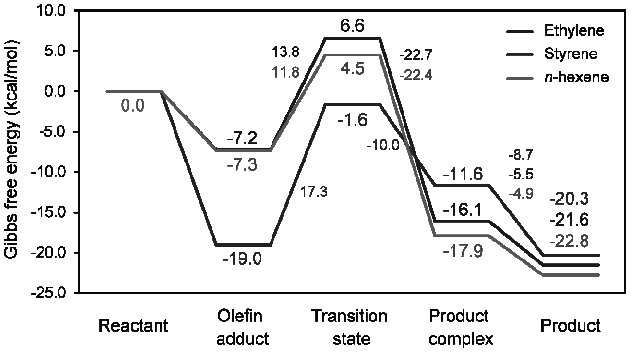
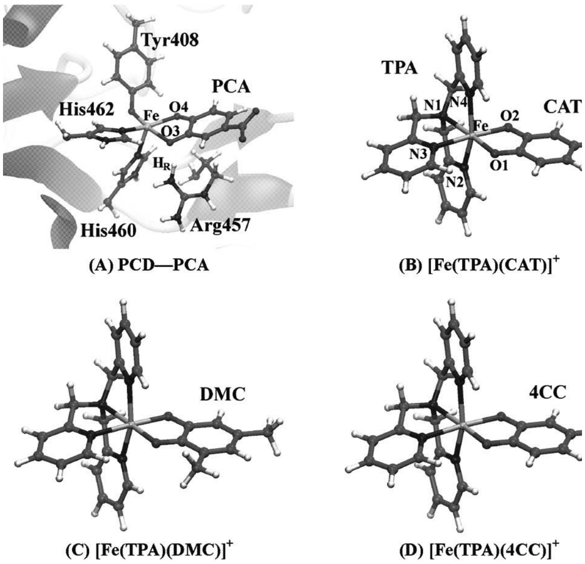


Fig. 3 Energy changes by epoxidation of three olefins by Ru-porphyrin

electronic structures of both the olefin adduct and the transition state are similarly influenced by the substituent of olefin.

(iii) MS-CASPT2 study of iron(III) complexes of catechol dioxygenase



(A) PCD—PCA (B) [Fe(TPA)(CAT)]$^+$

(C) [Fe(TPA)(DMC)]$^+$ (D) [Fe(TPA)(4CC)]$^+$

Fig.4 Model Fe(III) complexes examined here

Table 1. MS-CASPT2- and CAS-PT2-calculated LMCT transition energy of model complounds (in eV)

Compound	MS-CASPT2	CASPT2	TD-DFT	Expt.
PCD-PCA	1.57	0.74	0.81	1.75
[Fe(TPA)(CAT)]$^+$	1.45	0.46	1.41	1.53
[Fe(TPA)(DMC)]$^+$	1.25	0.23	1.45	1.39
[Fe(TPA)(3CC)]$^+$	1.54	0.62	1.36	1.58

In bioinorganic chemistry, non-hem iron complexes attract a lot of interest, because of their interesting catalytic reactions such as oxygenation of aromatic compounds. In such non-hem iron(III) catechole dioxygenase, the relation between activity and ligand-tometal charge-transfer (LMCT) transition energy was pointed out experimentally. We theoretically investigated the LMCT excitation of the native iron(III)-dependent catechol dioxygenase and its functionalmodel complexes with multistate complete active space second-order perturbation theory (MS-CASPT2). The ground state calculated by the MS-CASPT2 method mainly consists of the iron(III) catecholate electron configuration and moderately of the iron(II) semiquinonate electron configuration for both of the enzyme active centers and the model complexes when the active center exists in the protein environment and the model complexes exist in the solution. However, the ground-state wave function mainly consists of the iron(II) semiquinonate electron configuration for both the enzyme active site without a protein environment and themodel complexes in vacuo. These results clearly show that the protein environment and solvent play important roles to determine the electronic structure of the catecholatoiron(III) complex. The LMCT excitation energy clearly relates to the weight of the iron(III)-catecholate configuration in the ground state. The reactivity and the LMCT excitation energy directly relate to the ionization potential of the catecholate (IPCAT) in the model complex. This is because the charge transfer fromthe catecholatemoiety to the dioxygen molecule plays a key role to activate the dioxygen molecule. However, the reactivity of the native catechol dioxygenase ismuch larger than those of the model complexes, despite the similar IPCAT values, suggesting that other factors such as the coordinatively unsaturated iron(III) center of the native enzyme play a crucial role in the reactivity.

(iv) HS→LS Transition of the Hoffmann type MOF, {Fe^{II}(pz)[Pt^{II}(CN)$_4$]}, by CS$_2$ absorption

It is recently reported that a porous coordination polymer (PCP), {Fe^{II}(pz)[Pt^{II}(CN)$_4$]} (pz = pyrazine, Figure 4), adsorbs various guest molecules to induce spin transition between the LS and the HS states at room temperature. For instance, LS→HS transition is induced by adsorption of guest species whose size or occupation number per pore is large in many cases. This transition is understood by steric repulsion between bulky guests and the PCP framework, as follows. The steric repulsion is smaller in the HS framework than in the LS one because the HS framework is larger than the LS one. Hence, the HS framework is favorable for adsorption of bulky guests. This is the reason why the LS→HS transition is induced by bulky guests. In the case of adsorption of CS_2, on the other hand, reverse HS→LS transition is unexpectedly induced. The reason of this reverse transition is not clear at all.

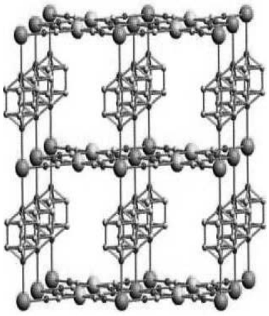


Fig. 4 Hoffmann-type MOF

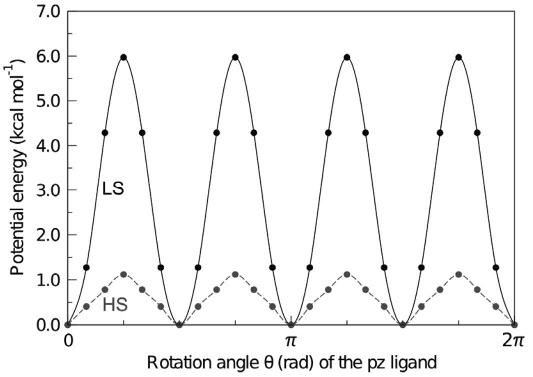


Fig. 5 Pyrazyne rotation around Fe-Fe axis

We investigated the mechanism of the CS_2-induced HS→LS transition of $\{Fe^{II}(pz)[Pt^{II}(CN)_4]\}$, considering hindered rotational entropy of the pz ligands. In the guest-free PCP, pz ligands rotate much easier in the HS framework than in the LS one, as shown in Fig. 4. This is because the steric repulsion in the HS framework is weaker than in the LS one. Thus, the entropy difference (ΔS_{rot}) between the LS and the HS states is positive. In CS_2 clathrate, however, CS_2 molecules are strongly adsorbed between pz ligands to suppress the pz rotation and to decrease $\Delta Srot$. We evaluated the $\Delta Srot$ value and estimated how much $T_{1/2}$ shifts through the CS_2 adsorption. The results indicate that the decrease in ΔS_{rot} induces the HS→LS transition. All computational results and discussion are consistent with the experimental ones. This is the first clear understanding of the $T_{1/2}$ shift based on the entropy difference between the LS and the HS states.

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(2) Naoki Nakatani, Yutaka Hitomi, and Shigeyoshi Sakaki
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(7) Shinya Tsukamoto and Shigeyoshi Sakaki
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between Transition Metal and Non-Transition Metal Elements; Geometry, Bond Strength,
and Prediction
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(8) Hideo Ando, Yoshihide Nakao, Hirofumi Sato, Masaaki Ohba, Susumu Kitagawa, Shigeyoshi Sakaki
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(9) Shibata, Naoto, Hirofumi Sato, Shigeyoshi Sakaki, Yuji Sugita
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(10) Hiroyuki Sakaba, Hiroyuki Oike, Masaaki Kawai, Masato , Takami, Chizuko Kabuto, Mausumi Ray, Yoshihide Nakao, Hirofumi Sato, and Shigeyoshi Sakaki
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Theor. Chem. Acc., 130, 237-250 (2011).

(12) Milind Deshmukh, Shigeyoshi Sakaki
Binding energy of gas molecule with two pyrazine molecules as organic linker in
meal-organic framework: its theoretical evaluation and understanding of determining
factors
Theor. Chem. Acc., 130, 475-482 (2011).

3. Presentation at academic conferences

(1) Shigeyoshi Sakaki
"Theoretical Study of Dinuclear Transition Metal Complexes: Interesting Electronic Structures and Molecular Properties, 4th Japan-Czech-Slovakia Joint Symposium for Theoretical and Computational Chemistry, Prague, 2011/5/18-20. (Invited Talk)

(2) Shigeyoshi Sakaki
"Heterolytic C-H σ-Bond Activation Reaction; Driving Force, Regioselectivity, Orbital Mixing, and Its Application to Pd-Catalyzed Direct Cross-Coupling Reaction", 9th World Association of Theoretical and Computational Chemists (WATOC2011), Sanchiago de Compostella, Spain, 2011/7/17-22. (Invited Talk)

(3) Shigeyoshi Sakaki, Milind Deshmukh, Hideo Ando, Yoshihide Nakao, Hirofumi Sato
"Theoretical Study of Gas-Adsorption to Metal-Organic-Framework (MOF)"
7th Congress of the International Society for Theoretical Chemical Physics (ISTCP-VII) at Waseda University, Tokyo, Japan on September 2-8, 2011. (Invited Talk)

(4) Shigeyoshi Sakaki
"Theoretical Study of σ-Bond Activation Reaction by Transition Metal Complex and Catalytic Reaction Including It", The 14th Asian Chemical Congress 2011 (14 ACC) Sept. 5-8, 2011 in Bangkok, Thailand. (Invited Talk)

(5) Shigeyoshi Sakaki
"C-H σ-Bond Activation Reaction and Catalytic Reactions by Transition Metal Complexes: Theoretical Study**"**, The 9th International Conference on Computational Methods for Science and Technology (ICCMSE), Oct., 2 to 7, Halkidiki, Greece (Invited Talk)

4. Others

（1）榊　茂好

“理論・計算化学の現在の成果と近未来：触媒反応、分子物性へのアプローチを例として” 計算分子科学拠点第１回　産学連携シンポジウム、野村コンファレンスプラザ日本橋、東京、2011年11月24日

(2) 榊　茂好　Hiroyuki Tamura, Shinkoh Nanbu, Toshimasa Ishida, and Hiroki Nakamura
“理論化学・計算化学と実験化学のインタープレイ：元素戦略への貢献を期待して“、CREST「元素戦略を基軸とする物質・材料の革新的機能の創出」理論と実験の連携強化を目指したシンポジウム（基調講演）　平成24年1月24日　東京（富士ソフトアキバプラザ）

(3) 榊　茂好
“遷移金属化学種の分子物性と反応過程：電子状態からの微視的理解と予測”、第２２回神奈川大学平塚シンポジウム　平成２４年３月９日　平塚(神奈川大学湘南ひらつかキャンパス)

３．特定助教（白眉）

Satoshi MAEDA
Visiting Assistant Professor (The Hakubi Center, Kyoto University),
Kenichi Fukui Memorial Research Group 1
(To 31 Jan. 2012)

1. Summary of the research of the year

1-0. Introduction

The mechanism of chemical reactions can be elucidated by exploring quantum chemical potential energy surfaces (PESs) and finding reaction pathways [1,2]. Search for transition state (TS) structures is the primal task in such studies, since a reaction path can be computed easily by the intrinsic reaction coordinate (IRC) method [3] once a corresponding TS structure is found. Reaction mechanisms of numerous chemical reactions have been elucidated by calculations of TS structures and corresponding reaction pathways.

One TS structure can be found by a geometry optimization starting from an initial guess structure [4]. However, an initial guess structure leads only to a TS structure anticipated from it. For finding unexpected pathways as well as anticipated ones, systematic search is necessary using an automated reaction path search method.

There had been no general method which can explore chemical reaction pathways automatically on quantum mechanical PESs until very recently. Hence, we have developed two such methods: global reaction route mapping (GRRM) method [5-7] and artificial force induced reaction (AFIR) method [8, original paper 7]. These two are independent but complementally to each other. Reaction pathways of type A → X (isomerization) and A → X + Y (dissociation) can be explored by GRRM, while AFIR can search for A + B → X (+ Y) type synthetic pathways.

We applied these methods to some complex chemical reactions: photolysis of atmospheric molecules [original papers 1 and 5], an organometallic catalysis [original paper 3], and a photoionization induced dynamics in a hydrogen-bond cluster [original paper 4].

We developed a set of Li-H-C-O DFTB parameters and it was employed in a simulation study on sputtering and reflection dynamics of lithiated carbon material bombarded by slow hydrogen atoms [original paper 2]. A very accurate calculation of the energetics of $POCl + e^- \rightarrow PO + Cl^-$ reaction was also performed to analyze experimental data concerned with electron catalyzed mutual neutralization reactions of $POCl_3^-$ and $POCl_2^-$ each with Ar^+ and Kr^+ [original paper 6].

Works in original papers 1, 2, 4, and 6 were conducted with experimental groups.

[1] Schlegel, H. B. *J. Comput. Chem.* **2003**, *24*, 1514.

[2] Jensen, F. *Introduction to Computational Chemistry, 2nd edn.*, Wiley, Chichester, **2007**.

[3] Fukui, K. *Acc. Chem. Res.* **1981**, *14*, 363.

[4] Schlegel, H. B. *WIREs Comput. Mol. Sci.* **2011**, *1*, 790.

[5] Ohno, K.; Maeda, S. *Chem. Phys. Lett.* **2004**, *384*, 277.

[6] Maeda, S.; Ohno, K. *J. Phys. Chem. A* **2005**, *109*, 5742.

[7] Ohno, K.; Maeda, S. *J. Phys. Chem. A* **2006**, *110*, 8933.

[8] Maeda, S.; Morokuma, K. *J. Chem. Phys.* **2010**, *132*, 241102.

1-1. No Straight Path: Roaming in Both Ground- and Excited-State Photolytic Channels of $NO_3 \rightarrow NO + O_2$ *(original paper 1)*

Roaming mechanisms have recently been observed in several chemical reactions alongside trajectories that pass through a traditional transition state. Here, we demonstrate that the visible light–induced reaction $NO_3 \rightarrow NO + O_2$ proceeds exclusively by roaming. High-level ab initio calculations predict specific NO Λ doublet propensities (orientations of the unpaired electron with respect to the molecular rotation plane) for this mechanism, which we discern experimentally by ion imaging. The data provide direct evidence for roaming pathways in two different electronic states, corresponding to both previously documented photolysis channels that produce $NO + O_2$. More broadly, the results raise intriguing questions about the overall prevalence of this unusual reaction mechanism.

1-2. Dynamics of Deuterium Retention and Sputtering of Li–C–O Surfaces *(original paper 2)*

Chemistry as well as sputtering and reflection dynamics of lithiated carbon material, bombarded by slow hydrogen atoms are studied. We present a realistic method for computational simulation of the dynamics of the polar Li–C–O–H material dynamics. It is based on an approximate, semi-empirical quantum mechanics of electrons and classical mechanics of nuclei. Results are validated qualitatively by comparison with experiments and with a first principle DFT computations. In particular, we explain observed details of the hydrogen bonding chemistry in lithiated carbon, showing that incoming hydrogen interacts preferably with Li-C rather than C structures.

1-3. Toward Predicting Full Catalytic Cycle Using Automatic Reaction Path Search Method: A Case Study on $HCo(CO)_3$-Catalyzed Hydroformylation *(original paper 3)*

Toward systematic prediction of reaction pathways in complex chemical reaction systems by quantum chemical calculations, a new automatic reaction path search approach has been proposed on the basis of the artificial force induced reaction (AFIR) method [*J. Chem. Theory Comput.* **2011**, *7*, 2335-2345.]. We demonstrate in this Letter that this approach enabled semi-automatic determination of the full catalytic cycle of the $HCo(CO)_3$-catalyzed hydroformylation. The search was fully systematic; no initial guess was required concerning the entire reaction mechanism as well as each transition state structure. This approach opens the door to non-empirical prediction of complex reaction mechanisms involving multiple steps in multiple pathways, such as full cycles of catalytic reactions.

1-4. Experimental and Theoretical Investigations of Isomerization Reactions of Ionized Acetone and Its Dimer *(original paper 4)*

Ionization dynamics of acetone and its dimer in supersonic jets is investigated by a combination of experimental and theoretical techniques, both of which have recently been developed. In experiments, the neutral and the cationic structures are explored by infrared predissociation spectroscopy with the vacuum-ultraviolet photoionization detection schemes. Reaction paths following the one-photon ionization of the acetone monomer and its dimer have been studied by the joint use of several theoretical methods including the ab initio molecular dynamics, the global reaction route mapping, the intrinsic reaction coordinate, and the artificial force induced reaction calculations. Upon one-photon ionization, the dimer isomerizes to the H-bonded form, in which the enol cation of acetone is bound to the neutral molecule, while this enolization is energetically forbidden in the acetone monomer. The enolization of the dimer cation occurs through a two-step proton-transfer from the methyl group of the ionized moiety, and is catalyzed by the neutral moiety within the dimer cation.

1-5. Exploring Multiple Potential Energy Surfaces: Photochemistry of Small Carbonyl Compounds *(original paper 5)*

In theoretical studies of chemical reactions involving multiple potential energy surfaces (PESs) such as photochemical reactions, seams of intersection among the PESs often complicate the analysis. In this paper, we review our recipe for exploring multiple PESs by using an automated reaction path search method which has previously been applied to single PESs. Although any such methods for single PESs can be employed in the recipe, the global reaction route mapping (GRRM) method was employed in this study. By combining GRRM with the proposed recipe, all critical regions, that is, transition states, conical intersections, intersection seams, and local minima, associated with multiple PESs, can be explored automatically. As illustrative examples, applications to photochemistry of formaldehyde and acetone are described. In these examples as well as in recent applications to other systems, the present approach led to discovery of many unexpected nonadiabatic pathways, by which some complicated experimental data have been explained very clearly.

1-6. Temperature Dependences of Rate Coefficients for Electron Catalyzed Mutual Neutralization *(original paper 6)*

The flowing afterglow technique of variable electron and neutral density attachment mass spectrometry (VENDAMS) has recently yielded evidence for a novel plasma charge loss process, electron catalyzed mutual neutralization (ECMN), i.e., $A^+ + B^- + e^- \rightarrow A + B + e^-$. Here, rate constants for ECMN of two polyatomic species ($POCl_3^-$ and $POCl_2^-$) and one diatomic species (Br_2^-) each with two monatomic cations (Ar^+ and Kr^+) are measured using VENDAMS over the temperature range 300 K-500 K. All rate constants show a steep negative temperature dependence, consistent with that expected for a three body process involving two ions and an electron. No variation in rate constants as a function of the cation type is observed outside of uncertainty; however, rate constants of the polyatomic anions ($\sim 1 \times 10^{-18}$ cm^6 s^{-1} at 300 K) are measurably higher than that for Br_2^- [$(5.5 \pm 2) \times 10^{-19}$ cm^6 s^{-1} at 300 K].

1-7. Finding Reaction Pathways of Type A + B → X: Toward Systematic Prediction of Reaction Mechanisms *(original paper 7)*

In these five decades, many useful tools have been developed for exploring quantum chemical potential energy surfaces. The success in theoretical studies of chemical reaction mechanisms has been greatly supported by these tools. However, systematic prediction of reaction mechanisms starting only from given reactants and catalysts is still very difficult. Toward this goal, we describe the artificial force induced reaction (AFIR) method for automatically finding reaction paths of type A + B → X (+ Y). By imposing an artificial force to given reactants and catalysts, the method can find their reactive sites very efficiently. Further pressing by the artificial force provides approximate transition state and product structures, which can be easily reoptimized to the corresponding true ones. This procedure can be executed very efficiently just by minimizing a single function called the AFIR function. All important reaction paths can be found by repeating this cycle starting from many initial orientations. We also discuss perspectives of automated reaction path search methods toward the above goal.

2. List of original papers

(1) M. P. Grubb, M. L. Warter, H. Xiao, S. Maeda, K. Morokuma, S. W. North, No Straight Path: Roaming in Both Ground- and Excited-State Photolytic Channels of NO_3 → $NO + O_2$, *Science*, **2012**, *335*, 1075-1078.

(2) P. S. Krstic, J. P. Allain, A. Allouche, J. Jakowski, J. Dadras, C. N. Taylor, Z. Yang, K. Morokuma, S. Maeda, Dynamics of Deuterium Retention and Sputtering of Li–C–O Surfaces., *Fusion Eng. Des.*, [doi:10.1016/j.fusengdes.2011.07.009].

(3) S. Maeda, K. Morokuma, Toward Predicting Full Catalytic Cycle Using Automatic Reaction Path Search Method: A Case Study on $HCo(CO)_3$-Catalyzed Hydroformylation., *J. Chem. Theory Comput.*, **2012**, *8*, 380-385.

(4) Y. Matsuda, K. Hoki, S. Maeda, K.-i. Hanaue, K. Ohta, K. Morokuma, N. Mikami, A. Fujii, Experimental and Theoretical Investigations of Isomerization Reactions of Ionized Acetone and Its Dimer., *Phys. Chem. Chem. Phys.*, **2012**, *14*, 712-719.

(5) S. Maeda, K. Ohno, K. Morokuma, Exploring Multiple Potential Energy Surfaces: Photochemistry of Small Carbonyl Compounds., *Adv. Phys. Chem.*, **2012**, *2012*, 268124 (13 pages).

(6) N. S. Shuman, T. M. Miller, J. F. Friedman, A. A. Viggiano, S. Maeda, K. Morokuma, Temperature Dependences of Rate Coefficients for Electron Catalyzed Mutual Neutralization., *J. Chem. Phys.*, **2011**, *135*, 024204 (8 pages).

(7) S. Maeda, K. Morokuma, Finding Reaction Pathways of Type A + B → X: Toward Systematic Prediction of Reaction Mechanisms., *J. Chem. Theory Comput.*, **2011**, *7*, 2335-2345.

3. List of review articles

(1) 大野公一・前田理「化学反応経路の自動探索」、*Mol. Sci.*, **2011**, *5*, A0042 (16 pages).

4. List of books

5. List of presentations at meetings

(1) (口頭発表)前田理・諸熊奎治、「反応経路自動探索法による触媒サイクルと選択性の量子化学的予測」、日本化学会第 92 春季年会(2012)、慶應義塾大学日吉キャンパス・矢上キャンパス、2012 年 3 月 25-28 日

(2) (招待講演) 前田理「人工力誘起反応法（AFIR）による化学反応経路探索」、シンポジウム「化学反応経路探索のニューフロンティア 2011」、北海道大学、2011 年 9 月 23-24 日

(3) (口頭発表)前田理・阿部恵里花・諸熊奎治、「反応経路自動探索法の有機金属触媒サイクルへの応用」、第 5 回分子科学討論会、札幌コンベンションセンター、2011 年 9 月 20-23 日

(4) (Oral) S. Maeda, K. Ohno, K. Morokuma, 16th International Workshop on Quantum Systems in Chemistry and Physics (QSCP- XVI), Kanazawa, Japan, September 11-17, 2011

(5) (Oral) S. Maeda, H. Xiao, R. Saito, K. Morokuma, Nonadiabatic Reactions Studied by Automated Reaction Path Search Methods., 7th Congress of the International Society for Theoretical Chemical Physics (ISTCP-VII), Waseda University, Tokyo, Japan, September 2-8, 2011

(6) (Invited talk) S. Maeda, Finding Chemical Reaction Pathways: Toward Systematic Prediction of Reaction Mechanisms., FISTC: Fukui International Symposium for Theoretical and Computational Chemistry, Kyoto, Japan, August 31 and September 1, 2011

(7) (ポスター発表)前田理・大野公一・諸熊奎治、「化学反応予測に向けた反応経路自動探索法の開発とその超並列化」、計算分子科学研究拠点（ＴＣＣＩ）第２回研究会、理化学研究所計算科学研究機構(AICS)、2011 年 8 月 11-12 日

(8) (Invited talk) S. Maeda, Finding Unexpected Reaction Pathways using Automated Reaction Route Finders., The World Association of Theoretical and Computational Chemists (WATOC) 2011, the Auditorio de Galicia and the Faculty of Medicine of the University of Santiago in Santiago de Compostela, Spain, July 17-22, 2011

(9) (口頭発表)前田理・諸熊奎治、「人工力誘起反応法による A + B → X 型反応経路の自動探索」、第 14 回理論化学討論会、岡山大学創立五十周年記念館、2011 年 5 月 12-14 日

(10) (Invited talk) S. Maeda, A New Paradigm for Finding Reaction Pathways for Organic Multicomponent Reactions., The First International Symposium on Computational Sciences (ISCS2011), Shanghai, China, April 18-21, 2011

6. Others

４．博士研究員

Zhuofeng KE

FIFC Fellow, Fukui Kenchi Memorial Research Group 1

1. Summary of the research of the year

I. Theoretical Study of Polymerization Catalyzed by Artificial Metalloenzymes.

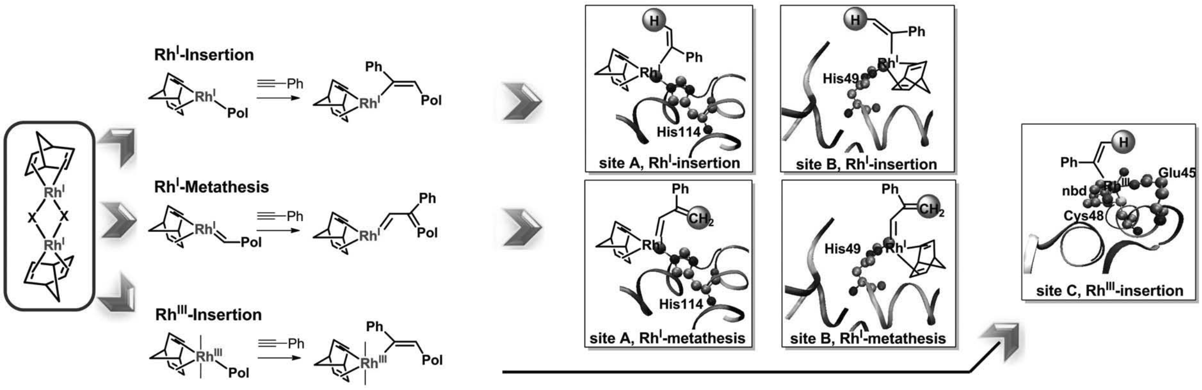


Figure 1. *Plausible active sites A, B and C inside Rh(nbd)•apo-Fr for the Rh-diene catalyzed polymerization of PA: the* Rh^I*-insertion,* Rh^I*-metathesis or* Rh^{III}*-insertion.*

Artificial metalloenzyme is a promising strategy to mimic enzyme catalytic functions or to develop novel enzyme-like catalysis, via combination of metal complex(es) into a host protein,. This strategy exhibits the advantages of metal complex in easy accessibility, broad substrate scope, and versatile reaction transformation, and the merits of enzyme in high efficiency, specific selectivity, and green chemistry. Therefore, it has intriguing potentials in the application and development of catalysis, through chemical evolution of metal complexes component and genetic evolution of the protein component. However, the design of new artificial metalloenzymes is rather challenging due to the complicated interactions between metal complex and protein, especially when the metal complexes have variable geometries in binding sites. To advance development of artificial metalloenzymes, it is important to detailedly understand the active site and the exact reaction mechanism inside host protein. Unfortunately, it is difficult to characterize the active species for the catalysis inside artificial metalloenzymes. Sometimes, only with some X-ray crystal structures of catalytic precursors or intermediates, the catalysis process inside artificial metalloenzyme is still less known. This study will clarify, with QM/MM studies, the complicated reaction polymerization mechanism for a recently developed artificial metalloenzyme system (**Rh(nbd)·*apo*-Fr**), with the X-ray proposed A, B, and C types of binding sites (Figure 1).

We have previously studied computationally the detailed mechanism of polymerization of PA catalyzed by the homogenous catalyst $[Rh(nbd)Cl]_2$ without protein environment. (J. Am. Chem. Soc. **2011**, 133, 7926-7941). The equilibriums of the reaction intermediates in the solution are more complicated than generally assumption. The Rh^I, Rh^{III}, and Rh-carbene types of intermediates are all thermodynamically and kinetically feasible. Among them, the Rh^{I} insertion mechanism is most preferred for the polymerization. In contrast, the Rh^{III} insertion and the Rh-carbene metathesis mechanisms need to overcome higher reaction barriers. Rh^{I} insertion shows perfectly regio- and stereoselectivity, i.e. the 2,1-inserion of PA leading to the head-to-tail *cis–transoidal* PPA. To elucidate how different is the polymerization mechanism inside artificial metalloenzyme from that in homogeneous solution, with the influence of the protein environment, we carried out a QM/MM study on the complicated polymerization mechanism for the (**Rh(nbd)·*apo*-Fr**) system, (nbd = norbornene) which is composed of a rhodium complex $[Rh(nbd)Cl]_2$ and the recombinant horse L-chain *apo*-Ferritin. We found that the binding sites A, B and C, from X-ray crystal structure, are only precursors/intermediates, not true active sites for the polymerization of phenylacetylene (PA). A new hydrophobic site D is suggested to be the most plausible active site for the polymerization. After the coordination of first monomer PA, the Rh^{I}(PA) complex is extruded from site B to the hydrophobic site D nearby. Then the polymerization occurs in site D via Rh^{I}-insertion mechanism. Importantly, a specific "hydrophobic region" composed by the hydrophobic active site D, the nonpolar 4-fold channel and other hydrophobic resides nearby is found to facilitate the accumulation, coordination and insertion of PA for the polymerization.

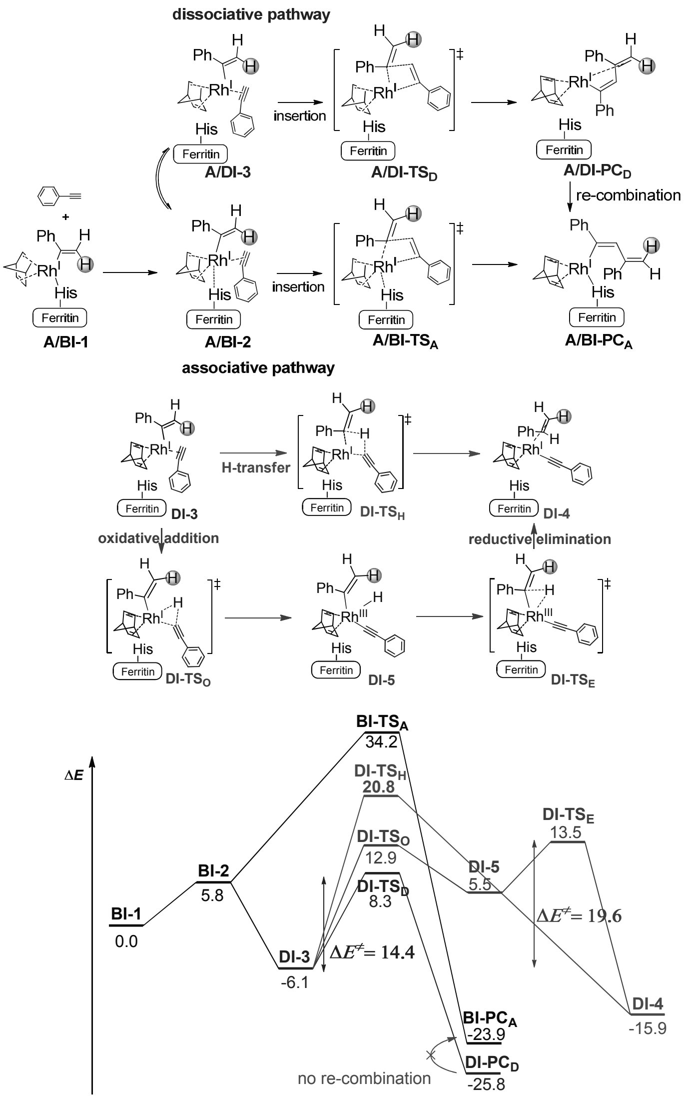
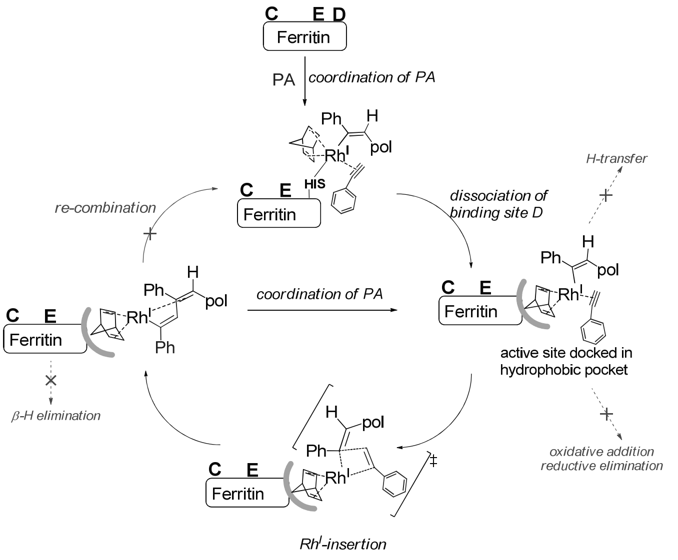


Figure 2. *The plausible active site in hydrophobic pocket near site D and the 4-fold channel.*

Scheme 1. *The overview mechanism of the polymerization of PA in the studied artificial metalloenzyme system.*



Our results also demonstrate that the hydrophobic active site D can retain the native regio and stereoselectivity of the Rh-catalyzed polymerization of PA without protein. The preferred potential energy surfaces, as well as reaction scheme, are shown in Figure 2. The overall reaction mechanism is shown in Scheme 1. This study highlights the importance of theoretical study in mechanistic understanding and rational design of artificial metalloenzymes, indicating that even with X-ray crystal structures at hand we may still be far from fully understanding the active site and the catalytic mechanism of artificial metalloenzymes.

II. Theoretical Study of Asymmetric Hydration Catalyzed by DNA-based Artificial Enzyme.

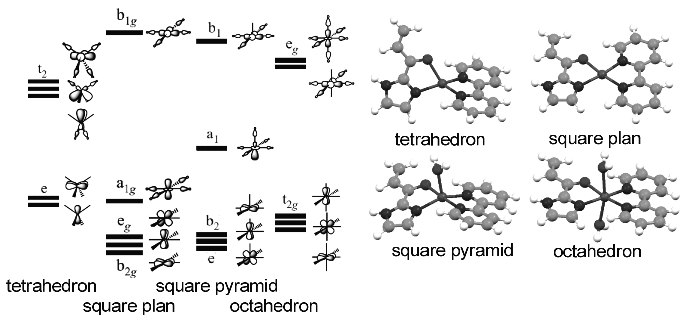


Figure 3. *The d orbital splitting in the ligand fields of tetrahedral, square planar, square pyramidal and octahedral transition metal complexes.*

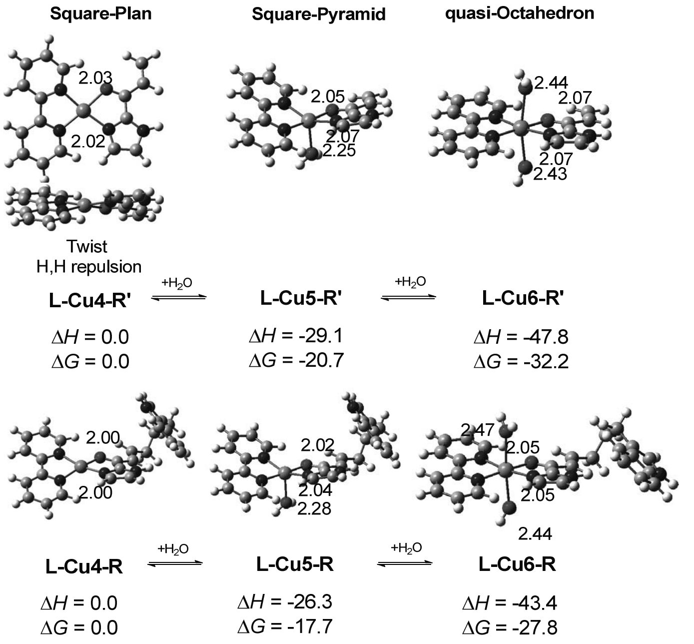


Figure 4. *The thermodynamic stabilities of the studied CuII complexes in aqueous.*

Biomacromolecule, like DNA, based catalysts recently emerges as an attractive strategy to the synthesis of enantiomerically pure compounds. Through recombination of DNA and metal complexes with a specific ligand, high stereoselectivity and rate enhancement had been achieved in several important applications, such as Diels–Alder, Michael addition, Friedel–Crafts reactions and hydration reactions. A novel non-enzymatic catalytic enantioselective hydration of enones was recently published by Ben L. Feringa, Gerard Roelfes and co-workers. The chiral b-hydroxy ketone product was obtained in up to 82% enantiomeric excess. Importantly, this diastereospecific and enantioselective reaction had no equivalent in conventional homogeneous catalysis. Herein, our theoretical study aims to understand the mechanism and the factors that controlling the enantioselectivity, which is of fundamental important to the development of these types hybrid catalysis with DNA

First, we studied the geometries and the thermodynamic stabilities of the studied Cu^{II}

complexes in aqueous. Copper plays important roles in metal-catalyzed and enzymatic processes. Natural copper compounds usually exist as Cu^{I} and Cu^{II} states. Cu^{II} with an open-shell d^9 electronic configuration is harder than Cu^{I} and softer than Cu^{III}, thus have complicated coordination situation, especially due to its Jahn-Teller effect(Figure 3). We performed DFT calculations for four, five and six-coordinated CuII complexes with model systems (L1-Cu-R') and real systems (L1-Cu-R) (Figure 4). The results for both model and real systems consist well with each other and suggest that the Cu^{II} complexes prefer five and six-coordinated structures with additional axial solvent ligands, rather than a four-coordinated square planar structure.

Table 1. Binding Energy from Docking Simulation.

Binding Energy (kcal/mol)	DNA1N(3.75) minor groove	DNA2N(3.75) minor groove	DNA1L(6.5) into layer	DNA2L(6.5) into layer
L1-Cu4-R'	-5.42	-4.58	-5.58	-5.42
L1-Cu5-R'	-6.29	-5.23	-5.95	-5.69
L1-Cu6-R'	-6.16	-5.69	-6.71	-6.50
L2-Cu-R	-8.89	-7.10	-9.25	-8.79

DNA1/2N is oligonucleotides with normal structures whose base-pair distance is 3.75 Å; DNA1/2L is oligonucleotides with artificial structures whose base-pair distance is elongated to 6.5 Å to estimate the capability of complex to insert into the DNA base-pair.

Secondly, we used combined docking and MD simulation to evaluate the binding modes and binding energies of Cu^{II} complexes to DNA molecules. The binding manners and binding free energies (**BE**) obtained by docking simulation are summarized in Table 1. We systematically compared the docking behaviors for the four-coordinated **L1-Cu4-R'**, the five-coordinated **L1-Cu5-R'**, and the six-coordinated **L1-Cu6-R'**. It is found that **L1-Cu6-R'** and **L1-Cu5-R'** have stronger binding affinities to both **DNA1** and **DNA2** than **L1-Cu4-R'** does. Compared with the binding manner in the minor groove (**DNA1/2N,** BE = -6.16/-5.69 kcal/mol), the **L1-Cu6-R'** prefers to insert into the base-pair of DNA (**DNA1/2L,** BE = -6.71/-6.50 kcal/mol). As for the **L2-Cu-R** complex (model for hydration reaction), we also found that it prefers a binding manner of insertion rather docking in the minor groove. The binding affinity of **L2-Cu-R** to the minor groove of **DNA1/2N** is calculated to be -8.89/-7.10 kcal/mol. A stronger binding free energy (-9.25/-8.79 kcal/mol) is obtained for **L2-Cu-R** for its insertion into the layer of **DNA1/2L**. MD simulation starting with the obtained docking binding modes as initial structural also found that the intercalations insertion should be more favorable than the minor groove aggregations, and the intercalations prefer specific layer of the base pairs.

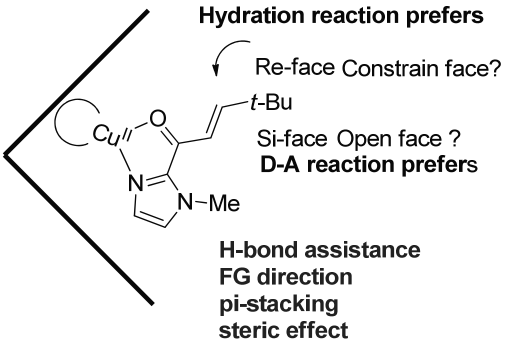
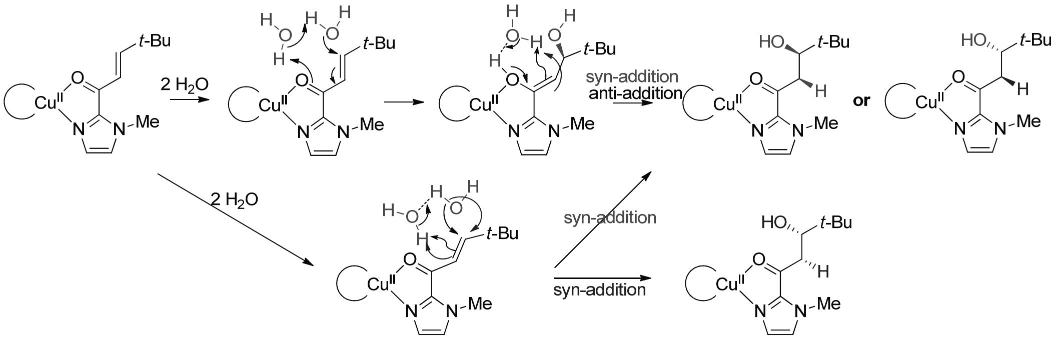


Figure 5. *The plausible stereoselective controlling factors for the asymmetric catalysis by DNA-based artificial enzyme.*

Thirdly, to reveal the plausible stereoselective controlling factors (Figure 5) that playing a role in the asymmetric hydration, we studied the Cu-catalyzed hydration reaction in the aqueous solution. Our calculation suggested that the general proposed hydration reaction assisted by coordinated water molecules is less feasible. Both the 1,4-addition and the 1,2-addition reaction mechanisms require to overcome reaction barriers of about 30 kcal/mol. However, with a deprotonated aqueous Cu^{II} complexes model, the hydration reaction barrier is only about 16 kcal/mol. Our results indicate that the acidity/basicity of the coordinated ligand or the base-pair/phosphodiester linkage may play an important role in the stereoselectivity.

Scheme 2. *Generally proposed Cu-catalyzed hydration reaction mechanism.*



2. Original papers

(1) Ke, Zhuofeng, Abe, S., Ueno, T., & Morokuma, Keiji, Catalytic Mechanism in Artificial Metalloenzyme: QM/MM Study of Phenylacetylene Polymerization by Rhodium Complex Encapsulated in apo-Ferritin. *J. Am. Chem. Soc.* Submitted.

(2) Ke, Zhuofeng, Abe, S., Ueno, T., & Morokuma, Keiji, Rh-catalyzed Polymerization of Phenylacetylene: Theoretical Studies of the Reaction Mechanism, Regioselectivity and Stereoregularity. *J. Am. Chem. Soc.* 133 *(20)*, 7926-7941 (2011). (***JACS beta Select issue 13: Current Applications of Computational Chemistry in JACS - Molecules, Mechanisms and Materials***)

3. Presentation at academic conferences

(1) Ke, Zhuofeng, Abe,S., Ueno, T., Morokuma, K., Catalytic Mechanism in Artificial Metalloenzyme: QM/MM Study of Phenylacetylene Polymerization by Rhodium Complex Encapsulated in apo-Ferritin. The 7th Symposium of Fukui Institute for Fundamental Chemistry, FIFC, Kyoto University, Kyoto, Japan. Jan. 6th. 2012. (poster)

4. Others

Joonghan KIM

FIFC Fellow, Fukui Kenichi Memorial Research Group 1

1. Summary of the research of the year

Determination of Local Chirality in Irregular Single-Walled Carbon Nanotube Based on Individual Hexagons

The chirality of single-walled carbon nanotubes (SWCNTs) has great importance since their physical and electronic properties strongly depend on it. In this respect the chirality-controlled SWCNT growth is an essential prerequisite for useful applications in nanotechnology. For the chirality-controlled growth, the preservation of predefined chirality of initial structures such as cap and seed SWCNTs is essential during the growth process. However, the chirality of irregular structures of SWCNTs, especially, those formed during the growth process, was difficult to define in contrast to the definition of the chirality of ideal SWCNTs, usually done using a graphene sheet with the direction of roll-up vector. This means that a new method is urgently required to define the chirality based not on the whole tube structure but on the individual hexagons that are formed during the growth process. Thus, we have recently developed the local chirality index (LOCI) method to determine the local chirality of arbitrary SWCNTs. For a growing, straight SWCNT structure, the principal axes (PAs), denoted as the *global* PAs (GPAs) may be calculated trivially. The *z*-component of the GPAs (GPAZ) is then assumed to be parallel to the growth axis of the SWCNT itself. We note here that if this assumption does not hold (*i.e.* if GPAZ and the growth axis are not approximately parallel) then the straightforward applicability of the LOCI method is limited, and a more involved methodology is required to determine GPAZ. Each constituent hexagon in the SWCNT structure is then identified, and its individual PAs, denoted as the *local* PAs (LPAs), are calculated. The angle (ϕ) between GPAZ and the *z*-axis of each hexagon's LPAs (LPAz) can then be used to determine the efficacy of the LOCI method for each hexagon. Hexagons with ϕ = 90º (*i.e.* the plane of the hexagon is parallel to the growth axis of the SWCNT) are ideally suited to the LOCI method, whereas ϕ = 0º (*i.e.* the plane of the hexagon is perpendicular to the growth axis of the SWCNT, such as in a cap) are not. All hexagons in the sidewall of an *ideal* SWCNT are categorized as the former. Intermediate cases (hexagons with ϕ between 0 and 90º) may be transformed to the suitable hexagon *via* two consecutive Euler rotations. Having done so, three angles (θ_1, θ_2, and θ_3) formed between the planes defined by GPAZ and three pairs of *para* carbon atoms in the hexagon are calculated. The effective average, θ ($\theta = [\theta_1 + \theta_2 + \theta_3]/3 - 60$), of θ_1, θ_2, and θ_3 is denoted as the *local chiral angle*. By definition, $0° \leq \theta \leq 30°$, and the overall chirality of a SWCNT can be described using a distribution of all constituent local chiral angles.

The present method has been applied to various SWCNT-like irregular structures as well as ideal SWCNTs, and the results of distributions of local chiral angles are shown in Figs. 1(a)-(h). The histograms were used for the representation of distributions of the local chiral angles θ for all hexagons, color-coded both in the structure and distribution, from red for zigzag (ZZ, θ=0°) through yellow to green for armchair

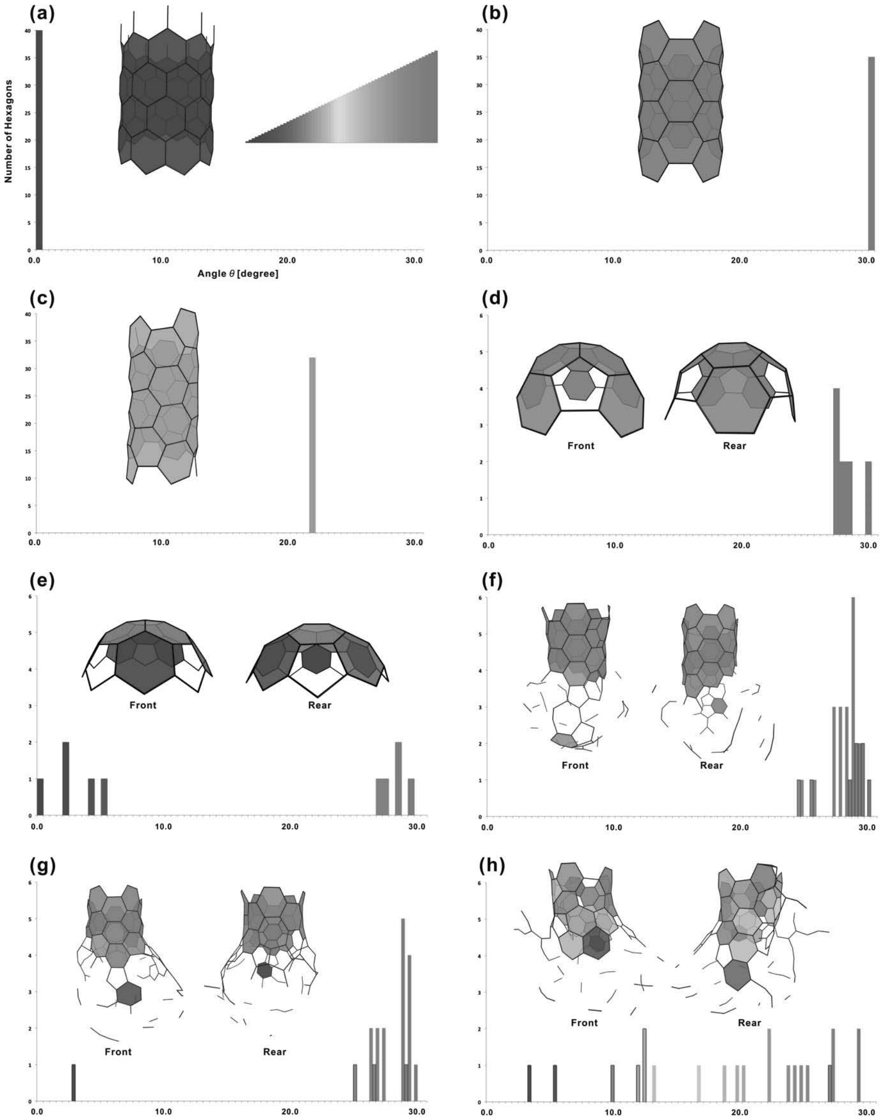


Fig. 1. Histograms of the local chiral angles of various ideal and irregular SWCNT-like structures. Color codes used are illustrated in (a) as a triangle, from red for 0 to green for 30°. (a) Ideal ZZ(10,0) SWCNT with a length of 11 Å. (b) Ideal AC(5,5) SWCNT with a length of 10 Å. (c) Ideal chiral(5,3) SWCNT with a length of 12 Å. (d) AC-type distorted C_{40} cap. (e) ZZ-type distorted C_{40} cap. (f) Irregular SWCNT obtained from DFTB/MD simulations in the trajectory A (T= 1000 K; at 45 ps of simulation). The magenta wire frames show new added C atoms during DFTB/MD simulations. The bars with black borderline indicate new added hexagons during DFTB/MD simulations. (g) Irregular SWCNT obtained from DFTB/MD simulations in the trajectory E (T= 1000 K; at 45 ps of simulation). (h) Irregular SWCNT obtained by DFTB/MD simulations in the trajectory G (T= 1000 K; at 45 ps of simulation).

(AC, θ=30°) (see inset in Fig. 1(a)). The width of each histogram bin is 0.5°. Firstly, we have calculated the local chiral angles of ideal seed SWCNTs of ZZ(10,0) with a length of 11 Å (total 40 hexagons), AC(5,5) with a length of 10 Å (total 35 hexagons), and chiral(5,3) with a length of 12 Å (total 32 hexagons). The results are shown in Figs. 1(a), (b), and (c), respectively. The histograms in these figures show only one peak each as we expected. The values of the local chiral angles of ZZ(10,0), AC(5,5), and chiral(5,3) SWCNT are exactly equal to the chiral angle, 0°, 30°, and 21.8°, respectively. Moreover, we calculated the local chiral angles for distorted C_{40} cap structures. These structures were optimized using DFTB method in the presence of a Fe_{38} cluster supporting the cap and are distorted from the ideal C_{5v} structures; they have been used as an initial structure in DFTB/MD simulations. The AC-type C_{40} cap has ten AC-type of hexagons and ZZ-type C_{40} cap has five AC and five ZZ-types of hexagons, which can be distinguished visually. Both AC-type and ZZ-type C_{40} caps have five *ill-suited* hexagons near top site of the cap. For the regular C_{5v}-symmetric caps, we should have obtained two sharp peaks near θ = 30° for AC-type and two peaks near θ = 30° and 0° for ZZ-type. The results of these distorted AC- and ZZ-type caps are shown in Figs. 1(d) and 1(e), respectively. The distributions are not sharply peaked and indicate that the present method can detect subtle changes in the chiral angle by distortion of the structure. Thus the present method provides a new accurate tool for detection of changes of local chiral environment during the dynamics of formation and annealing of SWCNT. The distributions of local chiral angles of three typical irregular SWCNTs obtained in DFTB/MD simulations of continued growth of a prepared AC hexagons during the growth simulation in Figs. 1(f)-(g). For example, in Fig. 1(f) a total of eight new hexagons were added, as shown in the black borderline in the histogram; the local chiral angles of preexisting and new added hexagons are found distributed near 30.0°. This result indicates that the local chirality of SWCNT shown in Fig. 1(f) is essentially retained. However, it does not mean a success of the chirality-controlled SWCNT growth since the one new added hexagon located on the underneath of SWCNT in Fig. 1(f) fortunately possesses AC chirality despite of the existence of defects (pentagon and heptagon) near the hexagon. This example in Fig. 1(f) shows very good growth of SWCNT except defects because of many newly added hexagons and the preservation of the original chirality. An example in Fig. 1(g) shows that all local chiral angles are distributed near 30.0°, except one whose local chiral angle is 2.9° (red colored hexagon). The value of 2.9° local chiral angle indicates that this hexagon is of ZZ-type. The formation of the ZZ-type hexagon was attributed to the existence of defect (pentagon in this case). Therefore, if any defect occurs and a new hexagon is added without healing process, the new added hexagon cannot maintain the chirality of the existing tube. The initial structure before MD simulation had twenty hexagons, and the present structure after MD growth process has also twenty hexagons. This indicates that some preexisting hexagons were broken by incoming feedstock (C atoms in this case) and defects are formed, which results in the failure of the chirality-controlled growth. Thus, the preservation of the preexisting hexagons seems to be crucial for the chirality-controlled SWCNT growth. In the example of Fig. 1(h), the distribution of the local chiral angles is very broad; containing hexagons with all kinds of local chiral angles. In particular, the local chiral angles for some newly added hexagons (with black borderline in the histogram) are different from those of the preexisting hexagons. As can be seen in these results, the LOCI method can monitor the state of the growth process and how the chirality is destroyed or maintained during the growth process.

Dynamics of Local Chirality during SWCNT Growth: Armchair versus Zigzag Nanotubes

We examine the time-evolution of SWCNT chirality and local chiral angles during SWCNT growth (TE-LOCI). This is achieved *via* monitoring the average local chiral angle or LOCI of all hexagons, and its standard deviation (σ), as a function of time. Despite of its simplicity, this analysis provides detailed understanding of the growth process and the dynamics of SWCNT chirality itself. We have applied TE-LOCI to AC(5,5) and ZZ(8,0) SWCNTs during their growth process. TE-LOCI analysis of trajectory $(5,5)_{\text{slow}}$-B (Fig. 2(a)) shows no dramatic change in the average θ and corresponding σ, from the original chirality of the SWCNT ((5,5) in this case) for the first 300 ps of growth. However, this does not indicate the success of chirality-controlled SWCNT growth, since SWCNT growth in this trajectory exhibited heptagon and pentagon defects (Fig. 2(b)). In particular, incoming carbon atoms readily initiated hexagon → heptagon transformation. This fact is reflected in the LOCI analysis; the total number of hexagons in the SWCNT at 300 ps (19 hexagons) was *decreased* compared to that in the initial SWCNT (20 hexagons). Alternatively,

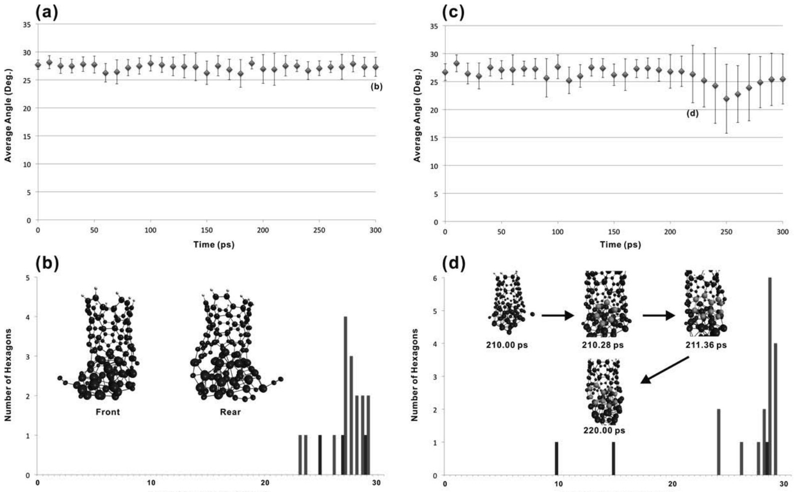


Fig. 2. TE-LOCI analysis of slow (5,5) SWCNT growth, demonstrating (a),(b) chirality-controlled (5,5) SWCNT growth observed in trajectory $(5,5)_{\text{slow}}$-B, and (c),(d) a loss of (5,5) SWCNT chirality during growth observed in trajectory $(5,5)_{\text{slow}}$-F. Data shown in (a),(b) are average θ values, error bars denote σ deviation. (c) Local chiral angles of all hexagons in trajectory $(5,5)_{\text{slow}}$-B at 300 ps. (d) Local chiral angles of all hexagons in trajectory $(5,5)_{\text{slow}}$-F at 220 ps. Red and blue bars denote original and added hexagons, respectively. Black, white, and brown spheres denote carbon, hydrogen, and iron, respectively. Cyan spheres denote carbon atoms discussed in the text.

the local chirality can change during the growth process, a phenomenon typically indicated by a sudden change in either/both θ and/or σ (for example, such as that observed at 220 ps in trajectory $(5,5)_{\text{slow}}$-F, Fig. 2(c)). In this case, this sudden change was caused by the formation of a single hexagon with a significantly different local chiral angle; this hexagon was the result of an incoming carbon atom attacking a pentagon at 210.28 ps (*i.e.* a defect-healing process, somewhat ironically). Nevertheless, this hexagon ultimately possessed a local chiral angle that is more typical of a zigzag SWCNT (θ=9.7°), since the adjacent heptagon defect was not removed. Another instance of 'defective' hexagon formation was observed in this trajectory at 211.36 ps, in this case θ=14.6°. Both hexagons here remained in the SWCNT structure for the remainder of the simulation. From these observations it is concluded that in order to accomplish chirality-controlled SWCNT growth, the *prevention* of defect formation is a key factor. Thus, chirality-controlled growth is not determined solely by the defect-healing process (such as in trajectory $(5,5)_{\text{slow}}$-F, Fig. 2(d)), but additionally by the ability to impede defect formation in the first place.

As can be seen in Fig. 3(a), local chirality is preserved in trajectory $(8,0)_{\text{slow}}$-A during growth. That is, no fluctuation in θ was observed. In addition, new hexagons exhibiting the 'original' chirality of the SWCNT were added during growth. Although this trajectory shows chirality-controlled growth, at least in the context of TE-LOCI analysis, it also exhibited a defect that resulted from the destruction of preexisting hexagons, as observed also in the case of (5,5) SWCNT growth. Abrupt changes in the local chirality were also observed during (8,0) SWCNT growth, as in the case of (5,5)

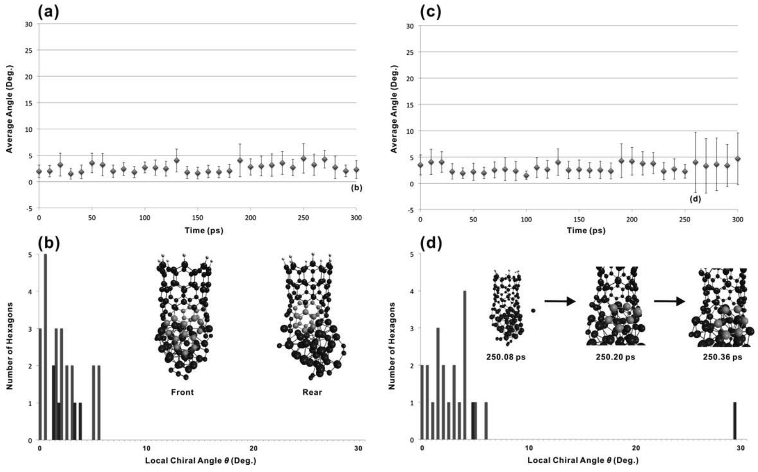


Fig. 3. TE-LOCI analysis of slow (8,0) SWCNT growth, demonstrating (a),(b) chirality-controlled (8,0) SWCNT growth observed in trajectory $(8,0)_{\text{slow}}$-A, and (c),(d) a loss of (8,0) SWCNT chirality during growth observed in trajectory $(8,0)_{\text{slow}}$-D. Data shown are average θ values, error bars denote σ deviation. (c) Local chiral angles of all hexagons in trajectory $(8,0)_{\text{slow}}$-A at 300 ps. (d) Local chiral angles of all hexagons in trajectory $(8,0)_{\text{slow}}$-D at 220 ps. Color schemes as in Fig. 2.

SWCNT growth. This is illustrated in Fig 3(c), which depicts the TE-LOCI of trajectory $(8,0)_{slow}$-D. Up until 250 ps, local chirality was conserved during growth at a value essentially equivalent to that of a pristine zigzag SWCNT. However, as shown in Fig. 3(d), an incoming carbon atom inserted directly into an existing pentagon defect at 260 ps, thereby creating a hexagon possessing near-armchair chirality (θ=29.2º). This structure was subsequently maintained for the remainder of the simulation. It is noted that the formation of this hexagon takes place *via* a route commonly associated with defect formation, *viz*. carbon atom insertion into an existing C–C bond. Following this result, we conclude that the preservation of local chirality during growth cannot be achieved in the absence of healing processes that remove defect structures located near the SWCNT-catalyst interface. That is, healing during SWCNT growth is necessary for the conservation of local chirality.

2. Original papers

(1) Joonghan Kim, Stephan Irle, and Keiji Morokuma,
"Determination of Local Chirality in Irregular Single-Walled Carbon Nanotube Based on Individual Hexagons", Phys. Rev. Lett. 107, 175505 (2011)

(2) Joonghan Kim, Alister J. Page, Stephan Irle, and Keiji Morokuma,
"Dynamics of Local Chirality during SWCNT Growth: Armchair versus Zigzag Nanotubes", submitted

3. Presentation at academic conferences

(1) Joonghan Kim and Keiji Morokuma
"Determination of Local Chirality of Irregular Single-Walled Carbon Nanotube Based on Individual Hexagons"
7th Congress of the International Society for Theoretical Chemical Physics, Tokyo, Sep. 4, 2011

4. Others

(1) Joonghan Kim, Alister J. Page, Stephan Irle, and Keiji Morokuma
"The dynamics of Local Chirality during SWCNT Growth: A QM/MD Investigation"
The 9th Symposium of Fukui Institute for Fundamental Chemistry, Kyoto, Jan. 6, 2012

Alister PAGE

Fukui Fellow, Fukui Kenichi Memorial Research Group 1

1. Summary of the Research of the Year

(A) Chirality-Controlled Carbon Nanotube Growth from Organic Templates

The electronic properties of single-walled carbon nanotubes (SWCNTs) are solely determined by their atomic structure, which is specified by a pair of chiral indices (n,m). Precise chirality control during SWCNT synthesis has become the 'holy grail' of nanotube research since it became clear that conventional high-temperature synthetic methods are incapable of achieving such control. Recent success in the synthesis of [n]cycloparaphenylenes ([n]CPPs) has fueled speculations on their use as organic templates in the 'bottom-up' synthesis of (n,n) SWCNTs and general carbon nanostructures. We have proposed a mechanism of SWCNT growth from [n]CPPs based upon the ethynyl (C_2H) radical. The formation of this radical from acetylene (C_2H_2) is known experimentally to take place at temperatures as low as 100 K on a variety of surfaces, including Fe, alumina and silica. The benefits of this radical-based mechanism over 'traditional', Diels-Alder cycloaddition-based approaches are numerous. Firstly, a decrease in the activation energy of approximately one order of magnitude is obtained using C_2H instead of C_2H_2. In addition, hydrogen abstraction from the growing SWCNT edge by C_2H (which we show to take place *ca*. 40 % of the time) produces radical centers on the growing SWCNT, which in turn facilitate much more labile SWCNT growth via C_2H_2 addition, see Fig. 1. For further details of our QM/MD simulations of SWCNT growth via C_2H addition to [n]CPPs, see the report of Dr Hai-Bei Li.

We have further demonstrated catalyst-free, chirality-controlled growth of chiral and zigzag SWCNTs from organic precursors using quantum chemical simulations. Comparison of C_2H- and C_2H_2-based growth mechanisms highlights the role of the C_2H radical in the growth of chiral and zigzag SWCNTs, as well as the growth of armchair SWCNTs. In agreement with current experimental and theoretical data concerning transition-metal catalyzed SWCNT growth, we have shown here that the SWCNT growth rate under significantly different (i.e. low temperature, catalyst-free) conditions correlates directly with the chiral angle θ of the SWCNT fragment. This relationship is

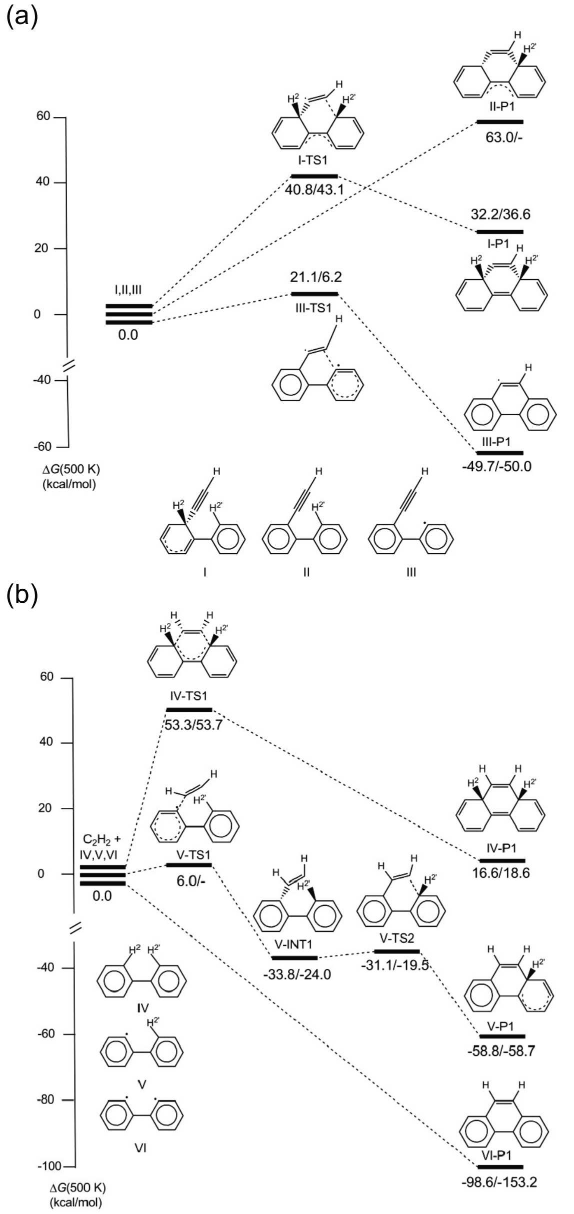


Fig. 1 (a) Reactive PES of C_2H and biphenyl/phenanthrene interaction, resulting in hexagon formation. In all cases, prior C_2H addition is a barrierless process. (b) Reactive PES of C_2H_2 and biphenyl/phenanthrene radical interaction, resulting in hexagon formation. Three possibilities, in which neither H^2/ $H^{2'}$ have been abstracted (*i.e.* DA cylcoaddition, IV), H has been abstracted (V) and both H^2/ $H^{2'}$ have been abstracted (VI) are shown. All data computed using B3LYP/6-31G(d); Gibbs free energies calculated at 500 K.

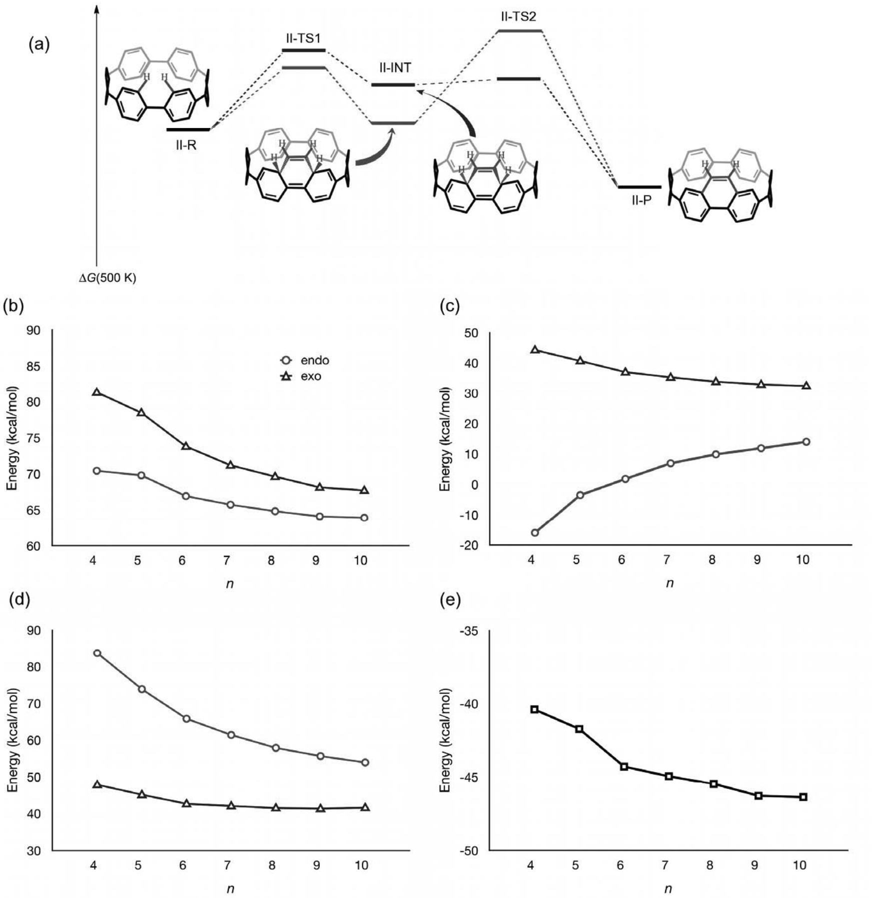


Fig. 2. (a) Reaction mechanism for hexagon addition to [*n*]CPP precursors (II-R) and H_2 renormalization *via* DA cycloaddition. (b) $\Delta G^{\ddagger}$(II-TS1), (c) ΔG(II-INT) (d) $\Delta G^{\ddagger}$(II-TS2) and (e) ΔG(II-P), relative to II-R, for [*n*]CPP precursors. All data computed using B3LYP/6-31G(d); Gibbs free energies calculated at 500 K.

therefore an intrinsic property of the SWCNT edge structure itself; the trend may presumably only be enhanced or minimized, but hardly reversed, by altering the conditions of growth. On the other hand, results presented here suggest that the relationship between the SWCNT's diameter and its rate of growth depends explicitly on the growth conditions. Contemporary theories of SWCNT growth rates, which are shown to be in good agreement with experimental data, are implicitly diameter-independent. Our simulations of C_2H-based SWCNT growth also show diameter-independent SWCNT growth rates. Conversely, the energetics of SWCNT growth via DA-based cycloaddition of C_2H_2 is influenced strongly by the SWCNT diameter, with the growth rate being proportional to the SWCNT diameter, see Fig. 2. Under such conditions, SWCNT diameter must therefore be taken into account if the mechanism and kinetics of SWCNT growth are to be understood. Most notably, our theoretical investigation points to the possibility that, for a given C_2H/C_2H_2 feedstock ratio, a SWCNT diameter/chirality combination that yields a maximum growth rate exists.

(B) Functionalization of Fullerenes Using a Genetic Algorithm

Functional carbon nanomaterials, such as graphene oxide, are being heralded as a cornerstone of the next generation of nano- and micro-scale devices. However, our understanding of the factors underpinning the functionalization of graphene, SWCNTs and fullerenes is relatively limited at this time. One of the mitigating factors in this respect is the combinatorial size of the problem; for example, to determine the thermodynamically most favorable hydroxylated adduct of C_{60} for M OH groups one must consider $M!/[60!(M-60)!]$ structures (and more generally $M!/[n!(M-n)!]$ for a structure with n possible functionalization sites). Clearly this cannot be achieved using QM methods, even for relatively modest cases. In the case of $C_{60}H_5$, the number of symmetrically distinct isomers is 45,010 (from a total of 5,461,512 structures in total). One possible alternative is to consider the use of π-Hückel theory as an approximation to a full QM description of functionalization, since the disruption to the π-conjugation of the carbon nanostructure presumably accounts for the majority of the energy associated with functionalization. In some cases this is certainly true; however, in others π-Hückel theory, and other topological approaches (such as the Zhang-Zhang polynomial approach) fail to describe functionalization completely. We have shown that this shortcoming of these simplified approximations coincides with those cases in which a large geometrical deformation of the functionalized structure takes place, see Figs 3 and 4. By definition, these simplified approaches cannot describe such geometrical considerations, and so in general one must employ more sophisticated methods to describe carbon nanostructure functionalization.

To this end, we have optimized a genetic algorithm (GA) that is designed to predict the most stable structural isomers of hydrogenated and hydroxylated carbon nanostructures. While this GA was parameterized using hydrogenated and hydroxylated C_{20} fullerenes, anticipate that it will applicable to the functionalization of any nanostructure, since it only considers energy of a given structure (which it is trying to minimize). Density functional theory (DFT) and density functional tight binding (DFTB) methods are both employed to compute isomer energies in the parameterization of the GA. We have shown that DFTB and DFT levels of theory are in good agreement with each other and that therefore both sets of optimized GA parameters are very similar. An energy decomposition analysis (EDA) for both $C_{20}H_n$ and $C_{20}(OH)_n$ systems reveals that, for only few functional groups, the relative stabilities of different structure isomers may be rationalized simply with recourse to π-Hückel theory. However, upon a greater degree of functionalization, π-electronic effects alone are incapable to describe the interaction between the functional groups and the distorted cage, and both σ- and π-electronic structure must be taken into account in order to understand the relative isomer stabilities.

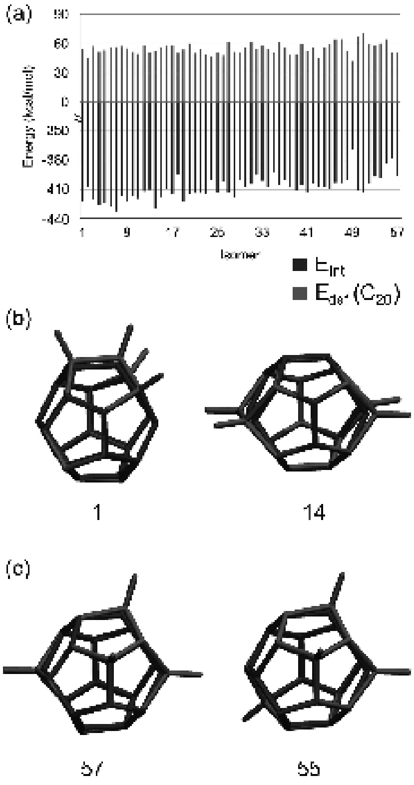


Fig. 3. (a) EDA of $C_{20}H_4$ functionalization. DFT $E_{def}(C_{20})$ and E_{int} for 57 distinct isomers shows that the isomers with the most favorable ΔE are those with the largest E_{int}. (b), (c) Structural deformation of the (b) most and (c) least stable $C_{20}H_4$ isomers according to Hückel (left) and DFT/DFTB (right). Structures shown are DFT-optimized. Functionalized structures are given in red and the pristine C_{20} cage is given in blue.

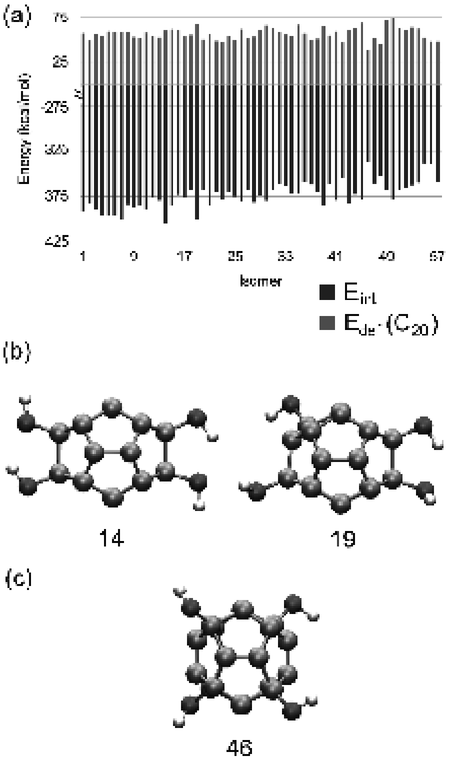


Fig. 4. (a) EDA of $C_{20}(OH)_4$ functionalization. DFT $E_{def}(C_{20})$ and E_{int} for 57 distinct isomers shows that the isomers with the most favorable ΔE are those with the largest E_{int}. However, hydrogen bonding between adjacent OH groups is seen to increase E_{int} substantially as shown in (b). Conversely, in the absence of these stabilizing hydrogen bonds, E_{int} is seen to decrease, as shown in (c).

(C) Effects of Molecular Dynamics Thermostats on Descriptions of Chemical Non-Equilibrium

The performance of popular molecular dynamics (MD) thermostat algorithms in constant temperature simulations of equilibrium systems is well known. This is not the case, however, in the context of non-equilibrium chemical systems, such as chemical reactions or nanoscale self-assembly processes. We have investigated the effect of popular thermostat algorithms on the natural dynamics of a non-equilibrium, chemically reacting system. By comparing constant-temperature quantum mechanical MD (QM/MD) simulations of carbon vapor condensation using velocity scaling, Berendsen, Andersen, Langevin and Nosé-Hoover Chain thermostat algorithms with 'natural' NVE simulations, we have shown that efficient temperature control and reliable reaction dynamics are mutually exclusive under conditions of chemical non-equilibrium, see Fig. 5. This problem may be circumvented, however, by placing the reactive system in an inert He atmosphere which is itself described using NVT MD, see Fig. 6. We have demonstrated that both realistic temperature control and dynamics consistent with natural NVE dynamics can then be obtained simultaneously. In essence, the thermal energy created by the natural dynamics of the NVE subsystem is drained by the thermostat acting on the NVT atmosphere, without adversely affecting the dynamics of the reactive system itself.

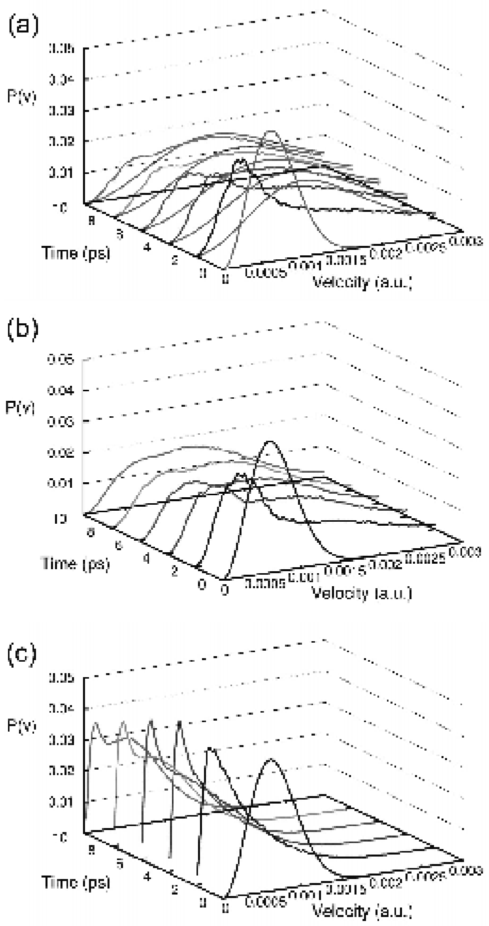


Fig 5. Comparison of time-dependent velocity distributions of a reactive C_2 system using (a) NVE C_2 and a Nosé-Hoover Chain thermostat coupled (b) strongly ($\omega = 188.37\ ps^{-1}$) and (c) weakly ($\omega = 0.19\ ps^{-1}$) to the degrees of freedom of the system. For reference, time-dependent Maxwell-Boltzmann velocity distributions at the corresponding NVE MDsimulation temperatures are included in (a) (grey lines). Temperature control comes at the cost of sacrificing a reliable description of the 'natural' reaction dynamics.

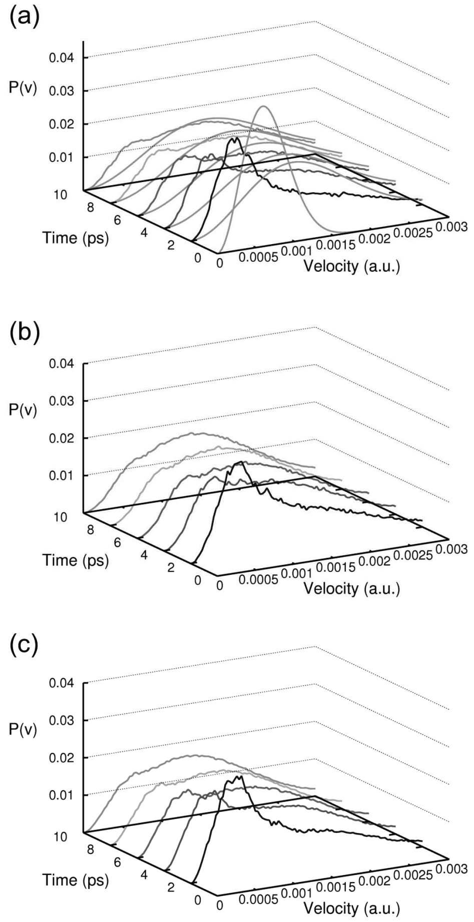


Fig 6. Comparison of time-dependent velocity distributions of a reactive C_2 system using (a) NVE C_2, (b) NVE C_2+He, and (c) NVE(C)-NVT(He) ensembles. For reference, time-dependent Maxwell-Boltzmann velocity distributions at the corresponding NVE MD simulation temperatures are included in (a) (grey lines). NVE/NVE(C)-NVT(He) simulations use C:He=1:1. P(v) shown only take into account carbon atom velocities.

2. Original Papers

(1) Y. Okamoto, Y. Ohta, A. J. Page, S. Irle, K. Morokuma, “QM/MD Study of Transition Metal Catalyst Particle Melting and Carbide Formation During SWCNT Nucleation”, *Journal of Theoretical and Computational Nanoscience*, **8**, 1755 (2011).
(2) Y. Wang, A. J. Page, H.-J Qian, Y. Nishimoto, S. Irle, K. Morokuma, “Template Effect in the Competition Between Haeckelite and Graphene Growth on Ni(111): Quantum-Chemical Molecular Dynamics Simulations”, *Journal of the American Chemical Society*, **133**, 18837 (2011).
(3) H.-B. Li, A. J. Page, S. Irle, K. Morokuma, “Theoretical Insights into Chirality-Controlled SWCNT Growth from a Cycloparaphenylene Template”, *ChemPhysChem*, **13**, 1479 (2012).
(4) M. A. Addicoat, A. J. Page, Z. Brain, L. Flack, S. Irle, K. Morokuma, “Optimisation of a Genetic Algorithm for the Functionalisation of Fullerenes”, *Journal of Chemical Theory and Computation*, **8**, 1841 (2012).
(5) J. Kim, A. J. Page, S. Irle, K. Morokuma, “The Dynamics of Local Chirality during SWCNT Growth: Armchair versus Zigzag Nanotubes”, *Journal of the American Chemical Society*, **134**, 9311 (2012).
(6) H.-B. Li, A. J. Page, Y. Wang, S. Irle, K. Morokuma, “Sub-Surface Nucleation of Graphene Precursors near a Ni(111) Step-Edge”, *ChemComm*, In press.
(7) A. J. Page, T. Isomoto, J. Knaup, S. Irle, K. Morokuma, “Effects of Molecular Dynamics Thermostats on Non-Equilibrium Systems.”, *Journal of Chemical Theory and Computation*, Submitted.
(8) H.-B. Li, A. J. Page, S. Irle, K. Morokuma, “SWCNT Growth from Chiral Carbon Nanorings: Prediction of Chirality and Diameter Influence on Growth Rates”, *Journal of the American Chemical Society*, In press.

3. Presentations at Academic Conferences

(1) “Modelling Carbon Nanotube Growth with Quantum-Mechanical Molecular Dynamics”. (Poster) A. J. Page, K. R. S. Chandrakumar, S. Irle, K. Morokuma, *Theoretical Modelling of Materials*, Abstract Page 67, Barcelona, Spain (2011).
(2) “Understanding Nanoscale Self-Assembly Processes Using QM/MD: Mechanisms of Carbon Nanotube Nucleation and Growth”. (Talk) A. J. Page, K. R. S. Chandrakumar, S. Irle, K. Morokuma, *2011 World Congress of WATOC*, Abstract Page OC098, Santiago de Compostela, Spain (2011).
(3) “Mechanisms of Carbon-Based Nanostructure Self-Assembly: Insights from Density-Functional Tight-Binding Molecular Dynamics”. (Talk) A. J. Page, K. R. S. Chandrakumar, S. Irle, K. Morokuma, *7th Congress of the International Society for Theoretical Chemical Physics*, Abstract Page 6A2-2C, Tokyo, Japan (2011).

4. Book Chapters

(1) “Atomistic Mechanism of Carbon Nanostructure Self-Assembly as Predicted by QM/MD Simulations” in *Practical Aspects of Computational Chemistry: An Overview of the Last Two Decades and Current Trends*. S. Irle, A. J. Page, B. Saha, Y. Wang, K. R. S. Chandrakumar, Y. Nishimoto, H.-J. Qian, K. Morokuma, Springer, New York, USA, In press. ISBN: 978-94-007-0918-8.

Miho HATANAKA

FIFC Fellow, Fukui Kenichi Memorial Research Group 1

1. Summary of the research of the year

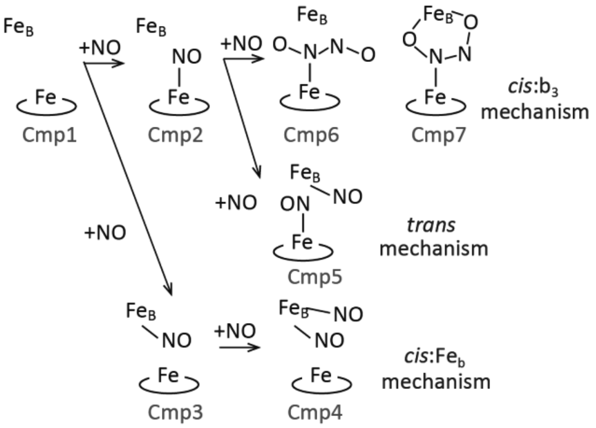
(A) DFT study of the mechanism of NO reduction in bacterial nitric oxide reductase

Nitrous oxide reductase (NOR) is a key enzyme for the reduction of NO which is a step in anaerobic respiration process.

$$2NO + 2H^+ + 2e^- \rightarrow N_2O + H_2O \qquad (1)$$

This reaction is interesting because it contains N-N bond formation and N-O bond cleavage. Additionally, NOR has a key to clarify the evolutional history of acquirement of aerobic respiration, because NOR has the same ancestor as Cytochrom c Oxidase (CcO) which catalyzes the reduction of O_2 in aerobic respiration. The overall structure of NOR is quite similar to that of CcO, though the structure of active site and proton pathway are different. The most notable difference in active site between NOR and CcO is that the active site of NOR has a heme-Fe and a non heme-Fe, so-called Fe_B, whilst that of CcO has a heme-Fe and a non heme-Cu. Therefore, the role of two metal centers could have a quite important key to clarify the evolutional change.

Although several mechanisms have been proposed in previous studies, such as the *cis*:Fe_B mechanism, the *trans* mechanism, and the *cis*:b_3 mechanism, it is a highly controversial issue. In this study, we performed density functional theory to understand the enzymatic mechanism of NO reduction. An X-ray structure of cytochrome *c*-dependent NOR (cNOR) from *Pseudomonas aeruginosa* (PDB code 3O0R) was used as a starting point for our calculations.



Scheme 1. *Possible reaction pathways for two NO addition*

As shown in Figure 1, we compare the reaction energy profile for three mechanisms, and clarify that first NO coordinates to heme-Fe and second NO form a stable N-N bond with NO coordinating to heme-Fe. The formation of N-N bond between two NO seems difficult, because it is well known that two neutral NO molecules cannot form a stable bond in gas

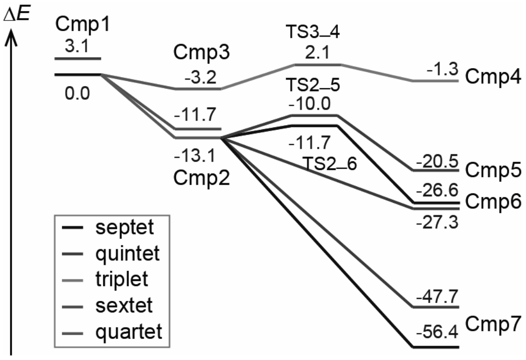
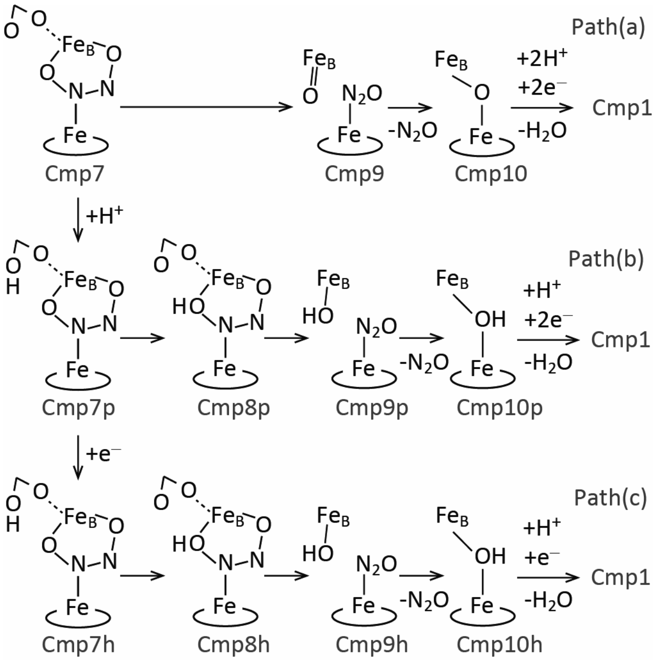


Figure 1. *The reaction energy (in kcal/mol) for two NO addition*

phase. However, NO coordinating to heme-Fe can coordinate to the second neutral NO molecule without reaction barrier, because NO in Cmp2 is partly reduced by heme-Fe, and has an anionic character.

After producing the five membered-ring complex (Cmp7), one N-O bond has to be cleaved to yield N_2O (Cmp9). Then, the remaining oxygen atom coordinates to both two Fe centers to form a μ-oxo complex (Cmp10). After the addition of two protons and two electrons, and the subsequent dissociation of a water molecule, Cmp10 can return to the starting point of this enzymatic cycle (Cmp1), as summarized in Path(a) in Scheme 2. However, the barrier of N-O bond cleavage from Cmp7 is 27.9 kcal/mol, which is too large compared with the experimental barrier of 13.3 kcal/mol.

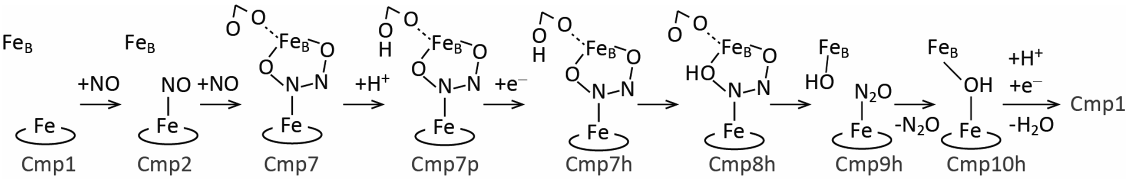
To find a favorable reaction path, protons and electrons adducts to Cmp7 are examined, because two protons and two electrons which are needed for this reaction can be added in any step of this reaction. Firstly, we focus on the NO cleavage mechanism of protonated Cmp7 (Cmp7p) as shown in Path(b) in Scheme 2. Surprisingly, the barrier of N-O bond cleavage from septet Cmp8p is only 11.1 kcal/mol, which is much lower than that from the deprotonated complex (Cmp7). However, combined with the energetics of proton transfer from Glu211 to hyponitrite (N_2O_2), which is endothermic by 7.4 kcal/mol, the barrier for N-O bond cleavage from Cmp7p is 18.6kcal/mol which is still larger than the experimental barrier of 13.3 kcal/mol. In other words, a proton addition does not promote the N-O bond cleavage.



Scheme 2. *Possible reaction pathways for NO bond cleavage and N_2O dissociation*

Secondly, reduced Cmp7p, which

means a proton and an electron adduct to Cmp7, is examined (Cmp7h) whose reaction pathway is shown in Path (c) in Scheme 2. In this case, the proton transfer from Glu211 to hyponitrite is endothermic by 2.6kcal/mol and the barrier of subsequent N-O bond cleavage reaction is 8.4 kcal/mol. Therefore, the barrier of N-O bond cleavage from sextet Cmp7h is 11.0 kcal/mol which is good agreement with the experimental barrier of 13.3 kcal/mol. To clarify the total barrier for NO bond cleavage, we need to estimate the energetics of electron transfer from heme *b* ,which is another heme in cNOR and a relay point of electron transfer, to Cmp7p. Although, it is difficult to calculate accurate absolute redox potentials because they depend on the surrounding environments, relative redox potential values for the same model can be calculated with much higher accuracy because the surroundings are the same. Therefore, we fit the parameter by using electron affinity of Cmp10p in our model to adjust its electron affinity calculated by Seigbahn et al. By using this parameter, energetics of electron transfer to Cmp7p can be estimated which is exoergic by -5.4 kcal/mol. Therefore, on the basis of the results of our DFT calculations, we propose an enzymatic reaction mechanism of NO reduction in cNOR as shown in Scheme 3. It should be noted that our proposed mechanism is the same as that of NO reduction in “heme Fe/ non heme Cu_B system” proposed by Seigbahn and coworkers.



Scheme 3. *Proposed mechanism for NO reduction in bacterial cNOR*

(B) Effect of protein environment on the NO reduction: An ONIOM study

As seen in the previous section, we found a reasonable pathway as seen in Scheme 3 and succeeded in explaining the experimental reaction barrier. Next, we recalculate the energetics of this reaction pathway by using ONIOM (DFT:MM) method to examine the effect of surrounding residues. We expected that the reaction barrier for the rate determining step (N-O bond cleavage step: TS_{8h_9h}) could be lowered by considering the surrounding environment because the typical role of enzyme is to promote the reaction by lowering the reaction barrier. However, the energetics from Cmp8h through Cmp10h calculated by ONIOM-ME and ONIOM-EE methods are quite similar to that calculated by DFT method, although there are differences of optimized geometries caused by the restriction from surrounding protein. To clarify the effect of protein, we focus on the

N-O bond cleavage step (Cmp8h→TS_{8h_9h}) and examine the following effect, such as (i) electrostatic (ES) and van der Waals (vdW) interactions between QM and MM region and (ii) deformation of QM region. Firstly, the effects of ES and vdW interactions are examined. If these interactions between QM and MM in TS_{8_9h} are smaller than those in Cmp8h, the reaction barrier obtained by ONIOM must have a lower value than that obtained by DFT in gas phase. To clarify how QM-MM interaction affects the value of reaction barrier, we calculate difference of ES and vdW interaction energies, and decompose them into contributions from each residue in the protein. However, the ES and vdW interactions lower the barrier of N-O bond cleavage only by 2.8 kcal/mol, and -0.1 kcal/mol, respectively, and only several residues near from the active site have the contributions. Both ES and vdW effects do not affect the reaction barrier so much, that means the mechanism of NO reduction can be controlled by the several residues coordinating to heme-Fe and non heme-Fe_B directly. Lastly, we focus on the effect of surrounding protein on the geometry of the active site, so-called the effect of deformation of QM region. One of the notable differences of geometry between DFT (in gas phase) and ONIOM is that heme obtained by DFT has a planar structure whilst heme obtained by ONIOM has a puckering structure because of the geometric restrain from surroundings. In addition, we notice that intermediates without bridged structures between heme Fe and non heme Fe dissociate only in gas phase. Therefore, it can be said that the most important role of surrounding protein is to keep a reasonable distance between upper part (non heme-Fe_B part) and lower part (heme-Fe part).

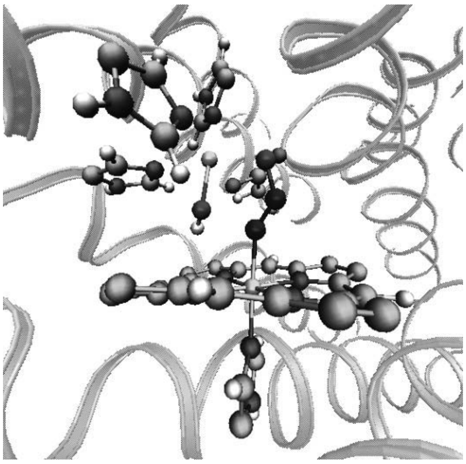


Figure 2. *Geometry of TS_{8h_9h} for NO bond cleavage calculated by ONIOM-ME method*

2. Original papers

(1) Miho Hatanaka, Keiji Morokuma, “The Mechanism of the reduction of nitric oxide in cytochrome *c*-dependent nitric oxide reductase (cNOR): A DFT study” Manuscript in preparation.

3. Presentation at academic conferences

(1) Miho Hatanaka, Keiji Morokuma
"Theoretical study of the reduction of nitric oxide in bacterial nitric oxide reductase"
52th Sanibel Symposium, St. Simons Island, Georgia, 2012/2/19

(2) 畑中美穂・諸熊奎治
「ヘム鉄・非ヘム鉄酵素を用いたNO還元反応に関する理論的研究」
第５回分子科学討論会 2011　札幌　2011/9/20 1P111

4. Others

(1) Miho Hatanaka, Keiji Morokuma
"Theoretical study on the reduction of nitric oxide in bacterial nitric oxide reductase"
第 9 回京都大学福井謙一記念研究センターシンポジウム 福井謙一博士ノーベル賞受賞 30 周年記念　京都　2012/1/6 P50

Xin LI

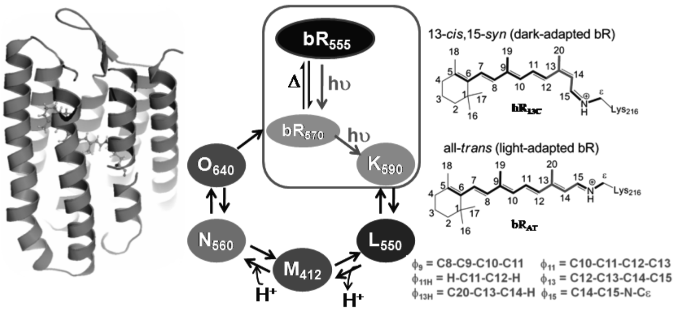
JST Fellow, Fukui Kenichi Memorial Research Group 1
(To 31 Dec. 2011)

1. Summary of the research of the year

Photodynamics and Isomerization Mechanisms of All-trans and 13-cis, 15-syn Retinal Protonated Schiff Base in the light-adapted and dark-adapted Bacteriorhodopsin

Bacteriorhodopsin (bR) is a transmembrane protein in the purple membrane of *Halobacterium salinarium*. All-*trans* retinal protonated Schiff base (RPSB) is covalently linked to Lys216 of the protein in the light-adapted bR. Absorption of a photon by RPSB can trigger a photocycle with several photostationary states (Scheme 1). In addition, there is a 40:60 mixture of all-*trans* (bR_{AT}) and 13-*cis*, 15-*syn* (bR_{13C}) in the dark-adapted bR (see Scheme 1). bR_{13C} can not release a proton but equilibrates thermally with bR_{AT} in the minute range. Photodynamics of all-*trans* and 13-*cis*, 15-*syn* retinal protonated Schiff base (RPSB) in bacteriorhodopsin and without an environment have been elucidated by nonadiabatic ONIOM(QM:MM) and QM simulations. For both all-*trans* and 13-*cis*, 15-*syn* RPSB, bR protein favors the C13=C14 bond-specific, ultrafast and unidirectional photoisomerization with a high quantum yield. The all-*trans* and 13-*cis*, 15-*syn* chromophore can be photoisomerized to 13-*cis, 15-anti* and 13-*trans*, 15-*syn* (not 13-*trans*, 15-*anti*) RPSB, respectively. Moreover, a thermal isomerization from 13-*trans*, 15-*syn* to 13-*trans*, 15-*anti* (all-*trans*) occurs by rotating the C15=N double bond. Therefore, there are light-induced and thermal isomerizations from 13-*cis*, 15-*syn* (dark-adapted bR) to all-*trans* RPSB (light-adapted bR). In addition, the thermal isomerizations between several intermediates 13-*cis*, 15-*syn* (bR_{13C}), 13-*trans*, 15-*syn* (K_{13C}), all-*trans* (bR_{AT}), and 13-*cis*, *15-anti* (K_{AT}) in bR protein have been further investigated by the ONIOM (QM:MM) method. The key role of protein environment is discussed. The isomerization mechanisms for the light-adapted and dark-adapted bR to their K states have been elucidated in the present work.

Scheme 1



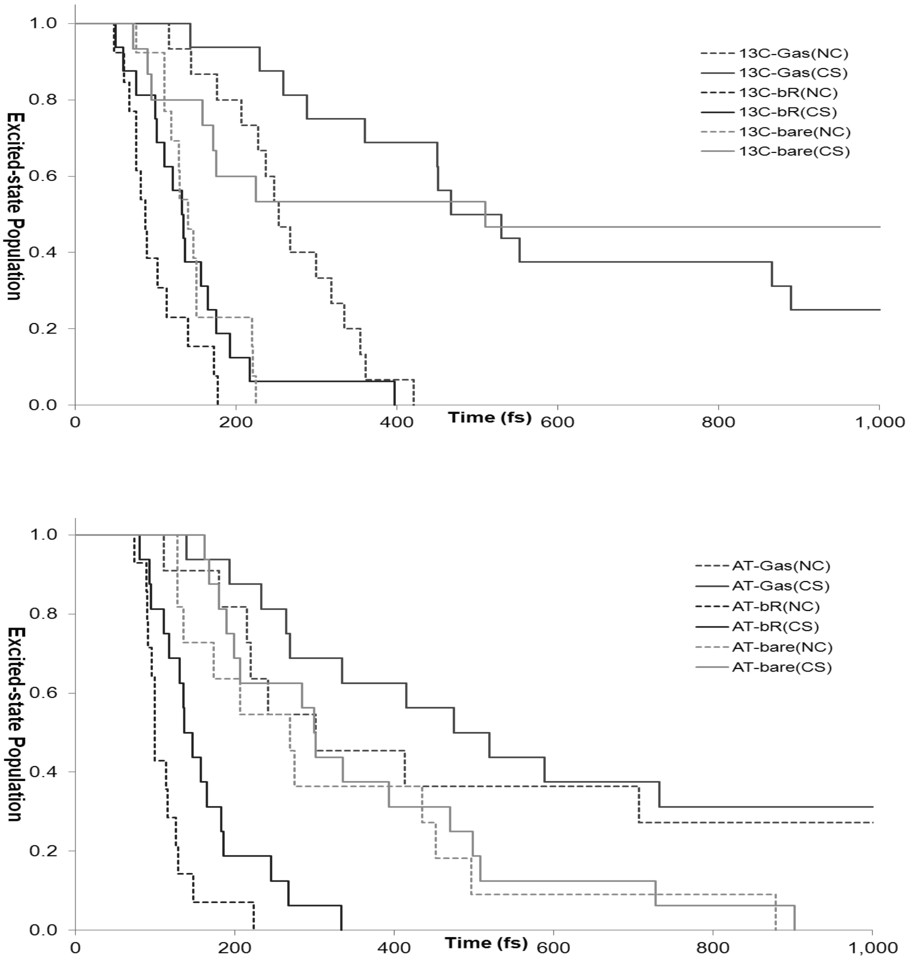


Figure 1. Excited-state population for photoisomerization of 13-*cis*, 15-*syn* (upper) and all-*trans* (lower) within and without bR protein.

2. Original papers

(1) Xin Li, Lung Wa Chung, and Keiji Morokuma, “Photodynamics of All-trans Retinal Protonated Schiff Base in Bacteriorhodopsin and Methanol Solution”, J. Chem. Theory Comp. (letter) 7, 2694-2698 (2011).

(2) Xin Li, Lung Wa Chung, and Keiji Morokuma, “*Modeling Photobiology Using Quantum Mechanics (QM) and Quantum Mechanics/Molecular Mechanics (QM/MM) Calculations,*” In “Computational Methods for Large systems: Electronic Structure Approaches for Biotechnology and Nanotechnology” Reimers, J. R. Eds. John Wiley & Sons, Inc., Hoboken, 2011**,** pp 397-433.

(3) Lung Wa Chung, Xin Li, Hajime Hirao, and Keiji Morokuma, “Comparative Reactivity of Ferric-Superoxo and Ferryl-Oxo Species in Heme and Non-Heme Complexes”, J. Am. Chem. Soc. (Commun.) 133, 20076-20079 (2011).

(4) Abdel-Azeim, S.; Li, X.; Chung, L. W.; Morokuma, K. “Zinc-Homocysteine Displacement in Cobalamin-Dependent Methionine Synthase and its Role in Substrate Activation: DFT and ONIOM Study”, J. Comput. Chem. 32, 3154-3167 (2011).

(5) Jiayun Pang, Xin Li, Keiji Morokuma, Nigel S. Scrutton, and Michael J. Sutcliffe, “Large-Scale Domain Conformational Change Is Coupled to the Activation of the Co−C Bond in the B_{12}-Dependent Enzyme Ornithine 4,5-Aminomutase: A Computational Study” J. Am. Chem. Soc. 134, 2367-2377 (2012).

(6) Chung, L. W.; Hirao, H.; Li, X.; Morokuma, K. “The ONIOM Method: Its Foundation and Applications to Metalloenzymes and Photobiology”, Wiley Interdisciplinary Reviews: Comput. Mol. Sci, 2, 327-350 (2012).

3. Presentation at academic conferences

(1) Xin Li, Lung Wa Chung, Hideaki Mizuno, Atsushi Miyawaki, and Keiji Morokuma, “*Primary Events of Photodynamics in Reversible Photoswitching Fluorescent Protein Dronpa*”, American Chemical Society 241th National Meeting, Anaheim, California, March 27-31, 2011.

(2) Xin Li, Lung Wa Chung, Hideaki Mizuno, Atsushi Miyawaki, and Keiji Morokuma, “*Primary Events of Photodynamics of GFP Chromophores in Proteins, Solution, and Gas-phase*”, 9th Triennial Congress of the World Association of Theoretical and Computational Chemists, Santiago de Compostela, Spain, July 17-22, 2011.

(3) Xin Li, Lung Wa Chung, and Keiji Morokuma, “*Primary Events of Photodynamics of All-trans Retinal Protonated Schiff Base in Bacteriorhodopsin, Methanol Solution and Gas Phase*”, 5th Asia and Oceania Conference on Photobiology, Nara, Japan, July 30-August 1, 2011.

K. R. S. CHANDRAKUMAR

JST Fellow, Fukui kenichi Memorial Research Group 1

(To 10 May 2011)

1. Summary of the research of the year 2012

Formation of Carbon Nanocapsule from Carbon Nanocone Aggregates around Nickel Nanocluster: An Insight from Density Functional Tight-Binding based Molecular Dynamics (DFTB-MD) Method

In our recent study, we have reported that interaction of nanohorns with the iron or nickel catalyst at higher temperature leads to the formation of a new form of carbon nanomaterials called as, nanooysters, a hollow graphene capsules containing metal particles that resemble pearls in an oyster shell. The structure of the oyster consists primarily of hexagons along with a few pentagons that are typically localized near the edges where the two cones are joined together. It may be noted that the formation of nanooysters has also been experimentally characterized. Herein, we demonstrate the effect of the change in disclination (apex) angle (DA) or cone angle of the nanohorns is very significant in such high temperature reactions. In particular, the nanohorns with DA-60 can lead to the formation of nanooysters while the carbon nanocapsule-like structure is preferably formed from the aggregates of the nanohorns with DA-120. The structural transformation of carbon nanocone into nanocapsules in the presence of iron and nickel nanoclusters as catalyst has been studied using the recently developed density functional tight binding (DFTB) based molecular dynamics simulation. In the present DFTB/MD simulations, we employed the self-consistent-charge DFTB (SCC-DFTB) method in combination with a finite electronic temperature approach with T_e=10000 K to evaluate the quantum chemical Born-Oppenheimer potential on the fly. In the molecular dynamics simulations the velocity-Verlet integrator was used with a time step of 1 fs, and the nuclear temperature was controlled by connecting the Nose−Hoover chain thermostat to the degrees of freedom of the present model system. We have annealed the initial starting structure at different temperatures 1500, 2000 and 2500 K for 10 ps, and ten such trajectories have been considered at the respective temperature for 30-40ps. Thus, the investigation in this work is comprised of a total of 60 trajectories plus a large number of less systematic supplementary simulations. As shown in Figure 1, Our initial structure comprise of the nanocone with definite length along with the iron nanocluster of size Fe_{38} and Ni_{38}.

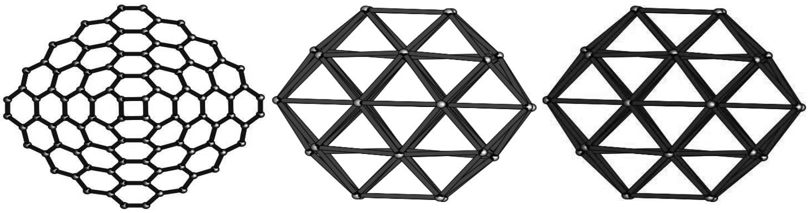


Figure 1: Structures of the Carbon nanohorn with apex angle 120°, as well as the catalysts Ni_{38} and Fe_{38}.

The nanohorn with DA-120 is structurally different from that of DA-60 and at the apex region of the nanocone, DA-120 is characterized by the presence of 4m-ring instead of 5m-ring of DA-60. We initially optimized the iron and nickel nanoclusters of size 38 along with the nanohorn DA-120 with diameter 5 Å. The metal clusters are found to have the face centered cubic structure with octahedron symmetry and the interaction of the cone is favored with the cluster at the face with 7-atom ring structure. The geometrical parameters along with the binding energy details are given in Table 1. Strikingly, it can be seen from Table 1 that the binding of strength of DA-120 is almost twice that of DA-60 with the iron or nickel nanoclusters. In addition, the binding of strength of the nanocone with the iron cluster is observed to be much stronger than nickel cluster.

Table 1: Binding energy and geometrical parameters of the nanocones (DA-60 and DA-120) interacting with iron and nickel nanoclusters

Metal Cluster (M)	Cone-Metal-Cone (C-M-C)		
	M-C	C-C@5/4m	BE
DA60-Fe_{38}	2.281	1.434/1.498	-3.91
DA120-Fe_{38}	2.205	1.544/1.547	-6.03
DA60-Ni_{38}	2.387	1.425/1.463	-2.15
DA120-Ni_{38}	2.334	1.486/1.584	-3.59

In all the MD trajectories, the above optimized structure of the individual complexes of iron and nickel is considered to the initial structures with different random seed numbers. Our initial results for iron complexes at 1500 and 2000 K reveal that part of the metal cluster is covered by one cone and the other cone either covers the metal cluster or it is in the suspended position. The apex part of the cone is always connected to the catalyst even at ~15ps and the 4m-ring is found to be stable. At 2000k, some of the trajectories show that the 4m-ring at the apex region is destroyed and metal encapsulated complex structure is observed. However, at 2500 K, only few trajectories exhibit the cone-cone interaction and most of the structures are found to be very much similar to the encapsulated complex or partially connected cone-cone types of structures even up to 30 ps. These results for the DA-120 are completely different from that of DA-60 wherein the structural transformation of cone into nanooyster-like transformation is observed at temperatures range of 1500 -2500 K within 6-8 ps. The reason for such differences may be due to the strong interaction of DA-120 with the iron cluster, the flexibility or movement of the cones is restricted and hence, the cones remains to be intact with the catalysts. In some cases, the 4m-rings are destroyed at the apex region and the resulting complex with such defect structure very strongly bound to the Fe surface. The thermal energy supplied even at 2500 K is not sufficient to overcome the interaction between the 4m-rings of the cones and the catalyst. However, at 3000 - 3500 K, the nanocones are decomposed into small carbon clusters and hence, the nanooyster-like transformation is not observed for the case of iron.

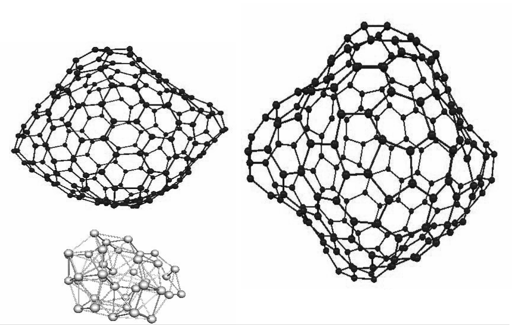


Figure 2: carbon Nanocapsule with the Nickel Catalyst

Let us now discuss the nature of interaction of nickel nanoclusters with nanocones, DA-120. More strikingly, the present results as shown in Figure 2, demonstrate that the resultant product is neither nanooyster nor the complex obtained for iron case. Herein, the observed product is nanocapsule-like structure, comprising mostly 6m-rings around the capsule and 5m-rings at the regions where the cones are interconnected to each other (interfacial region). This feature is very uniquely observed for the case of nickel catalyst.

The snapshots for the formation of carbon nanocapsule are presented in Figure 3 and the corresponding carbon polygonal ring formation dynamics is represented in figure 4. It can be seen from figure 3 that the nanocones slowly move from the catalyst surface, maintaining the metal-cone interaction through the 4m-ring of the apex region of the nanocone. The cone-cone interaction initially begins with the bonding at the peripheral regions of the cones and this process drives the formation of few polygonal carbon rings in the time interval of 9-12 ps (as shown in figure 4). Once the two cones are intact with each other, the contact of the cone with the catalyst becomes weak and the peripheral regions of both the cones are connected each other at 16 ps, this leading to the formation of carbon nanocapsule.

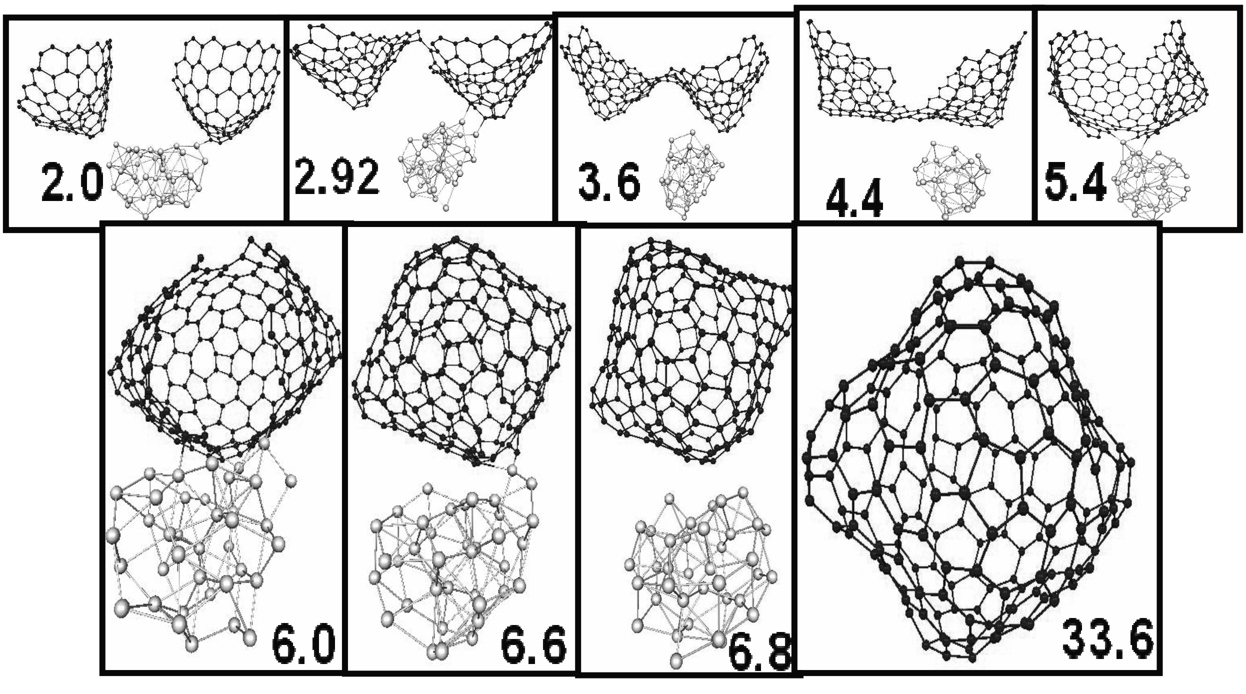


Figure 3: The mechanism of the nickel catalyzed nanocapsule formation. The numbers at each snapshot indicate the time in ps.

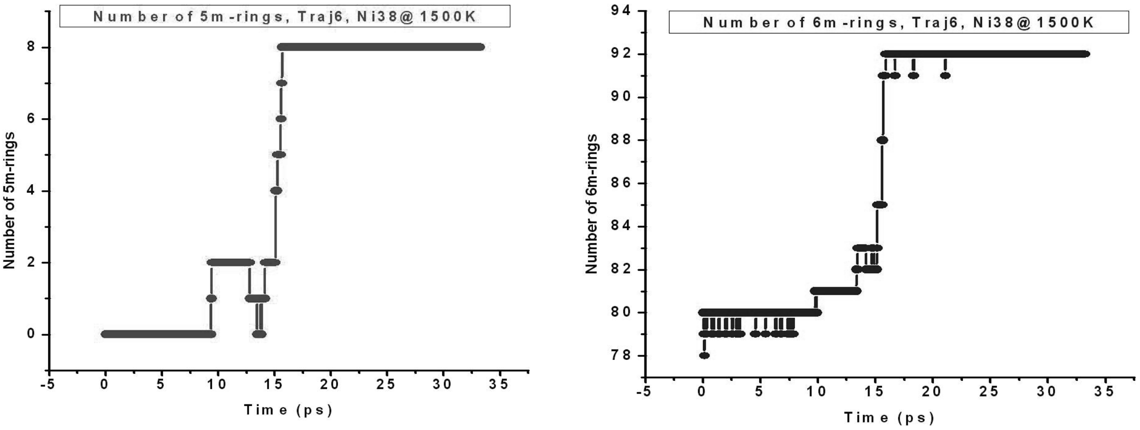


Figure 4: Carbon polygonal ring formation dynamics for one of the trajectories at 1500 K, catalyzed by Ni_{38} cluster.

From the Figures 3 and 4, it is evident that initially, both the cones have to move forward from the tip position to the edge and thereafter, both the cones are zipped together. The entire process is leading to the formation new 5m and 6m-rings as it is shown in Fig. 4. Considering the time scale, it can be mentioned that the flipping of the cones and the formation of the capsule-like structure takes place in the time range of 10-12 ps and 14-15ps, respectively. In addition, our simulation results illustrate that the transformation process is faster at 2500K compared to that of 1500K. It can be seen from Fig.4 that the nanocapsule growth process and the increment in the number of new 5m and 6m-rings at 1500K is quite sharp, indicating the growth process is quite fast with threshold time period. We have also observed that the 3m and 7m-rings are not formed. More strikingly, the structure of the tube is not changed after annealing the structure up to 34ps, which is also evident from the ring count (From Fig. 4). Since the interaction strength of the nanocapsule with the nickel cluster is found to be very weak, the nanocapsule is liberated from the catalyst surface. The irregular shape of the capsule can be attributed due to the presence of 5m-rings. In general, one 4m-ring is present at the capping region, which is surrounded by the five 6m-rings in the normal cones. However, the number of 5m-rings is increased to 8-10, during the growth of the capsule along with few 6m-rings. This type of arrangement of the rings causes the irregular types of structure. Since the nanocone has the zigzag as well as armchair types of edges, the formation of 5m, 6m and 7m rings is expected when two cones joins together especially at the interface region. These features are completely different from the case of iron cluster-nanocone interaction.

On comparing DA-120 nanocone interaction with the iron/nickel-catalyzed reaction, the mechanism of the formation of the nanocapsule structure is found to be profoundly different from the DA-60. In the present case, the basic structure of the zigzag as well as armchair types of edges are not destroyed at the peripheral region and hence, the mechanism of the formation of the nanocapsule has been explained in terms of the interface or bridge region at the intra-molecular junctions of the two cones which can have the 5m-rings around the tube. However, in case of nickel cluster-induced tube formation, the mechanism is not very apparent from the trajectories. The zigzags as well as armchair types of edges are found to have no role. Thus, although there are some similarities with the interaction of nanocones DA60 with different catalysts, the interaction of the cones DA-120 with the iron and nickel cluster is very different from each other.

2. Original Papers

1. DNA Base-Gold Nano Cluster Complex as a Potential Catalyzing Agent: An Attractive Route for CO Oxidation Process
   Naresh K Jena, KRS Chandrakumar, and Swapan K Ghosh J. Phys. Chem. C, **2012** (In Press) DOI: 10.1021/jp304660
2. Water Molecule Encapsulated in Carbon Nanotube Model Systems: Effect of Confinement and Curvature
   Naresh K. Jena, Manoj K. Tripathy, Alok K. Samanta, K. R. S. Chandrakumar and Swapan K. Ghosh Theo. Chem. Acc. 131, **2012**, 1205

3. High-Temperature Transformation of Fe-Decorated Single-Wall Carbon Nanohorns to Nanooysters: A Combined Experimental and Theoretical Study (Communicated to Nanoscale)

3. Presentations at Academic Conferences

Fengyi LIU

JST Fellow, Fukui kenichi Memorial Research Group 1

1. Summary of the research of the year

Ring-Opening and Ring-Closure Mechanism of Spiropyran-Merocyanine Photochromic Reaction

The photochromic reaction of Spiropyran-Merocyanine(SP-MC) photochromic reaction has been a hot but challenging subject for theoretical chemists. Due to the dramatic changes of electronic structure during the ring-open and ring-closure processes and highly flexible geometry of MC isomers, the potential energy surfaces of SP-MC are complex. The efficient nonadiabatic path from excited- to ground state, including crucial structures such as conical intersections and unusual intersystem crossing, have not been well understood.

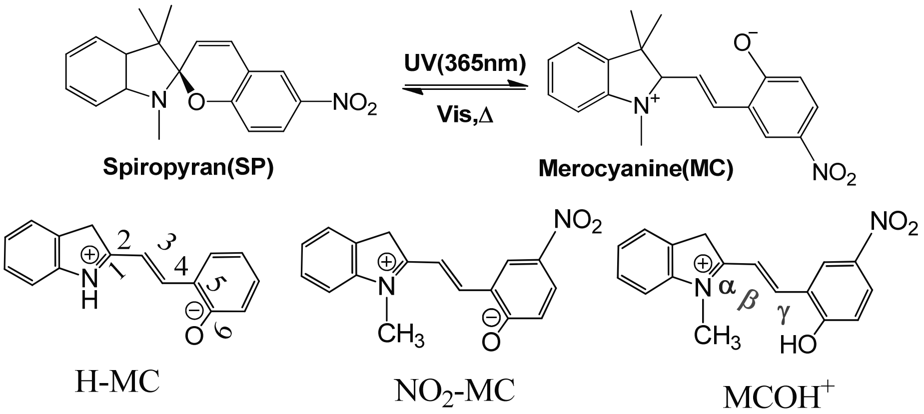
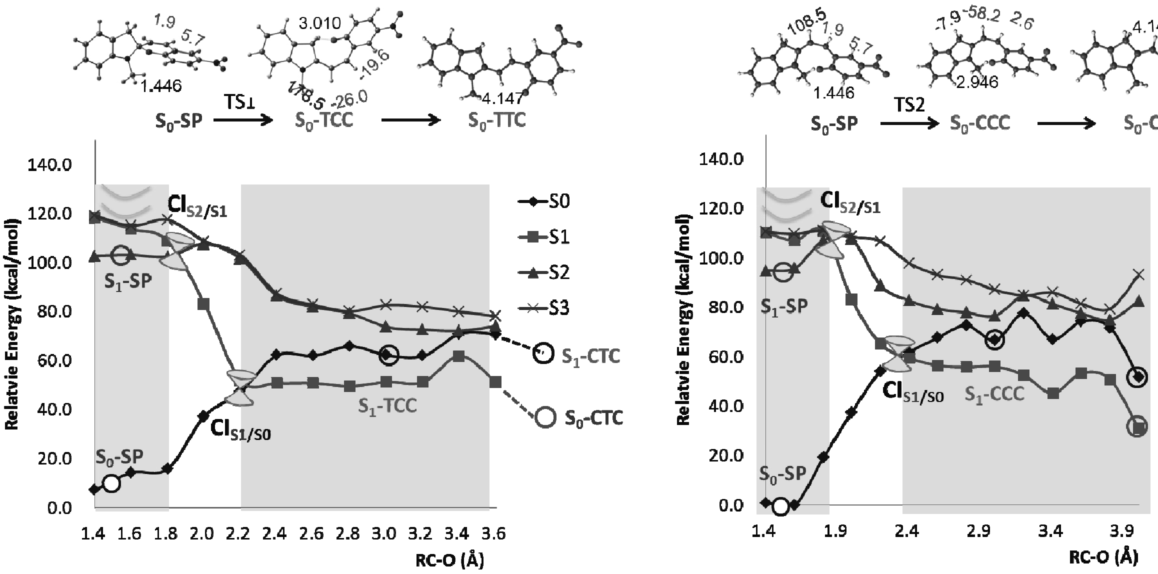


Figure 1. Spiropyran-Merocyanine photochromic reaction path and unsubstituted MC(H-MC), 6-NO_2 MC(NO_2-MC) and protonated MC($MCOH^+$).

Unsubstituted H-SP↔MC photoisomerization: We carried out CASPT2//CASSCF calculation to explore the ground- and excited-state PESs of the model molecule. The SP-MC ring-opening reaction takes place in two steps: (1) Photocleavage of C-O bond. Starting from the FC(S_0-SP), the molecules follow two primary reaction paths, S_1*-SP*→ S_1*-TCC* and S_1*-SP*→S_1*-CCC*, both are barrierless downhill MEP. Along the S_1-MEP, the S_0 and S_1 curve intersect with each other and form extensive state-interacting regions (S_1-S_0 gaps <10 kcal/mol). The torsional modes around dihedral angle α, β and γ (See Figure 1 for definition) regulate the branching ratio in the initio step, and are responsible for the strong state-interacting region along the reaction path. (2) Isomerization between MC Isomers. In principle, OBF, HT and BP can take place in MC photoisomerization. Considering of their relative long life time (~10ps), low isomerization barriers and flexible reaction paths, all MC conformers can be generated from the CCC and TCC. Several type of MECIs were located at the CASSCF level and are responsible to produce ground-state MC isomers.

The ring-closure mechanism of MC chromic reaction is studied. It is found the bond rotations around β are crucial for ring-closure, γ less important, and α bond are highly unfeasible. The most efficient reaction path corresponds to FC-TTC(S_2)→ CI (S_2/S_1,β2)→ TS(β2,S_1) → TCC(S_1) → CI2$_{S1/S0}$→SP(S_0). These results agree with the experimental findings.

NO_2-SP↔MC photoisomerization: The photochromic reaction for NO_2-SP-MC is more complicated than unsubstituted one, since the NO_2- substituent has significant to the electronic state, especially inducing charge-transfer process during C-O bond cleavage and formation.. The ring-opening mechanism for NO_2-SP was studied at the SA4-CASSCF(12,11) level with CASPT2 energy correction. NO_2-SP molecule is initially excited to S1 (π→π*) state, then the C-O bond cleavage take place along two paths (as shown in Figure 2). During this process, two type of CIs, CI(S_2/S_1) and CI(S_1/S_0) play their roles to form MC products. The experimentally undetectable excited-state intermediates, S_1-CCC and S_1-TCC were optimized and are located in the shallow well of the S1 PES. The NO_2-SP*→ TCC reaction path is more favorable than NO_2-SP*→ CCC.



(a) S_1-MEP: C-O cleavage via TS1

(b) S_1-MEP: C-O cleavage via TS2

Figure 2. The Ring-openning reaction paths for NO_2-SP→MC.

NO_2-SP↔MC acidichromic/photochromic reaction: Acidichromism stands for the phenomenon that the protonated form and the conjugate base of some compounds have distinctly different absorption spectra. It can occur in together with photochromism. In such cases, it is possible to take advantage them to construct interesting molecular devices. The reaction scheme of acdio-/photochromic reaction of SP and MC are shown in Figure 3.

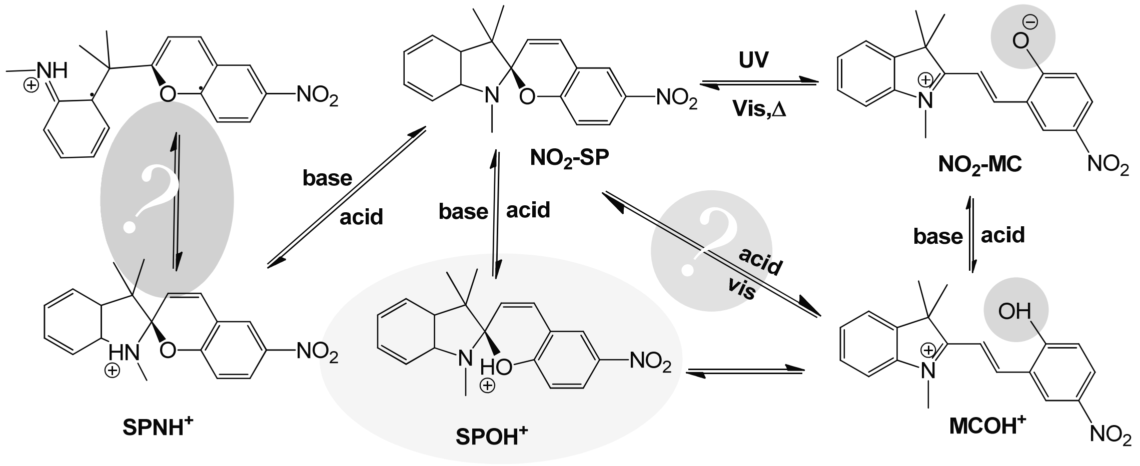


Figure 3. Schematic SP-MC Acido- and photochromic reaction path.

In this scheme, how does the reaction take place between neutral NO$_2$-SP and MCOH$^+$ is not known; in addition, the role of experimentally suggested side-reaction (C-N cleavage) is also to be understood. Therefore, 4SA-CASSCF(12-in-11)/6-31G calculation were carried out to locate the C-O and C-N cleavage. It is found the protonated MCOH$^+$ isomers are more stable that protonated SP, which reverses the direction of the SP-MC thermalchomism. Actually once the O15 in SP is attached by proton, the C-O bond dissociates instantly to produce CCCOH$^+$ or TCCOH$^+$; then isomerization take place among the MCOH$^+$ isomers. The protonation/deprotonation of molecule only occur in MC form (rather than SP).

We also found the C-N cleavage in N-protonated SP(SP-NH$^+$) as a competing side-equilibrium process, accounting for the unreactive “sink” reported by UV/vis spectroscopy experiment. The C-N dissociation on S$_1$ state is as low as ~6.5 kcal/mol so it take place easily though a CI between S$_1$/S$_0$ states (Figure 4).

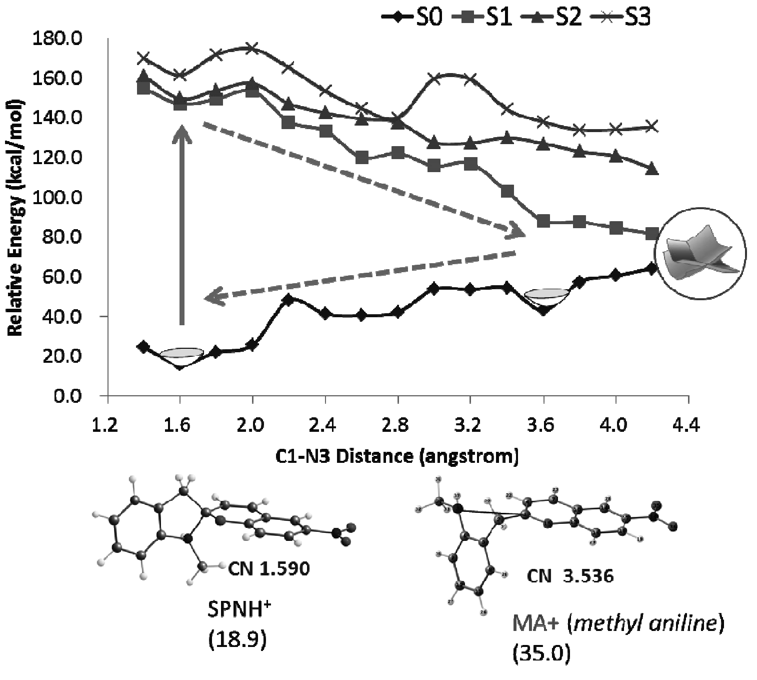


Figure 4. SPNH$^+$→MA$^+$ as an unreactive sink.

2. Original papers

(1) Fengyi LIU, Keiji MOROKUMA,
"Computational Study on the Working Mechanism of a Stilbene Light-Driven Molecular Rotary Motor: Sloped Minimal Energy Path and Unidirectional Nonadiabatic Photoisomerization",
J. Am. Chem. Soc., 2012, 134, 4864–4876.

(2) Fengyi LIU, Keiji MOROKUMA,
"Ring-Opening and Ring-Closure Mechanism of the Spiropyran-Merocyanine Photochromic Reaction: A CASSCF/CASPT2 Study"
manuscript in preparation.

3. Presentation at academic conferences

(1) Fengy Liu and Keiji Morokuma, Poster on:
"Theoretical study on the working mechanism of stilbene light-driven molecular rotary motor",
"7th Congress of the International Society for Theoretical Chemical Physics", September 2-8, 2011, Tokyo, Japan.

Hongyan XIAO

JST Fellow, Fukui Kenichi Memorial Research Group 1

1. Summary of the research of the year

I. Fitting Global *Ab Initio* Potential Energy Surfaces for Low-lying Doublet States of NO_3

Recently a joint experimental and theoretical work proved the exclusive excited-state roaming pathway in the reaction $NO_3 \rightarrow NO + O_2$ that eventually produced two different product channels (a) and (b).

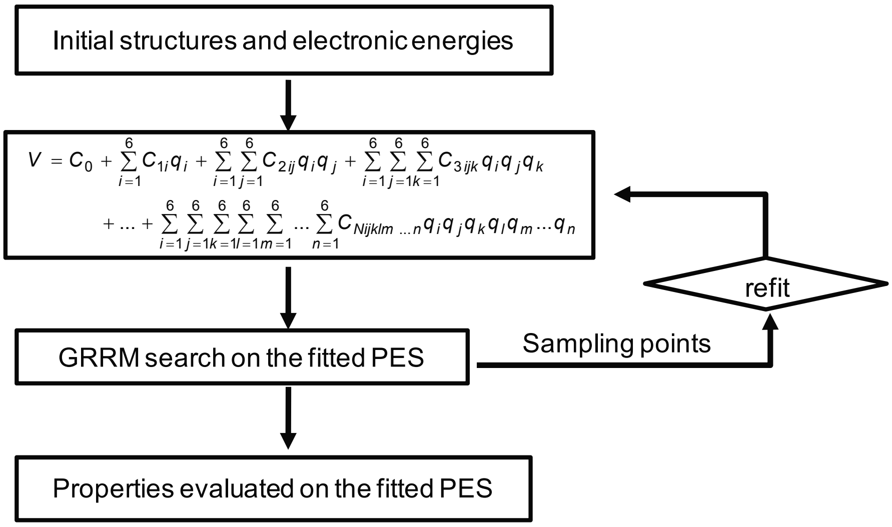
$$\begin{aligned} NO_3 + h\nu \quad & \rightarrow NO\,(^2\Pi_\Omega, \mathrm{v}=0-1, \text{low N}) + O_2\,(^3\Sigma_g^-, \mathrm{v}=5-10) \quad \text{major channel} \qquad (\mathrm{a}) \\ & \rightarrow NO\,(^2\Pi_\Omega, \mathrm{v}=0-1, \text{high N}) + O_2\,(^3\Sigma_g^-, \mathrm{v}=0-4) \quad \text{minor channel} \qquad (\mathrm{b}) \end{aligned}$$

The theoretical studies predicted specific NO Λ doublet propensities, namely, orientations of the unpaired electron with respect to the molecular rotation plane for the two product channels. The experimental studies using the ion imaging technique via multiple rotational branches proved that the major product channel with a high O_2 vibrational excitation produced a lower translational energy NO fragment in the A' Λ doublet state, while the minor product channel with a low O_2 vibrational excitation produced a higher translational energy NO fragment in the A" Λ doublet state, confirming the theoretical predictions.

In order to fully support the theoretical conclusions derived from potential energy surface (PES) characteristics and limited classical dynamics from dissociation transition states, it is highly desirable to perform classical and hopefully quantum dynamics calculations for complete evolution of the system from photoexcitation in the Franck-Condon region through succeeding nonadiabatic and dissociation processes to the product. In order to make this possible it is essential to have full PESs of multiple electronic states involved at a higher level than used in our previous reaction path characterization study. In particular, we are concerned with a small active space (11e,8o) used in such a study, which might have resulted in some errors in the very flat PESs in the roaming region as well as dissociation transition states.

In the present work, we develop such analytical global PESs for NO_3 on the basis of multistate (MS)-CAS(17e,13o)PT2/aug-cc-pVTZ *ab initio* calculations. The fits are made on roughly 74000 MS-CAS(17e,13o)PT2/aug-cc-pVTZ calculations of electronic energies, where these PESs are invariant of permutations of oxygen atoms (see below Fitting scheme). The surfaces describe two roaming pathways for $NO_3 \rightarrow NO_2$-----$O \rightarrow NO + O_2$ involving different electronic states discovered in the photolysis of NO_3 [Xiao, H. Y. et al. *J. Phys. Chem. Lett.* 2011, *2*, 934]. These pathways become accessible at excess energy of ~210 kJ/mol above the ground state global minimum of NO_3. The *ab initio* data below 360 kJ/mol are reproduced very well by the fitted PESs with the fitting RMS errors of less than 5.5 kJ/mol for all the three states. Moreover, key local minima and energy profiles along the roaming pathways on the fitted PESs are compared with those on the *ab initio* PESs. In addition, potential contour maps in the roaming region are also compared. These careful evaluations of the fitted PESs suggest that the present fitted PESs are well suited for future dynamics calculations of this system.

Fitting scheme



II. Theoretical Study of the Photodissociation Dynamic of Ketene

The photodissociation dynamics of ketene (H_2CCO) has been paid close attention by experiments and theories in the past several decades. At 193 nm the ketene photolysis has the following pathways:

$$\begin{array}{lll} \mathrm{H_2CCO} + h\nu \rightarrow & \mathrm{CH_2}(\tilde{X}^3B_1) + \mathrm{CO} & (1) \\ & \mathrm{CH_2}(\tilde{a}^1A_1) + \mathrm{CO} & (2) \\ & \mathrm{CH_2}(\tilde{b}^1B_1) + \mathrm{CO} & (3) \\ & \mathrm{HCCO}(\tilde{X}^2A'') + \mathrm{H} & (4) \\ & \mathrm{C_2O}(\tilde{X}^3\Sigma^-) + \mathrm{H_2} & (5) \end{array}$$

For the photochemical reactions of ketene in the near ultraviolet absorption region, the mechanism is very clear that the ketene molecule in the ground state (S_0) was first excited to the first excited singlet state (S_1) via a UV laser (300~360 nm), and the excited ketene underwent nonadiabatic transition to lower electronic states, i.e. S_0 and the first triplet state (T_1), the final leading to the C═C bond fission mainly occurred on the S_0 and T_1 states, which are relative to pathway (2) and pathway (1), respectively. In the higher excitation energy region (193~215 nm) within the banded S_2–S_0 absorption system, although there have been numerous experimental and theoretical reports, the photodissociation dynamics of ketene still need gain a further insight.

To be motivated by some experimental different conclusions and the fast development of the high level theoretical calculation methods, we will do a systemic study on the photodissociation dynamics of ketene considering the six lowest electronic states (S_0, S_1, S_2, T_1, T_2 and T_3), in order to explore the photodissociation mechanism of ketene under the higher excitation energy.

We proposed the main photodissociation mechanism of ketene as follows (see Figure 1), after one photon absorption to the S_2 state, ketene can decay to the $S_2/S_1/T_2$ intersection through S_2-TS along the minimum energy path on the S_2 state. Since the internal conversion is usually more efficient than the intersystem crossing from the $S_2/S_1/T_2$ intersection, it may further be inactive to the S_1 state. Due to a higher dissociation barrier (267.1 kJ/mol) on the S_1 state, S_1 will relax to the S_0 state via S_1/S_0-MSX. Finally, ketene directly dissociates into $\mathrm{CH}_2(\tilde{a}^1A_1) + \mathrm{CO}(\tilde{X}^1\Sigma^+)$ on the S_0 state. The result supported the experimental ones. In addition, we assigned the correlative dissociation pathways.

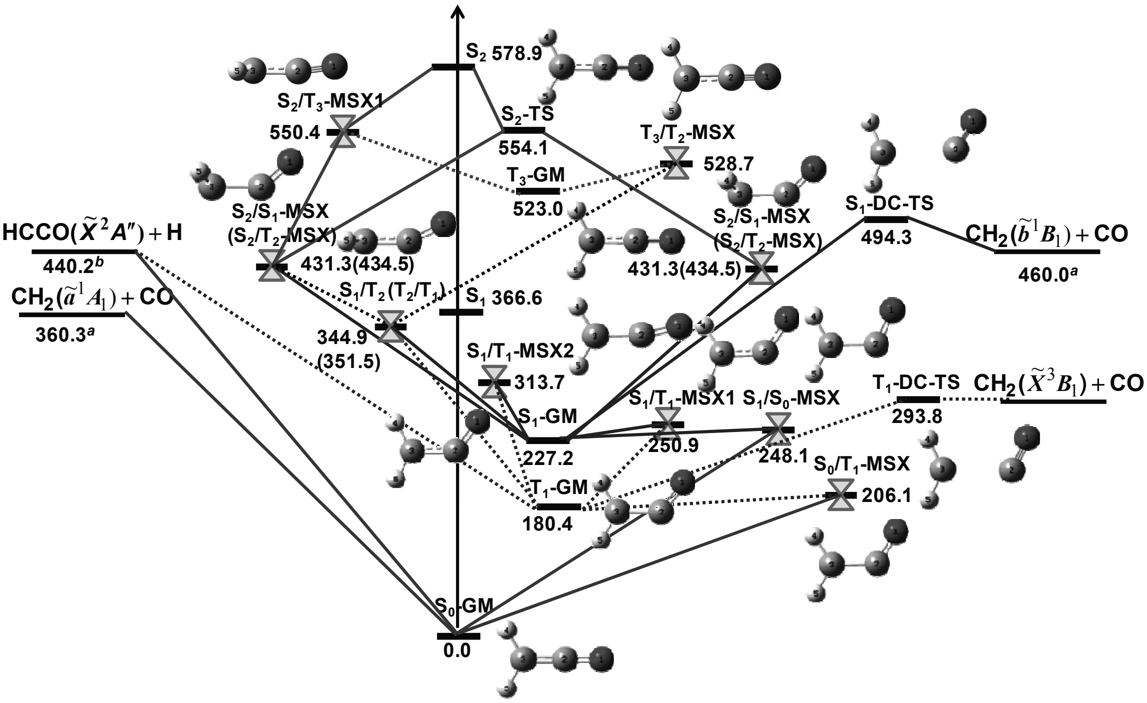
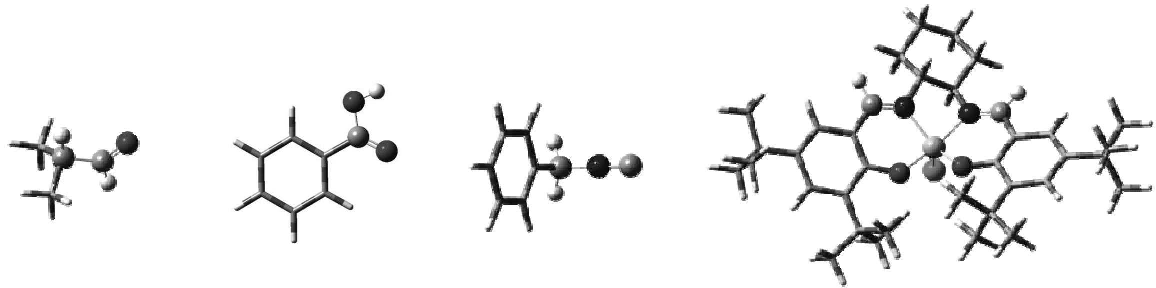


Figure 1. The PESs for the processes of ketene photoexcitation and photolysis. ^{a,b}The values are the dissociation energies in experiment.

III. Theoretical Study on Catalytic Enantioselective Mechanism of Passerini Reaction

The Passerini three-component reaction, which involves a carbonyl compound, a carboxylic acid and an isocyanide, has been investigated intensively during the past two decades. Recently, Maeda S. and coworkers used the artificial force induced reaction (AFIR) method to study on the mechanism of the Passerini reaction systematically and proposed that the Passerini reaction is actually a four-component reaction via four-component transition states (TSs) involved an extra carboxylic acid. Based on the previous study, we will continue to explore the mechanism and enantioselectivity of the Passerini reaction in relation to catalyst.



1 **2** **3** **Cat.**

Figure 2. The structures of reactants and catalyst in the Passerini reaction.

In this study we chose the real system in experiment (*Angew. Chem. Int. Ed.* 2008, 47, 388) to search, as shown in Figure 2. In comparison with the Passerini reaction involving catalyst, we also considered no catalyst reaction, that is to say only including reactants 1, 2 and 3. We used the ONIOM(M062X/6-31G:PM6) method in the initial AFIR search, where the mixing order of different species is based on the experimental procedure. Then, all the lower energy pathways were optimized by the ONIOM(M062X/6-31+G**:PM6) method. We also considered the solvent effect using PCM model, where toluene is as a solvent.

The present ONIOM(M062X/6-31+G**:PM6) results show that in no catalyst system, the products are racemic adducts. In the generation chirality step, the difference of the energy barrier between TSs to produce *S*-conformation and *R*-conformation is only 0.2 kJ/mol. For the involving catalyst system, we found eight TSs (4 *S*-conformation and 4 *R*-conformation) in the generation chirality step. In Figure 3, we take examples for the structures of TSs. (Si-face attack is relative to *R*-conformation; Re-face attack is relative to *S*-conformation.) The difference of the energy barrier among TSs is about 1.8 kJ/mol. Although the results are in agreement with the experimental ee value (*S*-conformation is major), the difference of the energy barrier is too small. Therefore, we are carrying on the high level calculations to validate the present results.

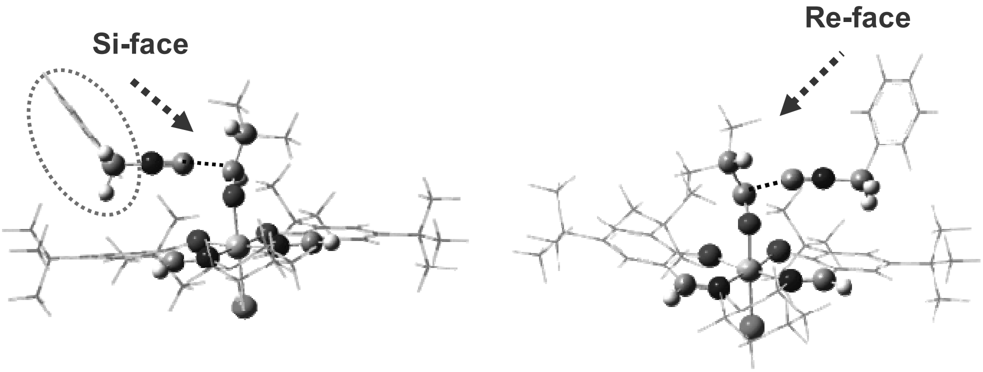


Figure 3. The structures of transition state in the generation chirality step.

2. Original papers

(1) Hongyan Xiao, Satoshi Maeda and Keiji Morokuma
“Excited-state roaming dynamics in photolysis of a nitrate radical”
J. Phys. Chem. Lett. 2, 934-938 (2011).

(2) Michael P. Grubb, Michelle L. Warter, Hongyan Xiao, Satoshi Maeda, Keiji Morokuma and Simon W. North.
“No straight path: roaming in both ground- and excited-state photolytic channels of $NO_3 \rightarrow NO + O_2$”
Science 335, 1075-1078 (2012)

(3) Hongyan Xiao, Satoshi Maeda and Keiji Morokuma
“Global *Ab Initio* Potential Energy Surfaces for Low-lying Doublet States of NO_3”
Submitted.

(4) Hongyan Xiao, Satoshi Maeda and Keiji Morokuma
"Multireference Theoretical Study of the Photodissociation Dynamics of Ketene"
Manuscript in preparation.

3. Presentation at academic conferences

(1) Hongyan Xiao, Satoshi Maeda and Keiji Morokuma (Poster)
"A theoretical study on the photodissociation of HNO_3 involving S_2, S_1 and S_0 states"
7th Congress of the International Society for Theoretical Chemical Physics, Abstract page 3PP-47, Tokyo, Japan, September 2~8, 2011.

(2) Hongyan Xiao, Satoshi Maeda and Keiji Morokuma (Poster)
"Multireference theoretical study of the photodissociation dynamics of ketene"
The 9th FIFC symposium, Kyoto, January 6, 2012.

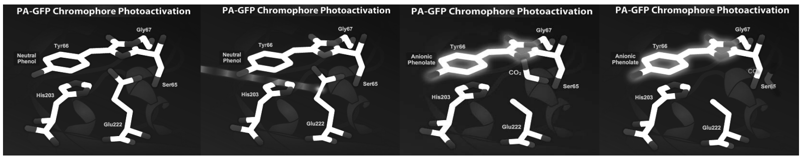
Lina DING

JST Fellow, Fukui kenichi Memorial Research Group 1

1. **Summary of the research of the year**

Reaction Mechanism of Photo-induced Decarboxylation of the Photoactivatable Green Fluorescent Protein:An ONIOM(QM:MM) Study

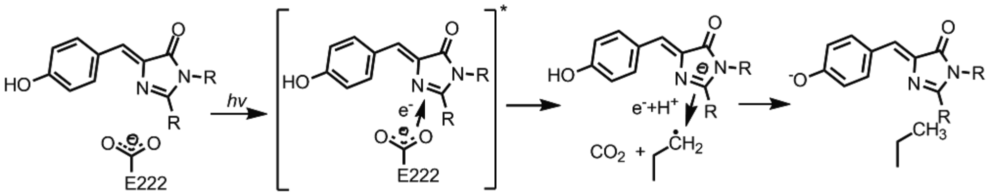
Green fluorescent protein (GFP) and its variants have played an important role in biological imaging and analysis. Photoactivatable fluorescent proteins have attracted a plenty of scientific interests, since dramatic contrast by emission upon an irradiation makes them particularly popular and important as optical markers.



http://zeiss-campus.magnet.fsu.edu/tutorials/fluorescentproteins/pagfpchroma/index.html

Photo-induced transformation between the neutral form (responsible to the A band) and anion form (the B band) of the GFP chromophore is essential to fluorescent emission. As shown in Scheme 1, an irreversible Type II and so-called Kolbe mechanism was proposed for the wild-type (WT) GFP which accompanies the photo-induced decarboxylation of GLU222, supported by X-ray crystallography and mass spectrometry. Due to the similarity to the well known thermal Kolbe reaction, the decarboxylation of GLU222 of GFP (or GLU219 of PA-GFP) was proposed to occur because of the photo-induced oxidation of GLU; upon photo-excitation one electron transfers from anionic GLU to the chromophore, followed by decarboxylation of the neutral species. The reported order of the decarboxylation rate (254 nm > 280 nm > 476 nm) showed clearly that it was excitation-wavelength dependent. Recently, X-ray crystal structures of native and photo-activated states of PA-GFP were also reported. In addition, rate measurements for irreversible photoactivation in WT-GFP and PA-GFP reveal similar kinetics.

Very recently, Roy et al. reported QM/MM and MD study of the decarboxylation process of IrisFP; here however one electron was arbitrarily removed from the QM system.; Nakatsuji and Krylov *et al.* have identified the critical CT states involved in the Kolbe mechanism which were proposed to be accessible via either directly one-photon absorption, or a two-step excitation via S_1.



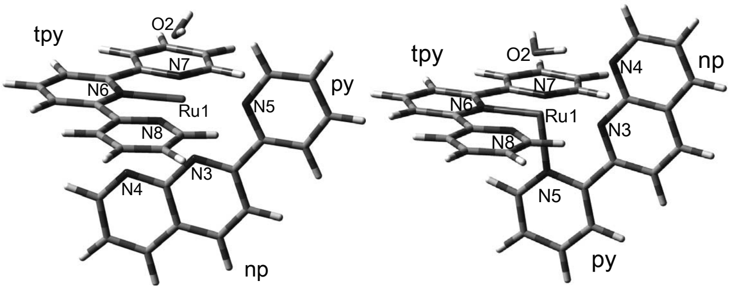
Scheme 1. Irreversible Type II Kolbe mechanism for the photo-decarboxylation.

Knowledge of potential energy surfaces (PESs) of the ground and excited states involved is of great importance in understanding the reaction mechanism. In particular, it is a challenge to characterize the nature of electronic structures involved and details of the decarboxylation process. Here, we investigated the reaction mechanism of the irreversible photo-induced decarboxylation of PA-GFP, which is still unclear and remains unresolved till now, by the ONIOM(CASSCF:Amber) and ONIOM(CASPT2:Amber) methods.

Mechanisic study on the Photoisomerization in Polypyridyl mononuclear ruthenium(II) aquo (PMRA) complexe

Polypyridyl mononuclear ruthenium(II) aquo (PMRA) complexes have considerable attractions as competent water oxidation catalysts, since the typical feature was established for a series of Ir complexes and polypyridyl ruthenium compounds. Relative to the higher nuclearity systems, the mononuclear systems that generally easier synthesis and study bring the important implications related to water oxidation catalysts. The proton-coupled electron-transfer reactions associated with the water splitting bring comprehensive studies on PMRA complexes because how electrons and protons are transferred is critical in developing our understanding of important biological reactions such as respiration, nitrogen fixation, and photosynthesis as well as energy conversion in artificial photosynthesis or fuel cells. Up to now, the rare photo-isomerization reaction has been surprisingly observed in cis-$[Ru(bpy)_2(OH_2)_2]^{2+}$ (bpy = 2,2-bipyridine) and trans-$[Ru(tpy)(pynp)OH_2]^{2+}$ by Meyer and Yagi, respectively. In case of cis-$[Ru(bpy)_2(OH_2)_2]^{2+}$, the trans form appeared to be a photo-stationary state and slowly reversed to the cis form. However, no evidence of a photostationary state was found between trans-$[Ru(tpy)(pynp)OH_2]^{2+}$ (A) and cis-$[Ru(tpy)(pynp)\text{-}OH_2]^{2+}$ (A') during 5-75 ℃. However, the forward process from trans- to cis- form can occur and the reverse cannot. The redox reactions and water oxidation catalyses are significantly controlled by the photoisomerization.

As a possible mechanism proposed by Yagi, the photoisomerization process should take place as following: visible-light irradiation can generate metal-ligand charge transfer (^{3}MLCT) state which is followed by the thermally accessible metal-center (^{3}MC) state, on which an aquo ligand dissociation could occur from A and a five-coordinate $[Ru(tpy)(pynp)]^{2+}$ intermediate could be formed; a water molecule re-coordinates to the metal center of the intermediate from the opposite side of tpy plane to form A' isomer. The Ru-O bond cleavage could be involved since the consistence between the photoisomerization activation energy(41.7 kJ mol^{-1}) and the water exchange activation enthalpy (50.6-87.8 kJ mol^{-1}) in ruthenium aquo complexes. However, no clear information could explain why the forward isomerization from A to A' can occur but the reverse process cannot, despite two compounds with similar UV-vis spectrum.



A A'

Figure 1 The structures of A and A' with labels on main atoms and group names

Theoretical study on the photo-isomerization pathways between trans-$[Ru(tpy)(pynp)OH_2]^{2+}$ and cis-$[Ru(tpy)(pynp)\text{-}OH_2]^{2+}$ would be interesting to clear the reason why two compounds with similar UV-vis spectrum have different reactivity. Also, the investigation study on the mechanism will be important for the new design of water splitting catalysts since the redox and oxidate reactions are significantly controlled by the photoisomerization.

2. Original Papers

(1) Lina Ding, Lung Wa Chung, Keiji Morokuma

"Reaction Mechanism of Photo-induced Decarboxylation of the Photoactivatable Green Fluorescent Protein:An ONIOM(QM:MM) Study"

To be submitted

(2) Lina Ding, Keiji Morokuma

"Mechanisic study on the Photoisomerization in Polypyridyl mononuclear ruthenium(II) aquo (PMRA) complexe"

In preparation

3. Presentation at academic conferences

(1) Lina Ding, Lung Wa Chung, Keiji Morokuma

"QM/MM study on the Photoinduced decarboxylation mechanism of Photoactivable Green Fluorescent Protein"

7th Congress of the International Society for Theoretical Chemical Physics (4PP-62), Tokyo, Sep. 2-8. 2011

(2) Lina Ding, Lung-Wa Chung, Keiji Morokuma. Theoretical Study on the Photoisomerization of Mononuclear Ruthenium(II) Monoaquo Complex,

福井謙一博士ノーベル賞受賞 30 周年記念 京都, 2012, Jan.01

Hai-Bei LI

JST Fellow, Fukui Kenichi Memorial Research Group 1

1. Summary of the Research of the Year

(A) SWCNT Growth from Chiral Carbon Nanorings: Prediction of Chirality and Diameter Influence on Growth Rates

Traditional CNT growth methods, such as carbon-arc, laser evaporation, and catalytic chemical vapor deposition (CCVD) are incapable of *in situ* control of (*n*, *m*) chirality during CNT synthesis, primarily due to the high temperatures employed. Recently proposed bottom-up strategy based upon organic synthetic methods represents a more realistic approach towards chirality-controlled SWCNT growth. While the relationship between cycloparaphenylenes (CPP) and the growth of armchair SWCNTs was at first a theoretical hypothesis, organic species including CPPs have been synthesized by a number of groups. It was originally imagined that chirality-controlled SWCNT growth could be achieved in this manner using low temperature CVD in conjunction with, for example, acetylene. In the present work, we illustrated the catalyst-free, chirality-controlled growth of chiral and zigzag single-walled carbon nanotubes (SWCNTs) from organic precursors using quantum chemical simulations. Growth of (6,6), (4,3), (6,5), (6,1), (10,1) and (8,0) SWCNTs was induced by ethynyl radical (C_2H) addition to organic precursors. Figure 1 depicts the evolution of (6,6)-SWCNT growth following the simulation time. About 7.5-Å-long (6,6) SWCNT with almost 5 belts is produced within 500 ps. The present QM/MD simulations have shown that C_2H radicals can facilitate the H abstraction, and act as sidewall growth agent, that is, the successful growth of (6,6)-SWCNT is proposed by H-abstraction and C_2H insertion mechanism, as shown in Figure 1. Figure 2 shows the six-membered ring counting statistics as a function of simulation times during (*n,m*)-SWCNT growth. All the simulations show a strong dependence of the SWCNT growth rate on the chiral angle. The SWCNT diameter however does not influence the SWCNT growth rate under these conditions. This agreement with a previously proposed screw-dislocation-like model of transition metal-catalyzed SWCNT growth rates [F. Ding, et al. *Proc. Natl. Acad. Sci.* **2009**, *106*, 2506] indicates that the

SWCNT growth rate is an intrinsic property of the SWCNT edge itself. Conversely, using *ab initio* simulation, we predict that the rate of SWCNT growth *via* Diels-Alder cycloaddition of C_2H_2 is strongly influenced by the diameter of the SWCNT, which suggests that the relationship between the SWCNT's diameter and its rate of growth depends explicitly on the growth conditions.

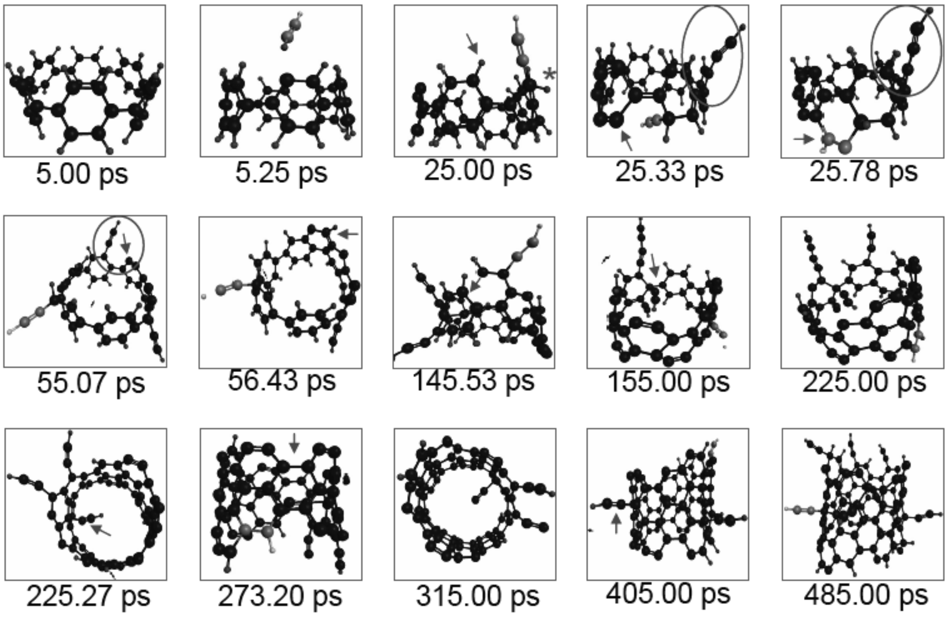


Figure 1. The snapshots of SCC-DFTB/MD simulations of (6,6)-SWCNT growth.

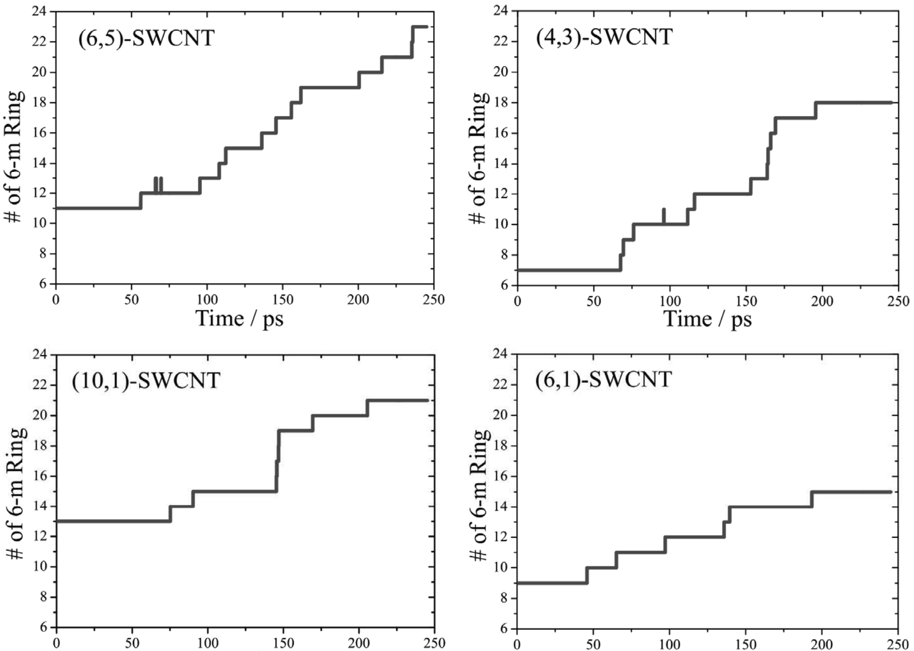


Figure 2. Six-membered ring counting statistics as a function of simulation times.

(B) Sub-Surface Nucleation of Graphene Precursors near a Ni(111) Step-Edge

Graphene, a two-dimensional honeycomb lattice of *sp*^{2} bonded carbon atoms, has attracted much attention due to its remarkable electronic, optical, and mechanical properties. Despite a great number of experimental and theoretical investigations on graphene nucleation and growth, the precise, atomistic nucleation and growth mechanism of graphene remains the topic of fierce debate. In the present work, graphene nucleation at a Ni(111) step-edge has been modeled by means of quantum chemical molecular dynamics (QM/MD) simulations at 1,180 K. These simulations demonstrate for the first time the nucleation of a graphene island precursor not on the Ni(111) surface, but in the Ni(111) subsurface. The mechanism of graphene nucleation observed in trajectory T1 is depicted in Figure 1. Nucleation occurs *via* three stages: (a) sub-surface diffusion of carbon atoms leads to the formation of small carbon chains; (b) coalescence of these chains leads to the formation of amorphous carbon clusters; (c) simultaneous sub-surface → surface precipitation, and amorphous→*sp*^{2} conversion of the carbon cluster. A sufficiently high local carbon concentration in the Ni(111) subsurface is a necessary prerequisite for graphene nucleation. These QM/MD simulations also shed light on the precise role of the step-edge on the graphene nucleation process. After precipitation of the graphene island precursor to the Ni(111) surface takes place, the step-edge defect provides anchoring points, *via* dominant σ C-Ni bonding. In contrast to common assumptions, these simulations demonstrate that the step-edge defect (and the Ni(111) surface in general) is a highly malleable and mobile entity, capable of being deformed, or even destroyed, by the precipitating carbon structure. While such deformation and destruction of the step-edge is observed during the nucleation process, we demonstrate the Ni(111) step-edges ability to ‘heal’ itself over longer periods of time.

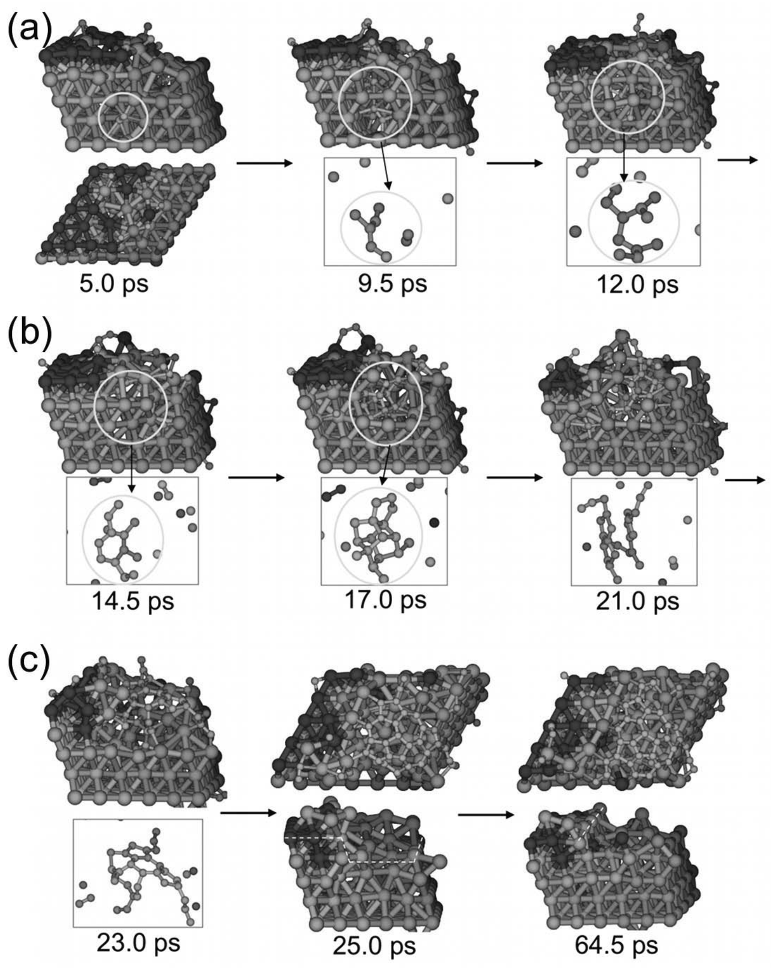


Figure 1. QM/MD simulation showing sub-surface nucleation of a graphene precusor on Ni(111) (trajectory T1). Cyan spheres represent C atoms; yellow/red spheres represent non-step-edge/step-edge Ni atoms, respectively.

2. Original papers

(1) H. B. Li, A. J. Page, S. Irle and K. Morokuma, “Theoretical Insights for Chirality-Controlled SWCNT Growth from a Cycloparaphenylene Template”, *ChemPhysChem*, **13**, 1479 (2012).

(2) H. B. Li, A. J. Page, Y. Wang, S. Irle and K. Morokuma, “Sub-Surface Nucleation of Graphene Precursors near a Ni(111) Step- Edge”, *ChemComm*, Accepted. DOI:10.1039/c2cc32995f.

(3) H. B. Li, A. J. Page, A. M. Mebel, S. Irle, and K. Morokuma, “SWCNT Growth from Chiral Carbon Nanorings: Prediction of Chirality and Diameter Influence on Growth Rates”, *Journal of the American Chemical Society*, (Submitted).

(4) H. B. Li, A. J. Page, A. M. Mebel, S. Irle, and K. Morokuma, “Fullerene Formation from

Hydrocarbon Combustions: Quantum Chemical Molecular Dynamics Study”, *Manuscript in preparation*.

(5) H. B. Li, S. Irle and K. Morokuma, “Growth Mechanism of Hexagonal-Shape PAH Fragments in H-Rich Environment”, *Manuscript in preparation*.

(6) H. B. Li, A. J. Page, S. Irle and K. Morokuma, “Surface Nucleation of Graphene Precursors under Lower Bulk Carbon Concentration”, *Manuscript in preparation*.

(7) H. B. Li, A. J. Page, S. Irle and K. Morokuma, “Dependence of the Catalyst-Free Bottom-up Growth of Single-Walled Carbon Nanotube on Temperature”, *Manuscript in preparation*.

3. Presentations at Academic Conferences

H. Li, S. Irle and K. Morokuma, “Fullerene Formation from Hydrocarbon Combustions: Quantum Chemical MD Study”, *7th Congress of the International Society for Theoretical Chemical Physics*, Abstract page 4PP-78, Tokyo, Japan (Septemper 2~8, 2011)

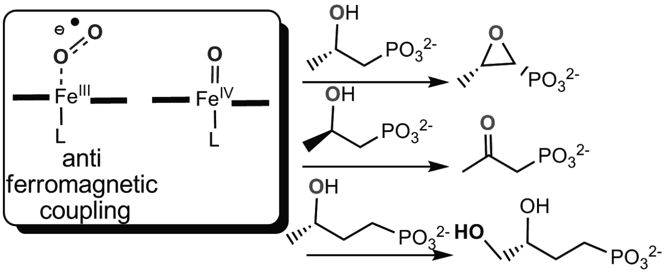
Lung Wa CHUNG

JST Fellow, Fukui kenichi Memorial Research Group 1

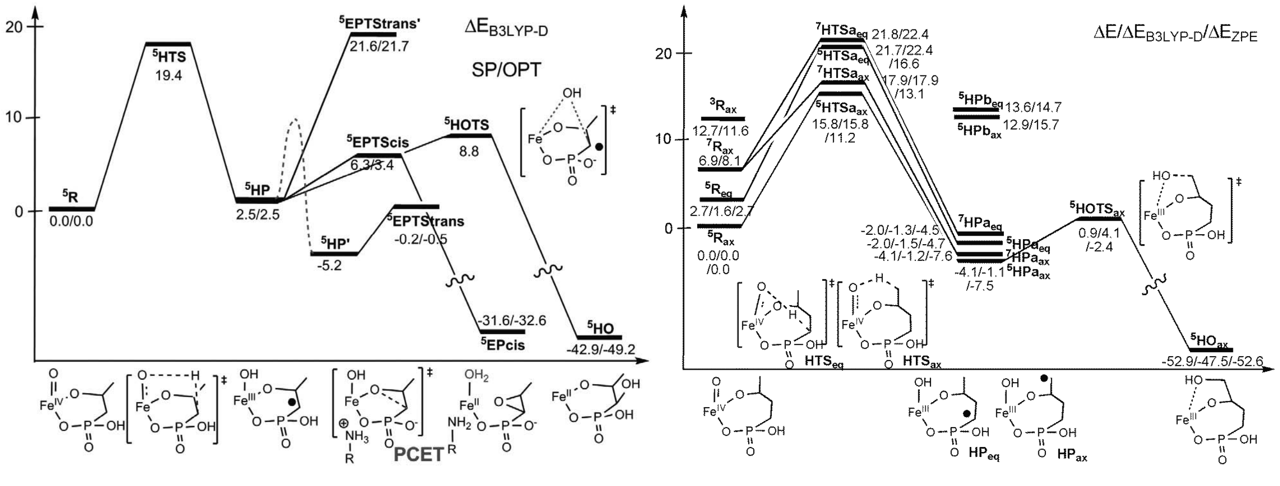
1. Summary of the research of the year

1a. Reaction Mechanism of Biosynthesis of Antibiotic Fosfomycin in HppE. Hydroxypropylphosphonic acid epoxidase (HppE) is a novel non-heme enzyme, that has a unique active site and catalyzes epoxidation from (S)-hydroxypropylphosphonic acid (HPP) to give antibiotic fosfomycin (Scheme 1). Interestingly, reaction can be changed to dehydrogenation or oxygenation, when (R)-HPP or (S)-hydroxybutylphosphonic acid (HBP) was used as the substrate. Ferryl-oxo and ferric-superoxo species have been proposed to be an active oxidant for the key hydrogen atom transfer (HAT) step in HPPE. We have carried out ONIOM(QM/MM) calculations to study reaction mechanisms of divergent reactions in HppE (Scheme 2). We found that conformation of the substrate can influence the reaction site for HAT and thus change the product.

Scheme 1.

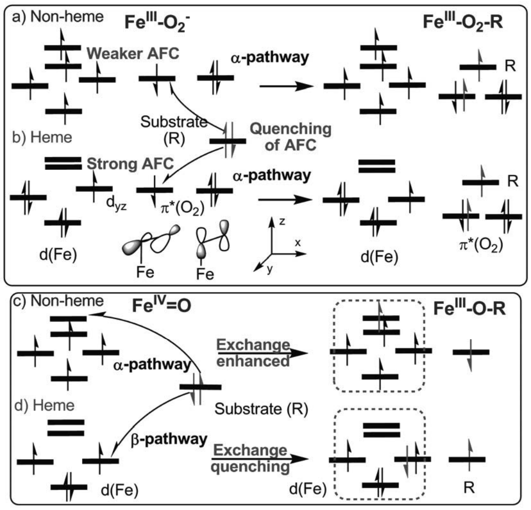


Scheme 2.



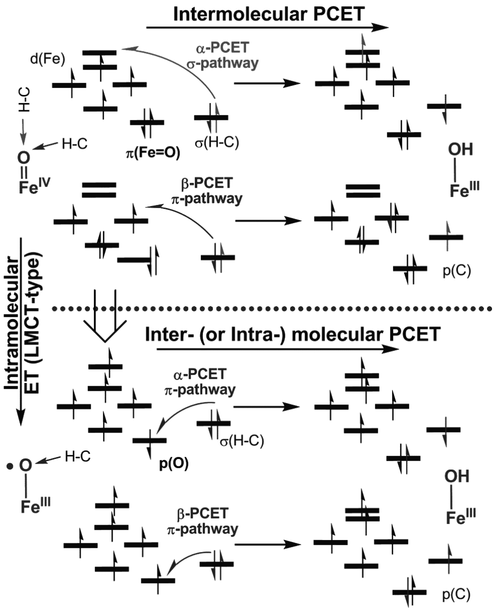
1b. Comparative Reactivity of Hydrogen Atom Transfer (HAT) with Important Metal-Oxo and Ferric-Superoxo Species. Heme- and non-heme-containing oxygenases and oxidases play vital roles in many selective and efficient biochemical oxidations. Several species including ferryl-oxo, ferric-hydroperoxo and ferric-peroxy were proposed or found to act as oxidants in these enzymes. In addition to the well-known high-valent ferryl-oxo species, not-well-characterized lower-valent ferric-superoxo species have recently been suggested or observed to be an alternative electrophilic oxidant, e.g. in isopenicillin N synthase (IPNS), hydroxyethylphosphonate dioxygenase (HEPD), and tryptophan 2, 3-dioxygenase (TDO). Furthermore, some recent synthetic ferric-superoxo and other metal superoxo complexes were reported to be capable of catalyzing oxidation, including C-H bond activation. Notably, many non-heme enzymes can use ferric-superoxo species as an oxidant, but only few heme enzymes (TDO, IDO and NOD so far) use ferric-superoxo species! We theoretically and systematically compare reactivity of several key ferric-superoxo and ferryl-oxo model complexes. Reactivity is found to correlate well with thermodynamic driving force and can increase with higher electrophilicity of the oxidant. Reactivity of the ferric-superoxo oxidants generally is not “superior” to the ferryl-oxo ones. Compared to the high-spin non-heme ferric-superoxo, the lower reactivity of low-spin heme ferric-superoxo, seldom utilized in nature, can be attributed to lower electrophilicity and more pronounced quenching of anti-ferromagnetic coupling between the ferric and superoxo parts (Scheme 3). On the basis of these results, I suggested that a cationic heme-like ferric-superoxo could be a reactive oxidant.

Scheme 3.



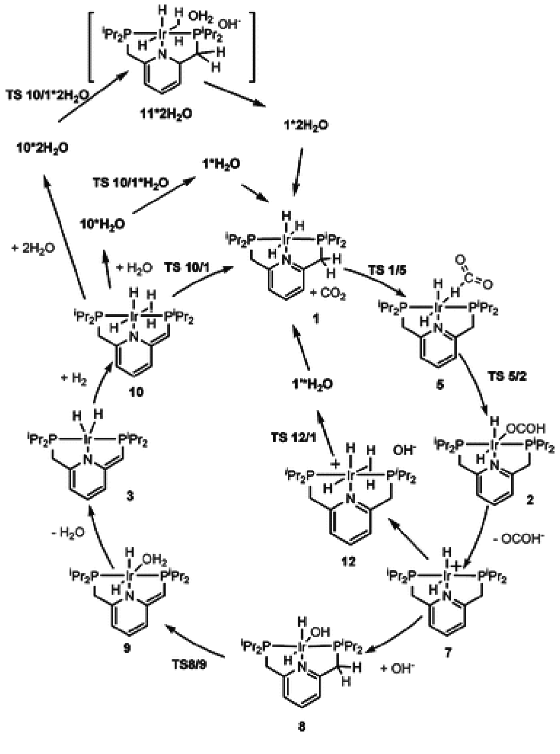
In addition, I further generalized HAT mechanisms (Scheme 4), based on the comparative study on HAT with important Fe-oxo species (heme, non-heme and synthetic model complexes). In general, there can be two classes of HAT mechanisms via either ferryl-oxo or ferric-oxyl type transition state. For the former case, type of ET (α or β) can affect the reaction path (σ or π-pathway). The σ-pathway via α-ET is generally more favorable in many non-heme complexes. While the π-pathway with stabilization of half-filled 3d orbital was found to take place in HPPE, in which ferric-oxyl type (i.e. ligand-metal charge-transfer state) transition state is involved.

Scheme 4.



1c. Reaction Mechanism of Hydrogenation of Carbon Dioxide Catalyzed by Ir-PNP Complex: A PNP-ligated iridium(III) trihydride complex **1** was reported to give the highest catalytic activity for hydrogenation of carbon dioxide in aqueous KOH by Nozaki group. The catalytic hydrogenation can be tuned to be a reversible process with the same catalyst at the expense of the activity, when triethanolamine was used as a base. DFT calculations were performed to understand reaction mechanism of hydrogenation of carbon dioxide. Our calculations suggested two competing reaction pathways: either the deprotonative dearomatization step or the hydrogenolysis step as the rate-determining step (Scheme 5). The results nicely explain our experimental observations, dependence of both the strength of the base and hydrogen pressure.

Scheme 5.



2. Original papers

(1) Chung, L. W.; Hirao, H.; Li, X.; Morokuma, K. “The ONIOM Method: Its Foundation and Applications to Metalloenzymes and Photobiology”, *Wiley Interdisciplinary Reviews: Comput. Mol. Sci.* **2012**, *2*, 327.

(2) Abdel-Azeim, S.; Li, X.; Chung, L. W.; Morokuma, K. “Zinc-Homocysteine Displacement in Cobalamin-Dependent Methionine Synthase and its Role in Substrate Activation: DFT and ONIOM Study”, *J. Comput. Chem.* **2011**, *32*, 3154.

(3) Li, X.; Chung, L. W.; Morokuma, K. “Primary Events of Photodynamics of All-trans Protonated Retinal Schiff Base in Bacteriorhodopsin, Methanol Solution and Gas Phase” *J. Chem. Theory Comput. (Lett.)* **2011**, *7*, 2694.

(4) Chung, L. W.; Li, X.; Hirao, H.; Morokuma, K. “Comparative Reactivity of Ferric-Superoxo and Ferryl-Oxo Species in Heme and non-Heme Complexes” *J. Am. Chem. Soc. (Commun.)* **2011**, *133*, 20076.

(5) Tanaka, R.; Yamashita, M.; Chung, L. W.; Morokuma, K.; Nozaki, K. “Hydrogenation of Carbon Dioxide Catalyzed by Ir-PNP Complex: Reversibility and Reaction Mechanism” *Organometallics* **2011**, *30*, 6742.

3. Presentation at academic conferences

(1) Xin Li, Lung Wa Chung, Hideaki Mizuno, Atsushi Miyawaki, Keiji Morokuma “*Reaction Mechanisms of Novel Fluorescent Proteins*”, (oral) the seventh Congress of the International Society for Theoretical Chemical Physics, Tokyo, September 4, 2011.

(2) Xin Li, Lung Wa Chung, Hideaki Mizuno, Atsushi Miyawaki, Keiji Morokuma “*Reaction Mechanisms of Photophysics and Photochemistry of New Fluorescent Proteins*”, 5th Asia and Oceania Conference for Photobiology, Nara, July, 31, 2011.

Galina PETROVA

JST Fellow, Fukui Kenichi Memorial Research Group I

1. Summary of the research of the year

Towards understanding the HppE catalytic mechanism

The formation of fosfomycin [*cis*-(1*R*,2*S*)-epoxypropylphosphonic acid, an antibiotic in clinical use] is catalyzed by the enzyme 2-hydroxypropylphosphonic acid epoxidase (HppE), which structure was defined several years ago. Systematic experimental studies with *S* and *R* forms of 2-hydroxypropylphosphonic acid (Hpp) suggest that the reaction mechanism includes two main steps: (*i*) H abstraction from C1/C2 atom of the substrate; and further (*ii*) formation of epoxide cycle after H-abstraction from C1 atom or formation of keto-structure after H-abstraction from C2 atom. The *S*-substrate results in *cis*-epoxide as the sole product of the reaction, while only the keto-compound is obtained from the *R*-substrate. Thus, based on the experimental hypotheses about the possible reaction pathways, we performed a DFT model study on the catalytic conversion of both *S* and *R* forms of Hpp, considering only the first coordination sphere of the iron cation (see Fig. 1a). The first step of H-abstraction and formation of alkyl radical is found to be the rate limiting step of the process, requiring above 30 kcal/mol in the case of ferric superoxo active species . A decrease in the energy barriers for H abstraction is observed with ferryl-oxo active species. Further simulations, applying two-layered ONIOM method, show that the influence of the environment is also important for the correct understanding of the catalytic role of HppE in the fosfomycin biosynthesis.

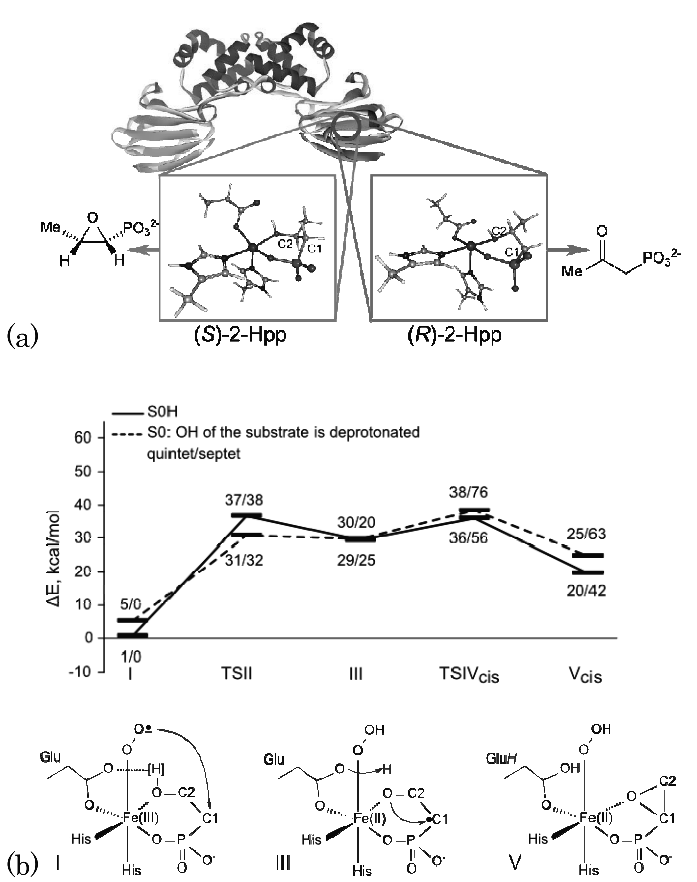


Figure 1. (a) Structure of HppE and model applied in the theoretical study. (b) Energy diagram (gas-phase calculations) for fosfomycin formation from *S*-Hpp in case of ferryl-superoxo active species. The schemes correspond to the structures of the reactant complex, the radial intermediate and the product (I, III and V, respectively).

Theoretical modeling of stereochemistry control of copper catalysts based on the chirality of DNA

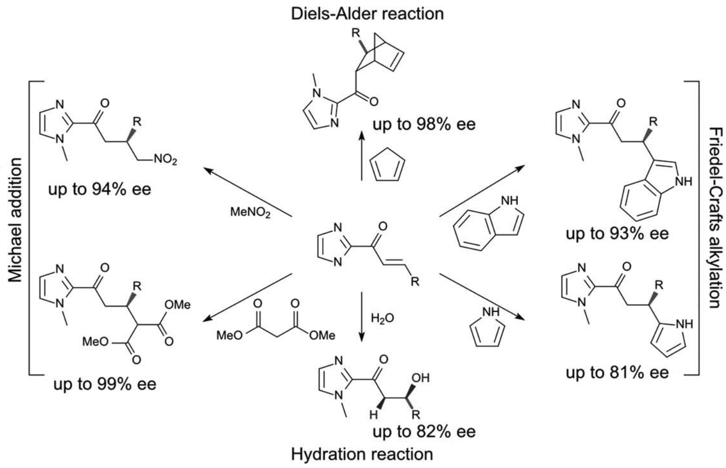


Figure 2. Scope of Cu(II)L/DNA catalyzed reactions (R = Ph, Me, *p*-MeOPh, *p*-ClPh, *o*-BrPh, 2-furanyl, cyclohexyl, etc.).

Another interesting topic on which we have been working is the theoretical investigation of the detailed mechanism of organic reactions catalyzed by hybrid Cu(II)L/DNA supramolecular catalysts and the options for stereo-control of the products. The idea to harness chiral biomolecules of natural origin in asymmetric organic synthesis is not a new one and proved to be quite a versatile one. In a series of experimental studies Feringa and co-authros have shown that such catalysts could be successfully applied in several types of reactions like Diels-Alder (DA), Friedel-Crafts (FC) and Michael addition (see Fig. 2). The DNA based catalysts combine the catalytic power of the transition metal complexes and the chiral architecture of the biopolymer resulting in both efficiency and high enantioselectivity of the reaction. Another important advantage of these catalytic systems is that they are water-soluble and do not require the usage of expensive and environment unfriendly organic solvents; while, on the other hand, the DNA component is cheap, readily available and desired oligo/polymers with designed nucleotide sequence and length could be prepared relatively easily.

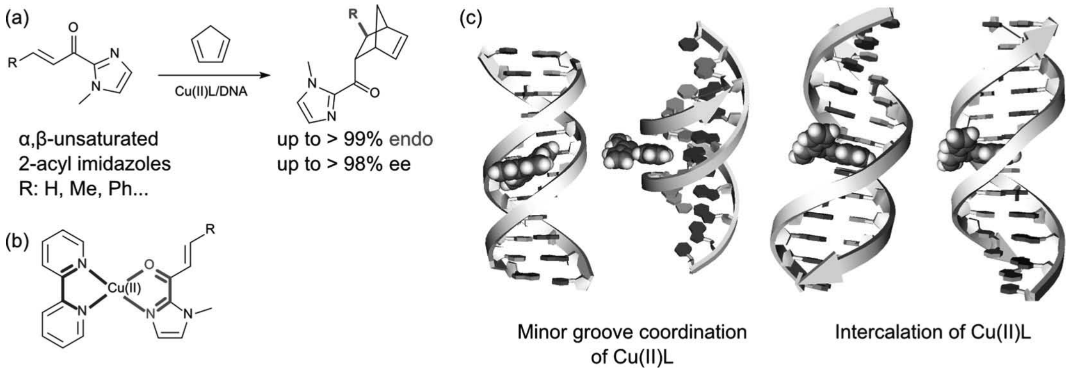


Figure 3. (a) Scheme of the reaction of interest - DA addition of cyclopentadiene to α,β-unsaturated 2-acyl imidazoles. (b) Scheme representing the local structure of the reactant complex consisting of Cu(II), L (L = bipyridine) and the dienophile reactant coordinated to the metal cation via the acyl oxygen and the pyridyl nitrogen. (c) Examples for coordination modes of Cu(II)L complex to a double-stranded DNA oligomer. Front and side view presented for minor groove coordination and two different complexes of intercalation via L with reactant facing the major (left structure) or minor (right structure) groove. The structures on this figure are tentative, not theoretically optimized or experimentally observed ones.

As we are mainly interested in DA and FC reactions for which Cu(II)-bpy complexes results in highest stereoselectivity, we considered Cu(II)-bpy complex and two different DNA dodecamer fragments: the AT rich $\mathrm{d(CAAAAATTTTTG)_2}$ and the CG rich one $\mathrm{d(CGCGCGCGCGCG)_2}$ and according to the experimental data CG rich sequences (DNA2) perform best for the DA and FC reactions. In case of intermolecular reactions (most common in the experimentally studies) the reactant molecule is α,β-unsaturated 2-acyl imidazole structure as the 2-acyl imidazole moiety ensures stable coordination of the organic structure to the Cu(II) ion (see Fig. 2 a & b).

Before studying the reaction mechanism of the catalyzed process and compare it with the referent reaction without a catalyst or with only Cu(II) complex as Lewis acid catalyst, it was important to propose a suitable model of the supramolecular complex. The available experimental data are not sufficient or ambiguous to define the structure of the supramolecular complex. A lot of other experimental studies (not connected with the role of DNA as asymmetric microenvironment) have revealed that organic molecules and metal complexes could interact with the DNA strand in two main modes: minor groove coordination or intercalation inbetween DNA base pairs (see Fig. 3c). It is possible that the metal complex including the ligand and the reactant is coordinated in mixed mode with the ligand anchored between the DNA base pairs and the reactant molecule nestling in the minor groove. In the search for a suitable structure we combined docking experiments and molecular dynamics (MD). The results from the MD simulations show that both types of interactions result in formation of stable supramolecular structures. In case of minor groove coordination of the metal complex with the ligand (bpy) nested in the groove the reactant is exposed for further interaction with dienophile (pentacyclodien) or nucleophile. However, such a structure of the complex catalyst will hardly favor the formation of a specific stereoisomer, i.e. will not show stereo specificity. Intercalation results in slightly more stable complexes (by ca. 8-10 kcal/mol) as in the obtained structures the attack to one site of the reactant is hinter due to sterical constraints. Further simulations of the reaction mechanism on QMMM level will be based on the most stable representatives.

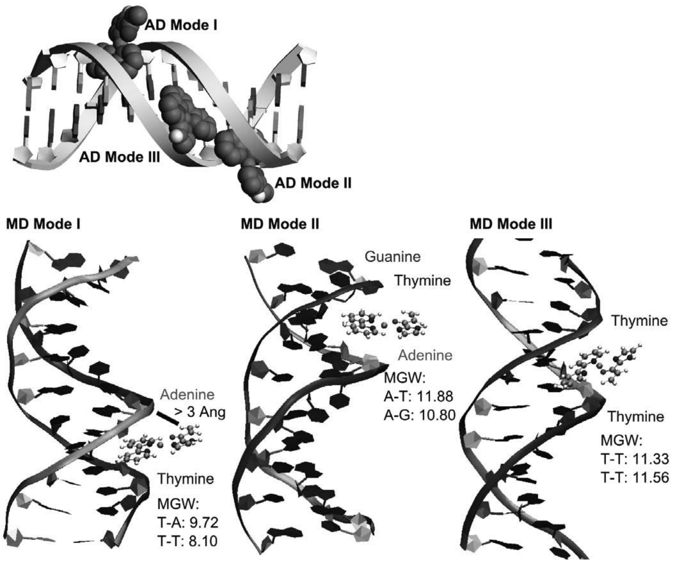


Figure 4. An example of minor groove coordination of LCu(II)R complex to DNA1. The upper panel shows the results from the docking while in the lower panel of the structures resulting from the MD simulations are given.

2. Original papers

Galina Petrova, Lung Wa Chung, Keiji Morokuma, DFT and ONIOM modeling of fosfomycin biosynthesis catalyzed by HppE. *In preparation*.

3. Presentation at academic conferences

Galina Petrova, Lung Wa Chung, Keiji Morokuma (FIFC)
“Towards understanding the HppE catalytic mechanism: theoretical modeling of fosfomycin biosynthesis” (Poster presentation)
9th FIFC Symposium, Kyoto, Japan (6 January 2012)

Raman Kumar SINGH

JST Fellow, Fukui kenichi Memorial Research Group 1
(To 31 Aug. 2011)

1. Summary of Research

The Reaction Pathway for C_4H_2 Polyyne Fusion Reactions: A Theoretical Investigation

The one dimensional (1D) carbon nanowire made of a long linear carbon chains inserted inside a multiwalled carbon nanotube (MWCNT) has attracted a great deal of attention for many researchers to trap its optical and electronic properties for the advancement of nanotechnology, material science and the basic research. The linear carbon chains can possess either cumulenic or polyynic structure. Recently, Shinohara and his co-workers succeeded in synthesising single(double)-wall carbon nanotubes encapsulating $C_{10}H_2$ polynne molecules and found that a high-temperature fusion reaction occurs to form long linear carbon chains inside the 1D nanospace of MWCNT. However, the reaction pathways for such fusion reactions are still unknown and unexplored either experimentally or theoretically, as far as we know. To address this issue, we have considered the minimal polyyne (C_4H_2) nano-fusion reactions (Fig. 1) as a first step to investigate theoretically using density functional theory.

$$2(C_{2n}H_2) \longrightarrow (C_{2n})_2H_2 + H_2 \quad ; n\geq 2$$

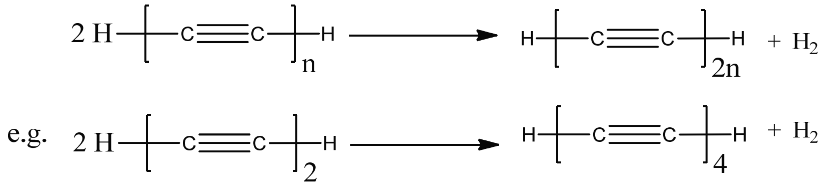


Figure 1: Schematic representation of nano-fusion reactions of polyyne in multiwalled carbon nanotube .

In this work, our focus is to find the reaction pathway of C_4H_2 polyyne fusion reactions in gas phase and then to see the effect of the single-wall carbon nanotube on the gas phase reaction pathways systems.

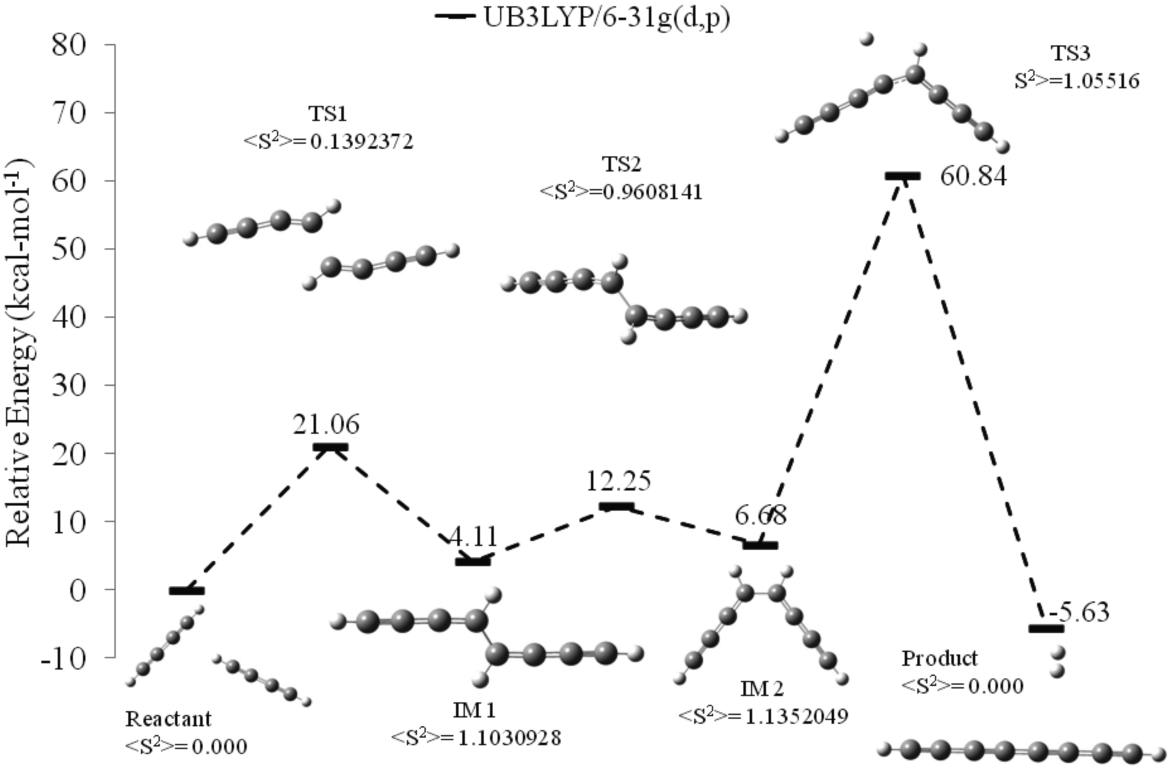


Figure 2: Open-shell singlet gas phase reaction pathway for C_4H_2 polyyne fusion reaction at the UB3LYP/6-31g(d,p) level.

Figure 2 shows that the reactants convert into the final product via two intermediates and three transition state (TS) structures in gas phase wherein all the intermediates and transition states structures are open shell singlet. It implies that C_4H_2 fusion reaction follows open-shell singlet reaction pathways. However, TS3 has very high barrier height in comparison to the rest TS structures.

To see the effect of single-wall carbon nanotubes (SWNTs) on the gas phase reaction pathways, a two layer ONIOM calculations (QM/MM) were performed in which (8,8)SWNT of length 20 Å was treated by the Dreiding force field molecular mechanics method and the gas phase reaction pathways systems inside the single-wall carbon nanotube were taken under quantum mechanical methods (i.e. UB3LYP/6-13g(d,p) : open-shell singlet) treatment. The optimized geometries are presented in figure 3. This figure shows that the hydrogen molecules are not adsorbed by the wall of the nano-tube. However, the relative energy profiles remained similar to the gas phase reaction pathways, as can be seen in the figure 4.

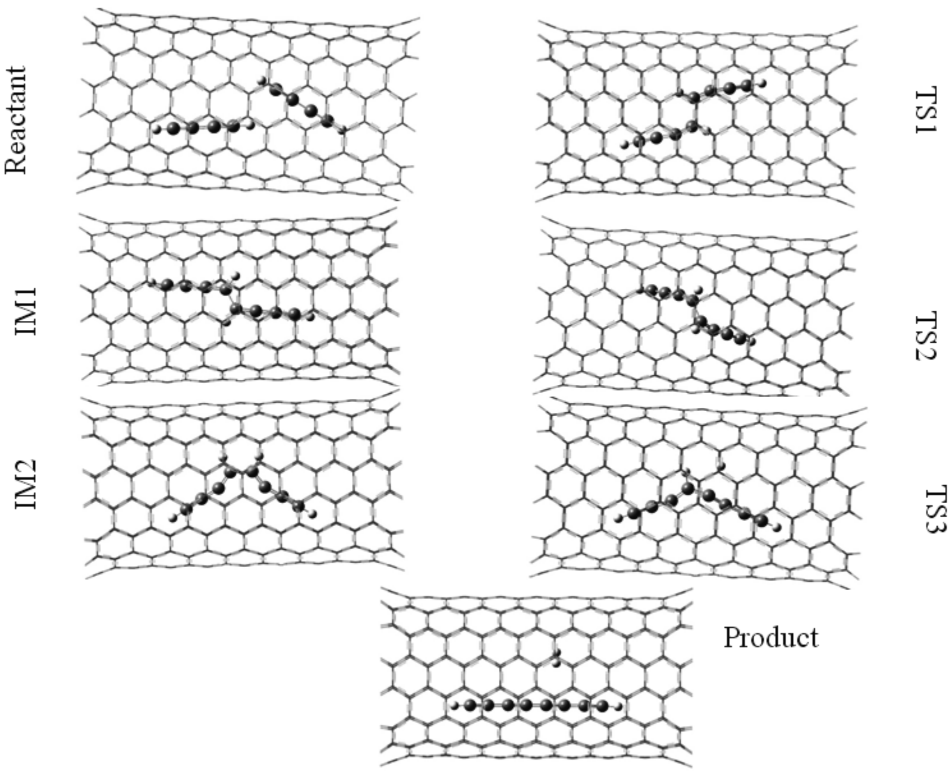


Figure 3: Optimized geometries of the gas phase reaction pathway inside the (8,8) SWNT of length 20 Å and diameter 10.77 Å at the ONIOM(UB3LYP/6-31g(d,p):Dreiding) level with open-shell singlet.

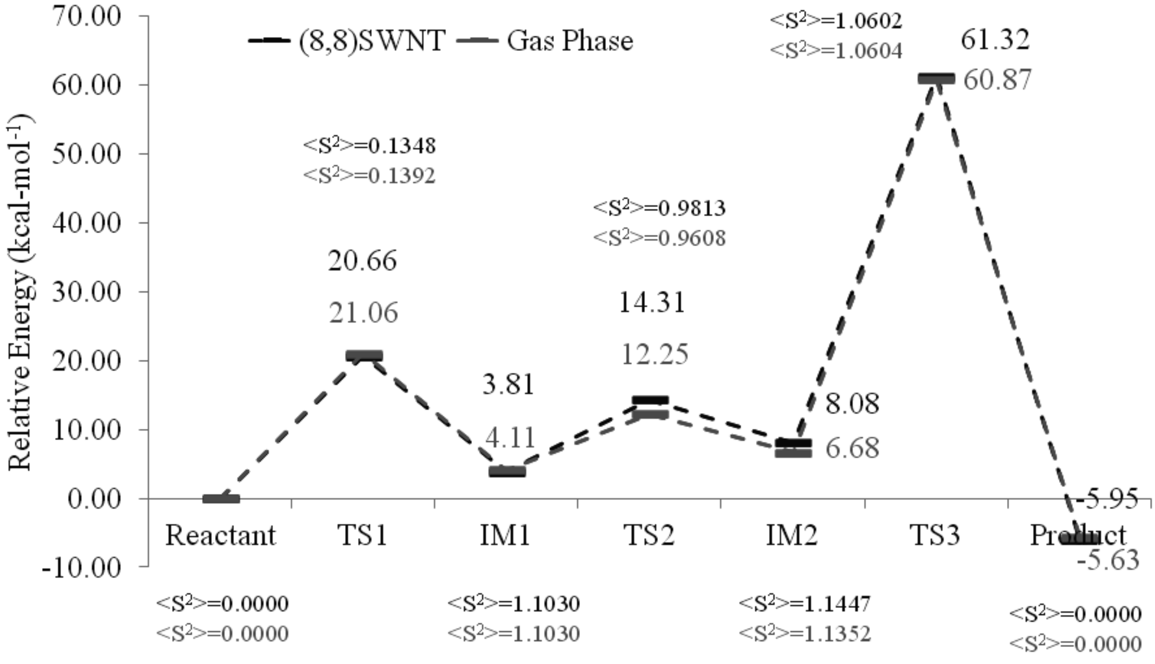


Figure 4: Open-shell singlet reaction pathway for C_4H_2 polyyne fusion reaction with and without the (8,8) SWNT (length 20 Å and diameter 10.77 Å).

In summary, this study shows that C_4H_2 fusion reaction follows open-shell singlet reaction pathways in gas phase as well as inside the SWNT. TS3 has the largest barrier height and the hydrogen molecules are not adsorbed by the wall of the nano-tube. These results also seem to indicate that these findings are not sufficient and needs to explore another reaction mechanism. Since the present investigation was carried out a zero-kelvin temperature and the polyyne nano-fusion reaction occurs at very high temperature and high vacuum. Therefore, the role of temperature is crucial and the temperature dependent reaction pathways need to be explored and investigated theoretically to capture the real essence of such polyyne nano-fusion reaction.

Travis HARRIS

JSPS Foreign Researcher, Fukui kenichi Memorial Research Group 1
(From 21 Jan. 2012)

1. Summary of the research of the year

ONIOM Investigation of Iron Uptake by Ferritin

Ferritins are the major iron storage proteins of animals, plants, and microorganisms, which are critical for preventing toxic radical chemistry and oxidative damage. Animal ferritins are composed of a 12 nm diameter protein shell (Figure 1a) surrounding an 8 nm cavity that can store up to 4500 iron atoms in the form of a hydrated iron oxide. This shell comprises 24 subunits, each structured as a 4-α-helix bundle (Figure 1b). Catalytically active, H or M, and inactive, L, subunits occur in animals in various ratios with tissue-specific distributions. The catalytic centers of H and M subunits are dinuclear ferroxidase sites (Figure 1b and c) where Fe^{2+} is oxidized by O_2, proceeding through a spectroscopically characterized di-ferric peroxo intermediate to a μ-oxo/hydroxo-di-ferric product (Fe-O-Fe) with release of H_2O_2. The Fe-O-Fe dimers move 20 Å through a channel in the subunit, aggregating with subsequently formed dimers to form tetramers and larger multimers before entering the cavity near the four-fold symmetry axis (Figure 1a and b).

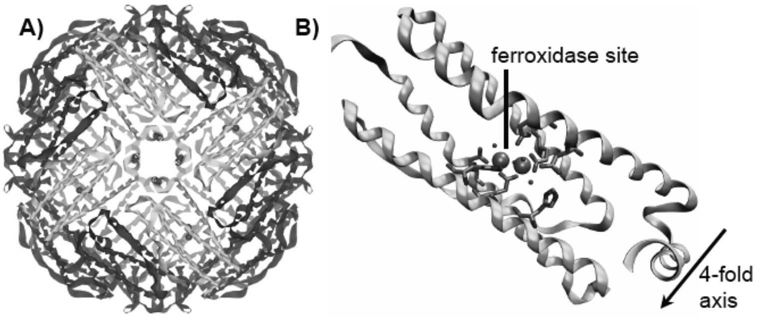


Figure 1. (A) Ferritin protein cage with four subunits in yellow forming a four-fold symmetry axis (PDB 1MFR). (B) A single subunit with iron indicated by purple spheres (PDB 3RBC).

The general mechanism of iron storage by ferritin has been outlined by years of experimental studies, but many aspects remain uncertain, including the role of water and the protein environment in the ferroxidase reaction, the peroxo coordination mode, and the protonation states of the intermediates and dimer products. The purpose of the current research is to theoretically define the structures of all intermediates and products in the reaction pathway through comparison with the available X-ray diffraction, EXAFS, Mössbauer, MCD, and Raman data.

Initial coordinates of the Fe(II)- and Fe(III)-bound states were taken from crystallographic structures of Cu(II)- (PDB 3RE7, 2.8 Å) and Fe(III)-bound (PDB 3RBC, 2.7 Å) bullfrog M ferritin, respectively. Each model was based on a single subunit containing ~3000 atoms. Structural optimizations were carried out for the 9 Å region surrounding the Fe centers using ONIOM-ME(B3LYP:Amber) with SDD(f) for Fe and 6-31G* for others. The QM layer for representative models including capping H atoms are shown in Figure 2. These models were also used in a separate series of QM-only calculations.

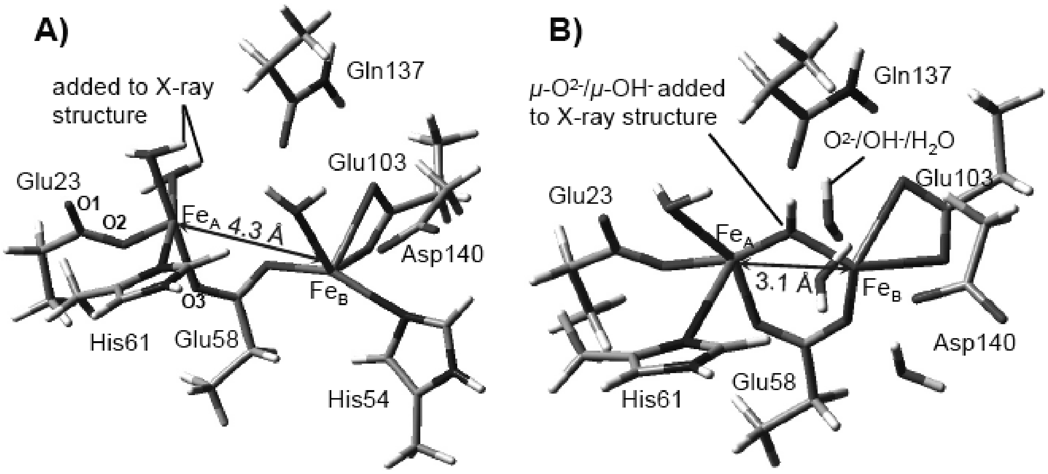


Figure 2. QM models of (A) Fe(II)-bound and (B) Fe(III)-bound ferroxidase sites with coordinates from crystallographic structures of Cu(II)-bound and Fe(III)-bound bullfrog M ferritin, respectively.

The Cu(II)-bound crystal structure on which the Fe(II) model is based (Figure 2a) defines a three-coordinate A site and five-coordinate B site; however, interpretation of MCD data led to assignments of a square pyramidal A site and trigonal bipyramidal B site. At 2.8 Å resolution the coordinates of water molecules are highly uncertain; thus, we examined models with one or two waters added to the A site, as well as models with and without the B-site water. Key structural parameters and Heisenberg exchange coupling constants of the optimized models are presented in Table 1. Model R1 can be ruled out due to a large rotation of the Glu23 side chain to an *anti* coordination mode and tetrahedral geometry at Fe_A. The discrepancy in the Glu23 side chain conformation is also described by the 81° change in the O_1-O_2-Fe_A-O_3 dihedral angle (see labels in Figure 2a) relative to that of the crystal structure (151°). To match the experimental 5-coordinate geometry at Fe_A, Glu23 can be bidentate as in R2 and R3, or an additional H_2O_A can be present as in R4 and R5. The dihedral angles show that the Glu23 bidentate coordination mode (126 or 142°) is achieved with less rotation than the *syn* monodentate mode (-165 or -157°), in which the uncoordinated Glu(O) is hydrogen bonding to a water ligand. On the other hand, it is this latter hydrogen bonding mode that is clearly present in the oxidized crystal structure and thus less rearrangement would be required. A further consequence of monodentate coordination is that it allows Fe_A to move closer to Fe_B in models R4 and R5, as shown by the shorter Fe...Fe distances (4.48 and 4.23 Å). While the crystallographic Fe…Fe distance has a large error bar (4.3 ± 0.4 Å), in R2 it is likely too long (4.88 Å) for it to be a reasonable candidate, in addition to the inconsistent tetrahedral geometry at Fe_B. R5 is also disfavored by the 6-coordinate geometry at each Fe, due to the H_2O_B migrating to a bridging position. R3 and R4 remain as the best models and neither is clearly favored. The Fe…Fe distances and J values are reasonable, but neither has the combination of trigonal bipyramidal and square pyramidal geometry indicated by MCD. Forthcoming TD calculations will provide another means to compare the models to the MCD results.

Table 1. Composition, structural parameters and exchange coupling constants for ONIOM-optimized Fe(II)-bound models

model	nH$_2$O$_A$	nH$_2$O$_B$	Glu23 coordination	O$_1$-O$_2$-Fe$_A$-O$_3$ (°)	Fe$_A$ geometry[a]	Fe$_B$ geometry[a]	Fe…Fe (Å)	J (cm^{-1})
R1	1	1	*anti*	70	Td	SP	4.71	-1.4
R2	1	0	bidentate	126	TB	Td	4.88	-0.8
R3	1	1	bidentate	142	TB	Td/TB	4.74	-0.6
R4	2	0	*syn*	-165	SP	SP	4.48	-0.9
R5	2	1	*syn*	-157	O	O	4.23	-0.9
Exp			*syn*	151	SP/TB	TB/SP	4.3 ± 0.4[b]	-0.8

[a] Td, tetrahedral; TB, trigonal bipyramidal; SP, square pyramidal; O, octahedral. [b] 4.63 Å in the subunit used for these optimizations.

The Fe(III) products of the ferroxidase reaction have a much shorter Fe…Fe distance of 3.1 ± 0.1 Å in the crystal structure (see Figure 2b) that is consistent with the 2.99 Å EXAFS value. Based on this distance, a μ-oxo/hydroxo ligand must be present but hidden by the electron density of the Fe centers in the crystal structure. The number and positions of water-derived ligands are again uncertain, and the one labeled $O^{2-}/OH^-/H_2O$ in Figure 2b is particularly interesting as it may be a second bridge. Mössbauer spectra show four quadrupole doublets which were attributed to a mixture of four μ-oxo/hydroxo-bridged species. To identify these products, ONIOM optimizations and Mössbauer calculations were carried out for models with various water-derived ligands, and representative results are presented in Table 2. The single μOH^--bridged model, Ox1, has the longest Fe…Fe distance of 3.50 Å, as the bridge is insufficient to maintain the crystallographic distance of 3.05 Å in the subunit used for the models. The stronger μO^{2-} ligand in Ox2 reduces the distance to 3.35 Å, which is still not within the experimental uncertainty. Further strengthening the bonds between the Fe sites, Ox3 has two μOH^- ligands, resulting in a 3.07 Å distance that is remarkably close to the initial 3.05 Å distance. The quadrupole splittings of Ox3 greatly differ between the two sites (0.49 and 1.25 mm/s), and match well with two of the experimental values, Exp4 (0.63 mm/s) and Exp3 (1.17). The corresponding calculated isomer shifts are systematically 0.03–0.04 mm/s higher than the experimental values if Exp4 is assigned to site A and Exp 3 to site B. Thus, the four experimental quadrupole

Table 2. Composition, Fe…Fe distances, isomer shifts, and quadrupole splittings of ONIOM-optimized Fe(III)-bound models

model	bridging ligands	Fe…Fe (Å)	δ(Fe$_A$, Fe$_B$) (mm/s)[a]	ΔE_Q(Fe$_A$, Fe$_B$) (mm/s)[a,b]
Ox1	OH^-	3.50	0.50, 0.50	0.43, 1.12
Ox2	O^{2-}	3.35	0.51, 0.50	1.77, 1.43
Ox3	$2OH^-$	3.07	0.56, 0.51	0.49, 1.25
Ox4	O^{2-}, OH^-	2.88	0.55, 0.47	1.33, 0.94
Exp1		3.1 ± 0.1	0.48[c]	1.95[c]
Exp2			0.55[c]	1.63[c]
Exp3			0.48[c]	1.17[c]
Exp4			0.52[c]	0.63[c]

[a] Calculated with B3LYP, Wachter's basis set for Fe, cc-pVDZ for other atoms according to Bochevarov et. al. *JCTC* 2010, 6, 3735. [b] ONIOM-EE values. [c] Parameters for four quadrupole doublets.

doublets may represent four sites rather than four dimers. Replacing one of the μOH$^-$ bridges with μO^{2-} results in the shortest distance of all, 2.88 Å, which is not within the reported crystallographic error bar; however, it is only 0.11 Å shorter than the EXAFS distance. The Fe$_A$ and Fe$_B$ isomer shifts (0.55 and 0.47 mm/s) agree well with Exp2 (0.55 mm/s) and both Exp1 (0.48 mm/s) and Exp3 (0.48 mm/s), respectively. The corresponding quadrupole splitting for FeA is 0.30 mm/s lower than that of Exp2, and similarly, FeB has a quadrupole splitting 0.23 mm/s lower than that of Exp3. Overall, doubly bridged structures are strongly favored over the singly bridged structures, and it is likely that both Ox3 and Ox4 are produced in the ferroxidase reaction.

This work has identified the most probably structures of the Fe(II)- and Fe(III)-bound states of the ferroxidase site, while eliminating many possible candidates. Ongoing TD-DFT calculations and an evaluation of the peroxo-intermediate will ensure that this is the most comprehensive theoretical study of the ferroxidase reaction to date.

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土方　優

FIFC フェロー

1．今年度の研究の要約

配位不飽和金属部位へのガス分子吸着に関する理論研究を行った．

【始めに】

金属と有機配位子の多彩な組み合わせによって生み出される多孔性配位高分子と呼ばれる新規物質群が近年注目を集め，ガス吸着材，ガス分離材，触媒，センシング材等への応用が期待され，近年盛んに研究が展開されている．多孔性配位高分子は規則的に配列したナノメートルオーダーの細孔を有し，その細孔内にはオープンメタルサイトと呼ばれる配位不飽和な金属部位を有する構造が報告されている．ガス分子の吸着においてはそのオープンメタルサイトが相互作用部位として有効に働いている事が示唆されており，そのような部位における相互作用を明らかにすることは，選択的吸着や触媒反応などに有用であると考えられる．実際，赤外分光や核磁気共鳴分光法など様々な実験的手法でその相互作用の存在を示す報告がなされている．その一方で，その相互作用に対する理論的研究の展開は発展途上であり，主に静電相互作用である事が示唆されつつあるが定量的な評価は行われていない．

そこで多孔性配位高分子の構成単位の一つである paddle-wheel 構造に注目した．Paddle-wheel 構造は４つのカルボキシレート誘導体配位子と二個の金属イオンから構成され，多くの多孔性配位高分子骨格中に見られる基本構造である．金属イオンとして Cu を対象とした．Cu は Zn と並んで多孔性配位高分子骨格の合成において最もよく用いられ

ている金属の一つであり，本研究で多様な骨格に対する知見を与える事ができると考えられる．

【研究目的と計算】

下の Figure 1 に，対象としたモデル構造を示した．二核の Cu と四つのカルボキシレート誘導体からなる配位子によって構築された paddle-wheel 構造において，軸位（z 軸方向）のガス分子（L）に対してオープンメタルサイトが相互作用部位として働く．

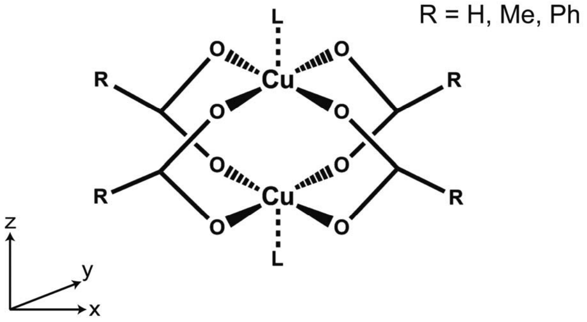

Figure 1

ガス分子が存在しない構造およびガス分子が捕捉された構造を DFT 法で構造最適化を行い，その相互作用エネルギーを下式で評価した．相互作用エネルギーの評価の際には BSSE 補正を行った．

$$E_{b,\,L} = \left\{E_{Cu-L} - \left(E_{Cu} + 2E_{L}\right)\right\}/2$$

本研究目的は，この相互作用の性質を明らかにすることで細孔中におけるオープンメタルサイトが果たす役割を明らかにすることである．

【研究結果】

Cu paddle-wheel 構造は，基底状態が open shell singlet であり，triplet 状態へ容易に励起し，その励起エネルギーは小さいことが知られている．そこで各々のスピン状態にお

ける相互作用エネルギーの違いについて検討を行ったが，その差はほとんどなかった．これはスピンが分布するのは Figure 1 において $d_{x2\text{-}y2}$ 軌道（x 軸と y 軸方向）であり，ガス分子が相互作用するのは z 軸方向（主に $4p_z$ 軌道）であるため，スピン状態の違いが直接，ガス分子との相互作用エネルギーに影響を与えないためと考えられる．

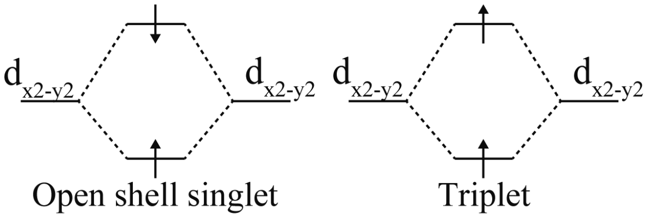

Figure 2

以下は全て triplet 状態における計算結果を示す．ガス分子として L = MeNC, MeCN, H_2O, C_2H_4, C_2H_2, CO, CO_2, N_2, CH_4, H_2 に対してその相互作用のエネルギーを Table 1 にまとめた．

（Table 1）各 L における相互作用エネルギー（$E_{b,\mathrm{L}}$）と構造

L	$E_{b,L}$ / kcal·mol^{-1}		Structure / Å	
	SCS-MP2	Exptl.	*r*(Cu-Cu)	*r*(Cu-L)
MeNC	17.2		2.650	2.174
MeCN	11.7		2.590	2.193
H_2O	12.2		2.562	2.241
C_2H_4	7.8		2.568	2.574
C_2H_2	6.9	7. 3	2.559	2.572
CO	5.8		2.573	2.267
CO_2	4.3		2.507	2.429
N_2	3.5		2.525	2.394
CH_4	1.8	4. 3	2.500	2.737
H_2	1.2	1. 6	2.508	2.221

相互作用のエネルギー評価は SCS-MP2 法によって行った．実験値が報告されている C_2H_2, H_2 については良い一致を示す一方で，CH_4 については実験値と合っていない．これは参考としている実験値が，CH_4 の吸着部位の周りには骨格の構成要素である芳香環が複数存在し，それら芳香環からなる細孔壁が構成するポテンシャル場によって捕捉された値となっているためである．つまり，今後はオープンメタルサイトとガス分子の相互作用だけでなく，細孔壁の効果を取り込んだ検討が必要である事が示唆される結果と言える．実際 Figure 1 のモデル構造においてカルボキシレート部分の置換基を R = H, Me, Ph で検討した場合も若干の相互作用エネルギーの違いが見られた．これは置換基による Cu の電荷の変化が影響しているためと考えられるが，今後は細孔中の環境を再現したモデル計算による検討も重要であることが示唆された．また，L = CO について，その電荷移動の評価を行った．その結果，CO 分子の σ 軌道からの供与については 0.322 e と大きな供与が見られる一方で，CO 分子の π*軌道への逆供与については 0.048 e とほとんど寄与が無いことが明らかとなった．実際，実験によっても赤外分光の CO 分子の伸縮振動の高波数シフトが見られており，その結果とも一致しており，その相互作用の性質としてこの電荷移動の寄与があることが明らかとなった．

Cu-Cu 金属間距離が，L との相互作用前（r(Cu-Cu) = 2.487 Å）に比べ長くなっている．これは上で述べたようにガス分子が z 軸方向で相互作用するため，d_{z2} 軌道との反発が大きくなり Cu-Cu 間の反発も大きくなるためである．相互作用エネルギーが大きくなるにつれその距離の変化も大きくなっている．しかし，相互作用エネルギーが小さいガス分子については，その電荷移動はほとんど見られず，CO の場合とは異なる相互作用によって捕捉されるものと考えられる．そこで静電相互作用に注目した．静電相互作用による安定化エネルギーを定量的に明らかにするためにエネルギー分割法による相互作用の解析を行った．

その結果，ガス分子とCu-paddle-wheelオープンメタルサイトにおける相互作用エネルギーと静電相互作用による安定化エネルギーに比例関係の相関があることを見出した．つまり，オープンメタルサイトはこれまで示唆されてきたように静電相互作用によるガス分子捕捉を可能にする部位であるということを定量的に評価することに成功した．

これは多孔性配位高分子において選択的ガス分子の捕捉・放出のための設計する上で重要な知見をあたえるものである．

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青野 信治

特推研究フェロー

1. 今年度の研究の要約

本年度は遷移金属錯体に対する溶媒和効果を中心に研究を行った。

【始めに】

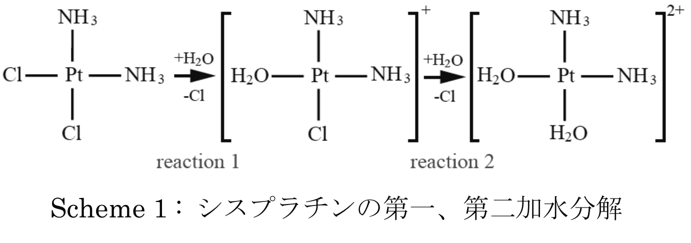
遷移金属錯体の特徴として電子状態が複雑で大きな分極性を持つ点などが挙げられるが、溶媒中での反応性や分子的性質を調べる上で、d 軌道の方向性に基づき遷移金属錯体の周囲の溶媒配置を空間的に考慮する事は重要である。無数の溶媒分子から成る分子集団性を扱う必要性からも現状このような計算を行う為に有用な方法としては、周囲の溶媒分子を古典的な MM モデルで陽に表す QM/MM 法、あるいは積分方程式により統計分布関数で表す 3D-RISM-SCF 法が主に挙げられる。近年の計算機の向上から CP-MD などの計算の適用範囲も広がりつつあるものの、これらは QM/MM 法と同様に溶媒群の箱サイズの点から解離反応などについては制限があり、3D-RISM-SCF 法による研究対象分野というものは、いまだ多く残されていると考える。

特に 1D-RISM-SCF 法では溶質の作る空孔領域を過大評価する点、また溶質周囲の静電ポテンシャルを点電荷近似により評価する点で、かさ高く分極性が大きな系への適用の際に問題が起こる事がしばしばあった。後者の点については近年考案された 1D-RISM-SCF-SEDD 法でも解消されているが、3D-RISM-SCF 法はこの２点について解消する可能性も持ち、溶液内の遷移金属錯体の反応や分子的性質を調べる上で有用であると期待される。本研究では 3D-RISM-SCF 法における静電ポテンシャルの計算を行う上で、波動関数から直接計算を行う近接領域、溶質点電荷から近似計算を行う遠方領域、またスイッチング関数を用いて近接領域と遠方領域の静電ポテンシャルを滑らかに繋ぐ為のスイッチング領域の３つの領域に溶媒空間を分ける事で記述精度を保ちつつコスト削減を行った。この 3D-RISM-SCF 法を白金錯体へと適応した研究について、以下報告する。

【プラチン錯体の加水分解反応に関する研究】

シスプラチン、cis-$PtCl_2(NH3)_2$ は抗癌活性を持つ事が知られ、古くから多くの実験的、理論的研究が広く行われて来た。その抗癌活性は、癌細胞の DNA 塩基に付加し DNA 合成を阻害する事に由来し、加水分解反応はその前段階の重要な反応と目されている（Scheme 1）。

第一、第二加水分解においてプラチン錯体はその電荷変化に示される通り、電子状態および溶媒和構造の大きな変化を伴う。特にこのようなイオン性解離は溶媒和エネルギーの定量的議論が難しい。本研究では 3D-RISM-SCF 法を適用して､溶媒効果の解析を試みた。



Scheme 1： シスプラチンの第一、第二加水分解

3D-RISM 法は平衡溶媒分布を解く際に必要な溶質まわりの静電ポテンシャルを波動関数から直接計算できる長所があり、Pt の孤立電子対が占める d 軌道の形等も反映できると期待した。また抗癌活性を持たない事が知られる trans-$PtCl_2(NH3)_2$ についても、同様に理論的検討を行った。

構造最適化計算は DFT 法により行い M06-2X を採用した。Pt の内殻電子は HW ECP で置き換えた LANL2TZ(f)基底を、残る原子については 6-31++G**を用いた。更に精度の向上のため 6-31++G**を cc-pVTZ に置き換え、Cl と O 原子に aug-cc-pVTZ を用いて MP2 計算を行った。特に高精度な電子状態計算として CCSD(T)と MP2 による電子相関エネルギーを cc-pVDZ 基底レベルにて評価を行い、MP2 自由エネルギーを補正する事で CCSD(T)自由エネルギーを計算した。また溶質運動に対する熱力学補正（零点、熱、エントロピー補正）について以下のように行った。振動運動項は計算コストの都合から PCM 法における調和振動数を用いて計算した。溶質分子の並進運動項については Whitesides らによる溶媒体積補正を利用して求めた。

例としてシスプラチンの加水分解反応の構造変化を図１に、またシス、トランスプラチンの自由エネルギー変化を図２に示した。

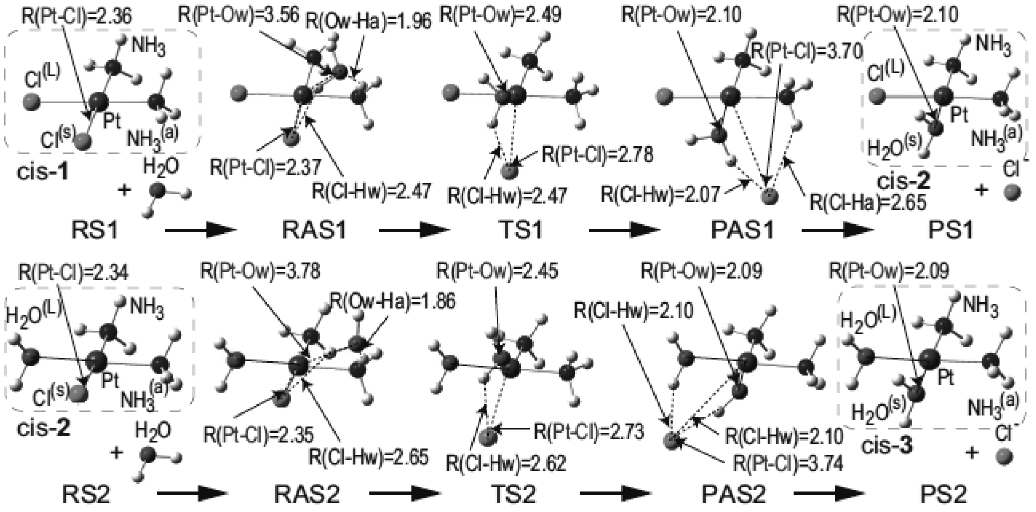


図１：シスプラチンの第一、第二加水分解反応における構造変化

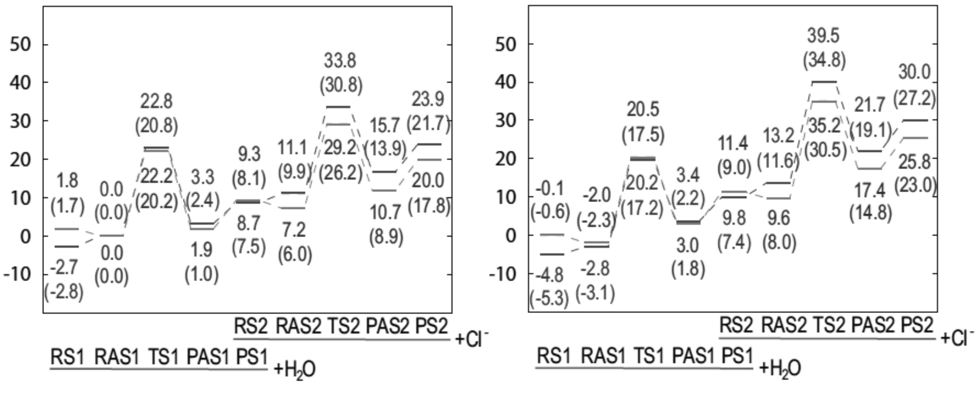


図２：シス、トランスプラチンの加水分解反応における MP2 自由エネルギー変化

左：シスプラチン 右：トランスプラチン　赤：熱力学補正後　緑：熱力学補正前 括弧内：CCSD(T)

これらの結果、第一加水分解における活性化自由エネルギーは、シス体で 20.8 kcal/mol、トランス体で 20.3 kcal/mol と見積もられ、第二加水分解においてシス体では障壁は変わらず 20.9 kcal/mol で

あるのに対し、トランス体では若干増加して23.2 kcal/molと見積もられた。この結果は実験値に適ったものであり、また得られた平衡定数pK1はシス体で3.74、トランス体で5.94、pK2はシス体で6.90、トランス体で9.69であり、この値は実験値に比べて大きいものの、その大きさの順序は上手く実験結果の傾向を再現したものである。特に気相中での反応と比較してPAS1からPS1への解離反応では100 kcal/mol、またPAS2からPS2への解離反応では200 kcal/molもの大きな反応障壁の低下があり、加水分解反応が進むためには溶媒効果が必要不可欠である事が確かめられた。また第一加水分解において置換されたClアニオンはその強い静電相互作用によってPt錯体の第一溶媒和圏に留まり易い傾向がある事を図２は示唆しており、Clアニオンが解離せずに進んだ場合の第二加水分解反応についても調べた結果、活性化自由エネルギー自体は変化しない事が分かった。従って、系の自由エネルギーの観点から、Clアニオンは第二加水分解が進んだ後で第一溶媒和圏から離れる方が反応経路として有利である点なども明らかにした。

【d^8平面４配位型金属錯体と水の相互作用に関する研究】

d^8平面４配位型金属錯体が正電荷を持つ場合、z軸上の水分子はO原子を中心金属へ向けた構造（O配向）をとる事が実験、理論研究から示唆されている。$[Pt(pyridine)_4]Cl_2$・３H_2O結晶などが例に挙げられるが、これは水素結合が電子的に富んだ領域と正に誘起された部位の静電相互作用に由来するという一般的理解に反しない。一方、全体で中性電荷となる金属錯体の場合、過去のMP2計算によれば、水分子のH原子が電子不足のd^8中心金属へ向いた構造（H配向）がエネルギー的に優位であると予測されており、一般的理解とは逆方向の水素結合を意味する。この存在は近年、実際にtrans-$PtCl_2(NH_3)$(N-glycine)・H_2O結晶における中性子散乱実験で立証された。

これらの実験、理論研究を踏まえて、本研究では正および中性電荷を示すd^8平面４配位型金属錯体のモデル系として、Pt^{2+}を中心金属とした$[Pt(NH_3)_4]^{2+}$と trans-$PtCl_2(NH_3)$(N-glycine)の錯体に対し、その z 軸上の水分子との相互作用について気相中での２つの配向の違いを明らかにした。更にdz^2軌道の影響を調べるため、電子分布の広がりの小さいPd^{2+}を中心金属とした系に対しても同様に、水分子の２つの配向における相互作用の違いを比較、検討した。

金属錯体とz軸上の水１分子をQM領域として扱い、水の２つの配向に関して次のように参照構造を決めた。O配向では水のO原子がz軸上に存在するように、またH配向ではH原子とO原子がz軸上に位置するように束縛条件を加えた上で、M06-2X汎関数によるDFT計算を行い、構造を最適化した。Ptは６０個の内殻電子を、Pdは２８個の内殻電子をHay-Wadt ECPに置き換えたLANL2TZ(f)を基底関数に選び、残る原子は6-31++G**基底を用いた。これにより得た金属錯体と水分子の内部座標は固定し、中心金属と水のO間の距離を変化させる事で気相中のエネルギーおよび水溶媒中の自由エネルギーの振る舞いを調べた。基底関数は水の O と配位子の Cl にaug-cc-pTVZを、残る配位子にcc-pTVZを用いてMP2計算を行い、BSSEを補正した。

結果、Pt錯体と水分子の相互作用系に対するH配向とO配向の参照構造を図３に示す。この参照構造に対して、H配向における解離状態を基準０にとった気相中のエネルギー変化は図４の通り、水の２つの配向構造で大きく異なる結果を得た。まず正に帯電したtetra-ammine錯体ではO配向の結合エネルギーがPtで-12.2、Pdで-13.7 kcal/molとH配向に比べて非常に大きな安定化を持つ。一方、中性のglycine錯体ではH配向の結合エネルギーがPtで-4.2、Pdで -2.7 kcal/molとO配向より優位な構造となる事が示され、先の結晶構造で見られる水の配向性に一致する。また

Pt、Pd錯体での結合エネルギーを比較するため、H配向とO配向に対して中心金属と水のO間距離が3.1、3.4Åの構造を参照にし、エネルギー分割法を用いて表１の結果を得た。

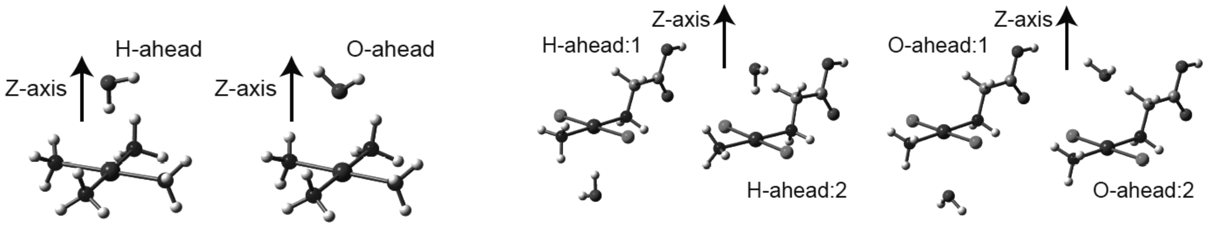


図３：$[Pt(NH_3)_4]^{2+}$ 及び trans-$PtCl_2(NH_3)$(N-glycine)錯体に対する水の配向性

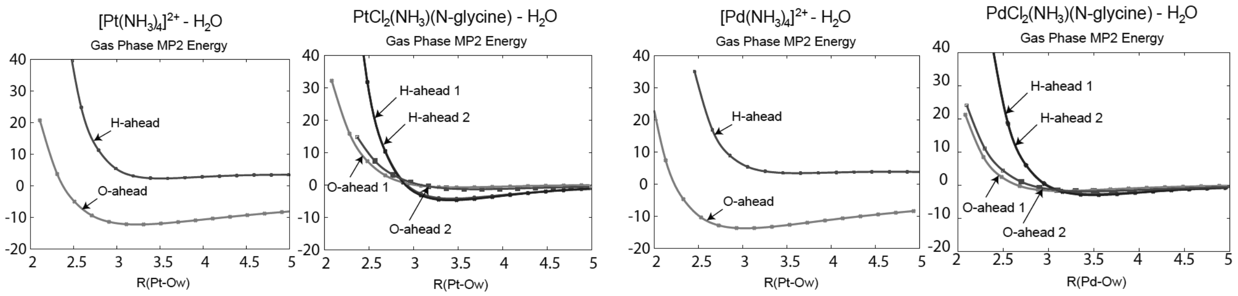


図４：気相中におけるPt及びPd錯体と水のエネルギー変化

赤：H配向１、緑：O配向１、青：H配向２、紫：O配向２。 エネルギー基準0はH配向の解離状態。単位：kcal/mol

中心金属、電荷に依らず、総じてMP2分散項(DISP)はH配向の方がO配向よりも約4 kcal/molの安定化を引き起こしており、またtetra-ammine錯体におけるO配向の大きな結合エネルギーは静電項(ES)に起因する事が分かった。Glycine錯体のH配向では分極項(POL)および電荷移動項(CT)の安定化も起こっているが、分散項による寄与が大半を占める。またPdのdz^2軌道がPt錯体よりも広がりが小さい事により、交換反発項(EX+REP)の不安定化は小さいが、分数値は予想に反し同程度であった。水溶媒中での自由エネルギー変化の比較を図５に示すが、気相中tetra-ammine錯体においてエネルギー的に不利であったH配向は、大きな溶媒和自由エネルギーの相対的安定化によって、Pt錯体の第一溶媒和圏のz軸方向において同程度に起こり得るという結果が得られた。更にtetra-ammine錯体でのH配向の大きな溶媒和安定化の原因として、O原子を向けた水溶媒分子が増加する領域を特定した結果、z軸上の水分子の近傍における溶媒和構造の違いのみならず、NH_3配位子→金属への電荷移動により間接的に引き起こされるNH_3配位子の周囲での溶媒和構造の違いというものも一因である事を明らかにした。

表１：相互作用エネルギー成分

	Pt-ammine 錯体		Pd-ammine 錯体	
	H配向	O配向	H配向	O配向
ES	+3.7	-13.3	+6.4	-14.0
EX+REP	+5.9	+5.2	+3.6	+3.2
POL+CT	-3.1	-2.8	-2.7	-2.7
DISP	-4.2	-0.8	-3.7	+0.0
	Pt-glycine 錯体		Pd-glycine 錯体	
	H配向１	O配向１	H配向１	O配向１
ES	-3.9	-3.8	-1.1	-4.3
EX+REP	+6.8	+6.0	+4.3	+3.8
POL+CT	-2.4	-1.3	-1.5	-1.0
DISP	-4.9	-1.3	-4.4	-0.6

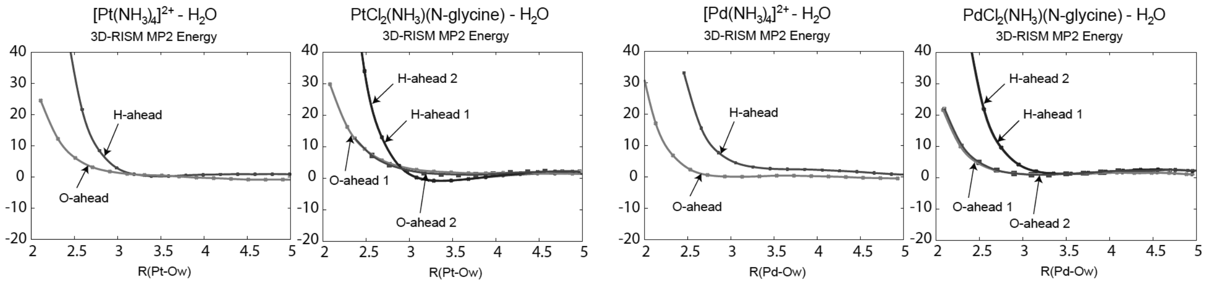


図５：水溶媒中での Pt 及び Pd 錯体と水の自由エネルギー変化

赤：H 配向１、緑：O 配向１、青：H 配向2、紫：O 配向２。　エネルギー基準 0 は H 配向の解離状態。単位：kcal/mol

2. 論文

3. 学会発表

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(3) 青野 信治・榊 茂好
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4. その他

(1) 青野 信治
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塚本　晋也

特推研究フェロー

1. 今年度の研究の要約

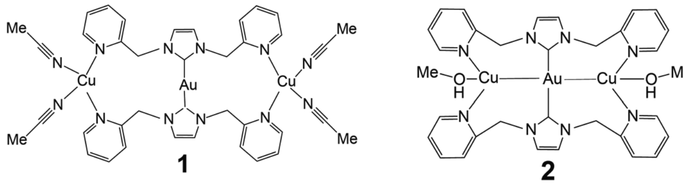
今年度は二つのテーマ 1. Au(I)-Cu(I)対を含む vapochromic 錯体の燐光の帰属と発光メカニズムについて理論研究 2. 五配位 Ni(II)錯体の結晶中でのスピンクロスオーバー現象の理論的考察　を行った。

Au(I)-Cu(I)相互作用を含む多核金属錯体の発光メカニズムと金属間相互作用

【背景及び目的】ガスの吸着によって発光する vapochromic 錯体は、有害ガスの検知に用いることが出来る。ガスの種類によって発光ピークが異なる場合、有害ガスの特定にも応用可能である。d^{10}-d^{10} 対を持つ金属錯体はその弱い相互作用のため、ガス吸着による構造変化が大きく、発光ピークの領域が大きいケースが多い。

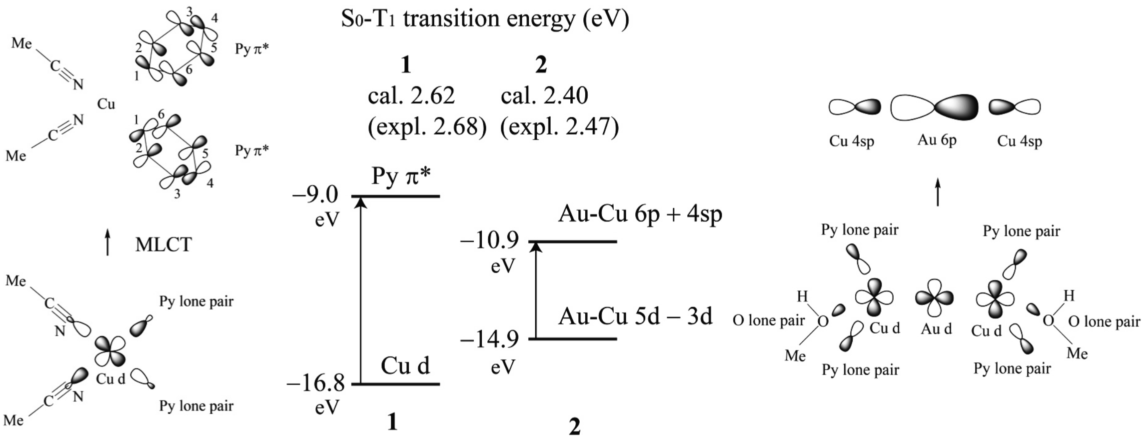
最近、Au(I)-Cu(I)対を含む三核錯体$[Au(im(CH_2Py)_2)_2(CuL_2)_2]^{3+}$ (**Scheme 1. 1**; L=MeCN, **2** ; L=MeOH)が合成され、MeOH、MeCN ガス雰囲気化で発光スペクトルのピークがそれぞれ 462nm(青), 520nm(緑)と異なることが報告された[1]。Au(I)-Cu(I)対を持つ vaporchromic 錯体は、この錯体が初めての合成例である。本研究では発光メカニズムと Au(I)-Cu(I)相互作用を調べることを目的に、DFT 法と SCS-MP2 法を用いて基底状態、励起状態の分子構造と燐光の帰属、Au-Cu 相互作用の評価を行い、MeOH、MeCN 雰囲気で燐光が異なる理由を解明した。

【計算方法】S_0 と T_1 状態について Au-Cu 距離を SCS-MP2 法で評価し、それ以外は B3PW91 汎関数を用いた DFT 計算で構造最適化した。基底関数は、Au と Cu 原子の内殻電子を Stuttgart ECP で置き換え 2*f* 分極関数を加えたものを用い、その他の原子には 6-31G(d), O 原子には 6-31+G(d)を用いた(BSI)。S_0-T_1 励起エネルギーは、配位子に cc-pVDZ, O 原子に aug-cc-pVDZ を用いて(BS II)、B3PW91 汎関数で評価した。



Scheme 1

[結果と考察] SCS-MP2 で最適化した **1**, **2** の Au-Cu 距離は実験値を良く再現した (**1**; cal. 4.631 Å, expl. 4.591 Å, **2**; cal. 2.767 Å, expl. 2.792 Å)。錯体 **1** の発光は Cu d → Py π*遷移(MLCT)と帰属され、錯体 **2** の発光は Au-Cu 5d-3d antibonding MO から Au-Cu 6p-4sp bonding MO への遷移と帰属された (Scheme 2)。**1**, **2** の S_0-T_1 遷移エネルギーは実験値と良く一致した (**1**: cal. 2.62 eV, expl. 2.68 eV, **2**: cal. 2.40 eV, expl. 2.47 eV)。Scheme 2 に示すように、**2** では S_0-T_1 遷移が anti-bonding MO → bonding MO 遷移であるため、**1** に比べて emission peak が red shift する。Au-Cu 相互作用は SCS-MP2 法で 0.89 kcal/mol と評価されたが (BSSE 補正後)、 Au-Au 相互作用(6-12 kcal/mol) と比較すると著しく小さい。Au-Cu 相互作用が弱く、NHC 分子が柔軟であるため、ガス分子の吸着により **1** と **2** の構造が容易に相互変換することが分かった。



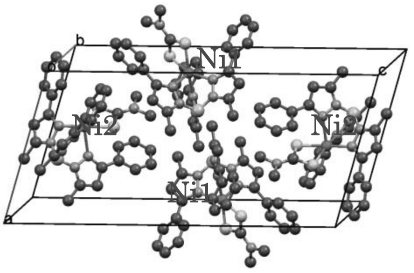
Scheme 2

[参考文献] [1] Strasser, C. E. *et al. J. Am. Chem. Soc.* 2010,*132*, 10009.

五配位 Ni(II)錯体の結晶中でのスピンクロスオーバー現象の理論的考察

【背景及び目的】遷移金属錯体の結晶中でのスピンクロスオーバー現象は、工業的な応用が期待される。近年、五配位 Ni(II)スピンクロスオーバー(SCO)錯体 $Tp^{Ph,Me}Ni(S_2CNMe_2)$[$Tp^{Ph,Me}$=hydrotris(3-phenyl-5methyl-1-pyrazolyl)borate]が、結晶中で二つの独立な構造 Ni1, Ni2 を持ち (Scheme1, Fig1)、磁気的性質が異なることが、X 線構造と磁化率の測定によって明らかにされた。Ni1 の構造は 123K と 293K で大きな違いがないが、Ni2 では 123K と 293K で構造が大きく異なる。このことは SCO が Ni1 で起こらず、Ni2 で起きていることを示している。

本研究では、単量体の構造と電子状態、及び結晶化の影響を考慮した場合の違いを電子状態計算から議論し、分子性結晶中のスピンクロスオーバー現象の理由を説明する。



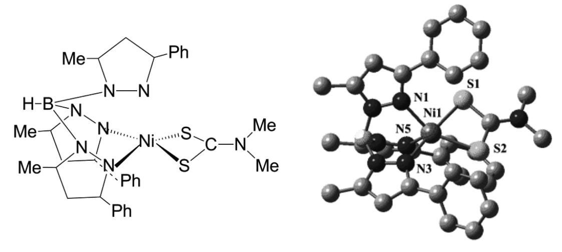


Fig.1 X-ray structure of $Tp^{Ph,Me}Ni(S_2CNMe_2)$ in 123K **Scheme 1** $Tp^{Ph,Me}Ni(S_2CNMe_2)$

【計算方法】単量体の構造最適化を行い X 線構造と比較した。Ph, Me を H 原子に置換したモデル錯体で電子状態と一重項、三重項の相対安定性を議論した。結晶の効果を取り入れるため、周囲の置換基の位置を X 線構造で固定した構造最適化を行った。基底関数は BSI (Ni: SDD ECP plus 2*f* polarization functions, C, H, N, B, S: 6-31G(d)), BSII (Ni: C, H, N, B, S: cc-pVDZ) を用い、構造最適化は B3PW91/BSI, 相対エネルギーは B3LYP*/BSII で計算した。

[結果と考察]単量体の構造と X 線構造を比較すると、Ni1 の 123K, 293K の構造は triplet の構造と良く一致した(Table 1)。Ni1 は低温から高温まで HS(high spin)を維持している。

Ni2 は 123K, 293K で構造が異なり SCO が起きていることが分かるが、計算結果との一致が悪く、結晶の効果が大きい。結晶化による影響で Ni2 の SCO が誘発されていることが示唆された。

Table 1. 単量体の最安定化構造と X 線構造との比較

	expl.				calcd.	
	Ni1		Ni2			
T (K)	123K	293K	123K	293K	singlet	triplet
Ni-N1 (Å)	2.038	2.048	2.401	2.149	2.927	2.069
Ni-N3 (Å)	2.111	2.111	2.003	2.083	1.929	2.128
Ni-N5 (Å)	2.048	2.058	1.972	2.046	1.913	2.063
Ni-S2 (Å)	2.3420	2.3435	2.2567	2.323	2.2191	2.3789
Ni-S1 (Å)	2.4006	2.3929	2.2721	2.3614	2.2273	2.4357

モデル錯体で singlet と triplet の構造を比較すると、triplet では Ni-N_{ax} が singlet より短く、Ni-N_{eq} と Ni-S が長い(Fig.2)。これは d_{z2}(HOMO)から d_{xy}(LUMO)への一電子励起により singlet と triplet の構造が変化するためである (Fig3)。

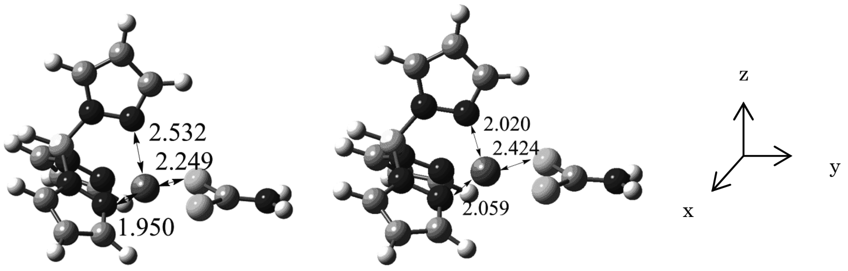
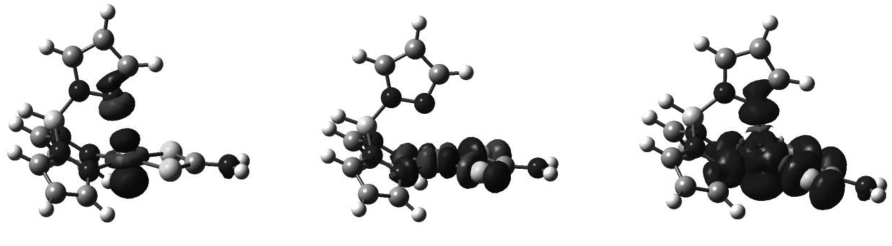


Fig.2 singlet and triplet structure of model complex



d_{z2}(HOMO) d_{xy}(LUMO) spin density of triplet

Fig.3 HOMO and LUMO and spin density of triplet

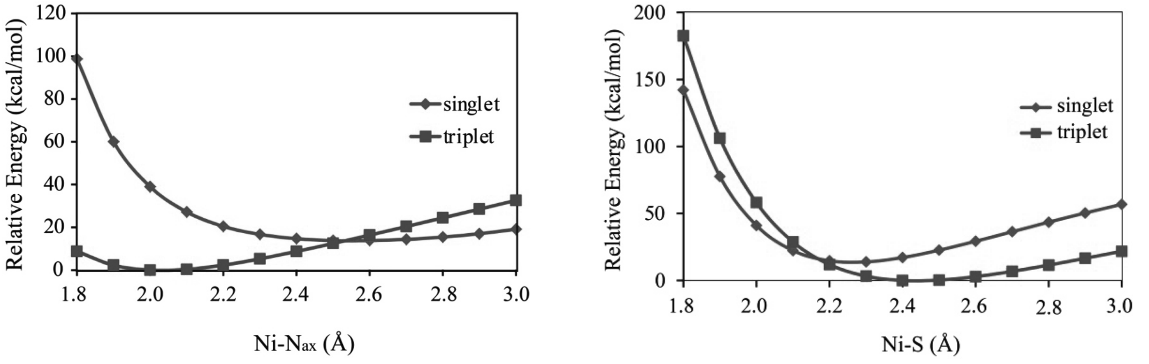


Fig.4 PES along Ni-N_{ax} and Ni-S distance

モデル錯体で Ni-N_{ax}, Ni-S 距離の変化に対する singlet と triplet の potential energy surface (PES) から、Ni-N_{ax}が長く Ni-S 距離が短い構造では、singlet が triplet より安定であることが分かった(Fig4)。Ni2 の Ni-S の分子面は *c* 軸に対して平行、Ni1 の Ni-S は *c* 軸に対して垂直であるため、結晶の *c* 軸方向の長さが短い場合(123K)、Ni2 の Ni-S が小さくなり triplet が不安定化することにより SCO が起きる。*c* 軸方向の短縮により、Ni2 の Ph と Ni1 の五員環との距離が短くなるため、Ni-N_{ax}の距離が大きくなり singlet が安定化する。モデル錯体の PES と低温高温の X 線構造の比較から Ni2 の SCO の原因を理解することが出来た。

論文

(1) Yumiko KATAOKA, Dharam PAUL, Hiroyuki MIYAKE, Tsuyoshi YAITA, Eisaku MIYOSHI, Hirotoshi MORI, Shinya TSUKAMOTO, Hiroshi TATEWAKI, Satoshi SHINODA, and Horoshi TSUKUBE
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Chem. A. Eur. J., 14, 5258-5266 (2008).

(2) Shinya TSUKAMOTO, Hirotoshi MORI, Hiroshi TATEWAKI, and Eisaku MIYOSHI
"CASSCF and CASPT2 calculations for lanthanide trihalides LnX3 using model core potentials"
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(3) Shigeyoshi SAKAKI, Daisuke KAWAI, and Shinya TSUKAMOTO
"Theoretical Study of Metallasilatranes; Bonding Nature and Prediction of New Metallasilatrane"
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(4) Shinya TSUKAMOTO and Shigeyoshi SAKAKI
"Theoretical Study of Pt(PR3)2(AlCl3) (R=H, Me, Ph, or Cy) Including an Unsupported Bond between Transition Metal and Non-Transition Metal Elements; Geometry, Bond Strength, and Prediction"
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2. 学会発表

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"Ab initio study for lanthanide trihalide by means of relativistic model core potentials"
WATOC 2008, Sydney, Australia (2008).

(2) Shinya Tsukamoto, Hirotoshi Mori, Hiroshi Tatewaki, and Eisaku Miyoshi
"Ab initio study for lanthanide fluorides by means of relativistic model core

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(3) Shinya Tsukamoto, Hirotoshi Mori, Hiroshi Tatewaki, and Eisaku Miyoshi
“CASSCF and CASPT2 calculations for lanthanide trihalides LnX3 using model core potentials” XIII-th ICQC, Helsinki, Finland (2009).

国内

2011年

(1) 塚本 晋也, 榊 茂好
“Pt(PR3)2(AlCl3) (R=H, Me, Ph, Cy) の理論研究：構造、結合、及びM-Alを持つ錯体の理論予測” 第14回理論化学討論会 5月12-14日、岡山大学、岡山市 1P19

(2) Shinya Tsukamoto, Shigeyoshi Sakaki
“Theoretical study of luminescent vapochromic complexes including AuCu2(NHC)2 core” International Society for Theoretical Chemical Physics (ISTCP-VII) September 2-8, Waseda University, Tokyo (Japan) 3PP-48

(3) 塚本 晋也, 榊 茂好
“Cu2Au骨格を持つ3核錯体の理論的研究:分子依存性とAu-Cu結合” 第61回 錯体化学討論会 9月17-19日、岡山理科大学、岡山市 2Bb-16

Milind Madhusudan DESHMUKH
SPR Fellow, Fukui kenichi Memorial Research Group 2

1. Summary of the research carried out during April 2011 to April 2012.

Theoretical Study of Complex Systems involving Non-covalent Interactions: Development of Computational Strategies and Application.

Non-covalent interactions plays dominant role in the structure and function of not only the biomolecular systems but are also important in supramolecular assemblies and material sciences. Accurate estimation of non-covalent interaction is extremely important to get insights into structure and stability of these systems. However, evaluation of intermolecular distance and binding energy (BE) of van der Waals complex/cluster at ab initio level of theory is computationally demanding when many monomers are involved.

Starting from MP2 energy, we reached a two step evaluation method of BE of van der Waals complex/cluster through reasonable approximations as given in equation 1;

$$\mathrm{BE} = \mathrm{BE(HF)} + \sum_{\mathrm{Mi>Mj}} \{\mathrm{BE}_{\mathrm{Mi\text{-}Mj}}(\mathrm{MP2\ or\ MP2.5}) - \mathrm{BE}_{\mathrm{Mi\text{-}Mj}}(\mathrm{HF})\} \qquad (1)$$

where HF represents the Hartree-Fock calculation, Mi, Mj etc. are interacting monomers, and MP2.5 represents the arithmetic mean of MP2 and MP3. The first term is the usual binding energy of the complex/cluster evaluated at the HF level. The second term is the sum of the difference in two-body binding energy between the correlated and HF levels of theory. This approximate evaluation methodology was applied to various van der Waals complexes from S22 data set consisting of up-to-four monomers at MP2 and MP2.5 levels of theory. We found that this method is capable of providing precise estimate of the binding energy. The nice correlation (Figure 1) between binding energy estimated with present approximate equation and standard approach ($\mathrm{BE}_{\mathrm{ref.}}$; see equation 2) was indeed encouraging.

$$\mathrm{BE}_{\mathrm{ref.}} = E^{\mathrm{MP2\ (or\ MP2.5)}}(\mathrm{M1, M2, M3, \ldots.}) - \sum_{\mathrm{Mi}} E^{\mathrm{MP2\ (or\ MP2.5)}}(\mathrm{Mi}) \qquad (2)$$

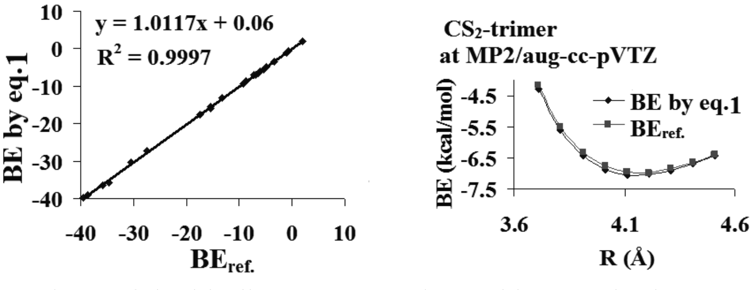
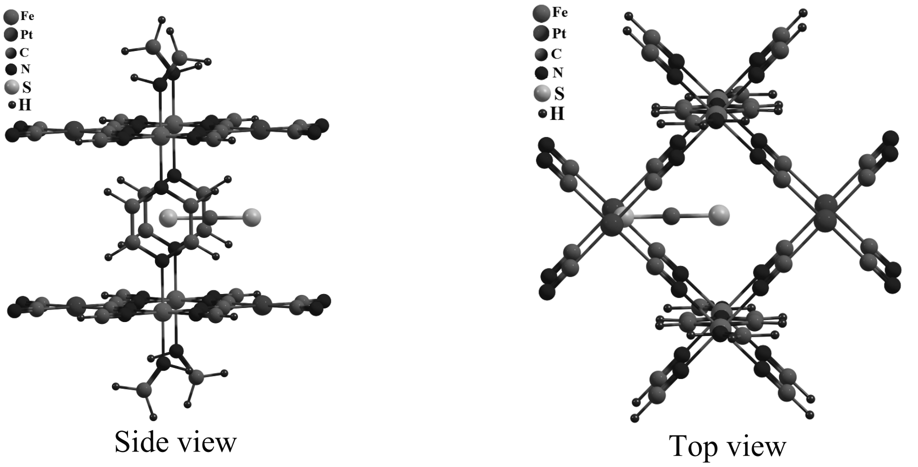


Figure 1: Comparison of the binding energy estimated by standard approach ($\mathrm{BE}_{\mathrm{ref.}}$) with that estimated by approximate eqs. 1

The maximum error of the BE is less than 1 kcal/mol and 1% in most cases except for several limited cases. The origins of error in these cases are discussed. Although moderately large error was found in some limited cases, it is noted that the equation 1 was able to reproduce precisely the potential energy surface in such case too (see Figure

1). The computation time with this approximate evaluation method decreases by about half than the conventional method. For details see reference 1 from publication list.

The above developed strategy was extremely useful in of our study of absorption/adsorption of CO_2 and CS_2 into porous coordination polymers (PCPs). PCPs recently attract much attention to the potential application to gas storage, gas separation, catalysis, and nanospace engineering. The flexibility in use of variety of organic linkers and/or metals leads to syntheses of many kinds of PCPs with required property. Among the desired properties of such compounds, selective uptake and storage of gas molecule have been investigated well. Recently, optical and magnetic properties and their responses to inclusion of a guest molecule have started to draw new attention in the chemistry of PCP. Recently the chemresponsive switching of spin-state was recently shown to occur by gas absorption in the Hofmann-type three-dimensional PCP $\{Fe^{II}(Pz)[Pt^{II}(CN)_4]\}_n$ (Pz=pyrazine). For instance, the absorption of such bulky molecules as benzene, pyrazine, water, methanol etc. stabilizes the high spin state; note that though water and methanol are not bulky, they forms bulky cluster in PCP. Of particular interest is the absorption of CS_2 molecule; despite of its small size, CS_2 absorption induces the spin transition from the high-spin to the low-spin state. This is the reverse to the spin transition by bulky molecules. On the other hand, the absorption of similar CO_2 does not induce any spin transition. In this work, we theoretically investigated the interactions of CS_2 and CO_2 molecules with a realistic model consisting of a unit cell of the Hofmann-type PCP $\{Fe(Pz)[Pt(CN)_4]\}_n$ as shown in Figure 2.



Side view Top view

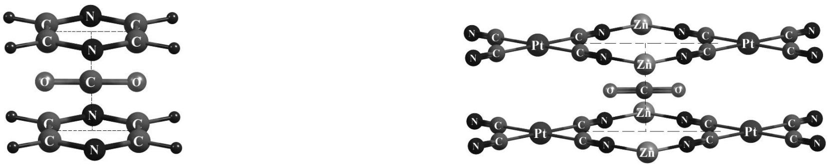
Figure 2: Realistic model (**RM**) of CS_2-absorbed PCP; Fe (green), Pt (pink), N (blue), C (gray), and S (yellow).

The purposes of the present work are to find the binding sites of these gases in the Hofmann-type PCP, to evaluate their binding energies, and to clarify the determining factors for absorption site and absorption energies of these gases with the PCP. We believe that the knowledge of such determining factors is indispensible to understanding the gas absorption with PCP and finding a gas molecule which induces the spin transition between high and low spin states.

The binding energy of gas molecule with framework was evaluated with ONIOM scheme, as shown in Eq. 3.

$$BE_{RM}^{ONIOM} = BE_{RM}^{Low} + \left\{ BE_{SM1}^{High} - BE_{SM1}^{Low} \right\} + \left\{ BE_{SM2}^{High} - BE_{SM2}^{Low} \right\} \qquad (3)$$

where superscripts "High" and "Low" represents the high quality calculation and low quality calculation, respectively and subscripts, "RM", "SM1", and "SM2" represents realistic model, small model 1 and small model 2; See Figure 3 for details of small model systems. The first term on the right hand side of Eq. 3 is the binding energy of gas molecule with realistic model, **RM**. This is a "real low" component of the ONIOM equation. The second term represents, binding energy of gas molecule with small model **SM1** and the third term represent binding energy of gas molecule with small model **SM2**. The M06-2X level of theory was employed with cc-pVTZ basis sets for low quality calculation and scaled MP2 methods[21] were used with aug-cc-pVTZ basis sets for high quality calculation.



(a) Small model 1 (SM1)

(b) Small model 2 (SM2)

Figure 3: Small models (a) SM1 and (b) SM2 representing the Pz and Pt interaction sites respectively. These models were used in ONIOM calculations.

The binding energies of CS_2 and CO_2 are evaluated to be -17.3 kcal mol^{-1} and -4.0 kcal mol^{-1}, respectively at the ONIOM(MP2.5:M06-2X) level and -25.0 kcal mol^{-1} and -6.0 kcal mol^{-1} at ONIOM(MP2:M06-2X) level, indicating that CS_2 strongly absorbs in PCP but CO_2 weakly. The absorption positions of these molecules are completely different between CO_2 and CS_2; CO_2 molecule exists between two Pt sites. To the contrary, one S atom of CS_2 exists between two Pz ligands and the other S atom is between two Pt sites. See Figure 4 and Figure 5 for the corresponding potential energy surface of CS_2 and CO_2 absorption in Hofmann-type PCP, respectively.

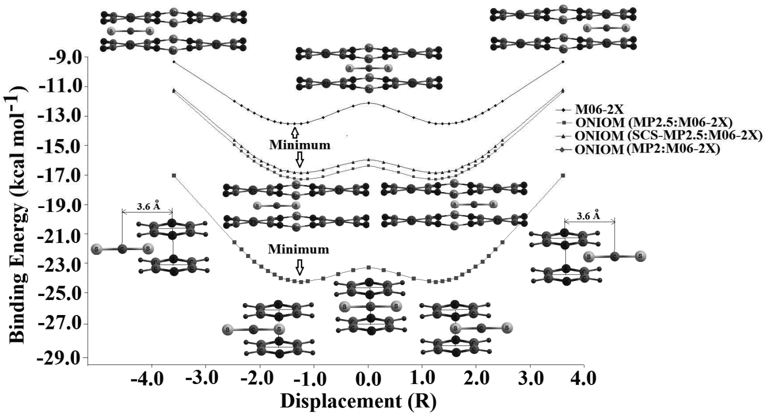


Figure 4: Comparison of potential energy surface between M062X and ONIOM for absorption of CS_2 in PCP.

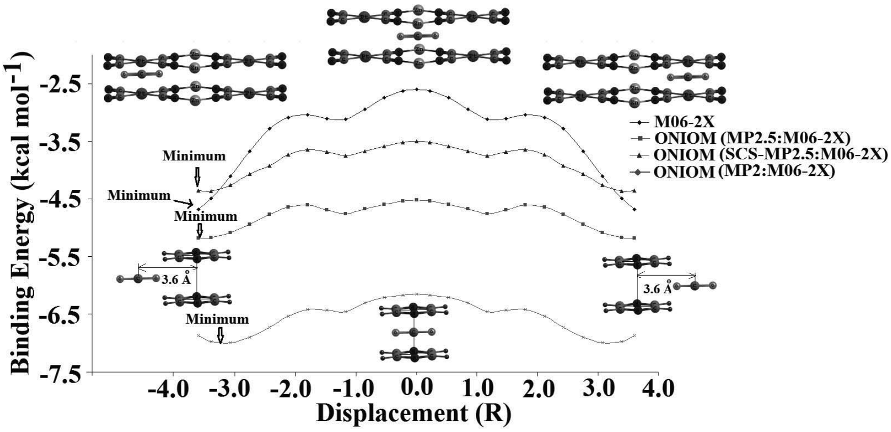


Figure 5: Comparison of potential energy surface between M062X and ONIOM for absorption of CO_2 in PCP.

Note that only model systems are shown in Figure 4 and 5 for brevity and the potential energy surfaces are scanned using ONIOM equation 3. The optimized position of CS_2 agrees with experimentally reported X-ray structure. Based on energy decomposition analysis and electrostatic potential of the PCP framework, it is concluded that both of the large binding energy and absorption position of CS_2 arise from large dispersion interaction between CS_2 and Pz. The different absorption position of CO_2 arises from large electrostatic interactions between CO_2 and Pt site, and small binding energy of CO_2 comes from weak dispersion interaction with both Pz and Pt site.

2. Original Papers

(1) Deshmukh Milind M. and Sakaki Shigeyoshi,
"Two-step Evaluation of Potential Energy Surface and Binding Energy of van der Waals Complexes"
J. Comput. Chem., 33, 617 (2012).

(2) Deshmukh Milind M. and Sakaki Shigeyoshi,
"Binding energy of gas molecule with two pyrazine molecules as organic linker in metal–organic framework: its theoretical evaluation and understanding of determining factors"
Theor. Chem. Acc., 130, 475 (2011).

(3) Deshmukh Milind M.; Ohba Masaaki, Kitagawa Susumu, and Sakaki Shigeyoshi,
"Absorption of CO_2 and CS_2 into Hofmann-type Porous Coordination Polymer: Theoretical Study of Binding Energy, Absorption Position, and Understanding of Determining Factors" (to be submitted). (2012).

3. Presentations at academic conferences

(1) Deshmukh Milind M. and Sakaki Shigeyoshi,
"Highly accurate approximate method for evaluation of binding energy of van der Waals complexes"
The 9th Triennial Congress of the World Association of Theoretical and Computational Chemist (WATOC), Santiago-de-compostela, Spain, July 17, 2011.

(2) Deshmukh Milind M. and Sakaki Shigeyoshi,
"Dispersion Energy of van der Waals Complex; Approximate Evaluation with Pair-wise Correlation Effect"
The 7th Congress of the International Society for Theoretical Chemical Physics (ISTCP-VII) at Waseda University, Tokyo, Japan on September 2-8, 2011.

(3) Deshmukh Milind M. and Sakaki Shigeyoshi,
"Highly accurate approximate method for evaluation of binding energy of van der Waals complexes"
The 14th Annual Meeting of Theoretical Chemistry Society, Okayama, Japan, May 2011.

4. Others

(1) Deshmukh Milind M. and Sakaki Shigeyoshi
"Absorption of Gases into Metal Organic Framework: A theoretical investigation"
The 8th symposium of Fukui Institute for Fundamental Chemistry, Kyoto, Dec.3, 2010.

(2) Deshmukh Milind M. and Sakaki Shigeyoshi
"Absorption of CO2, CS2 and OCS into Hofmann type Metal-organic Framework: Binding Energy, Absorption Position and Determining Factors"
The 9th symposium of Fukui Institute for Fundamental Chemistry, Kyoto, Jan. 6, 2012

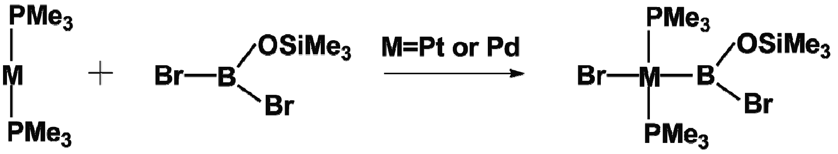
Guixiang ZENG

SPR Fellow, Fukui kenichi Memorial Research Group 2

1. Summary of the research of the year

Theoretical Study of Noble Features in Oxidative Addition of B−Br σ−Bond of Bromoborane to $M(PMe_3)_2$ (M= Pt or Pd)

Formation processes of cis−boryl complex via oxidative additions of B−H, B−B, and B−E (E═Si, Ge, or Sn) bonds to low−valent transition−metal complexes have been clarified theoretically. However, the mechanism for trans-boryl complex produced by the oxidative addition of B−X (X═Cl, Br, or I) bond to Pd(0) and Pt(0) complexes remains unclear yet, in which the cis−trans isomerization is proposed to be involved. In general, the cis-trans isomerization occurs via spin conversion process, but the cis-trans isomerization taking place on single potential surface has not been investigated well. Here, we theoretically investigated the oxidative addition of the B−Br bond of bromoborane Br2B(OSiMe3) to M(PMe3)2 (M ═ Pt or Pd) to explore possible reaction pathways and to clarify the process of the thermal cis−trans isomerization in the reaction presented in Eq. 1.



(1)

Geometry and frequency calculations were carried out by DFT method with triple-zeta quality basis sets. The singlet−triplet energy difference was evaluated with DFT and MP2 to MP4(SDQ) methods.

The first step is the coordination of $Br_2B(OSiMe_3)$ with $M(PMe_3)_2$ (M ═ Pt or Pd) to form a precursor complex. The next is the B−Br bond cleavage. In the Pt system, two reaction courses are possible (Figure 1);

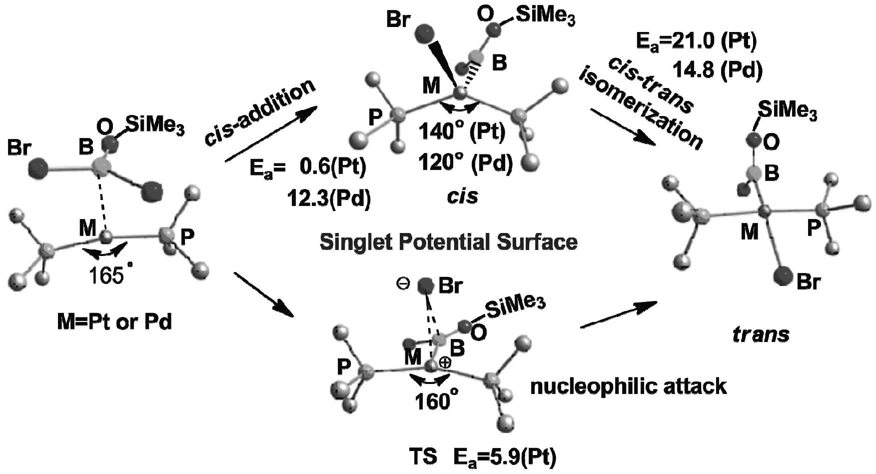
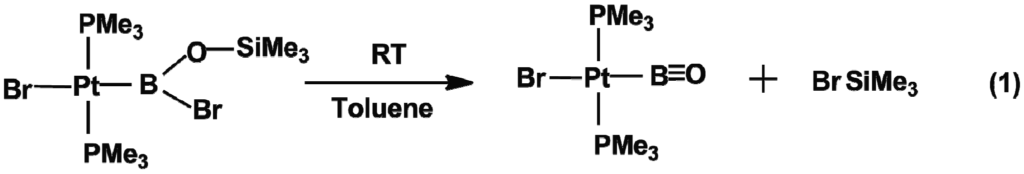


Figure 1. Oxidative addition of the B−Br bond to $M(PMe_3)_2$ (M ═ Pt or Pd). E_a (kcal/mol) is Gibbs energy barrier in solvent (toluene),

one is the nucleophilic attack pathway which directly affords the *trans*-product. The other one is the stepwise reaction pathway which includes the *cis*−oxidative addition followed by the cis−trans isomerization. The former reaction course is more favorable. In the Pd system, only the stepwise pathway was found. Interestingly, the thermal cis−trans isomerization was found to occur on the singlet potential energy surface due to the strong donation ability of the boryl group.

Theoretical Study on Transition−Metal Oxoboryl Complex: M−BO Bonding Nature, Mechanism of the Formation Reaction, and Prediction of New Oxoboryl Complex

The synthesis of B−O multiple−bonded compound has been very difficult for a long time. This is surprising because B≡N triple−bonded compounds were synthesized and well characterized. One of the reasons is that the B−O bond is highly polarized and easily undergoes oligomerization reaction to form B−O−B linkage rather than staying as B=O double or B≡O triple bond. In 2010, Braunschweig et al made a breaktrhough. They synthesized a remarkably stable neutral platinum(II)−oxoboryl complex $PtBr(BO)(PCy_3)_2$, as shown in Eq. 1.

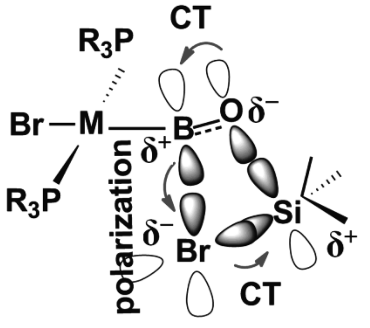


In this work, we theoretically investigated the M-BO bond nature, mechanism of the formation reaction, and make prediction of new oxoboryl complex with DFT method.

First, we make comparison of the Pt−BO bond with other Pt−L bond (L = CN^-, CO, and NO^+) is interesting. As shown in Table 1, the electron population on the LUMO of the $[PtBr(PMe_3)_2]^+$ moiety considerably increases in the order $NO^+ < CO < CN^- \ll BO^-$. Consistent with this result, the electron population on the HOMO (the lone pair orbital) of BO^-, CN^-, CO and NO^+ decreases in the order $NO^+ \gg CO > CN^- > BO^-$. On the other hand, the electron populations on the π* orbitals increase in the order $BO^- < CN^- < CO \ll NO^+$. These results indicate that the σ−donation ability becomes weaker in the order $BO^- \gg CN^- > CO > NO^+$, but the d_π−electron accepting ability becomes stronger in the reverse order.

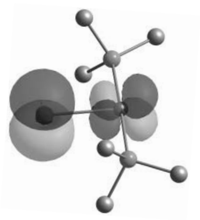
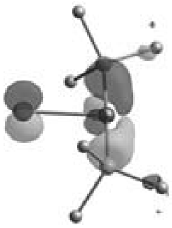
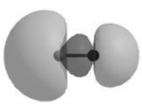
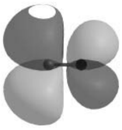
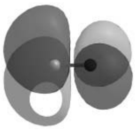
Second, the formation reaction of the oxoboryl complex $PtBr(BO)(PMe_3)_2$ was explored. It occurs through a four−center transition state (see Scheme 1), in which the $B^{\delta+}$−$Br2^{\delta-}$ polarization and the Br2→Si and the O p_π→B p_π charge transfer interactions play key roles. The electron−donating bulky phosphine ligand is favorable for the reaction by enhancing the $B^{\delta+}$−$Br2^{\delta-}$ polarization, stabilizing the transition state, and more destabilizing the boryl complex (reactant) than the oxoboryl complex (product).

Scheme 1.



Around Transition State

Table 1. Important Molecular Orbitals and Their Electron Populations[a] of $[MBr(PMe_3)_2]^+$ and L Ligand in $MBrL(PMe_3)_2$ ($L=BO^-$, CN^-, CO, and NO^+).

		$[MBr(PMe_3)_2]^+$			L		
		LUMO	**HOMO**	**HOMO−1**	**5σ**	π_2^*	π_2^*
L	**M**						
BO^-	Pt	1.174 *e*	1.946 *e*	1.972 *e*	0.702 *e*	0.068 *e*	0.042 *e*
	Pd	1.076 *e*	1.975 *e*	1.981 *e*	0.853 *e*	0.055 *e*	0.034 *e*
	Ni	0.999 *e*	1.976 *e*	1.985 *e*	0.857 *e*	0.053 *e*	0.023 *e*
	Ir	1.212 *e*	1.977 *e*	1.973 *e*	0.596 *e*	0.043 *e*	0.035 *e*
	Rh	1.190 *e*	1.910 *e*	1.979 *e*	0.729 *e*	0.040 *e*	0.024 *e*
CN^-	Pt	0.608 *e*	1.961 *e*	1.975 *e*	1.481 *e*	0.067 *e*	0.057 *e*
CO	Pt	0.413 *e*	1.841 *e*	1.881 *e*	1.636 *e*	0.210 *e*	0.183 *e*
NO^+	Pt	0.179 *e*	1.497 *e*	1.564 *e*	1.860 *e*	0.479 *e*	0.530 *e*

[a] The electron population of each MO is presented here. In the unoccupied orbital, the population increases from zero to the number here in the complex. In the doubly occupied orbital (HOMO, HOMO−1, and 5σ), the population decreases from two to the number here in the complex.

At last, $MBrCl(BO)(CO)(PR_3)_2$ (M=Ir and Rh) is predicted to be good candidate of stable oxoboryl complex based on the comparisons in the $\Delta G^{0\ddagger}$ and ΔG^0 values of the formation reaction, the M−BO bonding nature, and the M-BO interaction energy between $MBrCl(BO)(CO)(PR_3)_2$ and $PtBr(BO)(PR_3)_2$.

2. Original Papers.

(1) Guixiang ZENG and Shigeyoshi SAKAKI
"Noble Reaction Features of Bromoborane in Oxidative Addition of B−Br σ-Bond to $[M(PMe_3)_2]$(M = Pt or Pd): Theoretical Study" Inorg. Chem. 50, 5290–5297(2011)

(2) Guixiang ZENG and Shigeyoshi SAKAKI
"Theoretical Study on the Transition-Metal Oxoboryl Complex: M−BO Bonding Nature, Mechanism of the Formation Reaction, and Prediction of a New Oxoboryl Complex"
Inorg. Chem. 51, 4597−4605 (2012)

3. Presentation at academic conferences

(1) Guixiang Zeng and Shigeyoshi Sakaki
"Noble Reaction Features of Bromoborane in Oxidative Addition of B−Br σ-Bond to $[M(PMe_3)_2]$(M = Pt or Pd): Theoretical Study"
The 14th Symposium on theoretical chemistry (1P12), Okayama University, Okayama, May 12~14, 2011

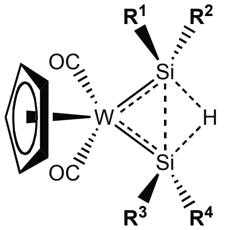
(2) Guixiang Zeng and Shigeyoshi Sakaki
"Noble Reaction Features of Bromoborane in Oxidative Addition of B−Br σ-Bond to $[M(PMe_3)_2]$(M = Pt or Pd): Theoretical Study"
The 7th Congress of the International Society for Theoretical Chemical Physics (ISTCP-VII) Waseda University, Tokyo, Japan, September 2-8, 2011.

Nozomi TAKAGI

SPR Fellow, Fukui kenichi Memorial Research Group 2

1. Summary of the research of the year

A Theoretical Study of Dynamic Behavior of Hydrogen-bridged Bis(silylene)tungsten Complexes



1 : $R^1 = H$, $R^2 = t$Bu, $R^3 = R^4 = Me$
2 : $R^1 = R^3 = R^4 = Me$, $R^2 = t$Bu
3 : $R^1 = R^3 = Me$, $R^2 = R^4 = t$Bu

Scheme 1

Hydrogen-bridged bis(silylene)tungsten complexes (**1** – **3** in Scheme 1) are of considerable interest, because these complexes are considered as a model of the transition state in H/D exchange of methane and silane by Cp_2MR (M = Ln; R = H, CH_3, SiH_3). The variable temperature ^{1}H NMR spectra show dynamic behavior involving site-exchanges of substituents (R^1 to R^4). Interestingly, only in **3** two different types of processes, the *cis*/*trans*-exchange (Process I) and the *trans*/*trans*-exchange (Process II), were observed independently and simultaneously depending on the temperature, though only Process I was observed in **1** and **2**. I investigated the mechanism of the dynamic behavior by density functional theory and post-Hartree-Fock calculations. The calculations indicate that in the Process I the 1,3-Me migration occurs easier than the W=silylene rotation (Figure 1). In

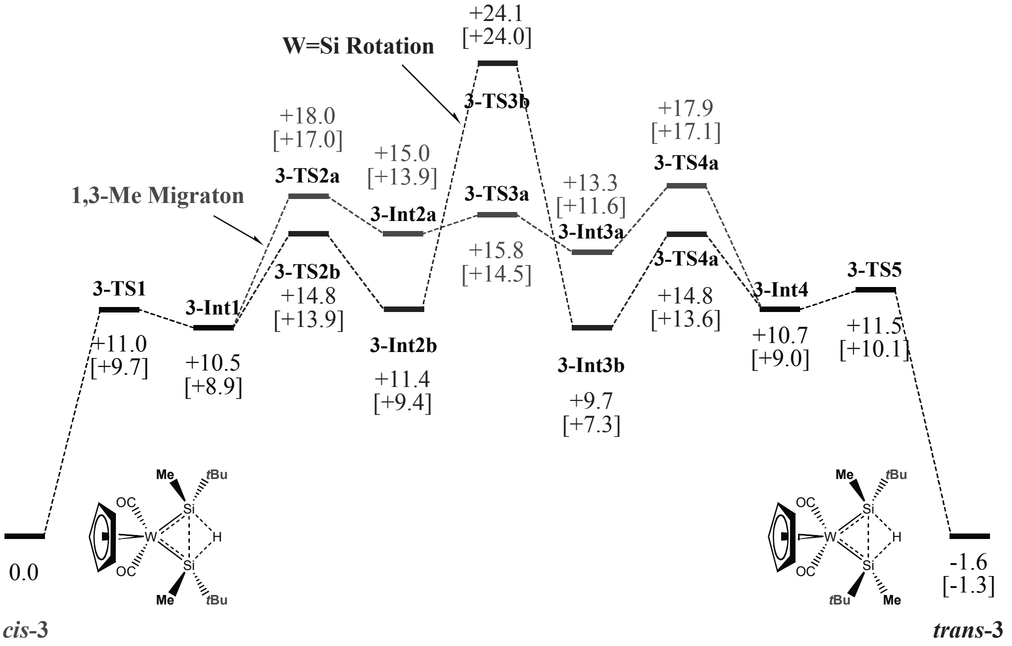


Figure 1. Energy profile for *cis*/*trans*-exchange process (Process I) of **3** calculated at the B3PW91 and the SCS-MP2 level. (in kcal/mol).

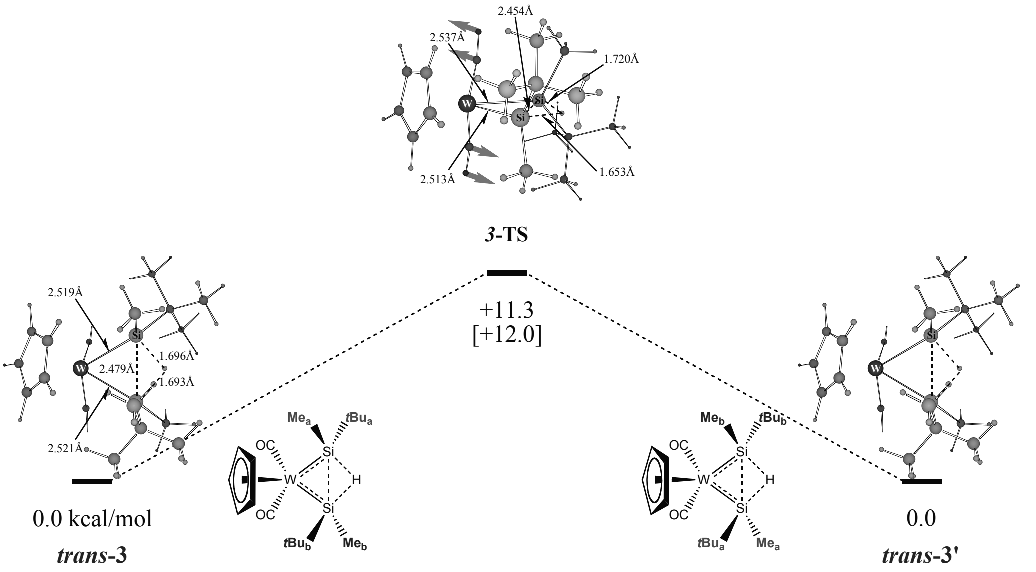


Figure 2. Energy profile for *trans*/*trans*-exchange process (Process II) of **3** calculated at the B3PW91 and the SCS-MP2 level. (in kcal/mol).

the Process II, the hydrogen-bridged bis(silylene) unit rotates with the smaller activation barrier than that of Process I (Figure 2). This result agrees well the experimental fact that the Process II takes place at lower temperature ($\Delta G^{\neq}_{298}$ = 12.3kcal/mol) than the Process I. The details of the reaction features as well as the characteristic bonding features of the three-center interaction of Si-H-Si, the W-Si double bonding nature, and the rather short Si-Si distance were also investigated.

A Theoretical Study of Unusual Y-Shaped Three-coordinate Pt Complex: Pt(0) σ-Disilane Complex or Pt(II) Disilyl Complex?

The unusual Y-shaped structure of the recently reported three-coordinate Pt complex Pt[NHC(Dip)$_2$](SiMe$_2$Ph)$_2$ (NHC = N-heterocyclic carbene; Dip = 2,6-diisopropylphenyl) was considered a snapshot of the reductive elimination of disilane. A density functional theory study indicates that this structure arises from the strong trans-influence of the extremely σ-donating carbene and silyl ligands. Though this complex can be understood to be a Pt(II) disilyl complex bearing a distorted geometry due to the Jahn-Teller effect, its ^{195}Pt NMR chemical shift is considerably different

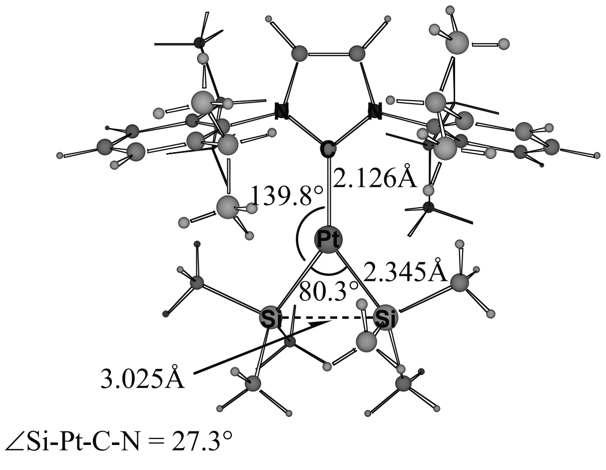
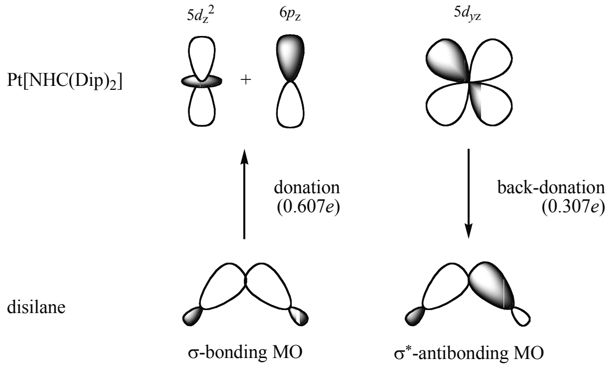
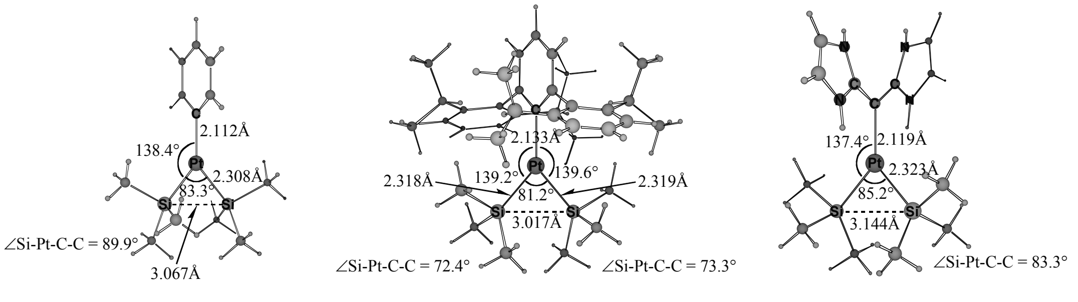


Figure 3. Optimized structure of Pt[NHC(Dip)$_2$](SiMe$_3$)$_2$ at the B3PW91 level.

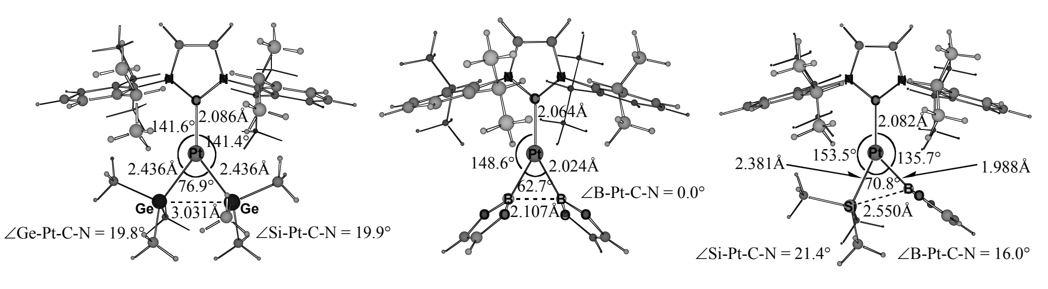


Scheme 2

from those of Pt(II) complexes but close to those of typical Pt(0) complexes. Its Si···Si bonding interaction is <50% of the usual energy of a Si-Si single bond. The interaction between the Pt center and the $(SiMe_2Ph)_2$ moiety can be understood in terms of donation and back-donation interactions of the Si-Si σ-bonding and σ*-antibonding molecular orbitals with the Pt center. Thus, we conclude that this is likely a Pt(0) σ-disilane complex and thus a snapshot after a considerable amount of the charge transfer from the two silyl groups to the Pt center has occurred. Phenyl anion (Ph^-) and $[R\text{-}Ar]^-$ [R-Ar = 2,6-(2,6-$i$$Pr_2C_6H_3)_2C_6H_3$] as well as the divalent carbon(0) ligand $C(NHC)_2$ also provide similar unusual Y-shaped structures. Three-coordinate digermyl, diboryl, and silyl-boryl complexes of Pt and a disilyl complex of Pd are theoretically predicted to have similar unusual Y-shaped structures when a strongly donating ligand coordinates to the metal center. In a trigonal-bipyramidal Ir disilyl complex $Ir(SiR_3)_2(NHC)(PH_3)_2$, the equatorial plane has a similar unusual Y-shaped structure. These results suggest that various snapshots can be shown for the reductive eliminations of the Ge-Ge, B-B, and B-Si σ-bonds (Figure 4).



(A) $[Pt(Ph)(SiMe_3)_2]^-$ **(B) $[Pt(R\text{-}Ar)(SiMe_3)_2]^-$** **(C) $Pt[C(NHC)_2](SiMe_3)_2$**



(D) $Pt[NHC(Dip)_2](GeMe_3)_2$ **(E) $Pt[NHC(Dip)_2](BO_2C_2H_2)_2$** **(F) $Pt[NHC(Dip)_2](SiMe_3)(BO_2C_2H_2)$**

Figure 4. Various snapshots for reductive elimination of Si-Si, Ge-Ge, B-B, and B-Si bonds calculated at the B3PW91 level.

2. Original papers

(1) "Bonding Situation in "Early-Late" Transition Metal Complexes $Cl_3M\text{-}M'(PCl_3)_4$ (M = Ti, Zr, Hf; M' = Co, Rh, Ir) - Theoretical Study for a Ligand Fine Tuning of M-M' Bonds -"
N. Takagi, A. Krapp, G. Frenking, *Z. Anorg. Alleg. Chem.* **637**, 1728-1735 (2011).

(2) "Carbodiphosphorane-Analogues $E(PPh_3)_2$ with E = C - Pb. A Theoretical Study with implications for ligand design"
N. Takagi, R. Tonner, and G. Frenking, *Chem. Eur. J.*, **18**, 1772-1780 (2012).

(3) "Synthesis of Kinetically Stabilized 1,2-Dihydrodisilenes"
T. Agou, Y. Sugiyama, T. Sasamori, H. Sakai, Y. Furukawa, N. Takagi, J. D. Guo, S. Nagase, D. Hashizume, N. Tokitoh, *J. Am. Chem. Soc.*, **134**, 4120-4122 (2012).

(4) "A Theoretical Study of Unusual Y-Shaped Three-coordinate Pt Complex: Pt(0) σ-Disilane Complex or Pt(II) Disilyl Complex?"
N. Takagi, S. Sakaki, *J. Am. Chem. Soc.*, *in press*.

3. Presentation at academic conferences

(1) "Characteristic Fluxional Behavior and Bonding Nature of Hydrogen-bridged Bis(silylene) Complexes"
N. Takagi, Y. Odagiri, H. Hashimoto, H. Tobita, S. Sakaki, The 7th Congress of the International Society for Theoretical Chemical Physics (ISTCP-VII), Tokyo, September 2 – 8, 2011.

(2) "A theoretical study of dynamic behavior of hydrogen-bridged bis(silylene)tungsten complexes"
N. Takagi, Y. Odagiri, H. Hashimoto, H. Tobita, S. Sakaki, The 61st Japan Society of Coordination Chemistry Symposium, Okayama, September, 17 – 19, 2011.

(3) "Characteristic Fluxional Behavior and Bonding Nature of Hydrogen-bridged Bis(silylene) Complexes"
N. Takagi, Y. Odagiri, H. Hashimoto, H. Tobita, S. Sakaki, The 9th Fukui Institute for Fundamental Chemistry Symposium, Kyoto, January 6, 2012.

Masayuki NAKAGAKI

SPR Fellow, Fukui kenichi Memorial Research Group 2

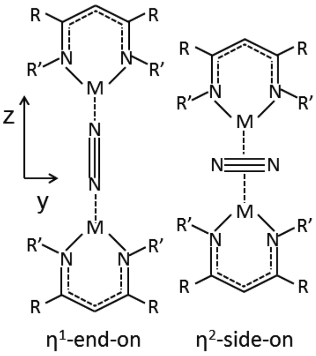
1. Summary of the research of the year

Theoretical Study of Inverted Sandwich Type Complexes of N_2

β-diketiminate ligands make low-valent and low-coordinate transition metal complexes and form the inversed sandwich type complexes (ISTCs). Especially, ISTCs bridged by dinitrogen molecule are interesting for its spin states and coordination mode of N_2. The (μ-N_2)[Fe(DDP)]$_2$ (DDPH = 2-{(2,6-diisopropyl-phenyl)imino}pent-2-ene, which is refer to "nacnac" in several works) was reported by Smith et al. and the coordination mode of N_2 is η^1-end-on. On the other hand, (μ-N_2)[Cr(DDP)]$_2$ was reported by Tsai et. al. and the coordination mode of N_2 is η^2-end-on mode (Scheme 1). The effective magnetic moment μ_{eff} of (μ-η^2:η^2-N_2)[Cr(DDP)]$_2$ at 293 K is 3.9 μ_B, which suggests antiferromagnetic coupling between the Cr atoms, though the values of (μ-η^1:η^1-N_2)[Fe(DDP)]$_2$ is 7.9 $\mu_{B,}$ which seems to ferromagnetic coupling between two metal atoms.

In this study, we investigated the electronic structure of the dinitrogen bridged ISTCs of chromium(I), manganese(I), and iron(I) and clarify the differences between these complexes.

Scheme 1 (μ-N_2)[M(AIP)]$_2$ (M= Cr, Mn, Fe; DDP: R=Me, R'=2,6-^{i}Pr$_2$C$_6$H$_3$; AIP: R=H, R'=H)



We replaced the DDP ligands with AIP (AIPH = 1-amino-3-imino-prop-1-ene; Scheme 1) for brevity. The validity of using the model complex was confirmed in our previous study of benzene complex. Geometry optimizations were carried out for each spin states by the complete active space self-consistent field (CASSCF) method. The active space consists of the d-orbitals of two metals and two π* orbitals of dinitrogen molecule. The second-order perturbation theory with a CASSCF reference function (CASPT2) calculations were carried out at CASSCF optimized structures. CASCI calculations with the orbitals were carried out to obtain the occupation number and spin density of each localized orbitals

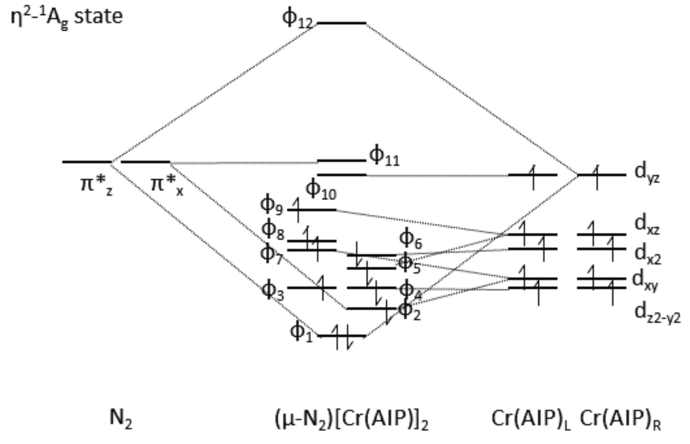
The relative energies of various spin states of (μ-N_2)[M(AIP)]$_2$ (M=Cr, Mn, Fe) with η^1-end-on and η^2-side-on coordination modes of N_2 are listed in Table 1. In the (μ-N_2)[Cr(DDP)]$_{2,}$ the singlet state is the most stable spin state, though the stability is similar to each other among singlet to nonet. Under the Boltzmann distribution at 293K, the effective magnetic moment estimated by CASPT2 is $\mu_{\mathrm{eff}} = 2.7$ $\mu_{B,}$ which is close to the experimental value (3.9 μ_B). In the (μ-N_2)[Fe(AIP)]$_2$, the septet state with η^1-end-on is the most stable, which agree with the experimental result. In the (μ-N_2)[Mn(AIP)]$_2$, nonet state with η^2-side-on is slightly more stable than that with η^1-end-on mode. Compare to the case of Cr complex, the energy differences of spin states are large, that is, strong high-spin coupling.

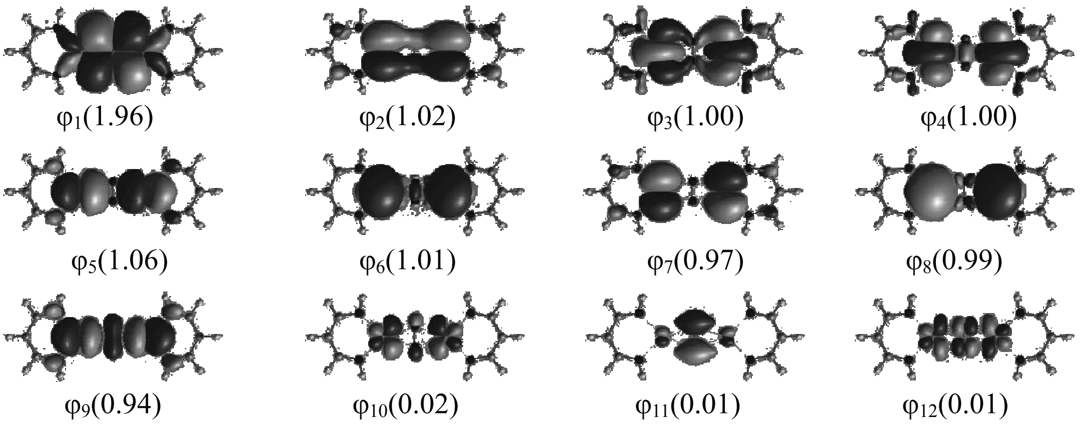
Table 1 Relative energies (kcal/mol) with end-on and side-on modes of (μ-N_2)[M(AIP)]$_2$ (M=Cr, Mn, Fe) calculated by CASPT2 method.

	(μ-N_2)[Cr(AIP)]$_2$		(μ-N_2)[Mn(AIP)]$_2$		(μ-N_2)[Fe(AIP)]$_2$	
	η^1-end	η^2-side	η^1-end	η^2-side	η^1-end	η^2-side
11tet			23.2	11.6		
9tet	22.5	4.0	0.2	0.0	28.9	14.8
7tet	17.8	2.6	5.2	5.0	0.0	3.6
5tet	13.2	1.4	9.6	9.4	7.4	9.8
3let	10.1	0.5	13.8	13.9	14.0	15.6
1let	8.4	0.0	18.4	18.7	21.8	22.0

Molecular orbital (MO) interaction diagram of (μ-η^2:η^2-N_2)[Cr(AIP)]$_2$ is shown in Scheme 2. The right hand is the orbital diagram of Cr(AIP) moiety and left hand is N_2 π^* orbitals. The energy destabilization of Cr d_{yz} orbital is large because of the overlap with the lone pair orbital of AIP ligand. The CASSCF(10,12) natural orbitals of (μ-η^2:η^2-N_2)[Cr(AIP)]$_2$, which correspond to the optimized orbitals in Scheme 2, are shown in Figure 1. Number in parentheses represents occupation number in the singlet state. The π-bond orbital (φ_1), which consists of two Cr d_{yz} orbitals and N_2 π^*_z orbital, is very stable and almost doubly occupied. Though the Cr d_{xy} orbital belong to same symmetry with N_2 π^*_x orbital, the $\delta(d_{xy})$-bond between N_2 and two Cr(AIP) is not confirmed. The other 8 electrons of active space singly occupy in d_{z2}, d_{xy}, d_{x2-y2} and d_{xz} orbitals (φ_2-φ_9). Generally, high spin state is more favorable than low spin state when orbital energies are similar. However, the d_{xy} orbital in b_{1g} (φ_2) is stabilized by unoccupied π^*_x orbital and d_{xz} orbital in b_{2u} (φ_9) is destabilized by occupied π_x orbital. Because the energy levels of degenerate d-orbitals split by these interactions, two electrons in paired d-orbitals prefer open-shell singlet. In fact, the occupation number of φ_2 is 1.02 and the one of φ_9 is 0.94.

Scheme 2 MO diagram of (μ-η^2:η^2-N_2)[Cr(AIP)]$_2$




φ_1(1.96) φ_2(1.02) φ_3(1.00) φ_4(1.00)

φ_5(1.06) φ_6(1.01) φ_7(0.97) φ_8(0.99)

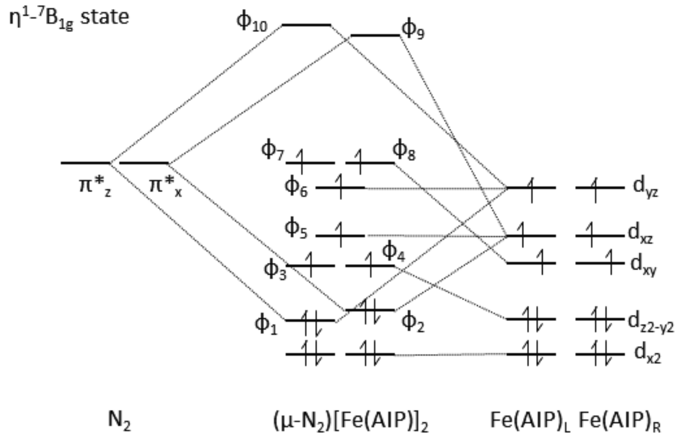
φ_9(0.94) φ_{10}(0.02) φ_{11}(0.01) φ_{12}(0.01)

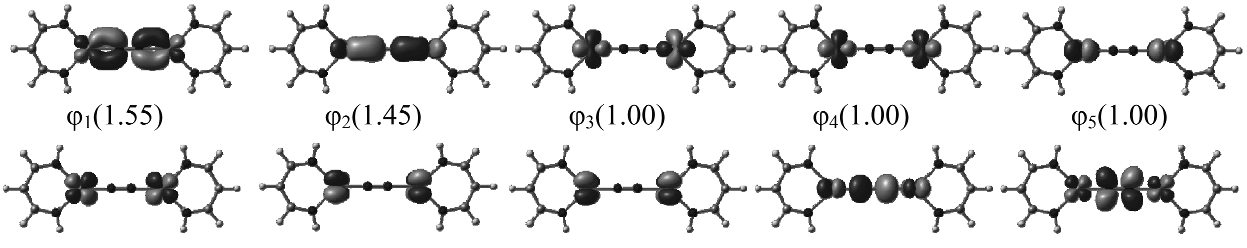
Figure 1. CASSCF orbitals of $(\mu\text{-}\eta^2\text{:}\eta^2\text{-N}_2)[\text{Cr(AIP)}]_2$.

The MO diagram of $(\mu\text{-}\eta^1\text{:}\eta^1\text{-N}_2)[\text{Fe(AIP)}]_2$ are shown in Scheme 3. In the isolate Fe(AIP), the A_1 state which has doubly occupied $d_{x2\text{-}y2}$ and d_{z2} orbitals is ground state, though the B_2 state which has doubly occupied d_{xz} and d_{y2} orbitals is only 0.6 kcal/mol higher at CASSCF level. At the η^1-end-on mode, bonding orbital is formed by Fe d_{xz} orbitals and N_2 π^*_x orbital. The CASSCF(10,10) natural orbitals of $(\mu\text{-}\eta^1\text{:}\eta^1\text{-N}_2)[\text{Fe(AIP)}]_2$, which correspond to the optimized orbitals in Scheme 3, are shown in Figure 2 with the occupation numbers of the septet state in parentheses. To avoid the convergence problem, the d_{x2} orbitals were excluded from the active space and taken as core orbitals. There are two bonding orbitals, $\pi(d_{yz})$-bond and $\pi(d_{xz})$-bond, and they are doubly occupied in main electron configuration. Two $d_{z2\text{-}y2}$, d_{xy} orbitals and non-bonding d_{xz}, d_{yz} orbitals are singly occupied and it takes high-spin coupling.

The electronic structure of $(\mu\text{-}\eta^2\text{:}\eta^2\text{-N}_2)[\text{Mn(AIP)}]_2$ is similar to that of $(\mu\text{-}\eta^1\text{:}\eta^1\text{-N}_2)[\text{Fe(AIP)}]_2$. By the forming of ISTC, the Mn d_{yz} and d_{xy} orbitals form $\pi(d_{yz})$-bond and $\delta(d_{xy})$-bond with the two N_2 π^* orbitals instead of $\pi(d_{xz})$-bond because of difference of coordination mode.

Scheme 3 MO diagram of $(\mu\text{-}\eta^1\text{:}\eta^1\text{-N}_2)[\text{Fe(AIP)}]_2$





φ_1(1.55) φ_2(1.45) φ_3(1.00) φ_4(1.00) φ_5(1.00)

φ_6(1.00) φ_7(1.00) φ_8(1.00) φ_9(0.55) φ_{10}(0.45)

Figure 2. CASSCF orbitals of $(\mu\text{-}\eta^1\text{:}\eta^1\text{-N}_2)[\text{Fe(AIP)}]_2$

Different from the π-bond of $(\mu\text{-N}_2)[\text{Cr(AIP)}]_2$, the occupation numbers of anti-bonding orbitals are large in $(\mu\text{-N}_2)[\text{Mn(AIP)}]_2$ and $(\mu\text{-N}_2)[\text{Fe(AIP)}]_2$. Table 2 shows the main electron configurations of $^9B_{2u}$ state of $(\mu\text{-}\eta^2\text{:}\eta^2\text{-N}_2)[\text{Mn(AIP)}]_2$ and $^7B_{1g}$ state of $(\mu\text{-}\eta^1\text{:}\eta^1\text{-N}_2)[\text{Fe(AIP)}]_2$ in CASSCF wavefunction. In fact, both states have several important configurations. In $^7B_{1g}$ state, the second reading terms are single or double excitation from bonding orbital to anti-bonding orbital. In $^9B_{2u}$ state, configurations which have excitation from bonding orbital to anti-bonding orbital of δ(d_{xy})-bond are more dominant. This multi-reference character results from the spin polarization of bonding orbitals. In $(\mu\text{-N}_2)[\text{Mn(AIP)}]_2$ and $(\mu\text{-N}_2)[\text{Fe(AIP)}]_2$, the non-bonding orbitals, which consist of the same d-orbitals as bonding one, are singly occupied, though the non-bonding d_{yz} orbital is vacant in $(\mu\text{-N}_2)[\text{Cr(AIP)}]_2$. The exchange integral between bonding and non-bonding orbital is clearly larger than the others. So the spin polarization, α-electron polarizes to metal side and β-electron polarizes to N_2 side, occurs to stabilize by the exchange interaction.

Table 4 Main electron configurations of CASSCF wavefunction. Orbital index correspond to Figure 5 and 6

State	Configuration												Coefficient
	φ_1	φ_2	φ_3	φ_4	φ_5	φ_6	φ_7	φ_8	φ_9	φ_{10}	φ_{11}	φ_{12}	
$(\mu\text{-}\eta^2\text{:}\eta^2\text{-N}_2)[\text{Mn(AIP)}]_2$													
$^9B_{2u}$	2	α	α	α	α	α	α	α	α	α	β	0	0.6135
	β	α	α	α	α	α	α	α	α	α	β	α	−0.5363
	2	2	α	α	α	α	α	α	α	α	0	0	0.3108
	α	2	α	α	α	α	α	α	α	α	0	β	−0.1912
	0	α	α	α	α	α	α	α	α	α	β	2	−0.1839
$(\mu\text{-}\eta^1\text{:}\eta^1\text{-N}_2)[\text{Fe(AIP)}]_2$													
$^7B_{1g}$	2	2	α	α	α	α	α	α	0	0			0.5804
	2	α	α	α	α	α	α	α	β	0			0.3707
	α	2	α	α	α	α	α	α	0	β			0.3236
	2	0	α	α	α	α	α	α	2	0			−0.2284
	0	2	α	α	α	α	α	α	0	2			−0.2096
	α	α	α	α	α	α	α	α	β	β			0.1861

The spin polarization can be recognized by localized orbital description. Table 3 shows the main electron configurations of CASCI wavefunction with the localized molecular orbitals under C_{2v} symmetry. In this set of orbitals, the $^9B_{2u}$ state of (μ-η^2:η^2-N$_2$)[Mn(AIP)]$_2$ and the $^7B_{1g}$ state of (μ-η^1:η^1-N$_2$)[Fe(AIP)]$_2$ could be mainly expressed by one configuration. In the configuration, β-electrons occupy the N$_2$ π* orbitals though the α-electrons occupy the d-orbitals of M(AIP), which can be regarded as three-center three-electron (3c-3e) bond.

Table 3 Main electron configurations of CAS-CI wavefunction with the localized molecular orbitals under C_{2v} symmetry. Parentheses represent double occupied (core) orbitals.

State	Configuration												Coefficient
	M1(AIP)					M2(AIP)					N$_2$		
	d_{x2-y2}	d_{z2}	d_{xy}	d_{xz}	d_{yz}	d_{x2-y2}	d_{z2}	d_{xy}	d_{xz}	d_{yz}	π^*_z	π^*_x	
(μ-η^2:η^2-N$_2$)[Mn(AIP)]$_2$													
$^9B_{2u}$	α	α	α	α	α	α	α	α	α	α	β	β	0.8136
	α	α	α	α	α	α	α	α	α	β	α	β	−0.1799
	α	α	α	α	β	α	α	α	α	α	α	β	0.1799
(μ-η^1:η^1-N$_2$)[Fe(AIP)]$_2$													
$^7B_{1g}$	(2)	α	α	α	α	(2)	α	α	α	α	β	β	0.7744
	(2)	α	α	α	α	(2)	α	α	α	β	α	β	−0.1769
	(2)	α	α	α	β	(2)	α	α	α	α	α	β	−0.1769

Summary

In the (μ-N$_2$)[Cr(AIP)]$_2$, the spin states of two Cr atoms take weak low-spin coupling and the open-shell singlet is the most stable state, though the spin states are near degenerated among singlet to nonet. The π-bond orbital, which consists of d_{yz} orbitals of two Cr atoms and π^*_z orbital of N$_2$, is very stable and almost doubly occupied. The degenerated d-orbitals of two Cr(AIP)s split because the d_{xy} orbital in b_{1g} is stabilized by unoccupied π^*_x orbital and d_{xz} orbital in b_{2u} is destabilized by occupied π_x orbital. Because of the energy splitting, eight single occupied d-electrons prefer the open-shell singlet.

In the (μ-N$_2$)[Mn(AIP)]$_2$ and (μ-N$_2$)[Fe(AIP)]$_2$, the spin states of two metal atoms take strong high-spin coupling, nonet and septet states are most stable states, respectively. They form two bond between N$_2$ and two M(AIP) moieties; π(d_{yz})-bond and π(d_{xz})-bond in η^2-side-on and π(d_{yz})-bond and π(d_{xz})-bond in η^1-end-on. The single occupation of non-bonding orbitals cause the spin polarization of bonding orbitals, α-electron localizes to metal side moieties and β-electron localizes to N$_2$ side, and the high-spin state is favorable.

In the (μ-N$_2$)[Cr(AIP)]$_2$, η^2-side-on coordination mode of N$_2$ is obviously stable than η^1-end-on mode because of the favorable orbital overlap between Cr d_{yz} and N$_2$ π_x* orbitals to form the π-bond. In the (μ-N$_2$)[Mn(AIP)]$_2$ and (μ-N$_2$)[Fe(AIP)]$_2$, the stabilities of two coordination modes are comparable, because the advantage of the π(d_{xz})-bond compared to the δ(d_{xy})-bond and destabilization of π(d_{yz})-bond cancel out.

2. Presentation at academic conferences

(1) Masayuki Nakagaki, Yusaku I. Kurokawa, and Shigeyoshi Sakaki
"Theoretical Study of Inverted Sandwich Type Dinuclear Complexes of ethylene and dinitrogen molecules"
7th Congress of the International Society for Theoretical Chemical Physics Tokyo (Waseda Univ.) 2011/9/3 3PP-52

(2) 中垣 雅之、黒川 悠索、榊 茂好
「クロム(I)-エチレン及び窒素分子の逆サンドイッチ型錯体及び類似錯体の電子構造に関する理論的研究」
第５回分子科学討論会 2011 札幌　札幌　2011/9/22 3P129

3. Others

(1) 中垣 雅之、黒川 悠索、榊 茂好
「クロム(I)及び鉄(I)-窒素分子の逆サンドイッチ型錯体の電子構造に関する理論的研究」
第9回京都大学福井謙一記念研究センターシンポジウム　京都 2012/1/6

(2) 中垣 雅之、黒川 悠索、榊 茂好
「クロム(I)及び鉄(I)-N_2錯体の理論的研究　—異常なスピン多重度とその起源—」
第１回協定講座シンポジウム「計算アルゴリズムと化学・生物学の融合」神戸（神戸大学）2012/2/17.

Terutaka YOSHIZAWA

SPR Fellow, Fukui kenichi Memorial Research Group 2

1. Summary of the research of the year

NMR shielding constants of CuX, AgX, and AuX (X = F, Cl, Br, and I) investigated by density functional theory based on the Douglas–Kroll–Hess Hamiltonian

Introduction

NMR shielding constants of heavy metal elements are of considerable interest in molecular science and theoretical chemistry, because those shielding constants reflect characteristic electronic structure, in particular, relativistic effects in the system including heavy elements. Actually, David and Restrepo recently reported that the paramagnetic term of the Au nuclear magnetic resonance (NMR) shielding constant of AuF molecule is more than three times as large as those of AuCl, AuBr, and AuI. They discussed that this result arises from spin-orbit (SO) effect enhanced by the high electronegativity of F atom. Since their report, the relation between the SO effect and the electronegativity attracts a lot of interests, because the SO effect does not seem to directly relate to electronegativity. However, the mechanism of the relation has not been elucidated yet.

In the present study, we combined the DFT method with the second-order DKH (DKH2) one-electron Hamiltonian and applied it to the calculation of the NMR shielding constant. Then, we applied this method to the NMR shielding constant of the metal in CuX, AgX, and AuX (X = F, Cl, Br, and I), investigated relativistic effects on the NMR shielding constant, and discussed the reasons why the electronegativity of halogen influences the NMR shielding constant.

Results and discussion

Cu, Ag, and Au shielding constants of MX (M = Cu, Ag, or Au; X = F, Cl, Br, or I)

NMR shielding constants of metal center are summarized in Table 1 The Cu shielding constant of CuI agrees well with the experimental value in the HF, B3LYP, and BP86 calculations.

In the Ag chemical shift, $AgNO_3$ in aqueous solution was experimentally taken as a reference. In general, it is difficult to calculate the shielding constant with solvation structure. Hence, we employed here the chemical shift relative to that of AgF. The HF-calculated δ(Ag) value is considerably negative in AgCl, AgBr, and AgI, which does not agree with the experimentally reported increasing order of δ(Ag); AgF < AgCl < AgBr < AgI. The B3LYP- and BP86-calculated δ(Ag) values are negative at AgCl but increase in the order AgF < AgBr < AgI. These results indicate that the DKH2-B3LYP and

DKH2-BP86 methods are better than the DKH2-HF method.

The DKH2-HF-calculated Au shielding constant decreases in the order AuF >> AuCl > AuBr ~ AuI, which agrees with the decreasing order of 4c-HF-calculated values. However, it is noted that the DKH2-HF method overestimates the Au shielding constant by about 1000 ppm, compared to the 4c-HF method. The similar overestimation was reported also in the ZORA-DFT-calculated Hg shielding constant of HgX_2, compared to the 4c-DFT value. These overestimations would be due to insufficiency of the higher order relativistic correction terms of the DKH Hamiltonian. Though the DKH2-DFT-calculated Au shielding constant of AuF is somewhat smaller and those of AuBr and AuI are somewhat larger than the 4c-HF values, the same trend of the Au shielding constant is observed, as will be discussed below.

As reported by David and Restrepo, the Au shielding constant of AuF is extremely larger than that of the other AuX in our DKH2-DFT and DKH2-HF calculations. However, the Cu and Ag shielding constants of CuF and AgF, respectively, are not very large; see Table 1 All these results indicate that the large Au shielding constant in AuF is characteristic and its reason is of considerable interest from the viewpoint of the relativistic effects, as follows: The Au shielding constants of AuF calculated by the scalar relativistic DKH2-B3LYP method is the smallest; 6926 ppm, 8658 ppm, 9186 ppm, and 9753 ppm for AuF, AuCl, AuBr, and AuI, respectively. This result clearly indicates that the scalar relativistic effect is not responsible for this characteristic feature and the SO effect plays an important role for the very large Au shielding constant of AuF.

Table 1. Metal shielding constant (in ppm) of MX (M = Cu, Ag, or Au; X = F, Cl, Br, or I) calculated by the DKH2-HF, DKH2-B3LYP, and DKH2-BP86 methods.

	Molecule	DKH2-HF	DKH2-B3LYP	DKH2-BP86	Exptl.	4c-HF[a]
σ(Cu)	CuF	2043	1754	1299		1787
	CuCl	2005	1708	1580		
	CuBr	2060	1899	1814		
	CuI	2112 (585)[b]	2166 (292)[b]	2143 (274)[b]	2184 (641)[b,c]	
σ(Ag)	AgF	5047 (0)[d]	4987 (0)[d]	4997 (0)[d]	(0)[d,e]	4634
	AgCl	4825 (–221)[d]	4794 (–193)[d]	4809 (–188)[d]	(65)[d,e]	
	AgBr	4830 (–217)[d]	5082 (95)[d]	5190 (193)[d]	(155)[d,e]	
	AgI	4830 (–217)[d]	5425 (438)[d]	5609 (612)[d]	(360)[d,e]	
σ(Au)	AuF	32635	25527	23747		31611
	AuCl	16130	14437	14196		14937
	AuBr	15501	15712	15891		14459
	AuI	15523	17669	18194		14454

[a]Ref [1]. [b]The value in parenthesis is the anisotropies of the shielding constants. [c]Ref [2]. [d]The values in parenthesis is relative value to σ(Ag) of AgF. [e]Ref [3].

Contributions of diamagnetic, paramagnetic, spin-dipolar, and Fermi contact terms to metal shielding constant of MX

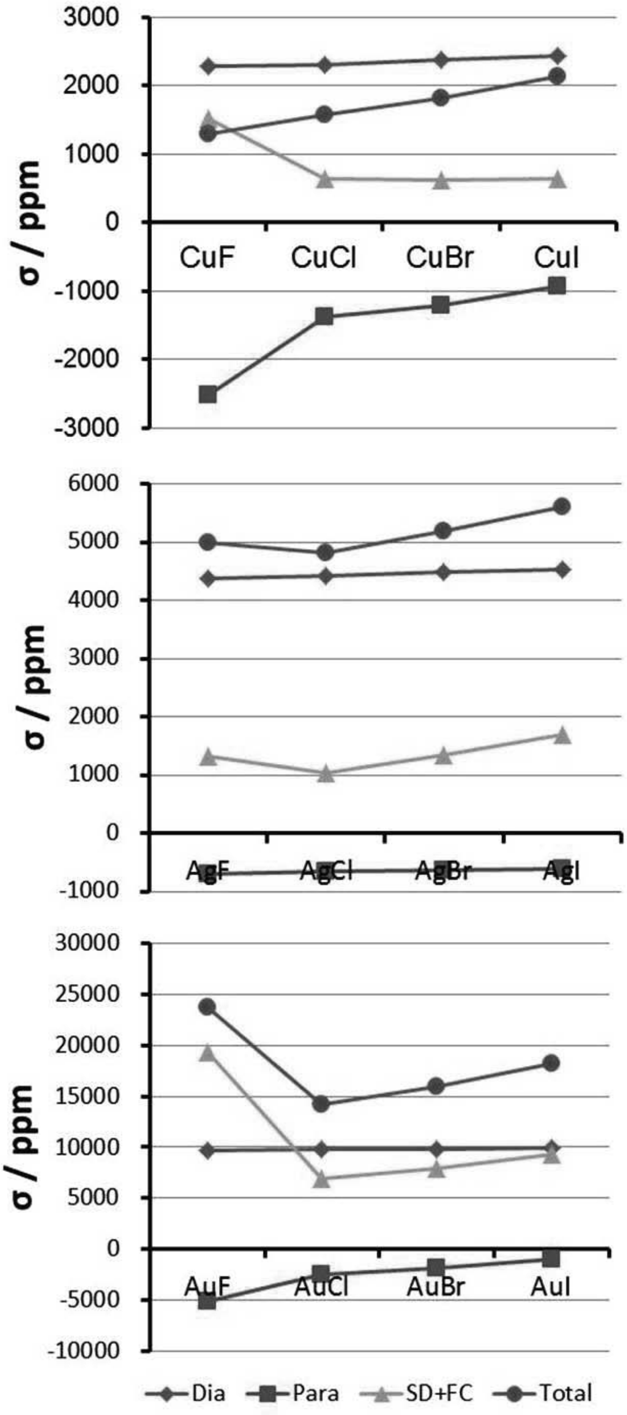


Figure 1. Diamagnetic, paramagnetic, and sum of spin-dipolar and Fermi contact terms of MX (M = Cu, Ag, or Au; X = F, Cl, Br, or I) calculated by the DKH2-BP86 method.

To elucidate the reason why the Au shielding constant is much larger in AuF than in AuCl, AuBr, and AuI unlike the Ag and Cu shielding constants of AgF and CuF, we decomposed the metal shielding constant into the diamagnetic, paramagnetic, and the sum of SD and FC terms, as shown in Figure 1. In all of CuX, AgX, and AuX, the diamagnetic term little depends on the kind of X. In CuX, on the other hand, when going from CuF to CuCl, the paramagnetic term considerably increases but the SD+FC term considerably decreases. The decrease in the SD+FC term largely cancels the increase in the paramagnetic term, leading to the moderate increase in the Cu shielding constant. When going from CuCl to CuI, the paramagnetic term moderately increases but the SD+FC term little changes. As a result, the Cu shielding constant monotonously increases when going from CuF to CuI. In AgX, the paramagnetic term little changes when going from AgF to AgI. This is against the general trend that the paramagnetic term of metal halide depends on the halide. In the Ga shielding constant of GaX_4^- and the In one of InX_4^-, however, the paramagnetic term little changes when going from X = Cl to I like AgX, (while the diamagnetic term largely changes). This means that the little dependence of paramagnetic term on halide in AgX is not surprising; the reason must be discussed in a near future. The SD+FC term moderately decreases when going from AgF to AgCl but then moderately increases when going from AgCl to AgI. As a result of these changes, the Ag shielding constant of AgF becomes moderately smaller than those of AgBr and AgI. In AuX, the paramagnetic term considerably increases but the SD+FC term extremely decreases, when going from AuF to AuCl. When going from AuCl to AuI, both terms moderately increase. Based on these results, it is concluded that the extremely large Au shielding constant in AuF arises from the extremely large SD+FC term in AuF. Thus, the next issue to be investigated is the reason why the SD+FC term is very large in AuF.

Reason why SD+FC term is very large in AuF.

We evaluated how much each transition between the occupied and virtual orbitals contributes to the paramagnetic term of CuX and AuX. In CuF, the HOMO → LUMO transition contributes the most to the paramagnetic term. In AuF, the HOMO–1 → LUMO transition contributes the most. Both of the HOMO of CuF and the HOMO–1 of AuF mainly consist of the metal d_π orbital into which the F p_π orbital mixes in an anti-bonding way, as shown in Figure 2. The LUMO mainly consists of metal s and d_σ orbital with which halogen p_σ orbital overlaps in an anti-bonding way. These two MOs are named (d_π–p_π) and (s+d_σ–p_σ), respectively, hereafter. On the other hand, the contribution of this transition is very small in the other MCl, MBr, and MI. More important is that this contribution decreases very much by about 3000 ppm when going from AuF to AuCl and by about 1000 ppm when going from CuF to CuCl. The HOMO-LUMO (or HOMO–1-LUMO) energy gap is not different very much; it is 1.82 eV, 1.92 eV, 1.85 eV, and 1.72 eV for CuF, CuCl, CuBr, and CuI, respectively, and 1.79 eV, 1.83 eV, 1.63 eV, and 1.42 eV for AuF, AuCl, AuBr, and AuI, respectively. These results suggest that not the denominator of Eq. (1) but the numerator is responsible for the large negative paramagnetic term of AuF:

$$\sigma_{tu}^{\mathrm{Para}} = -\sum_{i}^{\mathrm{Occ}}\sum_{a}^{\mathrm{Vir}} \frac{\langle\varphi_i|h_t^{(1,0)}|\varphi_a\rangle\langle\varphi_a|h_{u,\mathrm{SF}}^{(0,1)}|\varphi_i\rangle + \langle\varphi_i|h_{u,\mathrm{SF}}^{(0,1)}|\varphi_a\rangle\langle\varphi_a|h_t^{(1,0)}|\varphi_i\rangle}{\varepsilon_a - \varepsilon_i}. \tag{1}$$

As shown in Figure 2, the metal d-orbital component of the HOMO (or HOMO–1) is considerably larger than the F p-orbital component only in CuF and AuF. Moreover, the contributions of the metal d-orbital component is dominant in the HOMO (or HOMO–1)-LUMO contribution. The mixing (or overlap) between the metal d-orbitals of the HOMO (or HOMO–1) and of the LUMO is essential for the Cu and Au shielding constants. Actually, the metal part of the LUMO for CuF and AuF is the largest in CuX and AuX, respectively. On the other hand, the Ag d-orbital component is smaller than the F p-orbital one in the HOMO (d_π–p_π) of AgF, like the other halides. Therefore, the large paramagnetic terms of CuF and AuF are attributed to the large metal d-orbital component of the HOMO or HOMO–1 (d_π–p_π), respectively.

The d component of the d_π–p_π MO mainly depends on the relative energies of M d_π and X p_π orbitals; if the X p_π is at a lower energy than the M d_π, the M d_π component is larger than the X p_π component, as schematically shown in scheme 1. The 4d orbital of Ag is at considerably low energy, as well known. As a result, the 4*d* component of Ag is considerably smaller than the F p_π orbital in the d_π–p_π MO of AgF. On the other hand, the *d* orbitals of Cu and Au are at higher energy than the F p_π orbital, which leads to the large d_π component in the d_π–p_π MO. When going from MF to MCl, the halogen p_π orbital energy rises in energy, and hence the d_π orbital component decreases in the d_π–p_π MO of MCl.

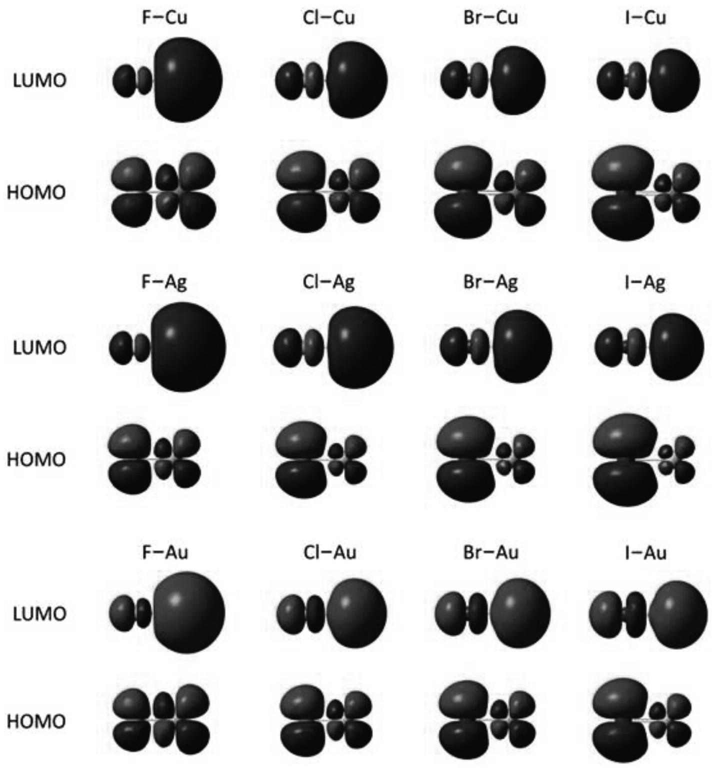
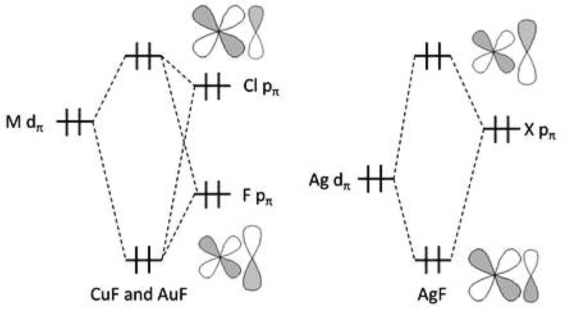


Figure 2. Frontier MOs of MX (M = Cu, Ag, or Au; X = F, Cl, Br, or I). HOMO–1 is shown only for AuF. Metal atom is in the right side and halogen atom is the left side. The bond axis corresponds to the Z-axis. These MOs are calculated by using the scalar relativistic DKH2-BP86 method in the Gaussian09 program package.



Scheme 1. MO diagram for MX (M = Cu, Ag, and Au; X = F, Cl, Br, and I).

References

[1] J. David, A. Restrepo, *Phys. Rev. A* **2007**, *76*, 052511.

[2] L. Bizzocchi, B. M. Giuliano, J.-U. Grabow, *J. Mol. Struct.* **2007**, *833*, 175.

[3] H. Looser, D. Brinkmann, *J. Magn. Reson.* **1985**, *64*, 76.

2. Original papers

T. Yoshizawa, S. Sakaki "NMR shielding constants of CuX, AgX, and AuX (X = F, Cl, Br, and I) investigated by density functional theory based on the Douglas–Kroll–Hess Hamiltonian" in preparation.

3. Presentation at academic conferences

T. Yoshizawa, S. Sakaki "NMR calculations of transition metal complexes containing M ≡ P triple bond" International Society for Theoretical Chemical Physics (ISTCP-VII), 3PP-57, September 2-8, 2011, Waseda University, Tokyo (Japan).

中谷　直輝

特推研究フェロー
（平成23年5月10日まで）

1. 今年度の研究の要約

今年度はパラジウム表面吸着CO分子の価電子励起スペクトルについて研究を行った。

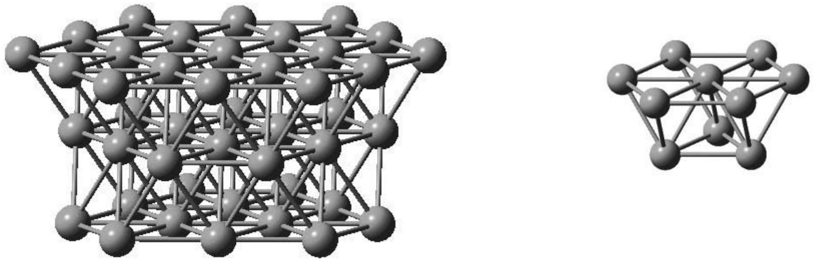
【始めに】金属表面に吸着した分子は、金属表面との相互作用により孤立分子とは全く異なった性質を持つようになり、例えば不均一触媒の開始反応の推進力となるため、反応機構を議論する上で非常に重要なステップである。しかしながら、金属表面のような反無限系を高精度かつ効率的に取り扱う理論的手法はほとんど提案されていない。

我々のグループではこれまで、クラスターモデルを基に有効ポテンシャルを用いて金属バルクの効果を取り込むことで金属表面の計算を行う手法の開発を行ってきた。本手法はクラスターモデルを用いているため、従来の高精度電子状態理論への応用が極めて簡単に行えることが最大の利点である。

本研究では、最も典型的な表面化学吸着現象として知られるパラジウム(111)表面へのCO分子の化学吸着に着目し、吸着CO分子の内殻イオン化スペクトルと価電子励起スペクトルを高精度励起状態計算手法の1つであるSAC-CI法を用いて計算し実験スペクトルとの比較を行った。

内殻イオン化スペクトルについては昨年度すでに検討を行っていたので、今年度は価電子励起スペクトルについて検討を行った。

【有効ポテンシャルの作成】ポテンシャルの作成はパラジウム43原子からなる参照クラスターに対して、中心10原子からなるモデルクラスターの表面軌道の軌道エネルギーを再現するように決定した（図・1）。ポテンシャル作成は密度汎関数法を用いて行い、基底関数はCristiansenの(541/541/211)基底および内殻28電子を有効内殻ポテンシャルで置き換えたものを使用した。


Pd_{43}　　Pd_{10}

図・1　参照クラスター(Pd_{43})とモデルクラスター(Pd_{10})

【パラジウム表面吸着 CO 分子の価電子励起スペクトル】以上のように作成した有効ポテンシャルを用いて、パラジウム(111)表面吸着 CO 分子の価電子励起スペクトルを SAC-CI 法を用いて計算した。計算は$Pd_{10}CO$クラスターモデルを用いて行い、CO の基底関数には Ahlrich の TZV を使用した。

表・1 に従来のクラスターモデルおよび有効ポテンシャルを用いた結果についてまとめた。

表・1 SAC-CI 法によるパラジウム(111)表面吸着 CO 分子の価電子励起スペクトルの計算結果

	$Pd_{10}CO$ without EP			$Pd_{10}CO$ with EP		
	ΔE_{Ex} / eV	Osc. stln.	Assign	ΔE_{Ex} / eV	Osc. stln.	Assign
S1	8.27	0.0005	d*←1π	7.78	0.0000	d*←1π
S2	8.49	0.0004	s*←1π	7.91	0.0003	d*←1π
S3	8.79	0.0057	s*←5σ	8.54	0.0006	s*←1π
S4	8.86	0.0058	s*←1π	8.97	0.0015	s*←5σ
S5	9.32	0.0005	Ryd←1π	9.10	0.0037	s*←1π
S6	9.62	0.0020	Ryd←5σ	9.34	0.0015	Ryd←1π

実験や過去の計算研究から、吸着 CO 分子の価電子励起(2π*←1π)は 8.0 - 9.0 eV 付近に観測されると予測されている。しかしながら、本研究ではその付近に CO の価電子励起に由来する状態は観測されず、パラジウム表面への電荷移動型の励起状態が観測された。そこで、今後の予備検討として、CIS 法を用いて基底状態から 14 eV までのおよそ 1600 状態を計算したが、CO 分子の価電子励起由来のピークは観測できず、さらに高エネルギー領域に存在するか、もしくは電荷移動型の励起と混合している可能性が考えられる。今後は、SAC-CI 法を用いてさらに高エネルギー領域まで計算を行う予定である。

2. 論文

(1) Naoki NAKATANI, Yutaka HITOMI, and Shigeyoshi SAKAKI,
“Multistate CASPT2 Study of Native Iron(III)-Dependent Catechol Dioxygenase and Its Functional Models: Electronic Structure and Ligand-to-Metal Charge Transfer Excitation”
J. Phys. Chem. B 115, 4781-4789(2011).

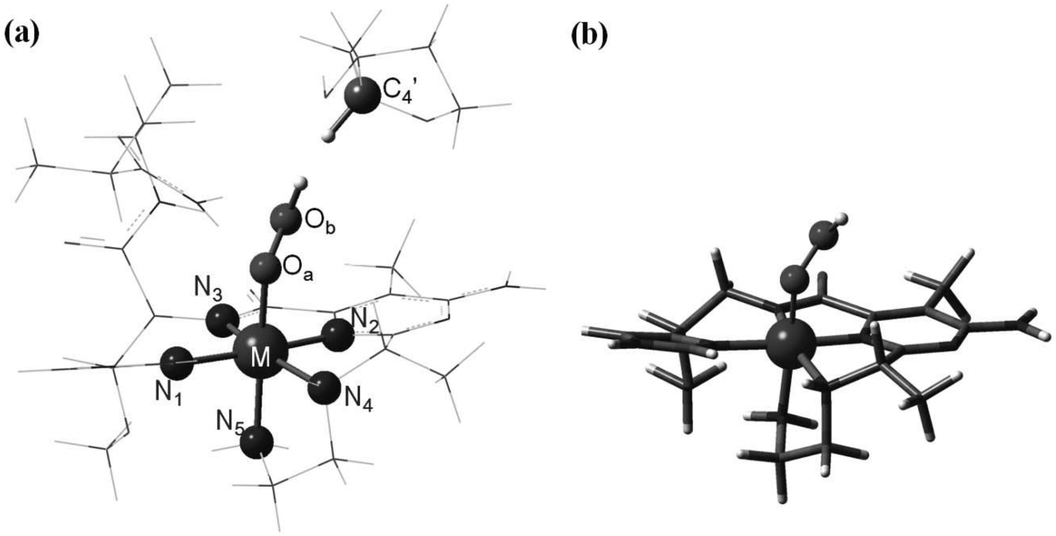
Toru MATSUI

Visiting Scholar, JSPS Fellow (Osaka University)

1. Summary of the research of the year

(A) DNA Scission Reaction by Metallo-Bleomycin: Similarities and Differences between Fe- and Co- Bleomycin

DNA scission reactions by Fe- and Co-bleomycins (BLMs, the model is shown in Scheme A-1) were theoretically investigated with the density functional theory (DFT) method. The geometry of transition states is similar between Fe- and Co-BLMs. In this study, we theoretically investigated the DNA scission reaction on the basis of the idea that DNA can be nicked by the ·OH radical via O-O homolysis. We reproduced the computed reaction barrier in Fe-BLM proposed by Decker et al. and estimated that the reaction barrier of DNA scission is too high in the case of Co-BLM. Especially in the case of Co-BLM, the triplet state is more stable than the open-shell singlet in the transition state. When we run the IRC calculation from the transition state in triplet state, we obtain the different geometry from the original ground state. From these results, we found that the DNA scission reaction by Co-BLM can occur in the triplet state and that there exist two triplet states as the excited state of Co-BLM. To obtain the whole image of photo-excited states of Co-BLM, we computed singlet and triplet excited states by using TD-DFT. Figure A-1 shows the results of computed UV-Vis spectrum of Co-BLM. This UV-Vis spectrum agrees well with the experimental data. When the excitation energy is small, the electronic state changes from the closed-shell singlet to the lowest excited triplet (T_1) state via S_9 state which corresponds to the small peak found in UV-Vis spectrum. After reaching T_1-opt geometry, this reaction occurs thermally through the cross point. From the result of potential energy surface, it is found that 22.1 kcal/mol more energy is needed to pass the cross point from the T_1-opt geometry.



Scheme A-1: Two models used in this study. (a) large model which contains a peptide part and DNA backbone. (b) small model which removes the peptide and DNA backbone

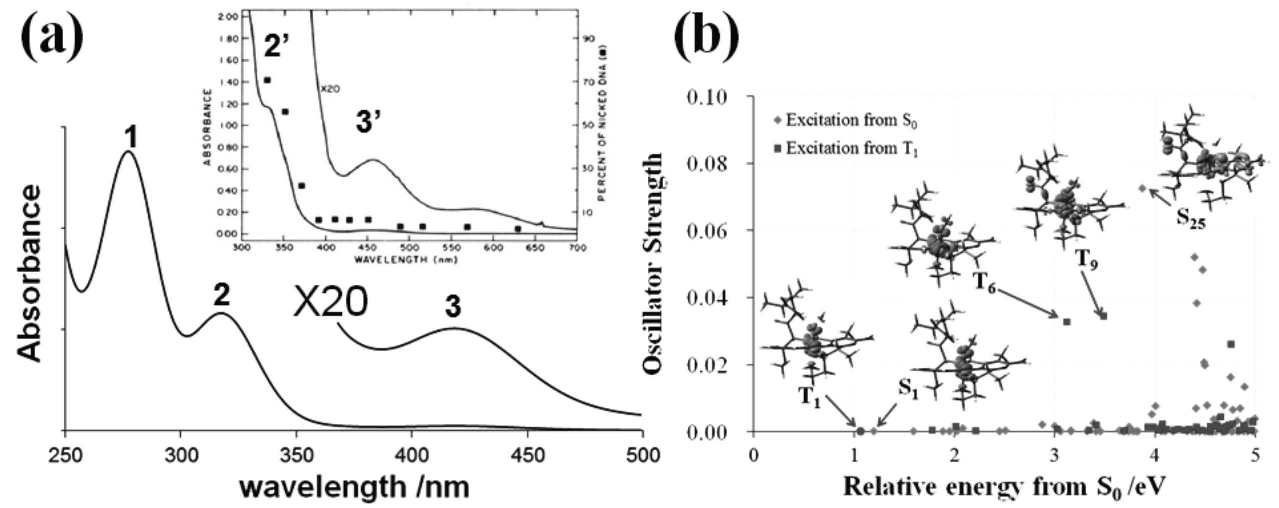


Figure A-1: (a) Computed (left) and observed UV-Vis spectra (right, *Taken from Chang and Meares, Biochemistry, 1984, 23, 2268, Figure 5.*) (b) Scatter plot of relative energy (in eV) from S_0 state and the subtracted electron densities of important excited state from S_0 state.

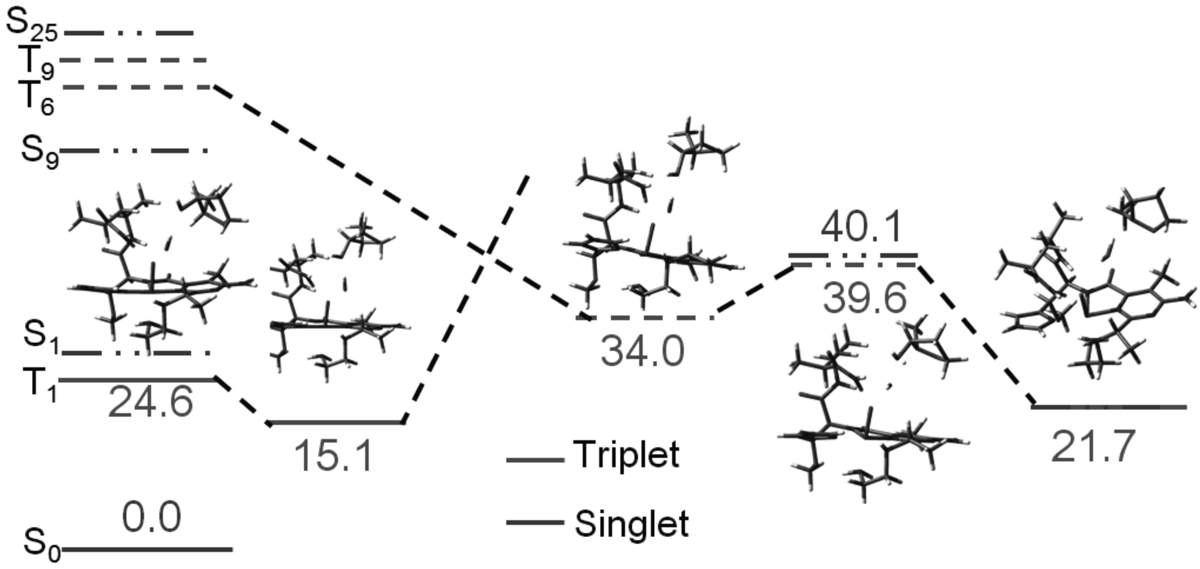


Figure A-2: Summary for the photo-induced reaction in Co(III)-BLM.

When the excitation energy is large enough, the electronic state changes to the T_r state via triplet states T_9, T_6 and singlet state S_{25} corresponding to the peak in UV-Vis spectrum. This excitation energy is so large that the reaction could occur spontaneously. The whole reaction diagram is shown in Figure A-2.

The difference of reactivity in DNA scission reaction between Fe-BLM and Co-BLM can be understood by using small model. When we devide the bond scission energy into several terms, it is found that the bond energy of metal-ooxygen bond mainly contributes to the difference.

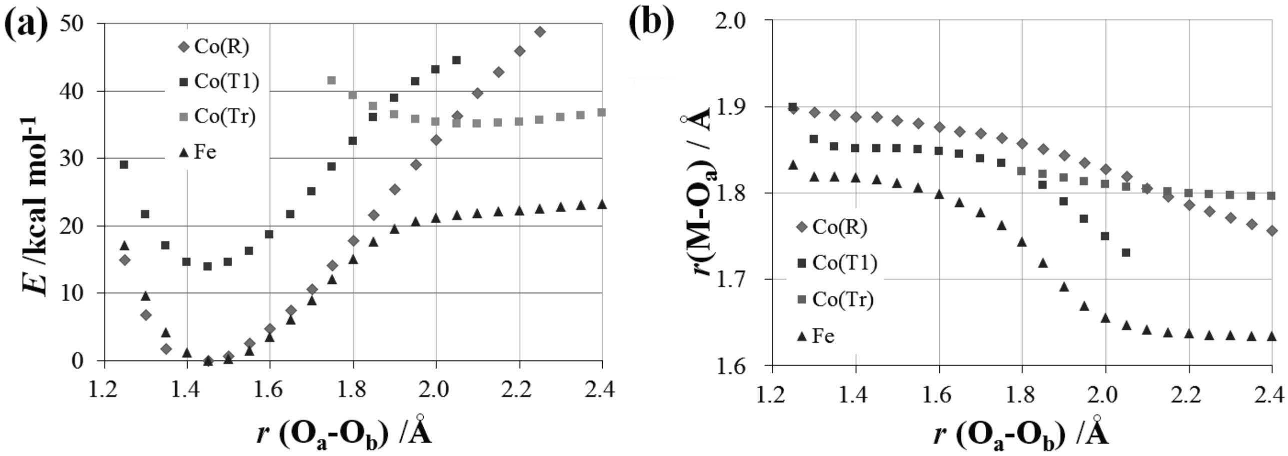


Figure A-3: (a) Potential energy surface for O-O in each metal. Co(T) has two local minima and a cross point between two electronic states. (b) The distance between metal and O atom in each optimized geometry in small model.

Next, we focused on the O-OH bond in HOO-M(III)-BLM with the 1D-potential energy surfaces for the bond length r(O_a—O_b). We draw the 1D- potential energy surface as shown in Figure A-3a. When O-O bond is 1.80 Å, the T_1 state is 5 kcal/mol more stable than T_r, whereas T_r is 4 kcal/mol more stable in O-O bond is 1.90 Å. Therefore, there exists a cross point between T_1 and T_r state around O-O: 1.80-1.90 Å. Within the single reference calculation, we cannot obtain the relative energy of cross point. After the cross point, we can obtain a local minimum of HOO-Co(III)-BLM (minimum of T_r state).

Figure A-3b shows the change of the distance between the metal and O_a atom. The distance between Fe and O_a decreases as the value $r(O_a—O_b)$ becomes larger, whereas the distance between Co and O_a does not strongly depend on the value $r(O_a—O_b)$.

The difference in metal-oxygen bond energy can be explained by the difference in occupation number of d-electron. Fe-OOH species can use the energy from d-π bond to decrease the energy for O-O cleavage. On the other hand, Co-OOH species cannot take the advantage and needs much more energy for the dissociation.

(B) A Consistent Scheme for Computing Standard Hydrogen Electrode and Redox Potentials

The standard hydrogen electrode (SHE) potential in aqueous solution was evaluated with new computational procedure which provides the Gibbs energy of a proton in aqueous solution from the experimental pK_a value and the Gibbs energy change by deprotonation reactions of several neutral alcohol molecules as shown in Figure B-1. Table B-1 lists the Gibbs energy of a proton and SHE potential obtained by our new computational schemes. The most reliable Gibbs energy of a proton is measured by Tissander et al. When we employ *ab initio* calculation method such as HF and post-HF calculations, the computed energy almost reproduces this value, whereas DFT tends to underestimate the $G(H^+, aq)$ by 4-7 kcal/mol.

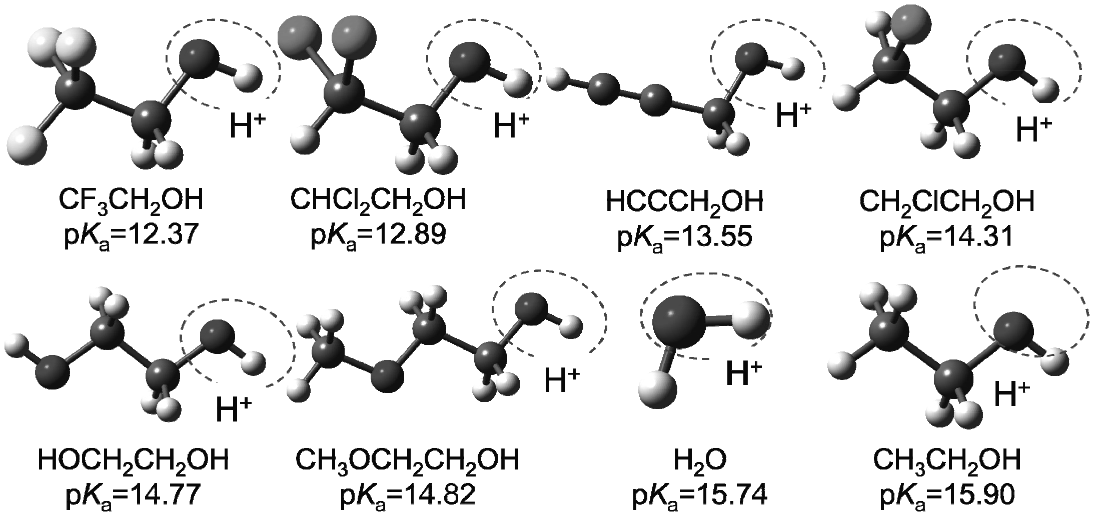


Figure B-1: The reference molecule and its observed pK_a.

Table B-1: Computed Gibbs energy of H$_2$(gas), Gibbs energy of proton and SHE potential in each computational method.

	H$_2$(gas)/ a.u.	H$^+$(aq)/a.u.	SHE / V
B3LYP/6-31G*	-1.176 831	-0.407 78^{b}	4.88
B3LYP/6-31+G*	-1.176 929	-0.404 371	4.99
B3LYP	-1.180 489	-0.413 945	4.80
BHandHLYP^{c}	-1.170 182	-0.417 645	4.54
BLYP	-1.170 171	-0.404 263	4.87
LC-BLY^{c}	-1.159 827	-0.415 463	4.44
M06	-1.171 108	-0.402 285	5.00
HF/CBS	-1.134 578	-0.427 640	3.80
MP2/CBS	-1.168 626	-0.422 656	4.40
MP3	-1.175 017	-0.422 550	4.49
MP4(DQ)	-1.176 600	-0.426 358	4.41
MP4(SDQ)	-1.176 646	-0.425 964	4.42
CCSD	-1.177 276	-0.424 967	4.45
CCSD(T)^{d}	-1.177 276	-0.422 578	4.52
G3MP2	-1.181 772	-0.423 967	4.54
G3	-1.178 832	-0.422 997	4.53
G3B3	-1.179 145	-0.423 041	4.53
Exp.		-0.423 739^{e}	4.44

When we employ MP3, and MP4(DQ), G(H$^+$, aq) are somewhat overestimated. The basis set effect on the Gibbs energy of a proton first examined at the B3LYP level. As shown in Table B-1, the inclusion of diffuse function such as 6-31+G* considerably changes the Gibbs energy. Because the Gibbs energy moderately changes when going to 6-31++G** from 6-31+G*, we employed 6-31++G** hereafter. Most of DFT methods overestimate the SHE potential. The overestimation in DFT calculation comes from the underestimation of energy of G(H+, aq) as discussed in the previous section. This overestimation corresponds to the 0.17-0.30 V compared with previously reported theoretical values. As the ratio of HF exchange increases in the hybrid functional, the computed SHE potential becomes closer to the experimental value; see B3LYP, BHandHLYP, and BLYP calculations in Table B-1. The importance of HF exchange is also seen in LC-BLYP-calculated values which better agrees with the experimental value than BLYP-calculated value. The HF/CBS method considerably underestimates the SHE potential as shown in Table B-1. Judging from the result that the HF-calculated Gibbs energy of a proton is almost the same as that calculated by the other method, the error arises from the energy of H_2 in gas phase. It is likely that the lack of the correlation energy in the HF method is a plausible reason. Most of post-HF methods reproduce the experimental SHE potential. CCSD(T)-calculated SHE potential slightly overestimates the IUPAC value of 4.44 V. G3, G3MP2, and G3B3 methods also provide a moderately different SHE potential from the other post-HF methods.

This scheme also reproduces well the redox potential of several typical reactions within almost 0.1 V. B3LYP also gives excellent redox potential of the same reaction with almost the same accuracy with our new computational scheme. This computational scheme will be applicable to compute many redox potentials.

2. Original papers

(1) Toru MATSUI, Takeshi BABA, Katsumasa KAMIYA, Yasuteru SHIGETA
"'An accurate density functional theory based estimation of pK_a value of polar residues combined with experimental data: from amino acids to minimal proteins"
Physical Chemistry Chemical Physics,14, pp. 4181-4187 (2012).

(2) Toru MATSUI, Hideaki MIYACHI, Takeshi BABA, Yasuteru SHIGETA
A Theoretical Study on Reaction Scheme of Silver (I) Containing 5-Substituted Uracils Bridge Formation"
The Journal of Physical Chemistry A, 115, 8524-8531 (2011).

(3) Katsumasa KAMIYA, Toru MATSUI, Takashi SUGIMURA, and Yasuteru SHIGETA
"Theoretical Insight into Stereoselective Reaction Mechanisms of 2,4-Pentanediol-Tethered Ketene-Olefin [2+2] Cycloaddition"
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"Electron Conductivity in Modified Models of Artificial Metal-DNA Using Green's Function-Based Scattering Theory"
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(5) Takeshi BABA, Katsumasa KAMIYA, Toru MATSUI, Naoki SHIBATA, Yoshiki HIGUCHI, Tatsuya KOBAYASHI, Seiji NEGORO, Yasuteru SHIGETA
"Molecular dynamics studies on mutational structures of a nylon-6 byproduct-degrading enzyme"
Chemical Physics Letters, 507, 157-161 (2011).

3. List of review articles

(1) **T. Matsui**, H. Miyachi and Y. Shigeta "Theoretical Studies on metal-containing artificial DNA bases", Progress in Theoretical Chemistry and Physics, Springer, 22, pp. 434-460.

4. List of books

(1) T. Matsui, H. Miyachi, Y. Shigeta and K. Hirao (2012) "Metal-Assisted Proton Transfer in Guanine-Cytosine Pair: An Approach from Quantum Chemistry", in Some Applications of Quantum Mechanics, ISBN 978-953-51-0059-1, edited by Mohammad Reza Pahlavani , InTech, p. 167-188.

5. Presentation at academic conferences

(1) (Poster) **T. Matsui**, H. Miyachi and Y. Shigeta, “Electronic structure and UV absorption spectra of metal-mediate DNA: an approach from theoretical chemistry”, The Seventh Congress of the International Society for Theoretical Chemical Physics (ISTCP-VII), **4PP-68**, Tokyo September 2-8, 2011.

(2) (口頭) 松井 亨，馬場 剛史，安田 奈都美，神谷 克政，北河 康隆，重田 育照，奥村 光隆
"タンパク質内アミノ酸側鎖の酸解離定数の新規算出法と応用", 第5回分子科学総合討論会, **1B02**, 北海道大学，札幌市, 2011年 9月

(3) (口頭) 松井 亨，馬場 剛史，安田 奈都美，神谷 克政，北河 康隆，重田 育照，奥村 光隆
"官能基の類似性を利用した酸解離定数の新規算出法と応用", 第92回日本化学会春季年会, **3A4-48**, 慶應義塾大学，横浜市, 2012年 3月

Wilfredo Credo CHUNG

FIFC Fellow

(To 30 Sept. 2011)

1. Summary of research for the year

A Nonadiabatic Ab Initio Dynamics Study on Rhodopsin and its Analog Isorhodopsin: Chemical Dynamics Reasons Behind Selection of Rhodopsin by Life

Rhodopsin (Rh) has 11-cis retinal as chromophore and is the photosensitive chemical found on the outer segment of rod-like cells in the retina, the light-sensing structure of the eye.[1] Isorhodopsin (isoRh) is an Rh analogue that contains 9-cis retinal embedded in the same opsin environment.[2, 3] Both are known to yield bathorhodopsin (bathoRh), a photoisomer that contains all-trans retinal, via cis-trans isomerization of the 11 or 9 position upon absorption of a photon. Despite their similarity, the photoisomerization period and quantum yield is largely different. Rhodopsin photoisomerization is experimentally known to be faster (t_{Rh} = 200 fs[4, 5], t_{isoRh} = 600 fs[6]) and more efficient (quantum yield: Φ_{Rh} = 0.65[7], Φ_{isoRh} = 0.22[8]).

We carried out a Quantum Mechanics/Molecular Mechanics (QM/MM) trajectory surface hopping (TSH) direct dynamics calculations in order to understand the origin of the discrepancy. Comparison is also made with our previous calculations[9, 10] The transition probability is estimated using the Zhu-Nakamura (ZN) theory[11] of nonadiabatic transitions. We call the present scheme the ZN-QM/MM-TSH scheme. The QM region is essentially a protonated Schiff base of retinal (see Figure 1 of reference 9 and Figure 2 of reference 10). The rest of the molecules were treated with MM using mechanical embedding. The QM treatment was the 6-electron-6-orbital complete active space self-consistent field (CASSCF) technique[12, 13] with the 6-31G basis set[14]. The MM part was described by AMBER parameters[15] in Gaussian 03[16]. 162 trajectories were calculated in total for both Rh and isoRh starting material at 300 K. Geometries of minima in the ground state and minimum energy conical intersections (MECI) are identified to analyze the dynamics results.

We have already shown[9, 10] that retinal molecule without opsin leads to rotations of ϕ_{11} and ϕ_9 rotates in a direction opposite to each other. Thus, the essential feature of isomerization motion after photo-excitation is intrinsic in retinal itself.

The experimental photoisomerization period and bathoRh quantum yield are reproduced reasonably (see Table 1). The slight discrepancy between the simulation and experiments are due to the failure of the chosen QM/MM treatment to reproduce a barrier[8, 17] in the excited state in isoRh reported in experiments. Even a tiny barrier would have slowed down the photoisomerization by trapping the trajectories in the excited state and yield a quantitatively accurate timescale and quantum yield.

Table 1. The ratio of photo products, quantum yield and photoisomerization period of rhodopsin in comparison with isorhodopsin. The values in square brackets are taken from the corresponding gas-phase PSB calculations[a].

		reactants	
		Rh(11-cis)	isoRh(9-cis)
photoproducts (%)	bathoRh(all-trans)	52 [27]	31 [13]
	isoRh(9-cis)	0 [22]	65 [82]
	Rh(11-cis)	48 [51]	0 [5]
	9,11-dicisRh	0 [0]	4 [0]
quantum yield	calc.	0.52	0.31
	expt.	0.65[7]	0.22[8]
photoisomerization period (fs)	calc.	187[185]	344[665]
	expt.	200[4, 5]	600[6]

[a] References 9 and 10.

Table 1 also shows that photoexcitation of Rh gives bathoRh (and the reactant) whereas the isoRh excitation yields a 9,11-dicis analog in addition to bathoRh (and the reactant). This byproduct formation in isoRh photoisomerization is another reason why life uses Rh rather than isoRh. Shown in Figure 1 are the plots of the time evolution of the active dihedral angles (=C_{10}-C_{11}=C_{12}-C_{13}= or ϕ_{11} and =C_8-C_9=C_{10}-C_{11}= or ϕ_9, respectively) for the (a) Rh and (b) isoRh trajectories. Clearly seen in Figure 1a is, for Rh, the lack of access of trajectories to a clockwise twist in ϕ_{11} in addition to rapid change in ϕ_{11} to -90°, where an MECI is located. Figure 1a shows that most of trajectories are in a similar and simultaneous way in the excited state, consistent with vibrational coherence revealed in an experiment on Rh[18] although the present treatment of the nuclei is classical except for transitions. In the case of isoRh (Figure 1b), a few trajectories are initiated by a clockwise twist of ϕ_9 in the excited state although the twist is unsuccessful and isoRh is regenerated in the ground state (S_0). Thus, all bathoRh photoproducts are formed via counterclockwise twist of the active dihedral ϕ_9 or ϕ_{11}. This obviously hindered isomerization is due to the constraints offered by the opsin environment especially by amino acid residues close to the binding pocket. In contrast, in our previous gas-phase PSB simulations, twists in both directions take place (cf. Figure 6, reference 10). The slower twist in isoRh is in the excited state. This is another consequence of the slower isoRh excited-state dynamics.

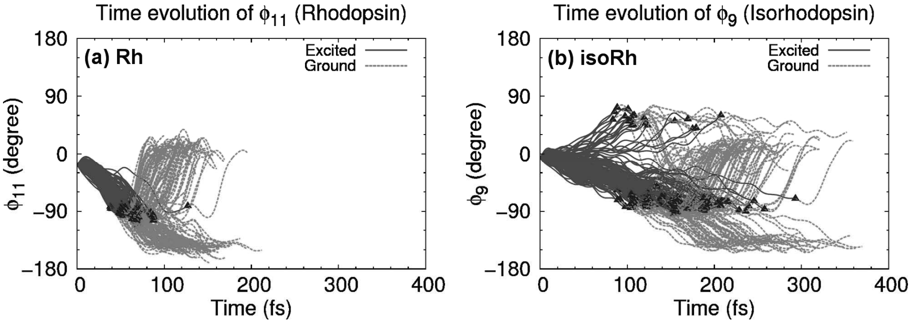

Figure 1. Time evolution of the dihedral angle of the twisting bond for the (a) Rh and (b) isoRh systems. Blue triangles are transition points from the excited state to the ground state.

Figure 2 shows the diagram of the active twist angle and the length of the active bond for five typical trajectories for Rh and isoRh. Fast and straightforward dynamics in Rh is shown in Figure 2a whereas complicated excited-state dynamics is evident in the isoRh case in Figure 2b.

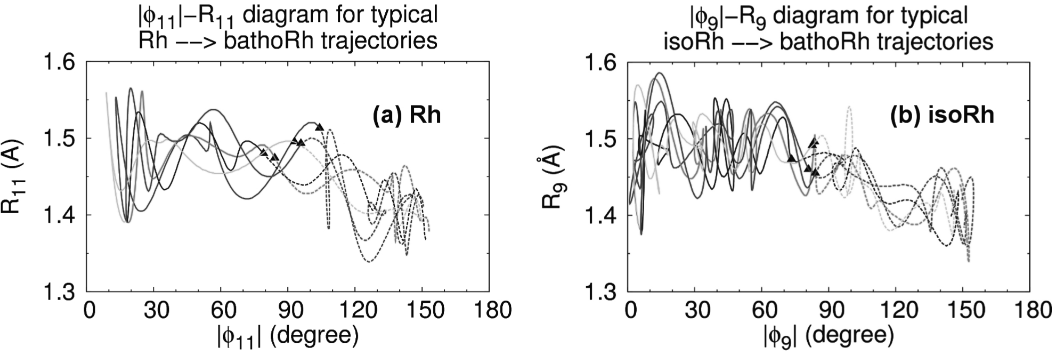

Figure 2. Change in length of the active bond -Cn-Cn+1- against the absolute value of the dihedral angle Cn-1-Cn-Cn+1-Cn+2 for typical (a) Rh (n = 11) and (b) isoRh (n = 9) trajectories leading to the all-trans form. The solid and dashed lines shows that trajectories are in the excited and ground states and the black triangles correspond to transition from the excitated state to the ground state.

Why is the isoRh photoisomerization more difficult compared to that of Rh? One reason is the atomic displacements required by the chromophore at the excited state potential energy surface to reach the conical intersection region. Shown in Figure 3 is a superimposed image of the S_0 optimized geometry and the geometry adapted by the chromophore at the crossing region. The pocket that contains the retinal chromophore is similar in shape for both the Rh and isoRh case. Opsin residues Thr118 and Tyr268 create a narrow gap near the -C_9=C_{10}-C_{11}= region of the retinal chain with the two residues coming as close as 7 Å to each other. The isoRh photoisomerization is more difficult compared to that of Rh because of at least two reasons: (1) the isoRh isomerization requires more space than that of Rh and (2) the dihedral that needs to be twisted in the isoRh case (-C_9=C_{10}-) is situated within the narrow gap between Thr118 and Tyr268.

Another reason is the initial acceleration of retinal atoms induced by surrounding residues. The initial force between two atoms for a few retinal-opsin atom pairs is listed in Table 2. Cys187, Thr118 and Tyr268 are close enough to the chromophore to significantly influence the isomerization. For example, for the atomic distance between the C_{12} hydrogen in retinal and the oxygen in Cys187, the projected inter-atomic force for Rh is about 15 times larger than the counterpart for isoRh. Also, a five-fold difference is found for the force between retinal C_{10} and Tyr268. Such differences partially explain the discrepancy in the speed and efficiency of the cis-trans isomerization between the Rh and isoRh chromophores.

Table 2. Initial interatomic forces between most relevant chromophore-opsin atom pairs

	Force (hartree-bohr^{-1})	
	Rh	isoRh
Ret C_{12}-H-Cys187 O	2.5×10^{-3}	1.7×10^{-4}
Ret C_{10}-Tyr268 CE2	2.2×10^{-3}	4.5×10^{-4}
Ret C_{11}-Thr118 N	1.8×10^{-3}	1.6×10^{-3}

CE2 = Tyr's second ε-carbon.

Comparison with the previous gas-phase simulations reveals three other consequences shown below.

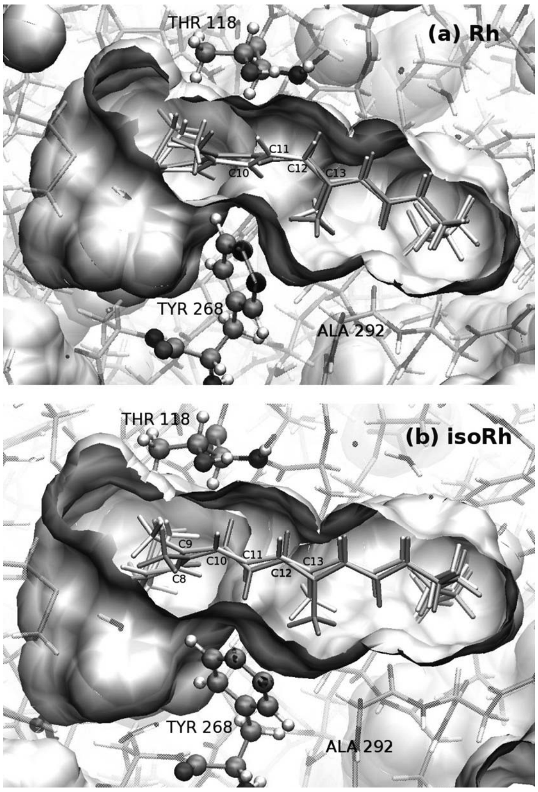

Figure 3. Superimposed structures of the S0 optimized geometry (gray) and geometry at the MECI (pink) for the (a) Rh and (b) isoRh case. Also shown is the opsin pocket that contains the chromophore. The pocket surface is the overlapped envelope of amino residues surrounding the retinal chromophore, which is generated using the S0 optimized geometry wherein the retinal chromophore is artificially removed.

The protein causes (almost) one-way twist of the active angle. In Figure 4, the values of the active dihedral angles ϕ_9 and ϕ_{11} at the time of hopping are plotted (compare with Figure 11, reference 9 and Figure 10, reference 10). All Rh trajectories go though only one MECI region with clockwise-twisted ϕ_9 and counterclockwise-twisted ϕ_{11} (Figure 4a). This MECI branches

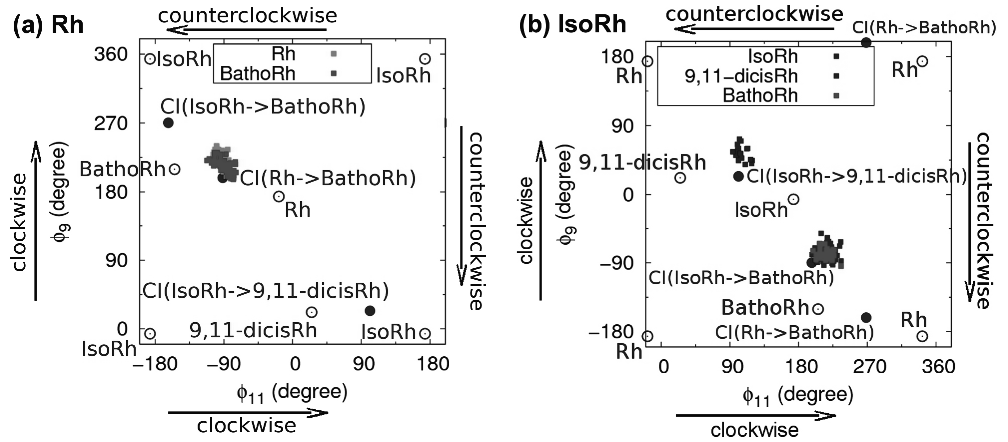

Figure 4. Diagram of the twist angles of -C_{11}=C_{12}- (ϕ_{11}) and -C_9=C_{10}- (ϕ_9) at the transition points. The minima in the ground state (open blue circles) and conical intersections (filled blue circles) obtained in the present calculations are plotted in the diagram. Rh = rhodopsin, isoRh = isorhodopsin, bathoRh = bathorhodopsin, 9,11-dicisRh = 9,11-dicis rhodopsin, CI=minimum energy conical intersection.

towards the formation of bathoRh and the regeneration of the reactant. The relaxation of the excited state of isoRh, on the other hand, goes through two MECI regions. Most of trajectories from isoRh go through the MECI region with ϕ_9 ~ -90° and clockwise-twisted ϕ_{11}, which is shown as CI(isoRh->BathoRh) in Figure 4b. This MECI is responsible for all of bathoRh generation. A few trajectories go through another MECI region (CI(isoRh->9,11-dicisRh)), which is responsible for the generation of a photoproduct with 9,11-dicis retinal as chromophore (we call this as 9,11-dicisRh hereafter). Thus, photoexcitation of Rh only gives bathoRh as a product whereas isoRh yields 9,11-dicisRh in addition to bathoRh, as shown in Table 1. Note that the reaction speeds through the two MECI in isoRh are significantly different. The reaction time is longer through CI(isoRh->BathoRh) (τ_{ave}=233 fs) than that through CI(isoRh->9,11-dicisRh) (τ_{ave}=188 fs). The difference is revealed in the dissimilarity in the twist speed of ϕ_9 in Figure 1(b).

Secondly, the protein environment enhances the production of bathoRh. When the opsin environment was totally ignored, the calculated bathoRh (all-trans PSB) quantum yield was only 0.27 and 0.13, respectively (in square brackets of Table 1). Explicit consideration of the opsin residues that envelop the chromophore significantly improves the theoretical quantum yield to 0.51 and 0.31, respectively. This is partly due to the unidirectional rotation in opsin environment.

The third effect of the opsin on the dynamics is to cause transitions to take place near MECIs. Comparison of transition points in Figure 4 with those in Figure 11 in reference 9 and Figure 10 in reference 10 reveals that the present transition points with the opsin environment are nearer the MECI points than the points without the opsin. In our previous opsin-free simulations, it was observed that inefficient, premature hops (excited-to-ground state hops that occur far from the MECI region) occur often especially in the isoRh case. The opsin environment enhances the dynamics by drastically reducing the probability of premature hopping, in particular in the isoRh case with transitions occurring near the MECI region. The protein may keep large energy gaps between the excited state and S_0 except for the MECI region.

In conclusion, the faster and more efficient photoisomerization of Rh than of isoRh is due to a straightforward and fast excited-state dynamics for Rh in contrast with a complicated dynamics in a back and forth fashion especially in the excited state for isoRh. The dynamics is governed by the differences (1) in volume-saving motions of retinal molecules, (2) in space gaps formed by surrounding residues, and (3) in the initial acceleration by repulsive force from the surrounding amino residues. The formation of 9,11-dicis Rh byproduct from isoRh photoisomerization is another reason why organisms adopt rhodopsin rather than isorhodopsin. The other effects of the opsin environment are (1) to cause the active dihedral angle in retinal to rotate one way, (2) to enhance the bathoRh quantum yield and (3) to cause transitions to take place near the MECIs. The present ZN-QM/MM-TSH scheme is found to be applicable to photoreactions of biomolecules.

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2. Original Papers

1. W. C. Chung, S. Nanbu and T. Ishida, QM/MM Trajectory Surface Hopping Approach to Photoisomerization of Rhodopsin and Isorhodopsin: The Origin of Faster and More Efficient Isomerization for Rhodopsin, J. Phys. Chem. B, 2012, 116 (28), 8009–8023.
2. W. C. Chung, S. Nanbu and T. Ishida, A Nonadiabatic Ab Initio Dynamics Study on Rhodopsin and Its Analog Isorhodopsin: Chemical Dynamics Reasons behind Selection of Rhodopsin by Life, Chemistry Letters 2011, 40, 1395-1397.
3. W. C. Chung and T. Ishida, An MD simulation of the decoy action of Epstein–Barr virus LMP1 protein mimicking the CD40 interaction with TRAF3, Theoretical Chemistry Accounts 2011, 130, 401-410.

3. Presentation at academic conferences

1. W. C. Chung, S. Nanbu and T. Ishida *Nonadiabatic ab initio dynamics of rhodopsin and isorhodopsin: a QM/MM trajectory surface hopping (TSH) approach based on the Zhu-Nakamura theory* 14th Asian Chemical Congress, Bangkok, Thailand, September 5 – 11, 2011 (Poster).
2. W. C. Chung, S. Nanbu and T. Ishida *Nonadiabatic ab initio dynamics of rhodopsin and isorhodopsin: a QM/MM trajectory surface hopping (TSH) approach based on the Zhu-Nakamura theory* 27th Symposium on Chemical Kinetics and Dynamics, June 8-10, 2011, Tokyo, Japan (Poster).

Takafumi IWAKI

FIFC Fellow

1. Summary of the research of the year

Confinement Effect of Folding Transition for Semiflexible and Flexible Polymer Chains

Living organism is constituted by lots of biopolymers, which are confined in a tiny cell. For example, DNA in vivo is usually confined in a nucleus of which size is extremely smaller than the contour length of DNA. Readout of gene information is done in such a narrow confinement. However, the effect of confinement to the structure and behavior of polymeric molecules has not been well understood.

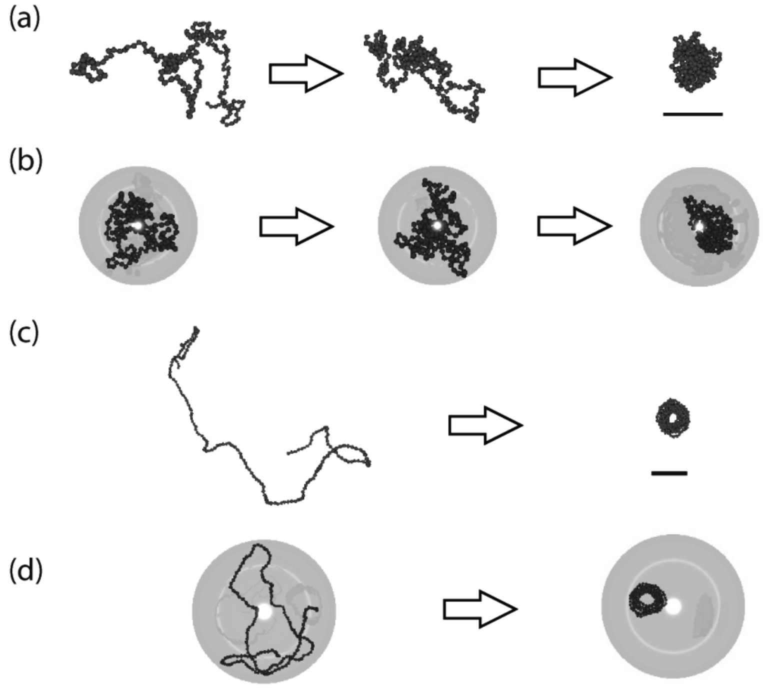

Figure 1: Snapshots of the folding transition of linear polymer chains. (a) A flexible polymer in a free solution. (b) A confined flexible polymer. (c) A semiflexible polymer in a free solution. (d) A confined semiflexible polymer.

To get insight into this problem, we performed a Langevin dynamics simulation of a simplified model polymer confined in a spherical cavity. In Fig. 1, typical snapshots of polymeric chain undergoing a folding transition under confined and free conditions are shown. It is known that folding transition of a flexible polymer is a continuous transition, and the folded structure is in a liquid-like or amorphous state. On the other hand, a semiflexible polymer undergoes a discontinuous transition, and the folded structure is in an ordered state. From the present simulation study, we found that the confinement effect shifts the transition point in the opposite direction between a flexible polymer and a semiflexible polymer. That is to say, for a flexible polymer, the confinement retards the transition, and, for a semiflexible polymer, it promotes the transition. This fact comes from the difference of an essential mechanism to determine the transition points between the two cases. For a flexible polymer, the transition occurs continuously so that the transition point is defined as compared with the ideal chain as a reference state. In this case, an excluded volume of an actual polymer is the origin of the retardation of the transition. For a semiflexible chain, the transition occurs abruptly with a great change of a volume of a chain expansion. In this case, conformational entropy of a swelling state is the reason of the promotion of the transition. We successfully explained this qualitative difference of the confinement effect by a simple scaling argument.

Study of DNA Double Strand Breaking Produced by Ionizing Radiations

DNA double-strand breaks (DSBs) represent a serious source of damage for all living things and thus there have been many quantitative studies of DSBs both in vivo and in vitro. Despite this fact, the processes that lead to their production have not yet been clearly understood, and there is no established theory that can account for the statistics of their production, in particular, the number of DSBs per base pair per unit Gy, here denoted by P1, which is the most important parameter for evaluating the degree of risk posed by DSBs. Using the single-molecule observation method with giant DNA molecules (166 kbp), we evaluate the number of DSBs caused by γ-ray irradiation. We found that, in the dependence of P1 to the DNA concentration, there are two characteristic regions. In a low DNA concentration region, P1 is nearly constant to the DNA concentration. On the other hand, P1 is nearly inversely proportional to the DNA concentration above a certain threshold DNA concentration. We calculate the probability to occur double strand breaking on the basis of a simple model, which well accounts for the marked profile of P1 over all measured region. Based on this argument, we show that it is necessary to consider the characteristics of giant DNA molecules as semiflexible polymers to interpret the intrinsic mechanism of DSBs. This work is now submitted to a scientific journal.

Numerical Fluid Dynamics Study of a Heated Oil Droplet on Air-Water Interface

A centimeter-sized droplet of liquid paraffin on water can be accelerated by a laser irradiation. In this scale of experiments, the origin of the migration force is attributable to the Marangoni effect: a surface force arising from a local difference of surface tensions. For example, as shown in Fig. 2, irradiation of the laser induces flows outside and inside the droplet by thermal Marangoni effect, which in turn influences a temperature distribution of the heated droplet. In actual experiments, we found that the presence/absence of surfactant (SDS) changes the migration direction to the opposite side. Since this system has a low symmetry, we performed a CFD simulation to analyze an essential mechanism of this change

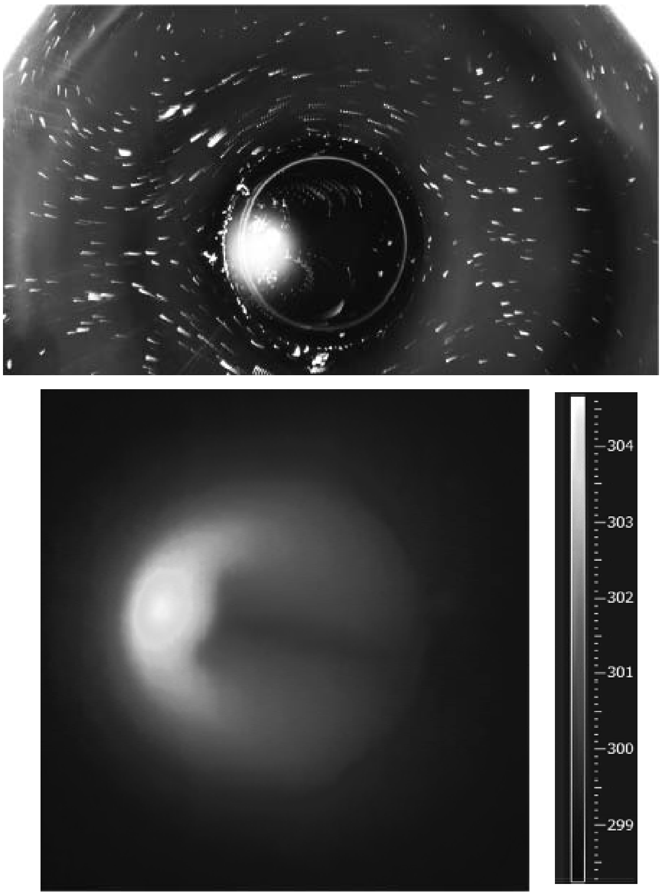

Figure 2: Flow pattern and temperature distribution of a paraffin droplet on pure water heated by a laser irradiation.

in the acceleration direction.

Here, we performed a numerical simulation of thermal fluid on an irregular lattice with a finite volume method. Several causes were assumed for the above-mentioned effect of SDS. For example, the difference in the shape of the droplet might have induced a different flow mode inside the droplet. Nonlinear effect of the hydrodynamics might have promoted the appearance of the different modes in similar experimental systems. These expectations were, however, denied by a sequence of simulations. We found that the migration direction changes due to the temperature coefficients of surface tensions changed by the presence/absence of SDS. The Marangoni effect on an oil droplet on an air-water interface caused by local heating induces two types of actions on the droplet. One is the viscous friction force from an external flow induced by caterpillar-like action of the droplet surface. This force always accelerates the droplet to approach a heating spot. The other is the Young force arising from a dynamical breaking of a surface tension balance in a periphery of the droplet. This force is determined by the weight of the temperature coefficient of surface tension in each of interfaces. When the magnitude relation of the temperature coefficients between air-water interface and oil surfaces reverses, the Young force changes its direction.

Thus, we simulated a thermal flow for two typical sets of temperature coefficients of surface tensions. Consequently, we obtained flow patterns and temperature distributions very similar to experimentally obtained ones in the presence/absence of SDS, respectively, which rationalize that the above-mentioned mechanism is applicable to the interpretation of the experimentally observed effect of SDS. This work is now submitted to a scientific journal.

Study of the Dynamical Mechanism of the Self-Organization of the Tooth Germ

In the development process of the tooth germ, the enamel knot is formed simultaneously with the epithelial invagination. The epithelial invagination is considered as the buckling of the growing surface layer of the tooth germ. However, the mechanism of the formation of the enamel knot is not understood well in terms of both physics and molecular biology. In order to solve this problem from the perspective of physics, we performed Brownian dynamics simulations of a coarse-grained toy model of cell population. In the simulations, we found that according to the proliferation rates of the surface layer and the interior of the dental epithelial, the buckling formation undergoes several courses. In particular, when the proliferation rate of the surface layer is considerably larger than that of the interior, the bending is not uniform, and the plural buds are formed similarly to the actual development process. This fact suggests that the formation of the enamel knot is governed by a rather simple mechanical process. To get a further insight, we calculate the “free energy of time course” of the buckling process of elastic continuous segment for the several given paths, and found that the shrinking speed of the end-to-end distance determines the favored type of buckling. In fact, when this speed is faster, buckling along with a growth of plural peaks is more favored. This well corresponds to the simulation result and also the actual development process. We are now writing the manuscript of these results, which is to be submitted to a scientific journal.

2. Original papers

(1) S. N. Watanabe, T. Iwaki, M. I. Kohira, N. Magome, and K. Yoshikawa,
“Negative photophoresis of smoke particles observed under microgravity”
Chem. Phys. Lett. 511, 447-451(2011).

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“Stiffness causes opposite trend on the folding transition of a single polymer chain in a confined space”
Physical Review E, 84, 021924 (5 pages) (2011).

3. Presentation at academic conferences

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4. Others

(1) ““細胞の自己組織化”に物理の視点から迫る” (“Physical approach toward a “self-organization of a biological cell””), Kenichi Yoshikawa and Takafumi Iwaki, パリティ (parity), vol. 26, No. 05, pp. 13-21 (issued on Apr. 25, 2011)

Natsuhiko YOSHINAGA

FIFC Fellow

(To 15 Dec. 2011)

Assitant Professor, WPI-AIMR, Tohoku University

1. Summary of the research of the year

Spontaneous motion of a droplet coupled with a chemical wave

Spatiotemporal patterns are widely seen in living systems; target, spiral, stripe, and dot patterns have been observed at various scales from the interior of a cell to a swarm of cells. Most of studies have focused on patterns at larger scales, which can be successfully reproduced using reaction diffusion dynamics. In contrast, it is only recently that internal patterns in a single cell have been visualized. These patterns are expected to relate to cellular functions; examples include calcium ions for signal transduction, Min proteins for cell division, and actin cytoskeltons for mechanical properties. Although pattern formation in a cell is expected to be analyzed in the framework of a reaction-diffusion system, as demonstrated in in vitro experiments, sufficient understanding of the connection between pattern formation and cellular function is lacking. In this paper we focus motility, as a typical aspect of cellular functions, arising from internal patterns. Several artificial systems imitating cell motility have been proposed as self-propelled particles. Although no external force is exerted on the particles (a force-free condition), the motion is induced by the asymmetric distribution of an electric field, concentration of chemicals, temperature, and so on. These asymmetric distributions are either a priori embedded in the asymmetry of the surface properties of the self-propelled objects or a posteriori created by nonlinear effects; motion itself destabilizes a symmetric distribution, for instance, through advective flow. In both cases, however, most studies have focused on motion under steady distributions.

In order to understand the dynamic features of cell motility, a system connecting the dynamic pattern with motion is desirable. In fact, experimental and numerical evidence of chemo-mechanical coupling in such systems has been demonstrated. In this work we propose a theoretical framework for a chemical system exhibiting self-organized patterns, leading to spontaneous motion. We consider that the Marangoni effect is suitable for this purpose as it has been shown to drive an object under force-free conditions by an inhomogeneous interfacial tension arising from a gradient in the chemical concentration. In our system, the energy supply and consumption can generate a pattern in a droplet through nonlinear chemical kinetics and the pattern at the interface of the droplet creates inhomogeneous interfacial tension. This generates a flow surrounding the droplet, resulting in motion.

Rigidity Sensing Explained by Active Matter Theory

Living cells respond to mechanical as well as biochemical cues. Rigidity sensing designates the web of complex mechanisms whereby a cell will adapt, as a function of the elastic modulus of its environment, diverse aspects of its phenotype, including motility, gene expression, proliferation, and fate after differentiation. The traction forces that a cell exerts on a flat, elastic plate depend in a nontrivial way on the extracellular stiffness, being roughly proportional to the elastic modulus in a softer environment and saturating to a finite value for stiffer substrates. Similar force-rigidity data are obtained whether forces are measured locally or globally for both integrin-mediated and cadherin-mediated adhesion, and even when the traction forces are exerted by assemblies of cells in a monolayer epithelium. Single-cell rheology assays show that cells respond to sudden changes in substrate rigidity too rapidly to be detected at the data acquisition rate. These observations call for a simple, generic explanation that is valid for short timescales where cell signaling cannot operate.

It is found that the magnitude of traction forces exerted by living animal cells on their environment is a monotonically increasing and approximately sigmoidal function of the stiffness of the external medium. We rationalize this observation using active matter theory, and propose that adaptation to substrate rigidity results from an interplay between passive elasticity and active contractility.

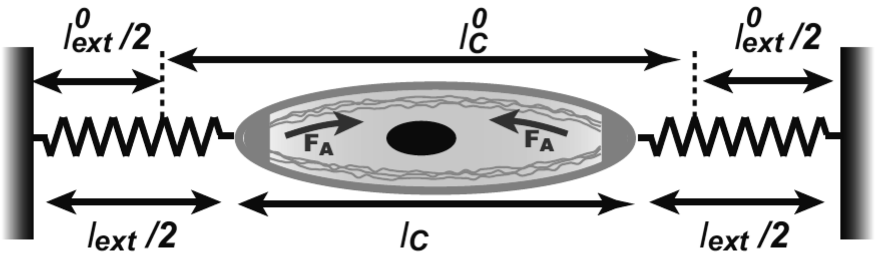

Fig. 1: Schematic representation of the model

Self-propelled motion of a fluid droplet under chemical reaction

Self-propelled motion of particles has attracted much attention recently from the viewpoint of nonlinear physics far from equilibrium. There are several experiments of self-propulsion of droplets in fluids. It has been shown that the Belousov-Zhabotinsky reaction composed in a fluid droplet triggers a spontaneous motion of a droplet. Computer simulations of convective droplet motion and nano-dimer motors driven by chemical reactions have also been carried out. There are theoretical studies of droplet motion due to an interfacial tension gradient along the droplet surface. However, these theories are concerned only with the steady velocity of a droplet. As a related theoretical study, the mesoscopic description of the thermo-capillary effect has been formulated. A transition between a motionless and migrating droplet driven by chemical reactions has been studied in a system where a droplet is on a solid substrate.

We study self-propelled dynamics of a droplet due to a Marangoni effect and chemical reactions in a binary fluid with a dilute third component of chemical product which affects the interfacial energy of a droplet. The equation for the migration velocity of the center of mass of a droplet is derived in the limit of an infinitesimally thin interface. We found that there is a bifurcation from a motionless state to a propagating state of droplet by changing the strength of the Marangoni effect.

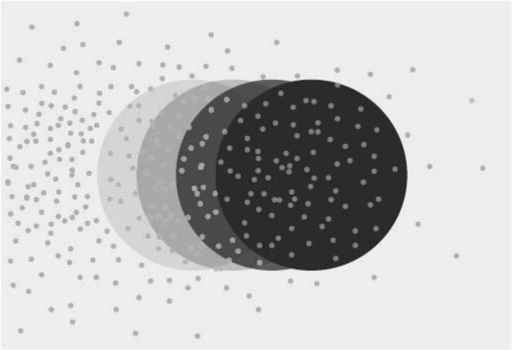

Fig. 2: Translational motion of a droplet. The droplet is migrating to the right under the non-uniform distribution of the c component indicated by the small dots.

2. Original papers

(1) Shunsuke Yabunaka, Takao Ohta, and Natsuhiko Yoshinaga
“Self-propelled motion of a fluid droplet under chemical reaction”
J. Chem. Phys. 136, 074904 (2012).

(2) Hiroyuki Kitahata, Natsuhiko Yoshinaga, Ken H. Nagai, and Yutaka Sumino
" Spontaneous motion of a droplet coupled with a chemical wave""
Phys. Rev. E. Rapid Communications 84, 015101 (2011).
selected by PRE Kaleidoscope Images: July 2011

(3) Philippe Marcq, Natsuhiko Yoshinaga, and Jacques Prost
“Rigidity sensing explained by active matter theory”
Biophys. J. 101, L33-L35 (2011).

3. Presentation at academic conferences

(1) Natsuhiko Yoshinaga, Ken Nagai, and Yutaka Sumino, and Hiroyuki Kitahata
“Self-propulsion of a drop driven by Marangoni flow”
Regional Bio-Soft Matter Workshop: Non-equilibrium statistical Physics in Bio-Soft Systems, Taipei, Taiwan, (27-29 Oct., 2011)

(2) Natsuhiko Yoshinaga, Ken Nagai, and Yutaka Sumino, and Hiroyuki Kitahata
“Self-propulsion of a drop driven by Marangoni flow”
Workshop: Collective Dynamics and Pattern Formation in Active Matter Systems, Dresden, Germany, (29 Aug. - 16 Sep., 2011)

(3) Natsuhiko Yoshinaga, Jean-Francois Joanny, Jacques Prost, and Philippe Marcq
“Polarity Patterns of Stress Fiber ”
7th International Conference on Biological Physics 2011, UCSB, USA, (22-24 June, 2011)

4. Others

嶺澤　範行

センターフェロー
（平成 23 年 10 月 1 日から）

1. 今年度の研究の要約

今年度は時間依存密度汎関数理論を用いて、光化学反応において重要な役割を果たしている円錐交差の解析を行った。

【始めに】

円錐交差は、電子励起状態からの非常に速い無輻射遷移を説明する非常に重要な機構である。電子状態計算による円錐交差の解析には、静的および動的な電子相関をバランスよく記述する手法が要求される。円錐交差の領域では複数のポテンシャルエネルギー面が縮退しているため、様々な電子配置(静的電子相関)を考慮する必要がある。また動的電子相関の有無により、円錐交差の近傍における分子の構造やポテンシャルエネルギー面の形状は定性的に異なる。動的電子相関の寄与は電子状態によって異なるため、円錐交差の探索過程でこの効果を無視するわけにはいかない。動的電子相関の取り扱いに優れた方法として、線形応答に基づく時間依存密度汎関数(LR-TDDFT) 法が知られている。しかし LR-TDDFT 法では、単純なエチレン分子でさえ正しい円錐交差の構造を与えることが出来ない[1]。これは、静的電子相関の取り扱いが不十分であるためである。スピン反転励起に基づく LR-TDDFT (SFDFT) 法[2]は、部分的にではあるが静的電子相関を取り入れることができる。SFDFT 法を用いることでエチレンの円錐交差が正しく記述できることを、私は過去に報告した[3]。得られた計算結果は、波動関数に基づく高精度の *ab initio* 計算を非常によく再現した。これは、円錐交差を解析する手段として LR-TDDFT 法の可能性を示している。

【スチルベン分子の光化学】

SFDFT 法は、波動関数に基づく計算に比べて計算コストが小さく、電子相関もあらわに考慮されている。その特性を生かし、スチルベン分子の計算に適用し、励起状態のポテンシャル面を解析した。スチルベンは、エチレンの水素原子をベンゼン環で置き換えた化合物であり、過去のエチレンの研究の自然な拡張である。また、スチルベンの光異性化の反応機構を理解することは、光駆動分子モーターやフォトクロミック材料など、材料科学の分野における分子設計で重要な知見を与える。

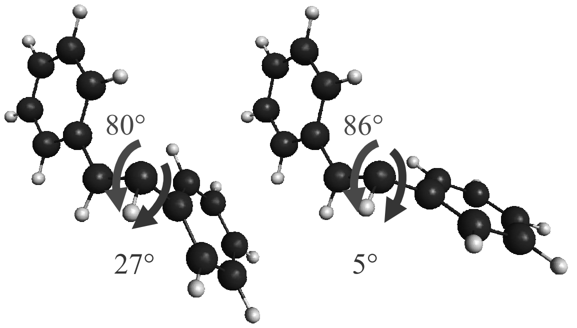

図１ ねじれたスチルベン分子の構造: 円錐交差(左)、エネルギー極小点(右)

図１に示したのは、ねじれたスチルベンにおける円錐交差およびエネルギー極小点の構造である。２つの構造の主な違いは、ベンゼン環の回転によるものである。円錐交差の構造は、エチレンのそれと非常によく似ており、スチルベンの二重結合もエチレンのそれで定性的に理解できることがわかる。一方、エチレンと異なり、エネルギー極小点が存在することを示した。エチレンでは、円錐交差が同時に励起状態のポテンシャル面のエネルギー最小点になる。最近の実験結果[4,5]によると、ねじれたスチルベンにおいて、この極小点の存在(phantom state)が示唆されており、本研究における計算結果は、それを支持するものである。

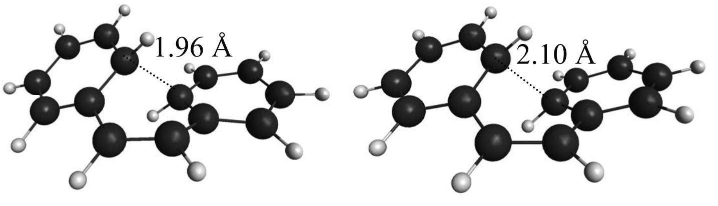

図２ シス - スチルベンの構造: 円錐構造(左)、DHP(右)

また、本研究ではもう一つ別の円錐交差の構造を指摘した(図２)。スチルベンの光化学反応では、シス - トランス異性化のほかに環化した生成物(DHP)を得る。今回明らかにした円錐交差の構造はDHPに似ており、環化反応のメカニズムに関与していることが推定される。

これらをふまえ、基底状態および励起状態のポテンシャル面において重要な構造を同定し、まとめたものが図３である。トランス体は光励起された後、反応障壁を超えてねじれた構造をとる。そこから、円錐交差から基底状態へ戻るあるいは励起状態でシス体を生成する。一方シス体の場合、ねじれた構造の円錐交差を経て基底状態、あるいはもう一つの円錐交差から DHP を生成する２つの経路が考えられる。将来的には、非断熱分子動力学を用いて、シス - トランス光異性化および環化反応のメカニズムを明らかにしたいと考えている。

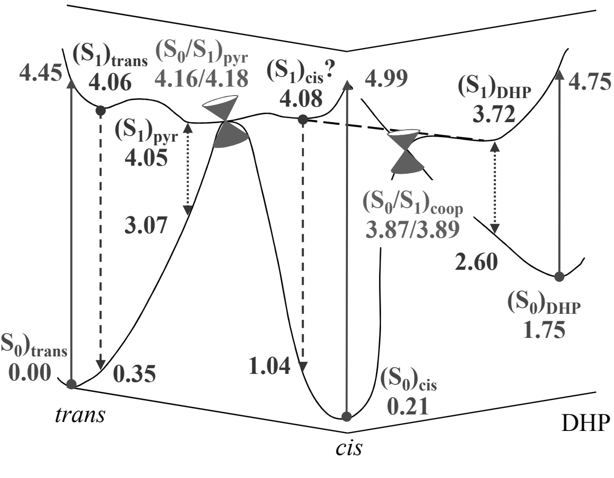

図３ スチルベン分子のポテンシャル面のまとめ (単位: eV)

【溶媒効果を考慮した円錐交差の記述】

溶液内分子の電子励起状態を理解するためには、量子力学に基づく溶質分子の記述と溶質 - 溶媒間の相互作用の表現を両立させる必要がある。しかし、実験で取り扱われている分子はサイズが大きく、従来の波動関数に基づく計算手法では計算コストが莫大なものになる。私は、LR-TDDFT 法とプログラムパッケージGAMESSに実装されている電子分極を考慮した溶媒モデル(EFP)を組み合わせ、その解析的エネルギー微分を導入した[6]。これは，励起状態における分子動力学シミュレーションを低コストで実現し、動的過程を解析する手法として重要な寄与である。

この方法を拡張し、上で述べたように円錐交差の解析に優れた SFDFT 法に適用した。そして、SFDFT/EFP 法の解析的エネルギー微分を実装した。同時に、円錐交差の探索プログラムを導入し、溶液内分子の円錐交差を記述できるようにした。開発した方法を緑色蛍光タンパク質(GFP)の発色団 (HBI)に適用した。GFP の発色団は、水溶液中で蛍光が著しく減少することが知られている。これは、円錐交差を介した速い緩和過程が存在するためであるといわれている。

図４に示したのは、緑色蛍光タンパク質(GFP)の発色団の水和クラスターにおける円錐交差の構造の一例である。溶液内では、C=C 周りのねじれ角が 104 度から 90 度に減少し、C=C の imidazolinone 環に対する面外角が 30 度からほぼ 0 度の平面となった。

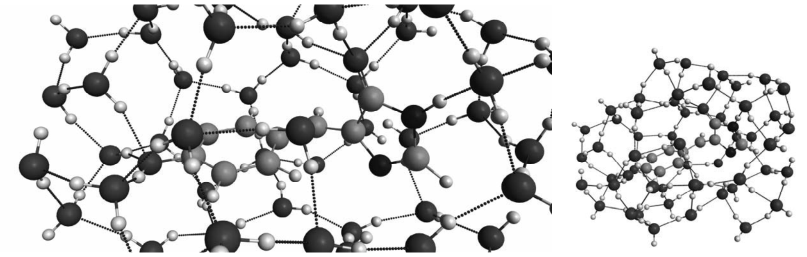

図４　GFP 発色団の水和クラスターの円錐交差

溶媒効果により、ポテンシャルエネルギー面も、定性的に異なる描像となった。表１に示したように、溶媒和クラスターではππ*状態の極小点が存在せず、直接、円錐交差にいたる反応経路であることが示唆される。これは、GFP 水溶液では蛍光が抑制され、非常に速い緩和を起こすことと対応している。

Geometry	State	Gas	+1 water	+1 water +50 EFP
S_0	S_0	0.00	0.00	0.00
	ππ*	3.94	3.85	3.88
$(\pi\pi^*)_{twi}$	S_0	2.46	2.49	N/A
	ππ*	2.89	2.71	N/A
$(S_0/\pi\pi^*)_{CI}$		3.022	2.744	2.128
		3.022	2.744	2.128

表１　GFP 発色団のエネルギー (単位: eV)

本研究では、ポテンシャルエネルギー面に基づく解析を行った。すなわち、限られた数の溶媒和構造を発生させ、それを初期条件として円錐交差などの構造を求めた。しかし、溶液系では溶媒分子の自由度が非常に大きいため、自由エネルギーに基づいた議論のほうが便利である。例えば、

QM/MM 法や積分方程式による円錐交差の記述法[7,8]が提案されている。これらを SFDFT 法と組み合わせることで、溶液内における円錐交差の議論が行うことが可能になると期待している。

【文献】

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2. 論文

(1) N. Minezawa and M. S. Gordon, “Photoisomerization of stilbene: A spin-flip density functional theory approach”, J. Phys. Chem. A **115**, 7901-7911 (2011).

(2) A. Defusco, N. Minezawa, L. V. Slipchenko, F. Zahariev, and M. S. Gordon, “Modeling solvent effects on electronic excited states”, J. Phys. Chem. Lett. **2**, 2184-2192 (2011).

(3) N. Minezawa and M. S. Gordon, “Optimizing conical intersections of solvated molecules: The combined spin-flip density functional theory/effective fragment potential method”, J. Chem. Phys., *accepted*.

3. その他

(1) 嶺澤 範行
「SFDFT法による緑色蛍光タンパク質発色団のポテンシャル面の理論的研究」
第９回京都大学福井謙一記念研究センターシンポジウム　京都　2012/01/06

(2) 嶺澤 範行
「時間依存密度汎関数理論による非断熱過程の解析」
化学反応のポテンシャル曲面とダイナミックス　京都（京都大学）　2012/03/30

Kunkun GUO

FIFC Fellow

(From 1 Mar. 2012)

1. Summary of the research of the year

Vesicle shapes encapsulated by two aqueous phase systems

Liquid ordered domains enriched in sphingolipids and cholesterol, known as lipid rafts, have received widespread attention from the cell biology and membrane biophysics during the last decade because they are believed to play a key role in several important cellular functions, including membrane sorting and trafficking, signal transduction, and cell polarization.

The interior of living cells is crowded with macromolecules and organelles. The weight fractions of proteins, RNAs, and polysaccharides in the interior of living cells are on the order of 20-30 %. In such a concentrated environment, local phase separation may occur, involving local composition differences and microcompartments, e.g. cell functioning and the performance of cytoplasmic proteins. As a simplistic model of the cytoplasmic medium, the solutions of the water-soluble macromolecules polyethylene glycol (PEG) and dextran would undergo phase separation with the concentrations of the polymers increasing. Dynamic microcompartmentation of macromolecules between the enclosed phases are found to resemble similar partitioning behavior as proposed in cytoplasm of living cells. Interesting phenomena associated with the phase separation processes, such as wetting transition, vesicle budding, fission of vesicles, and the formation of membrane nanotubes, are observed in the recent experiments.

Here, we theoretically consider such a system that a vesicle membrane which is consisted of two components is encapsulated by aqueous two-phase polymer, see Fig. 1. The system is assumed to be homogeneous with the same density ρ_0. The two components of the vesicle are assumed to be locally incompressible, and that the total amounts of amphiphiles A and B on the vesicle membrane are conserved during evolution. The local bending modulus of the membrane, κ, is determined by the local concentration of amphiphiles ϕ_A and ϕ_B, where $\phi_A+\phi_B=1$, as well as their bending modulus, κ_A and κ_B . The local bending modulus obeys with a linear relationship that is $\kappa=\kappa_A\phi_A+\kappa_B\phi_B=\kappa_0+\zeta\phi_m$, where $\phi_m=\phi_A-\phi_B$, $\kappa_0=(\kappa_A+\kappa_B)/2$ and $\zeta=(\kappa_A-\kappa_B)/2$. Similarly, the local spontaneous curvature c_m is also known as composition-dependent and can be expressed as $c_m=c_A\phi_A+c_B\phi_B=c_0+\varepsilon\phi_m$ with the average spontaneous curvature given by $c_0=(c_A+c_B)/2$ and the difference of the spontaneous curvatures between the two components given by $\varepsilon=c_A-c_B$. n_α polymer α with chain length N_α and n_β polymer β with chain length N_β dispersed in a good solution S are encapsulated inside the vesicle membrane with volume

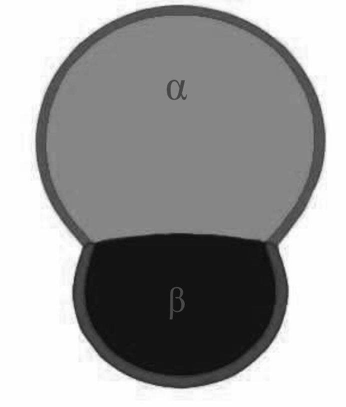

Fig. 1: The schematic illustration of the system that a two-component vesicle indicated by the contour is encapsulated by aqueous two phases α and β.

fraction $\phi_\alpha=n_\alpha N_\alpha/(\rho_0 V_m)$, $\phi_\beta=n_\beta N_\beta/(\rho_0 V_m)$, respectively. The small solution molecules S can be freely penetrate into the membrane which is dependent on the chemical potential across the membrane, but the two kinds of polymer can not penetrate into the membrane and are always located inside the membrane. Therefore, the volume fraction of polymer α and polymer β will be changed along with the vesicle volume. At the same time, the solvents can be assumed as the background of such a compound system and then its effects can be neglected. Therefore, the free energy of such a system corresponding to the membrane and the components inside the membrane can be written as

$$\begin{aligned}\beta F \ =\ & \int [\frac{1}{2}b(\nabla\varphi_m)^2 + f(\varphi_m) + \frac{1}{2}(\kappa_0 + \zeta\varphi_m)(2H + c_0 + \epsilon\varphi_m)^2]\sqrt{g}\,du\,dv + \int \triangle P\,dV \\ & + \int dr[\frac{1}{N_\alpha}\varphi_\alpha(r)\ln\varphi_\alpha(r) + \frac{1}{N_\beta}\varphi_\beta(r)\ln\varphi_\beta(r) + \chi_{\alpha\beta}\varphi_\alpha(r)\varphi_\beta(r) + \chi_{A\alpha}\varphi_A(r)\varphi_\alpha(r) \\ & + \chi_{A\beta}\varphi_A(r)\varphi_\beta(r) + \chi_{B\alpha}\varphi_B(r)\varphi_\alpha(r) + \chi_{B\beta}\varphi_B(r)\varphi_\beta(r) + w(r)(\varphi_\alpha(r) + \varphi_\beta(r))]\end{aligned}$$

The free energy function βF_m which is related to the membrane can be written based upon the discrete space and given by

$$\begin{aligned}\beta F_m \ =\ & \sum_{k=1}^{N}\frac{1}{2}b(\varphi_m(k) - \varphi_m(k-1))^2|\tau(k)| + \sum_{k=1}^{N} f(\varphi_m(k))\frac{|\tau(k)| + |\tau(k+1)|}{2} \\ & + \sum_{k=1}^{N}\frac{1}{4}(\kappa_0 + \zeta\varphi_m(k))(2H(k) + c_0 + \epsilon\varphi_m(k))^2](|\tau(k)| + |\tau(k+1)|) + \frac{P}{2}\sum_{k=1}^{k=N} r(k)n(k)|\tau(k)| \\ & + \sum_{k=1}^{N}\chi_{A\alpha}\varphi_A(k)\varphi_\alpha(k)\frac{|\tau(k)| + |\tau(k+1)|}{2} + \sum_{k=1}^{N}\chi_{A\beta}\varphi_A(k)\varphi_\beta(k)\frac{|\tau(k)| + |\tau(k+1)|}{2} \\ & + \sum_{k=1}^{N}\chi_{B\alpha}\varphi_B(k)\varphi_\alpha(k)\frac{|\tau(k)| + |\tau(k+1)|}{2} + \sum_{k=1}^{N}\chi_{B\beta}\varphi_B(k)\varphi_\beta(k)\frac{|\tau(k)| + |\tau(k+1)|}{2}\end{aligned}$$

Likewise, the free energy βF_{in} of three components inside the vesicle can be written as

$$\begin{aligned}\beta F_{in} \ =\ & \frac{1}{N_\alpha}\phi_\alpha\ln\phi_\alpha + \frac{1}{N_\beta}\phi_\beta\ln\phi_\beta + \chi_{\alpha\beta}\phi_\alpha\phi_\beta \\ & + \chi_{A\alpha}\phi_A\phi_\alpha + \chi_{A\beta}\phi_A\phi_\beta + \chi_{B\alpha}\phi_B\phi_\alpha + \chi_{B\beta}\phi_B\phi_\beta + w(\phi_\alpha + \phi_\beta)\end{aligned}$$

Another two parameters, ψ and η, are therefore introduced and defined as follows,

$$\psi(r) = \varphi_\alpha(r) - \varphi_\beta(r)\ ,\quad \eta = \varphi_\alpha(r) + \varphi_\beta(r).$$

Then, the model free energy βF_{in} for the mixtures inside the vesicle in terms of ψ is written as

$$\beta F_{in}\{\psi\} \ =\ \int dr[f_\psi(\psi) + f_{int}(\psi, m)] + \frac{D_\psi}{2}\int dr(\nabla\psi(r))^2$$

The kinetic equations which describe the evolution of the order parameter ψ inside the vesicle and the phase separation coupled with vesicle deformation can be solved using the simplest dissipative models and are written as the Time-dependent Ginzburg-Landau equations and given by,

$$\frac{\partial\psi}{\partial t} = M_\psi\nabla^2\frac{\beta\delta F_{in}\{\psi\}}{\delta\psi}$$

$$\frac{\partial r(k)}{\partial t} = -L_r \frac{\delta\lfloor \beta F_m + \sum_{k-1}^{N} \gamma(k)|\tau|\rfloor}{\delta r(k)}$$

$$= -L_r[A(k)n(k) + B(k)|\tau(k)|\tau]\left(\frac{|\tau(k)| + |\tau(k+1)|}{2}\right)^{-1}$$

$$\frac{\partial \varphi_m(k)}{\partial t} = -L_{\varphi_m} \nabla^2\left[\frac{\delta\beta F_m}{\delta\varphi_m(k)}\left(\frac{|\tau(k)| + |\tau(k+1)|}{2}\right)^{-1}\right]$$

The initial vesicle shape encapsulated aqueous two-phase systems are randomly generated. The initial positions of the vesicle and distributions of the order parameters, ψ and ϕ_m, are inserted into right hand of the above equations. Then, the positions of the vesicle and distributions of these order parameters in the next time step are obtained. This procedure can be iterated until the unchanged shape and the stable distributions of these order parameters have both been reached.

The vesicle shape encapsulated by two aqueous phase systems at the final simulation step is presented in Figure 2. After simulations, the shape of vesicle is not a sphere, and become shape deformations. The polymer systems also separate from homogeneous phase into two aqueous phases. However, the system of the vesicle shape encapsulated by two aqueous phase systems still do not explain all experimental results, but we would like to provide deep insights into the experiment in further work.

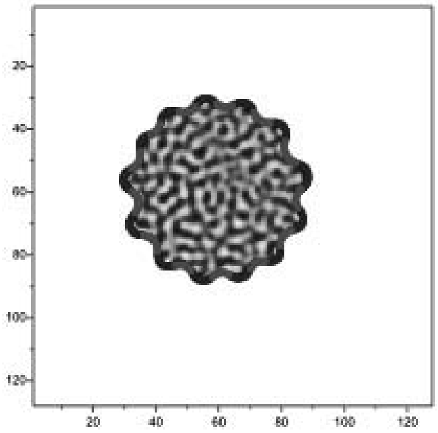

Fig. 2: the vesicle shape encapsulated by two aqueous phase systems, membrane indicated by red and blue lines, the phase encapsulated by vesicle indicated two phase colored by white and black.

2. Original papers

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“Exploration of the shapes of double-walled vesicle with a confined inner membrane”
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3. Presentation at academic conferences

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Seminar in Prof. Yoshikawa group, Kyoto, March, 2012

河津　励

分子科学研究所　専門研究職員(長谷川グループ所属)

1. 今年度の研究の要約

GFPc-X-CFPc モデルペプチドにおけるアミノ酸経由励起エネルギー移動[1]

【始めに】

生化学分野の実験において、GFP(緑蛍光蛋白質)とその色素変異ファミリーの間の励起エネルギー移動(EET)が、近年、分子の会合を測る蛍光プローブとして使われている。EET プロセスは主にFRET(蛍光共鳴エネルギー移動)機構によって起こるが、それとは別に蛋白質が介在する超交換相互作用の寄与が存在している。この寄与は通常 FRET の項と比べて小さいが、まれに相対的に無視できないほど大きいこともある。量子化学的手法を元に、GFPc(GFP 色素)と CFPc(シアン蛍光蛋白質色素)間の励起エネルギー移動について、架橋するブリッジのアミノ酸残基の種類による超交換相互作用項の大きさの依存性を調べた。GFPc-X-CFPc 系では、Through-residue X の項の違いで超交換相互作用項全体の大きさが制御されることがわかった。

【方法】

以前開発したEET電子カップリング計算法およびEET トンネル移動経路決定法[2]をGFPc-ブリッジ-CFPc のモデルシステムに適用して、この系の電子カップリングに対する蛋白質の寄与、特にアミノ酸の種類に拠る違いを調べた。GFPc と CFPc を両端に持ち、間にアミノ酸 X を持つ、GFPc-X-CFPc ペプチドモデル系を作り、GFPc と CFPc の間の励起エネルギー移動の電子カップリングを計算し、その間接項の寄与の成分を調べた。その結果得られたアミノ酸 X に対する依存性について報告する。X には Ala, His, Phe, Trp, Tyr, Val のうち一つが入る。電子カップリング計算の前に、X 以外の部分については X=Ala として B3LYP/6-31G*で構造最適化してあり、そのあと X のみを再び構造最適化している。その最適化構造を図１に示す。以降の計算では CIS/D95 を用いている。計算手順としては、まず参照分子として GFPc (両端に CH3 を含む)、CFPc (両端に CH3 を含む)および、X (側鎖及びα炭素を含む)の３つを用いた MOD 法[3]により、それぞれのフラグメントに局在化した分子軌道を作り、残りのペプチド部分を Pipek-Mezey 法で局在化するというハイブリッド局在化法[4]を行いてモデル全域における局在化分子軌道を得た。この結果得られる、分子軌道は GFPc-pep1-X-pep2-CFPc の 5 か所のフラグメントに局在化する (図１)。これらの局在分子

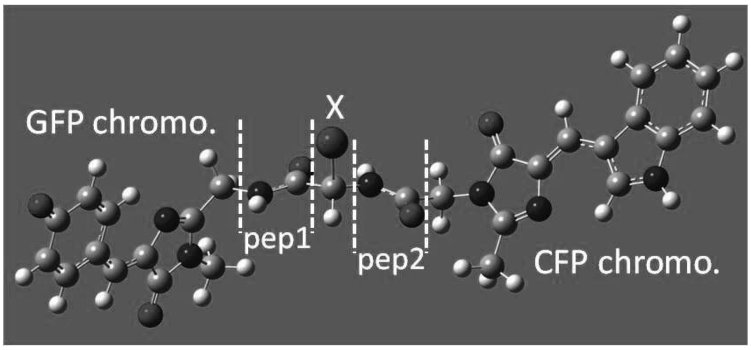

図 1. GFPc-X-CFPc モデル。

軌道から作られるSlater determinantを基底として、EETトンネル経路を計算し、そのアミノ酸ごとの違いを調べた。電子トンネル経路の計算にはグリーン関数法を用いており、トンネルエネルギーはCFPcとGFPcのそれぞれの第一励起エネルギーの平均値を用いた(4.12eV=0.1515au)。

【結果】

まず、計算された結果から、この系では直接項の寄与が特に大きいことがわかり、そのため、ここで考えているような系ではドナー、アクセプター状態に直接関与しないブリッジアミノ酸のミューテーションは全体のカップリングにはあまり寄与しないことがわかる。一方で、超交換項についてはアミノ酸の種類に依存して大きく変動することがわかった。そこで、それぞれのアミノ酸Xに関して、超交換項に主要な寄与を与えるExcitonタイプのSlater determinantを通るEET経路の寄与を計算し、結果をペプチドボンド経由の経路の結果と合わせて表1に示す。A->BはAにあるexcitonがBに移る経路であることを表す。アミノ酸の種類を変えることに拠り、X経由経路の寄与だけが主に変動していることがわかる。超交換相互作用の項の中では、ペプチドの寄与とアミノ酸残基の寄与は競合しており、アミノ酸の種類によってその大小が入れ替わりうる。表1ではXはアミノ酸残基の第一励起エネルギーとトンネリングエネルギーの差ΔEが大きい順に並んでおり、X経由経路の寄与の大きさとΔEに依存関係があるのがわかる。このほかに、ドナー、アクセプターとアミノ酸残基の間の相互作用もいくらか関係している。今回のモデルについては主成分である直接項に対してペプチド項は正、残基項は負の位相を持って計算されているので、有効な残基の場合ほど全体の電子カップリングは小さくなっているが、このようなケースでも、ちゃんと個別の寄与の大小を議論できるのが我々の解析方法の特色である。

表1. 局在Exciton経由EETトンネル経路の寄与

X	CFPc->X/ X->GFPc	CFPc->pep1/ pep1->GFPc	CFPc->pep2/ pep2->GFPc
Ala	-7.32/ -6.63	-13.3/ -13.5	-8.77/ -8.50
Val	-3.11/ -2.76	-12.8/ -12.6	-8.71/ -8.43
His	14.7/ 14.7	-13.6/ -13.3	-9.33/ -8.79
Phe	27.5/ 28.5	-13.1/ -13.2	-8.20/ -8.48
Trp	35.9/ 36.9	-13.3/ -13.8	-8.09/ -8.53
Tyr	35.2/ 36.4	-12.8/ -12.8	-8.40/ -8.76

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(2) Tsutomu Kawatsu, Jun-ya Hasegawa, and Kenji Matsuda, “Bridge-mediated excitation energy transfer pathways through protein media: a Slater determinant-based electronic coupling calculation combined with localized molecular orbitals,” J. Phys. Chem. A 115(39), 10814-10822(2011).

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3. 学会発表

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4. その他

(1) 河津励、長谷川淳也
「GFP-X-CFPモデルペプチドにおけるアミノ酸経由励起エネルギー移動」
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外国人共同研究者受入れ状況（平成23年度）

氏名	受入れ身分	受入れ期間	所属機関・職	受入れ教員	研究内容
Jiayun Pang	外国人 共同研究者	平成23年3月19日～ 平成23年4月16日	University of Manchester （イギリス）・研究員	諸熊奎治	複雑分子系の シミュレーション
Burger, Steven K.	外国人 共同研究者	平成23年4月11日～ 平成23年5月26日	McMaster University （カナダ）・研究員	諸熊奎治	複雑分子系の シミュレーション
Sivakumar Sekharan	外国人 共同研究者	平成24年2月29日～ 平成24年3月21日	Emory University （アメリカ）・研究員	諸熊奎治	複雑分子系の シミュレーション

海外渡航一覧（平成23年度）

職　　名	氏　　名	期間（自）	期間（至）	目 的 地
特定研究員	Alister Page	2011.4.8	2011.4.14	アメリカ合衆国
特定研究員	岩城　貴史	2011.4.3	2011.4.8	アメリカ合衆国
特定助教	前田　　理	2011.4.17	2011.4.20	中華人民共和国
研究員（学術研究奨励）	諸熊　奎治	2011.5.14	2011.6.8	アメリカ合衆国
研究員（学術研究奨励）	諸熊　奎治	2011.6.23	2011.6.30	チェコ
研究員（学術研究奨励）	諸熊　奎治	2011.7.15	2011.7.24	スペイン
研究員（学術研究奨励）	榊　　茂好	2011.5.17	2011.5.26	チェコ
研究員（学術研究奨励）	榊　　茂好	2011.5.31	2011.6.3	シンガポール
特定研究員	義永　那津人	2011.6.21	2011.6.26	アメリカ合衆国
准教授	石田　俊正	2011.7.15	2011.7.30	スペイン
特定研究員	Alister Page	2011.7.11	2011.7.26	スペイン
産学官連携研究員	Li Xin	2011.7.13	2011.7.24	スペイン
研究員（学術研究奨励）	榊　　茂好	2011.7.17	2011.7.25	スペイン
研究員（科学研究）	DESHMUKH, Milind Madhusudan	2011.7.15	2011.7.24	スペイン
特定助教	前田　　理	2011.7.16	2011.7.25	スペイン
研究員（学術研究奨励）	諸熊　奎治	2011.8.11	2011.8.18	中国
研究員（学術研究奨励）	榊　　茂好	2011.8.17	2011.8.19	中国
研究員（学術研究奨励）	Wilfredo C. Chung	2011.8.16	2011.8.21	フィリピン共和国
特定研究員	義永　那津人	2011.8.27	2011.9.28	ドイツ　フランス
研究員（学術研究奨励）	諸熊　奎治	2011.9.2	2011.9.9	タイ
研究員（学術研究奨励）	Wilfredo C. Chung	2011.9.4	2011.9.9	タイ
研究員（学術研究奨励）	榊　　茂好	2011.9.2	2011.9.8	タイ
研究員（学術研究奨励）	榊　　茂好	2011.10.2	2011.10.10	ギリシャ
研究員（学術研究奨励）	諸熊　奎治	2011.10.7	2011.10.31	アメリカ合衆国
特定研究員	義永　那津人	2011.10.26	2011.10.30	台湾
研究員（学術研究奨励）	諸熊　奎治	2011.12.8	2011.12.15	ニュージーランド
研究員（学術研究奨励）	諸熊　奎治	2012.1.8	2012.1.21	アメリカ合衆国
特定研究員	畑中　美穂	2012.2.18	2012.2.27	アメリカ合衆国
研究員（学術研究奨励）	諸熊　奎治	2012.3.25	2012.3.28	シンガポール

研究業績一覧（2011 年度）

№	Authors	Title	Journal	Volume(Number), first page to last page	year
長谷川　淳也					
1	J. Hasegawa, T. Kawatsu, K. Toyoya, and K. Matsuda	Chemical-intuition based LMO transformation simplifies excited-state wave functions of peptides	*Chem. Phys. Letters*	508(1-3), 171-176	2011
2	Y. Kitagawa, K. Matsuda, and J. Hasegawa	Theoretical Study of the Excited States of the Photosynthetic Reaction Center in Photosystem II: Electronic Structure, Interactions, and Their Origin	*Biophys. Chem.*	159(2-3), 227-236	2011
3	T. Kawatsu, K. Matsuda, and J. Hasegawa	Bridge-Mediated Excitation Energy Transfer Pathways through Protein Media: a Slater Determinant-Based Electronic Coupling Calculation Combined with Localized Molecular Orbitals	*J. Phys. Chem. A*	115(39), 10814-10822	2011
4	J. Hasegawa and K. Matsuda	Theoretical study of the excited states and the redox potentials of unusually distorted β-trifluoromethylporphycene	*Theoret. Chem. Acc.*	130(2-3), 175-185	2011
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7	T. Sakano, J. Hasegawa, K. Higashiguchi, and K. Matsuda	Chronological Change from Face-On to Edge-On Ordering of Zinc Tetraphenylporphyrin at Phenyloctane-HOPG Interface	*Chem. Asian J.*	7(2), 394-399	2012
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13	Yoshihiro Matano, Kazuaki Matsumoto, Hironobu Hayashi, Yoshihide Nakao, Tatu Kumpulainen, Vladimir Chukharev, Nikolai V. Tkachenko, Helge Lemmetyinen, Soji Shimizu, Nagao Kobayashi, Daisuke Sakamaki, Akihiro Ito, Kazuyoshi Tanaka, and Hiroshi Imahori	Effects of Carbon–Metal–Carbon Linkages on the Optical, Photophysical, and Electrochemical Properties of Phosphametallacycle-Linked Coplanar Porphyrin Dimers	*J. Am. Chem. Soc.*	134, 1825–1839	2012
14	Ken Saito, Yoshinori Eishiro, Yoshihide Nakao, Hirofumi Sato, Shigeyoshi Sakaki	Oscillator strength of symmetry-forbidden d-d absorption of octahedral transition metal complex: theoretical evaluation.	*Inorg. Chem.*	51, 2785-2792	2012
石田　俊正					
15	Suhara, Masanori; Ozaki, Hiroyuki; Endo, Osamu; Ishida, Toshimasa; Katagiri, Hideki; Egawa, Toru; Katouda, Michio	Changes in the Electronic Structures of a Single Sheet of Sashlike Polydiacetylene Atomic Sash upon Structural Transformations	*J. Phys. Chem. C*	115(19), 9518-9525	2011
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17	Jun-ichi Aihara, Rika Sekine and Toshimasa Ishida	Electronic and Magnetic Characteristics of Polycyclic Aromatic Hydrocarbons with Factorizable Kekule Structure Count	*J. Phys. Chem. A*	115(33), 9314-9321	2011
18	Wilfredo Credo Chung, Shinkoh Nanbu, and Toshimasa Ishida	A Nonadiabatic Ab Initio Dynamics Study on Rhodopsin and its Analog Isorhodopsin: Chemical Dynamics Reasons Behind Selection of Rhodopsin by Life	*Chem. Lett.*	40(12), 1395-1397	2011
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19	Hidekazu Ikeno, Teruyasu Mizoguchi, Yukinori Koyama, Zenpachi Ogumi, YasuharuUchimoto, and Isao Tanaka,	Theoretical Fingerprints of Transition Metal $L_{2,3}$ XANES/ELNES for Lithium Transition Metal Oxides by ab Initio Multiplet Calculations	*J. Phys. Chem. C*	115, 11871-11879	2011
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25	S. Maeda and K. Morokuma	Finding Reaction Pathways of Type A + B → X: Toward Systematic Prediction of Reaction Mechanisms,	*J. Chem. Theo. Comp.*	7, 2335-2345.	2011
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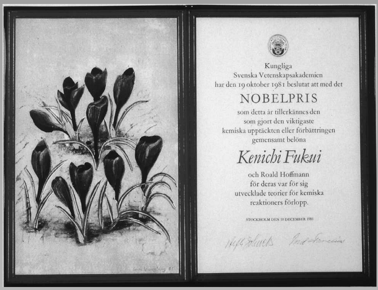
124	N. Takagi, R. Tonner, G. Frenking	Carbodiphosphorane-Analogues E(PPh_3)$_2$ with E = C - Pb. A Theoretical Study with implications for ligand design	*Chem. Eur. J.*	18, 1772-1780	2012
125	T. Agou, Y. Sugiyama, T. Sasamori, H. Sakai, Y. Furukawa, N. Takagi, J. D. Guo, S. Nagase, D. Hashizume, N. Tokitoh	Synthesis of Kinetically Stabilized 1,2-Dihydrodisilenes	*J. Am. Chem. Soc.*	134, 4120-4122	2012
126	N. Takagi, S. Sakaki	A Theoretical Study of Unusual Y-Shaped Three-coordinate Pt Complex: Pt(0) σ-Disilane Complex or Pt(II) Disilyl Complex?	*J. Am. Chem. Soc.*	in press	2012
吉澤　輝高					
127	T. Yoshizawa, S. Sakaki	NMR shielding constants of CuX, AgX, and AuX (X = F, Cl, Br, and I) investigated by density functional theory based on the Douglas–Kroll–Hess Hamiltonian	*in preparation*		

№	Authors	Title	Journal	Volume(Number), first page to last page	year
中谷　直樹					
128	Naoki Nakatani, Yutaka Hitomi, and Shigeyoshi Sakaki	Multistate CASPT2 Study of Native Iron(III)-Dependent Catechol Dioxygenase and Its Functional Models: Electronic Structure and Ligand-to-Metal Charge-Transfer Excitation	*J. Phys. Chem. B*	115, 4781-4789	2011
松井　亨					
129	T. Baba, K. Kamiya, T. Matsui, N. Shibata, Y. Higuchi, T. Kobayashi, S. Negoro and Y. Shigeta	Molecular dynamics studies on mutational structures of a nylon-6 byproduct-degrading enzyme	*Chem. Phys. Lett.*	507, 157-161	2011
130	Y. Nakanishi, T. Matsui, Y. Kitagawa, Y. Shigeta, T. Saito, Y. Kataoka, T. Kawakami, M. Okumura and K. Yamaguchi	Electron Conductivity in Modified Models of Artificial Metal-DNA Using Green's Function-Based Scattering Theory	*Bull. Chem. Soc. Japan*	84, 366-375	2011
131	T. Matsui, H. Miyachi, T. Baba and Y. Shigeta	A Theoretical Study on Reaction Scheme of Silver (I) Containing 5-Substituted Uracils Bridge Formation	*J. Phys. Chem. A*	115, 8504-8511	2011
132	K. Kamiya, T. Matsui, T. Sugimura and Y. Shigeta	Theoretical Insight into Stereoselective Reaction Mechanisms of 2,4-Pentanediol-Tethered Ketene-Olefin [2+2] Cycloaddition	*J. Phys. Chem. A*	116, 1168-1175	2012
133	T. Matsui, T. Baba, K. Kamiya and Y. Shigeta	An accurate density functional theory based estimation of pKa value of polar residues combined with experimental data: from amino acids to minimal proteins	*Phys. Chem. Chem. Phys.*	12, 4181-4187	2012
Wilfredo Credo Chung					
134	Wilfredo Credo Chung, Shinkoh Nanbu, Toshimasa Ishida	QM/MM Trajectory Surface Hopping Approach to Photoisomerization of Rhodopsin and Isorhodopsin: The Origin of Faster and More Efficient Isomerization for Rhodopsin	*J. Phys. Chem. B*	116 (28), 8009–8023.	2012
135	Wilfredo Credo Chung, Shinkoh Nanbu, Toshimasa Ishida	A Nonadiabatic Ab Initio Dynamics Study on Rhodopsin and Its Analog Isorhodopsin: Chemical Dynamics Reasons behind Selection of Rhodopsin by Life	*Chemistry Letters*	40, 1395-1397	2011
136	-Wilfredo Credo Chung, Toshimasa Ishida	An MD simulation of the decoy action of Epstein–Barr virus LMP1 protein mimicking the CD40 interaction with TRAF3	*Theoretical Chemistry Accounts*	130, 401-410	2011
岩城　貴史					
137	S. N. Watanabe, T. Iwaki, M. I. Kohira, N. Magome, and K. Yoshikawa	Negative photophoresis of smoke particles observed under microgravity	*Chem. Phys. Lett.*	511, 447-451	2011
138	Y. Higuchi, K. Yoshikawa, and T. Iwaki	Stiffness causes opposite trend on the folding transition of a single polymer chain in a confined space	*Physical Review E*	84, 021924 (1-5)	2011

№	Authors	Title	Journal	Volume(Number), first page to last page	year
義永　那津人					
139	Shunsuke Yabunaka, Takao Ohta, and Natsuhiko Yoshinaga	Self-propelled motion of a fluid droplet under chemical reaction	*J. Chem. Phys.*	136, 074904	2012
140	Philippe Marcq, Natsuhiko Yoshinaga, and Jacques Prost	Rigidity sensing explained by active matter theory	*Biophys. J.*	101, L33-L35	2011
141	Hiroyuki Kitahata, Natsuhiko Yoshinaga, Ken H. Nagai, and Yutaka Sumino	Spontaneous motion of a droplet coupled with a chemical wave	*Phys. Rev. E Rapid Communications*	84, 015101	2011
嶺澤　範行					
142	Noriyuki Minezawa and Mark S Gordon	Photoisomerization of Stilbene: A Spin-Flip Density Functional Theory Approach	*J. Phys. Chem. A*	115(27), 7901-7911	2011
143	Albert DeFusco, Noriyuki Minezawa, Lyudmila V Slipchenko, Federico Zahariev, and Mark S Gordon	Modeling Solvent Effects on Electronic Excited States	*J. Phys. Chem. Lett.*	2(17), 2184-2192	2011
Kunkun Guo					
144	Kunkun Guo, Wenjia Xiao, and Dong Qiu	Polymerization of actin filaments coupled with adenosine triphosphate hydrolysis: Brownian dynamics and theoretical analysis	*J. Chem. Phys.*	135(10), 105101(1)-105101(6)	2011
145	Kunkun Guo, Jianfeng Li	Exploration of the shapes of double-walled vesicles with a confined inner membrane	*J. Phys.: Condens. Matter*	23, 285103 (12pp)	2011
河津　励					
146	Tsutomu Kawatsu, and Jun-ya Hasegawa	Excitation energy transfer in GFP-X-CFP model peptides (X = amino acids): Direct Versus through-bridge energy transfers	*Int. J. Quantum Chem.*	published online	2012
147	Tsutomu Kawatsu, Jun-ya Hasegawa, and Kenji Matsuda	Bridge-mediated excitation energy transfer pathways through protein media: a Slater determinant-based electronic coupling calculation combined with localized molecular orbitals	*J. Phys. Chem. A*	115(39), 10814-10822	2011
148	Jun-ya Hasegawa, Tsutomu Kawatsu, Kazuo Toyota, and Kenji Matsuda	Chemical-intuition based LMO transformation simplifies excited-state wave functions of peptides	*Chem. Phys. Lett.*	508, 171-176	2011

若い人に贈る福井謙一先生ノーベル化学賞受賞30周年記念公開講座

―最近の基礎化学の進展―



Kungliga
Svenska Vetenskapsakademien
har den 19 oktober 1981 beslutat att med det
NOBELPRIS
som detta år tillerkännes den
som gjort den viktigaste
kemiska upptäckten eller förbättringen
gemensamt belöna
Kenichi Fukui
och Roald Hoffmann
för deras var för sig
utvecklade teorier för kemiska
reaktioners förlopp.

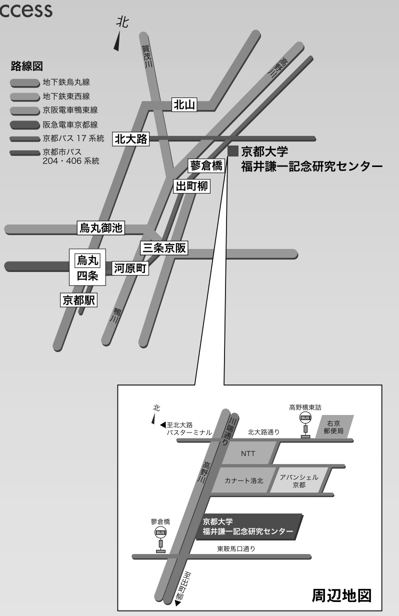
STOCKHOLM DEN 10 DECEMBER 1981

日時　平成23年7月30日（土）13:00～16:00

場所　京都大学福井謙一記念研究センター 3F大会議室

〒606-8103
京都市左京区高野西開町34-4
Tel : 075-711-7708
http: //www.fukui.kyoto-u.ac.jp/

Access



プログラム

13:00～13:10	**開会の挨拶** センター長　田中　功（京都大学工学研究科教授）
13:10～13:55	**福井謙一博士の生い立ちとノーベル化学賞までの軌跡** 副センター長　田中 一義（京都大学工学研究科教授）
13:55～14:10	休憩
14:10～14:55	**コンピュータで化学反応の世界を探る** センター リサーチリーダー　諸熊 奎治
14:55～15:10	休憩
15:10～15:55	**基礎化学から応用への展開** センター運営委員　今堀　博（京都大学工学研究科教授）

・休憩時間や講座終了後に、福井先生記念の展示物を見学頂きます。
・参加費は無料ですが、会場の都合上，事前に参加申込下さい。希望者多数の場合は、先着順とさせていただきます。

申込方法

所属学校等で○名参加というように、まとめていただければありがたいですが、
個人参加も受け付けます。引率の先生、ご父兄の方々も歓迎です。
申込は電子メールで school@fukui.kyoto-u.ac.jp あるいは Fax：075-781-4757まで。

Fukui International Symposium for Theoretical Chemistry (FISTC)

Place: **Fukui Institute for Fundamental Chemistry, Kyoto University**
Schedule: **Wednesday, August 31, 1300: opening, lectures and banquet**
Thursday, September 1, 2011, 900: lectures; 1700: closing
Banquet: Aug. 31 PM 7:00-9:00
Organizers: **Keiji Morokuma and Shigeyoshi Sakaki**

Fukui Institute for Fundamental Chemistry of Kyoto University is planning to organize International Symposium for Theoretical and Computational Chemistry for August 31 to September 1, 2011 at Kyoto. Fukui Institute was built by late Professor Kenichi Fukui at 1985 after he retired from Kyoto University to continue his research with young colleagues. After he has passed away, the Institute has become a part of Kyoto University.

In this symposium, we would like to invite excellent theoretical and computational chemists from abroad and Japan including young researchers, to provide high quality lectures about new methods, new targets for molecular science and new theoretical and computational results, and to deepen contact and enhance cooperative works between Japan and other countries. In this small symposium we hope to provide ample time for open and personal discussion. Another important purpose is to encourage excellent young theoretical and computational chemists. They are performing excellent works but they do not have many chances to present their oral talks in international conferences. In this symposium, we will provide such opportunities to young researchers.

We hope that many people join to this international symposium at Fukui Institute for Fundamental Chemistry. We believe that you will have good chances to listen excellent talks and to enjoy direct discussion with excellent speakers.

Speakers (Alphabetical)

Marcus Elstner (Karlsruhe)
Gernot Frenking (Marburg)
Jurgen Gauss (Mainz)
Jyunya Hasegawa (Kyoto)
Shigehiko Hayashi (Kyoto)
So Hirata (Illinois)
Toshimasa Ishida (Kyoto)

Kwang S. Kim (Pohan)
Kazuo Kitaura (Kyoto)
Shuhua Li (Nanjing)
Satoshi Maeda (Kyoto)
Masayoshi Nakano (Toyonaka)
Yoshihide Nakao (Kyoto)
Josef Noga (Blatislaba)
Yu-ki Ohtsuka (Okazaki-Kobe)
Kiyoshi Yagi (Osaka)
Shusuke Yamanaka (Toyonaka)
Koichi Yamashita (Tokyo)
Kazunari Yoshizawa (Fukuoka)

Program (temporary)

Wednesday, August 3

13:00-13:10	Opening
13:10-13:40	Koichi Yamashita(Tokyo)
13:40-14:20	Kwang S. Kim(Pohan)
14:20-15:00	
15:00-15:20	Masayoshi Nakano(Toyonaka)
15:20-16:00	Josef Noga(Bulatislava)
16:00-16:40	Kiyoshi Yagi(Osaka)
16:40-17:00	Break
17:00-17:20	Toshimasa Ishida(Kyoto)
17:20-17:40	Shusuke Yamanaka, Keita Kanda, Toru Saito,Yasutaka Kitagawa, Takashi Kawakami,Masahiro Ehara, Mitsutaka Okumura,Haruki Nakamura, Kizashi Yamaguchi(Toyonaka)
17:40-18:00	Yuhki Ohtsuka, Seiichiro Ten-no, Shigeru Nagase(Okazaki-Kobe)
18:00-18:20	Satoshi Maeda(Kyoto)
18:20-18:40	Yoshihide Nakao(Kyoto)
19:00-21:00	

Thursday, September 1

9:00-9:40	Kazunari Yoshizawa(Fukuoka)
9:40-10:20	Gernot Frenking(Marburg)

10:20-10:40	Break
10:20-11:00	Shigehiko Hayashi (Kyoto)
11:00-11:40	Marcus Elstner(Karlsruhe)
11:40-12:20	Junya Hasegawa(Kyoto)
12:20-14:00	Lunch
14:00-14:40	Kazuo Kitaura (Kyoto)
14:40-15:20	Shuhua Li(Nangin)
15:20-15:40	Break
15:40-16:20	Jurgen Gauss(Mainz)
16:20-17:00	So Hirata(Illinois)
17:00-17:10	

Registration

Please send e-mail to the office of Fukui Institute with the information described below:

Your Name:
Affiliation(Company/Intitute/University):
Address:
E-mail Address:
Banquet (¥5,000): Yes or No
(The payment will be accepted at the conference desk)

Send the above information to; higashida@adm.t.kyoto-u.ac.jp

Kyoto University Junior Campus 2011

京都大学
ジュニアキャンパス
2011

世界から日本を診てみよう

- ●日　　時　2011（平成23）年9月17日㊏／18日㊐
- ●会　　場　京都大学吉田キャンパス・宇治キャンパス・桂キャンパス 他（各講義室／実験室／実習室／研究室）
- ●プログラム　特別講義、中学生向けゼミ、特別協賛ゼミ、大学院生等によるポスターセッション
- ●主　　催　京都大学
- ●共　　催　京都市教育委員会
- ●問い合わせ先　京都大学学務部教務企画課ジュニアキャンパス担当 TEL:075-753-2548

詳細はホームページにも掲載しています。 http://www.kyoto-u.ac.jp/ja/education/open/junior.htm

吉 田	A 7	**太陽の素顔をさぐる** －花山天文台における 太陽観測実習 **柴田　一成** （理学研究科教授）	最近の観測が明らかにした太陽の驚くべき素顔を最新の映像などを用いて紹介・講演し、のち、花山天文台のシーロスタット７０ｃｍ望遠鏡を用いた太陽スペクトル観測、１８ｃｍ屈折望遠鏡を用いた黒点スケッチ、Ｈα観測実習などを行うことにより、太陽の素顔にせまる。	保護者 参加型 花山 天文台
吉 田	A 8	**化学** －フロンティア軌道理論と 電子計算機で化学が分かる？ **田中　功** （福井謙一記念研究センター教授）	化学反応はなぜ起きるのでしょう。フロンティア軌道理論を発見し、その疑問に明快に答えたのが、1981年にノーベル化学賞を受賞された福井謙一先生です。フロンティア軌道理論をやさしく説明し、先生の人柄と研究の姿勢を紹介するとともに、最新の計算機を使って化学反応の詳細がどのように分かるようになったかを説明します。	保護者 参観型 福井謙一 記念研究 センター
宇 治	A 9	**低温物理学** －196℃の世界を楽しもう ：超伝導と磁石の不思議 **寺嶋　孝仁** （低温物質科学研究センター教授）	液体チッソ(－196℃）を使った基礎的な物理実験を行います。 空気の収縮・膨張、超伝導体の磁気浮上、磁石にくっつく液体酸素などの実験を通して低温物理学、物質科学の面白さを実感してもらいます。また、中学生にも分かるレベルでその背景にある物理の解説も行います。	保護者 参加型
宇 治	A 10	**地震学** －地震をはかろう－ **加納 靖之** （防災研究所助教）	地震が発生したときに報道される震度やマグニチュードはすべて地震計で測定した地面の揺れをもとに算出しています。また、地震がつくりだす地面の揺れ方を調べることによって、地震の起こった場所（震源）や断層の動き方、地下や地球内部の構造などがわかります。この実習では地震計によるデータをもとに、どこでどのような地震が起こっているか考えてみましょう。	保護者 参加型

特別協賛ゼミ①

日時：平成２３年７月３０日（土）13：00〜16：00

テーマ・講師	ゼミの内容等	備考
若い人に贈る 福井謙一先生ノーベル化学賞受賞 ３０周年記念公開講座 － 最近の基礎化学の進展 － 田中　一義 （工学研究科教授） 諸熊　奎治 （福井謙一記念研究センターリサーチリーダー） 今堀　博 （物質－細胞統合システム拠点教授）	中学生・高校生・大学生と引率者・保護者を対象に、福井謙一先生のノーベル化学賞受賞の対象となった研究業績を紹介し、それに関連して最近の基礎化学の進展を分かりやすく解説し、化学（科学）への親しみを感じてもらう。 あわせて、本センターの福井先生関連展示コーナーを見学してもらい、研究業績のみならず、その人柄をも紹介する。	

（注）このゼミの申込みは、ジュニアキャンパスの申込みとは別に、福井謙一記念研究センターに行ってください。

申込方法　電子メール、郵便あるいはFAXで、郵便番号・住所・氏名・学校名・学年を記載し、下記宛に**７月２０日まで**に送付ください。

申 込 先
〒606-8103　京都市左京区高野西開町３４－４
福井謙一記念研究センター　記念公開講座係
▶**FAX：075-781-4757**　▶**E-mail：school@fukui.kyoto-u.ac.jp**

実施場所　福井謙一記念研究センター　３階大会議室

募集人数　中学生・高校生・大学生と引率者　合計１００名

特別協賛ゼミ②

日時：平成２３年８月５日（金）13：00〜16：30

テーマ・講師	ゼミの内容等	備考
『放射線って何だろう？』 川本　卓男 （放射線同位元素総合センター長ほか センターの教職員）	(1)　我々の身の回りに存在する放射線に関する講義を行う。 (2)　放射線測定器（サーベイメーター）を使って、身の回りの放射線量を実際に測ってみる。 (3)　手近な材料で放射線検出器（霧箱）を作成し、放射線の飛跡を観察する。	

（注）このゼミの申込みは、ジュニアキャンパスの申込みとは別に、放射線同位元素総合センターに行ってください。

申込方法　FAXまたはE-mailに氏名、ふりがな、住所、電話番号、ＦＡＸ番号、電子メール、学校名、学年を記載し、下記宛に**７月２９日（必着）まで**にお申し込みください。

申 込 先
〒606-8501 京都市左京区吉田近衛町
京都大学環境安全保健機構附属放射性同位元素総合センター
▶**FAX：075-753-7504**　▶**E-mail：taiken@barium.rirc.kyoto-u.ac.jp**

実施場所
京都大学環境安全保健機構附属
放射性同位元素総合センター　教育訓練棟３階講義室

募集人数　中学生５０名　※保護者同伴可

第9回

京都大学 福井謙一記念研究センターシンポジウム

福井謙一博士ノーベル賞受賞30周年記念

福井謙一博士記念展示コーナー 除幕式 10:00–10:45

［司会］田中 一義（福井謙一記念研究センター 副センター長）

［開式の辞］田中 功（福井謙一記念研究センター長）
［挨　　拶］江﨑 信芳（京都大学 理事・副学長）
小森 悟（京都大学 工学研究科長）
テープカット
ご見学

講演会（3階大会議室）

［司会］太田 隆夫（福井謙一記念研究センター 副センター長）

玉尾 皓平（理化学研究所 基幹研究所 所長）
「深化・拡大を続ける有機元素化学：実験と理論の連携の舞台」 11:00–12:00

– 昼食 –

［司会］榊 茂好（福井謙一記念研究センター リサーチリーダー）

諸熊 奎治（福井謙一記念研究センター リサーチリーダー）
「化学反応の理論研究：フロンティア理論から現在，未来へ」 13:30–14:15

平尾 公彦（理化学研究所 計算科学研究機構 機構長）
「コンピュータと福井先生」 14:15–15:00

– コーヒーブレイク –

ポスターセッション（3階大会議室） 15:30–17:20
懇親会（1階多目的ルーム） 17:30–19:00

平成24年1月6日（金）

会場：京都大学 福井謙一記念研究センター

京都大学福井謙一記念研究センター
〒606-8103　京都市左京区高野西開町34-4
問合せ先：長谷川 淳也 ／ E-mail:hasegawa@fukui.kyoto-u.ac.jp　Tel:075-711-7867
事務室 ／ Tel:075-711-7708　Fax:075-781-4757

http://www.fukui.kyoto-u.ac.jp

第9回京都大学福井謙一記念研究センターシンポジウム

プログラム

日時　2012(平成24)年1月6日（金）
場所　京都大学福井謙一記念研究センター

福井謙一博士記念展示コーナー　除幕式（1階展示コーナー　10:00-10:45）

司会：田中　一義（福井謙一記念研究センター　副センター長）

- 開会の辞　田中　功（福井謙一記念研究センター長）
- 挨拶　江崎　信芳（京都大学　理事・副学長）
- 挨拶　小森　悟（京都大学　工学研究科長）
- テープカット
- ご見学

講演会（3階大会議室　11:00-17:20）

司会：太田　隆夫（福井謙一記念研究センター　副センター長）

- 玉尾　皓平（理化学研究所　基幹研究所　所長）
  「深化・拡大を続ける有機元素化学：実験と理論の連携の舞台」　11:00-12:00

－昼食－

司会：榊　茂好（福井謙一記念研究センター　リサーチリーダー）

- 諸熊　奎治（福井謙一記念研究センター　リサーチリーダー）
  「化学反応の理論研究：フロンティア理論から現在、未来へ」　13:30-14:15
- 平尾　公彦（理化学研究所　計算科学研究機構　機構長）
  「コンピュータと福井先生」　14:15-15:00

－コーヒーブレイク－

ポスターセッション（3階大会議室　15:30-17:20）

懇親会（1F多目的ルーム　17:30-19:00）

ポスターセッション　15:30-17:20 (3F 大会議室)

※ 番号が奇数の方は前半(15:30-16:25)に、番号が偶数の方は後半(16:25-17:20)にポスターの場所にて発表を行ってください。

※ Please present your poster at the first half (15:30-16:25) when your poster number is odd and do it at the second half (16:25-17:20) when the number is even.

1. Ab initio MO 量子マスター方程式法に基づく動的第一超分極率密度解析法の開発
（阪大院基礎工）○岸亮平、藤井宏旭、岸本真悟、村田裕介、重田育照、中野雅由

2. CAM-B3LYP 法によるジアリールエテン誘導体の励起エネルギー計算
（阪大院基礎工）○奥野　克樹、重田　育照、中野　雅由、宮坂　博

3. PCM 法に基づく超分極率計算手法の開発
（阪大院基礎工[1]、阪大院理[2]）○乾　智也[1]、井上　雄大[1]、奥野　克樹[1]、岸　亮平[1], 重田　育照[1]、久保　孝史[2]、中野　雅由[1]

4. Comparative Study of Diradical Characters and Third-Order Nonlinear Optical Properties of Linear/Cyclic Acenes versus Phenylenes
(Osaka Univ.) ○Shabbir Muhammad, Takuya Minami, Hitoshi Fukui, Kyohei Yoneda, Shu Minamide, Ryohei Kishi, Yasuteru Shigeta, Masayoshi Nakano

5. 最適化長距離補正時間依存密度汎関数法に基づく非対称 π 共役分子系の電子遷移特性と第一超分極率についての理論的研究
(阪大院基礎工) ○藤井宏旭、岸本真悟、伊藤聡一、山田大志、岸亮平、重田育照、中野雅由

6. Broken-Symmetry TDDFT 量子マスター方程式法による開殻一重項分子系の線形吸収スペクトルの理論研究
（阪大院基礎工）○岸本真悟、岸亮平、村田裕介、重田育照、中野雅由

7. アンチドット構造を有する四角形グラフェンナノフレークの開殻性と第二超分極率に関する理論研究
（大阪大学大学院基礎工学研究科）○米田京平、元村脩人、南出秀、伊藤聡一、山田大志、山本耕平、 岸亮平、重田育照、中野雅由

8. Polyacene および Dicyclopenta-fused acene における開殻性ー芳香族性ー非線形光学物性の相関の研究
（阪大院基礎工[1]、Facultés Universitaires Notre-Dame de la Paix[2]）○元村脩人[1]、米田京平[1]、Raphaël Carion[2], Benoît Champagne[2]、中野雅由[1]

9. ペンタセン／C_{60} 界面の電荷移動励起状態に対する誘電分極の効果
（阪大院基礎工、Université de Bordeaux）○南拓也、Castet Frédéric、伊藤聡一、中野雅由

10. ペンタレノジアセンの開殻性に関する理論的研究
(阪大院基礎工) ○伊藤 聡一、南 拓也、岸 亮平、重田 育照、中野 雅由

11. 理論と実験によるゼトレン誘導体の非線形光学特性についての研究
(阪大院基礎工[1]、産総研ユビキタスエネルギー[2]、國立成功大學化學系[3]) ○南出秀[1]、鎌田賢司[2]、太田浩二[2]、米田京平[1]、岸亮平[1]、重田育照[1]、中野雅由[1]、WU Tsun-Cheng[3]、WU Yao-Ting[3]、日比大治郎[1]、清水章弘[1]、戸部義人[1]

12. 二核遷移金属錯体のジラジカル性に対する配位子効果の理論的研究
(阪大院基礎工) ○井上雄大、山田大志、福井仁之、岸亮平、重田育照、中野雅由

13. 一次元 Ni 多核錯体の磁性と伝導性
(阪大院理[1]、阪大院基礎工[2]) ○北河康隆[1]、松井亨[1]、重田育照[2]、安田奈都美[1]、畑ヶ宇宙[1]、川上貴資[1]、 山中秀介[1]、 奥村光隆[1]

14. Self-diffusion in crystalline silicon: A Car-Parrinello molecular dynamics study
(東大院工[1]、IPCMS[2]、阪大基礎工[3]) ○小泉健一[1]、Mauro Boero[2]、重田育照[3]、押山淳[1]

15. First-layer initial oxidation process of a Si(100) surface: A Car-Parrinello molecular dynamics investigation of the atomic-scale mechanism
(東大院工[1]、IPCMS[2]、阪大基礎工[3]) ○小泉健一[1]、Mauro Boero[2]、重田育照[3]、押山淳[1]

16. 理論研究に基づくナイロンオリゴマー分解酵素に対するアミノ酸効果についての研究
(兵庫県立大院生命[1]、筑波大院数理[2]、阪大院理[3]、兵庫県立大学院工学[4]、阪大院基礎工[5]) ○馬場剛史[1]、神谷克政[2]、松井亨[3]、根来誠司[4]、重田育照[5]

17. ゲルの体積相転移における添加物の効果
(京大理) ○植松祐輝、荒木武昭

18. 溶液内におけるフェノール誘導体の電子・プロトン移動反応
(京大院理) ○稲垣泰一、山本武志

19. 平均場 QM/MM 計算における点電荷近似の問題点を解決する計算手法の開発
(京大院理) ○中農 浩史、山本 武志

20. 好冷性 α-Amylase の酵素活性に及ぼす構造揺らぎの役割に関する理論的研究
(京大院理) ○小杉 貴洋、林 重彦

21. 多重極子を含む RESP 法を用いた QM/MM 自由エネルギー計算
(京大院理) ○井上 雄介、小杉 貴洋、林 重彦

22. Theoretical Analysis of Chalcone Isomerase Catalyzed Reaction
(京大院理[1]、分子科学研究所[2]) ○喜田 龍一[1]、東 雅大[2]、林 重彦[1]、加藤 重樹[1]

23. MS-CASPT2 法を応用したピリジンの超高速緩和過程の理論的研究
(京大院・理[1]、スタンフォード大[2]) ○中野勝博[1]、森俊文[2]、林重彦[1]、加藤重樹[1]

24. 結晶セレンの電荷移動とバンド構造: 平面波 DFT 法での Charge Decomposition
(京大・院) ○松井 正冬

25. Atoms-in-Molecules Analysis of Dipole Moment Enhancement in Hydrogen-Bonded Molecular Crystal 5-Bromo-9-hydroxyphenalenone
（京大理）○大滝大樹、安藤耕司

26. Thermally Induced Synthesis and Properties of Low-Bandgap Conjugated Polymers Containing Isothianaphthene Dimer Subunits
（京都大学大学院工学研究科）○広瀬公平、梅山有和、俣野善博、小野昇、今堀博

27. テレケリック会合高分子の構造形成とレオロジー
(京都大学大学院工学研究科高分子化学専攻) ○古賀毅、田中文彦

28. Reentrant Volume Phase Transition of Cross-linked Poly(N-isopropylacrylamide) Gels in Mixed Hydrogen-Bonding Solvents
(Kyoto Univ.) ○Hiroyuki Kojima, Tsuyoshi Koga, and Fumihiko Tanaka

29. 水素結合超分子系におけるレオロジーの分子機構
(京都大学大学院 工学研究科 高分子化学専攻) ○高橋 孝太郎

30. セルフヒーリングゴムに関する破断と修復の分子シミュレーション
(京都大学大学院 工学研究科 高分子化学専攻) ○鈴村 圭史

31. 感熱高分子水溶液における多層水和と協同性の発現機構
(京都大学大学院 工学研究科 高分子化学専攻) ○松尾 麻子

32. Palladium-Catalyzed Asymmetric Reactions Using Polymer-Based Chiral Phosphine Ligand PQXphos
（京大院工）○山本武司、赤井勇斗、足立拓海、長田裕也、杉野目道紀

33. 遷移金属触媒によるピリジンへのホウ素反応剤の付加
（京大院工）○大嶌和幸、大村智通、杉野目道紀

34. 第一原理計算によるフォノンの非調和項の直接計算
（京大工）○東後 篤史、田中 功

35. 第一原理計算による Eu^{2+}ペロブスカイト酸化物の磁気的相互作用
(京都大学) ○赤松 寛文、熊谷 悠、大場 史康、藤田 晃司、田中 勝久、田中 功

36. 微量元素添加ハイドロキシアパタイトの X 線吸収スペクトルの第一原理計算
(京大院工[1]、大阪府立大院工[2]、名大院工[3]) ◯村田 秀信[1]、設楽 一希[1]、田中 功[1]、中平 敦[2]、松永 克志[3]

37. 水溶液環境下でのハイドロキシアパタイト表面における陽イオン置換固溶に関する第一原理計算
（京大工[1], 名大工[2]）◯森 正弘[1], 松永 克志[2], 田中 功[1]

38. 2D lattice liquid models - 2 次元膜の流体模型
(京大工) ◯石本 志高、村島 隆浩、谷口 貴志、山本 量一

39. 参照軌道を用いた分子軌道の局在化法：レチナール蛋白質の励起状態への応用
(京大福井セ[1]、神戸大情報[2]) ◯長谷川淳也[1]、藤本和宏[2]、河津励[1]

40. GFP-X-CFP モデルペプチドにおけるアミノ酸経由励起エネルギー移動
(京大福井セ[1]、分子研[2]、京大院工[3]、量化研[4]) ◯河津 励[1,2]、 長谷川淳也[1,3,4]

41. 第一原理分子動力学法によるサーモクロミック銅(II)錯体に関する理論的研究
(京大福井セ[1]、京大院工[2]) ◯中尾 嘉秀[1]、竹中 裕喜雄[2]、佐藤 啓文[2]

42. A Nonadiabatic Ab Initio Dynamics Study on Rhodopsin and its Analog Isorhodopsin
(京大福井セ[1]、上智大理工[2]) Wilfredo C. Chung[1]、南部 伸孝[2]、◯石田 俊正[1]

43. 遷移金属酸化物における X 線磁気円二色性の第一原理計算
(京大福井セ) ◯池野 豪一

44. レーザー加熱によるマランゴニ効果の熱流体数値シミュレーション
(京大福井セ) ◯岩城 貴史

45. SFDFT 法による GFP 発色団の理論的研究
(京大福井センター) ◯嶺澤範行

46. 人工力誘起反応法による有機金属触媒反応機構の自動解析と予測
(京大白眉センター[1]、京大福井謙一研究セ[2]、エモリ―大化学[3])
◯前田 理[1,2]、 諸熊 奎治[2,3]

47. Multireference theoretical study of the photodissociation dynamics of ketene
（京大福井セ）◯Hongyan Xiao, Satoshi Maeda, Keiji Morokuma

48. Catalytic Mechanism in Artificial Metalloenzyme: QM/MM Study of Phenylacetylene Polymerization by Rhodium Complex Encapsulated in apo-Ferritin
(FIFC, Kyoto University[1], iCeMS, Kyoto University, [2]) ◯Zhuofeng Ke[1], Satoshi Abe[2], Takafumi Ueno[2], and Keiji Morokuma[1]

49. The Dynamics of Local Chirality during SWCNT Growth: A QM/MD Investigation
(Fukui Institute for Fundamental Chemistry[1], Department of Chemistry, Graduate School of Science, Nagoya University[2], Cherry L. Emerson Center for Scientific Computation and Department of Chemistry, Emory University[3]) ○Joonghan Kim[1], Alister J. Page[1], Stephan Irle[2], and Keiji Morokuma[1,3]

50. Theoretical study on the reduction of nitric oxide in bacterial nitric oxide reductase
(FIFC[1], Emory Univ.[2]) ○Miho Hatanaka[1], Keiji Morokuma[1,2]

51. Photochemistry and Photophysics behind Light-Driven Molecular Rotary Motor
(FIFC, Kyoto Univ.) ○Fengyi Liu, Keiji Morokuma

52. Comparative Reactivity of Ferric-Superoxo and Ferryl-Oxo Species in Heme and Non-Heme Complexes
(FIFC) ○Lung Wa Chung, Xin Li and Keiji Morokuma

53. Chirality-controlled SWCNT growth from hydrocarbon templates
(FIFC) ○Hai-Bei Li, Alister J. Page, Stephan Irle, and Morokuma Keiji

54. Chirality Controlled SWCNT Growth from an Organic Template: The Role of the C_2H Radical
(FIFC) ○Alister J. Page, Haibei Li, Stephan Irle, Keiji Morokuma

55. Theoretical study on the photoisomerization of Mononuclear Ruthenium(II) Monoaquo Complex
(FIFC) ○Lina Ding, Lung Wa Chung, Keiji Morokuma

56. Towards understanding the HppE catalytic mechanism: theoretical modeling of fosfomycin biosynthesis
(FIFC) ○Galina Petrova, Lung Wa Chung, Keiji Morokuma

57. 金属-ブレオマイシンの DNA 損傷機構に関する理論的研究
(京大福井セ) ○松井 亨、 榊 茂好

58. 相対論的 DFT 法による NMR の計算
（京大福井セ） ○吉澤輝高、榊茂好

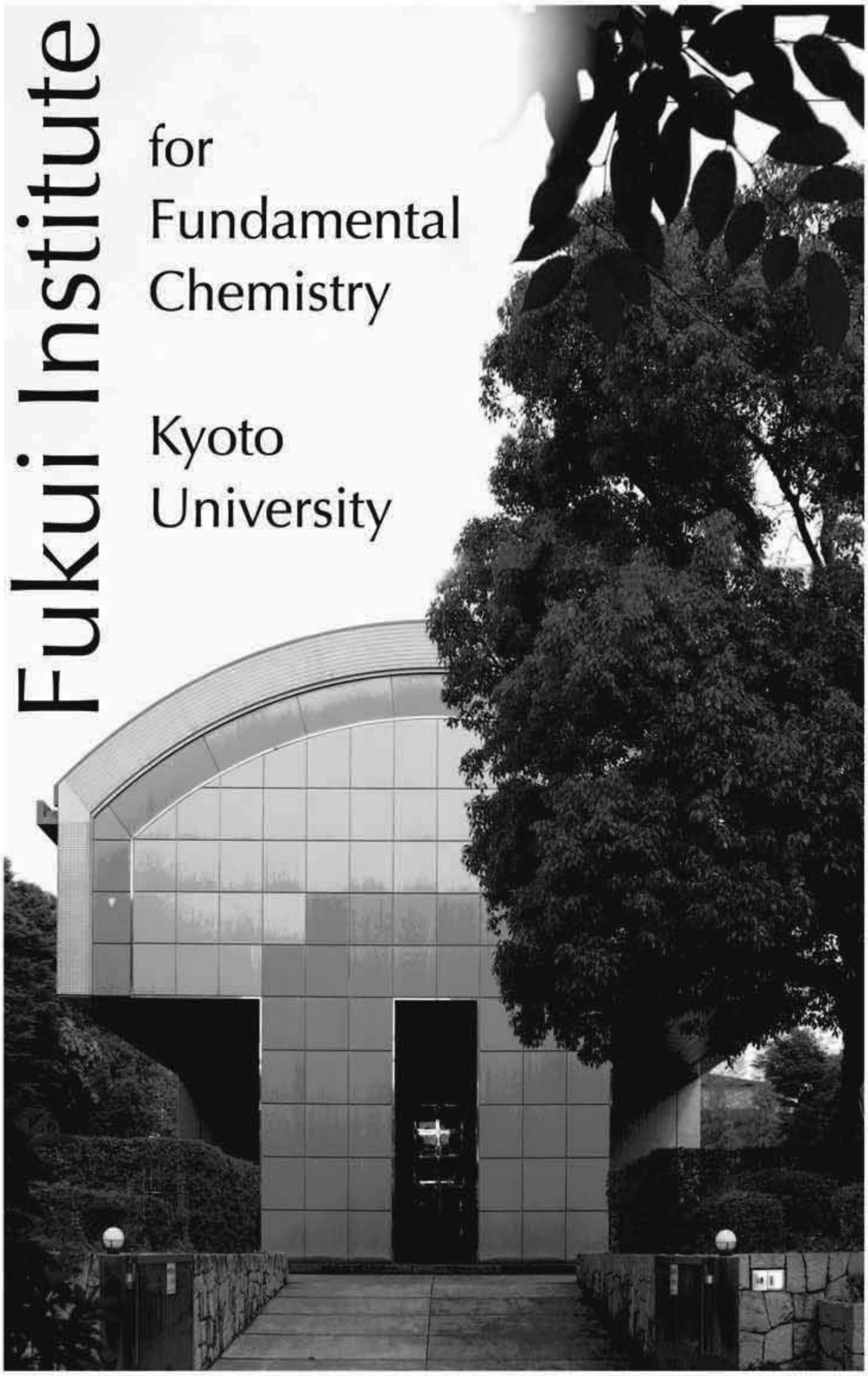
59. 平面4配位型金属錯体と水の相互作用の理論的研究
（京大福井セ）○青野 信治、榊 茂好

60. 金属配位不飽和サイトへの気体分子吸着に関する理論的研究
（京大福井謙一研究セ） ○土方 優、榊 茂好

61. **Theoretical study of Absorption of CO_2, CS_2 and OCS into Hoffman type Metal Organic Framework: Binding Energy Evaluation, Absorption Position and Understanding of Determining Factors**
    (FIFC [1], Grad. School of Sciences, Kyushu Univ.[2], Grad. School. of Eng. Kyoto Univ.[3])
    ◯Milind Deshmukh [1], Masaaki Ohba [2], Kitagawa sususmi [3], Shigeyoshi Sakaki [1]

62. **クロム(I)及び鉄(I)-窒素分子の逆サンドイッチ型錯体の電子構造に関する理論的研究**
    (京大福井謙一研究センター[1]、QCRI[2]) ◯中垣　雅之[1]、黒川　悠索[2]、榊　茂好[1]

63. **水素架橋したビス（シリレン）タングステン錯体の動的挙動に関する理論的研究**
    (京大福井セ[1]、東北大院理[2]) ◯高木望[1]、小田桐悠斗[2]、橋本久子[2]、飛田博実[2]、榊茂好[1]



第9回福井謙一記念研究センターシンポジウム
2012年(平成24年)1月6日(金)
京都大学福井謙一記念研究センター

第9回
福井センターセミナー
The 9th FIFC Seminar

2012年3月16日(金)　14:00-17:00

京都大学福井謙一記念研究センター 3F 大会議室
〒606-8103 京都市左京区高野西開町34-4
（℡075-711-7708)
http://www.fukui.kyoto-u.ac.jp/
(at FIFC, Kyoto Univ. on March, 16(Fri.), 2012)

14:00～15:00 Shinkoh NANBU (Sophia Univ., Tokyo)

“Nonadiabatic dynamics in photochemical processes"

15:00～15:30 Yoshihide NAKAO (FIFC)

“Theoretical Study of Physical Properties in First-Row Transition Metal Complexes”

Coffee break

16:00～17:00 Shoji TAKADA (Kyoto Univ.)

“Coarse-grained molecular simulations of large biomolecules: From theory to applications”

多数の方のご来場を歓迎いたします
We welcome all of you to join.

社会へのアウトリーチ活動

科学技術フェスタin Kyoto 2011（平成23年12月17-18日）

榊リサーチリーダーが、国立京都国際会館にて開催された「科学技術フェスタ in Kyoto 2011」に出展しました。コンピュータを使う化学の研究について、特に、金属などに現れるd電子、d軌道の面白さを伝えました。

ウォークイン　サイエンス（平成24年2月25-26日）

諸熊グループのオフィスアシスタントの三木さん、堀さん、延山さんが、理学研究科・社会交流室が主催する「ウォークイン　サイエンス」に出展し、Zest御池　河原町広場にて理論化学のデモンストレーションをしました。


京都大学アカデミックデイ（平成24年3月10日）

諸熊リサーチリーダーが、「京都大学アカデミックデイ」に出展し、理論化学のおもしろさを伝えました。


── その人と学問 ──

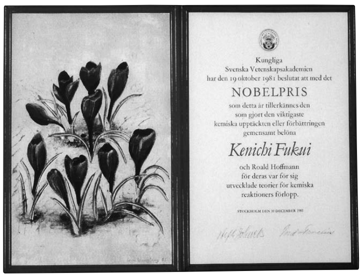
福井謙一博士記念展示コーナー

福井謙一博士は、1981年に日本人として初めてノーベル化学賞を受賞されました。
本センターでは、ノーベル化学賞受賞３０周年という節目の年に、博士の生い立ちから研究生活を通して、ノーベル賞受賞までの軌跡を辿っていただくための展示コーナーを設置しました。
博士の人間としての奥行きの広さや学問への情熱を感じとっていただければと思います。

福井謙一（1918年～1998年）
1981年ノーベル化学賞受賞

化学反応がおきるすべての仕組みが示せるような理論がなかったころ、福井謙一とロアルドホフマンは「フロンティア軌道理論」という、化学反応のほとんどをカバーできる画期的な理論を共同で導きました。この理論が全ての化学における根源的なものになりました。

ノーベル賞メダル（レプリカ）**：1981 年**
ノーベル賞受賞者に贈られる。
メダルの表にはアルフレッド・ノーベルの横顔、裏には自然の女神と科学の女神が刻まれている。
Nobel Prize Medal, 1981, replica

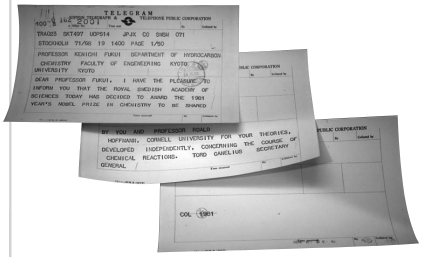


Kungliga
Svenska Vetenskapsakademien
har den 19 oktober 1981 beslutat att med det
NOBELPRIS
som detta år tillerkännes den
som gjort den viktigaste
kemiska upptäckten eller förbättringen
gemensamt belöna
Kenichi Fukui
och Roald Hoffmann
för deras var för sig
utvecklade teorier för kemiska
reaktioners förlopp.

STOCKHOLM DEN 10 DECEMBER 1981

ノーベル賞賞状（レプリカ）**：1981 年**
メダルと同時に授与される。
受賞者一人一人に対して、異なる絵が手書きされている。
福井博士のものは、サフラン（クロッカス）である。
Nobel Prize Diploma,1981, replica

カエルの勲章（レプリカ）**：1981 年**
ノーベル賞受賞者時に、スウェーデンの大学生主催のパーティ席上でノーベル賞受賞者たちがカエル跳びをさせられた。そのときのご褒美。
Frog Prize Gifted by Swedish Students, 1981, replica



TELEGRAM
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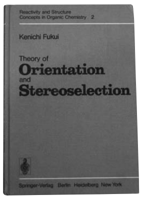
STOCKHOLM 71/68 19 1400 PAGE 1/50
PROFESSOR KENICHI FUKUI DEPARTMENT OF HYDROCARBON CHEMISTRY FACULTY OF ENGENEERING KYOTO UNIVERSITY KYOTO
DEAR PROFESSOR FUKUI, I HAVE THE PLEASURE TO INFORM YOU THAT THE ROYAL SWEDISH ACADEMY OF SCIENCES TODAY HAS DECIDED TO AWARD THE 1981 YEAR'S NOBEL PRIZE IN CHEMISTRY TO BE SHARED
BY YOU AND PROFESSOR ROALD HOFFMANN, CORNELL UNIVERSITY FOR YOUR THEORIES, DEVELOPED INDEPENDENTLY, CONCERNING THE COURSE OF CHEMICAL REACTIONS. TORD GANELIUS SECRETARY GENERAL
COL 1981

ノーベル化学賞授賞通知電報（コピー）**：1981 年**
Information Telegram for Nobel Prize in Chemistry, 1981, copy

愛読書（中学時代）
ファーブル「昆虫記」（コピー）
赤鉛筆で書き込みが見える。1925 年版。
Favorite Book, Souvenirs Entomologiques, by J-H.Fabre, 1925,copy

愛用の旅行用小辞書（レプリカ）
博士は語学が好きで、海外旅行のときにはこのような辞書をいつも携帯していた。
Portable Dictionaries during World Travels; replica

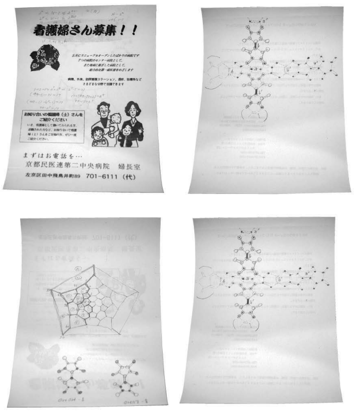


Reactivity and Structure
Concepts in Organic Chemistry 2
Kenichi Fukui
Theory of Orientation and Stereoselection
Springer-Verlag Berlin Heidelberg New York

著書「Theory of Orientation and Stereoselection」
（ドイツから出版）
Theory of Orientation and Stereoselection Written by K. Fukui Published in Germany

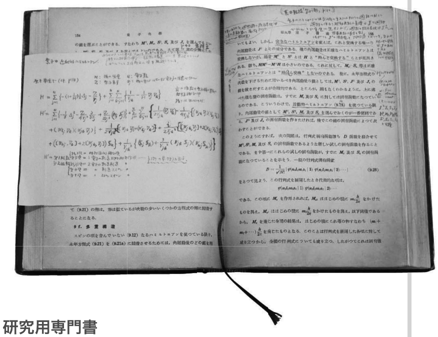
化学反応と電子の軌道
福井謙一
著
丸善株式会社

著書「化学反応と電子の軌道」
Chemical Reactions and Electron Orbitals Written by K. Fukui

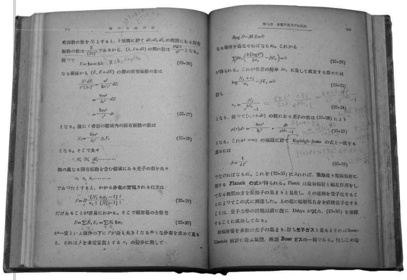


看護婦さん募集！！
5月にリニューアルオープンしたばかりの病院です
7つの病院のセンター病院として、
また地域に根ざした病院として、
総合的な第一線医療をめざします
病棟、外来、訪問看護ステーション、透析、診療所など
さまざまな分野で活躍できます
お知り合いの看護婦（士）さんを
ご紹介ください
いま、看護婦として働いておられる方、退職された方など、お知り合いで看護婦（士）さんをご存知の方、ぜひ一度ご紹介ください。
まずはお電話を…
京都民医連第二中央病院　婦長室
左京区田中飛鳥井町89　701-6111（代）

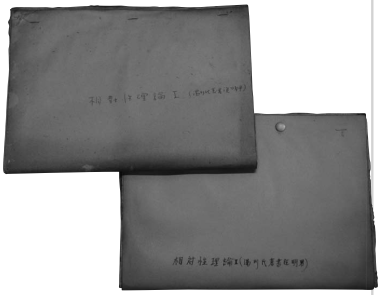
絶筆研究メモ（コピー）**：1997 年**
フラーレン分子の軌道相互作用の解析である。
Final Research Memo, Analysis of Orbital Interaction of Fullerenes, 1977, copy



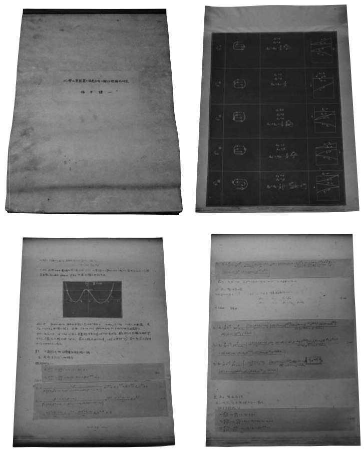
研究用専門書
（アイリング・ウォルター・キムボール 量子化学）（コピー）
多くの書き込みメモがある。1953 年版。
Quantum Chemistry
by H. Eyring, J. Walter, and G. E. Kimball, 1953, copy



研究用専門書
（湯川秀樹 量子力学序説）（コピー）
この中の数式を誘導したものが研究メモとして残っている。
1947 年版。
Introduction to Quantum Mechanics by H. Yukawa, 1947, copy



研究メモ
湯川博士「相対性理論Ⅰ」
説明用（コピー）
Research Memos for
“Theory of Relativity I”
by Dr. H. Yukawa, copy

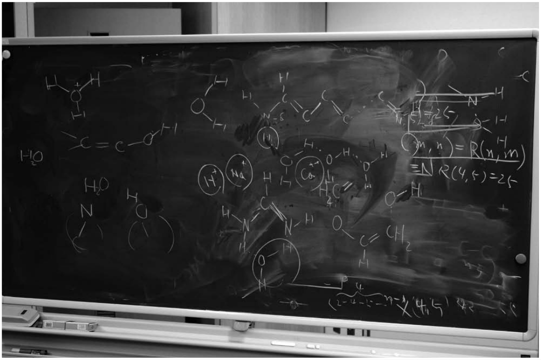


工学博士の学位論文
「化学工業装置の温度分布に関する理論的研究」（コピー）
1948 年
Dissertation, 1948, copy

モンロー電動式計算機
福井研究室での研究に使われた。
Monroe Electric Calculator used in Fukui’s Laboratory

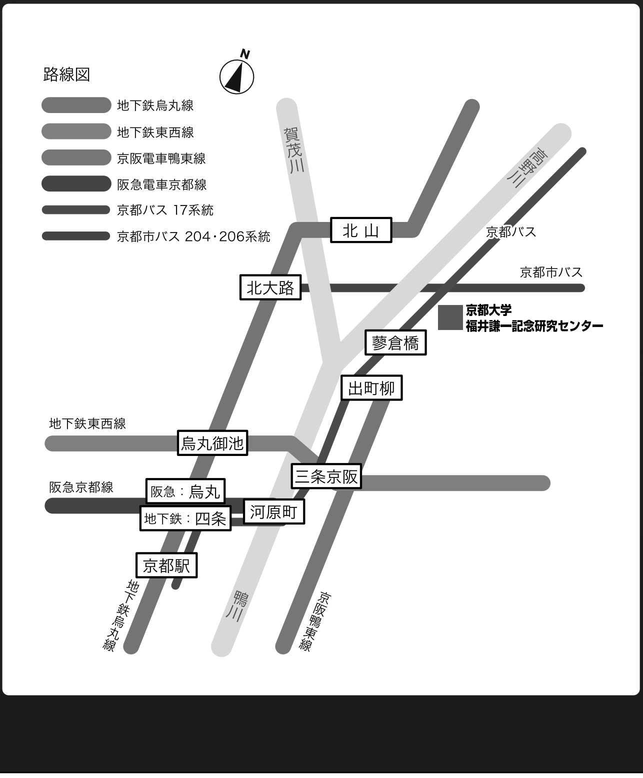
肖像切手（5 ケ国）（コピー）
福井博士の肖像をデザインした切手が各国から出ている。
Postage Stamps Featuring Dr. Fukui from Five Countries, copy

福井謙一博士記念室



博士が記述した黒板をそのまま保存している

地図



京都大学福井謙一記念研究センター

http://www.fukui.kyoto-u.ac.jp

毎日新聞　2012年1月7日　朝刊

21　京都　市内　2012年（平成24年）1月7日（土）

京都

福井謙一博士ノーベル化学賞受賞30年

ゆかりの品でしのぶ

京大センター
コーナー開設

ノーベル賞のメダルを前に思い出を語る福井友栄さん＝左京区の京都大福井謙一記念研究センターで

ノーベル化学賞を1981年に受賞した福井謙一博士（1918～98年）ゆかりの品を集めた記念展示コーナーが6日、京都大福井謙一記念研究センター（京都市左京区高野西開町）にオープンした。

受賞30年を記念したもので、ノーベル賞のメダルや賞状のレプリカのほか、細かい文字でぎっしり書き込みされた専門書、研究室で使われていた電動式計算機、中学生の頃に愛読したファーブル昆虫記などを展示。博士が亡くなる少し前に、新聞の折り込みチラシの裏側に分子軌道に関する計算式を書き込んだ研究メモなど、最後まで研究に打ち込んだ生涯をしのばせる遺品もある。

除幕式に参加した夫人の友栄さん(86)は「もう30年もたったのかと感慨深い。主人は独創性を持てと常に若い人に言っていた。また技術と科学が相互作用でどんどん進歩していくなかで、それをコントロールする見識が大切だと話していた。そうした精神をくみ取ってほしい」と話した。また田中功・同研究センター長は「先生の学問への情熱を若い人に感じ取ってほしい」と述べた。

一般見学も可能。同センター（075・711・7708）。

【榊原雅晴】

2012年(平成24年)1月16日 読売新聞朝刊 14頁(科学面)

福井謙一さんの足跡たどる展示

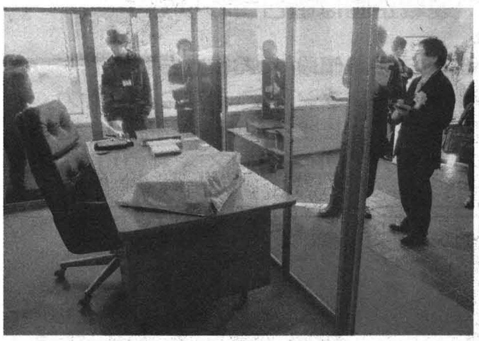
京大

1981年に日本人で初めてノーベル化学賞を受賞した福井謙一氏の足跡をたどる展示コーナーが、京都大福井謙一記念研究センター（京都市）の1階ロビーに開設された＝写真＝。筆箱や辞書を置いた愛用の机などを常設展示する。

福井氏は、どのような化学反応が起きるかを計算で予測する「フロンティア電子理論」で同賞を受賞。98年に亡くなるまで、同センター前身の財団法人基礎化学研究所所長を務めた。

2011年で受賞30周年になるのを機に、京大が展示を決めた。82年の京大退官まで学内で20年間使った机、同賞の賞状とメダルのレプリカや授賞式の写真、亡くなる直前に折り込み広告の裏に記した研究メモのコピーなど、約40点が並べられている。

6日に行われた除幕式には、妻の友栄さん（86）が出席。「生前、若い人には独創的な考えで技術を発展させてほしいと願っていた。展示品から、その思いを感じ取ってもらえれば」と話していた。大学休校日を除く平日午前9時～午後5時に一般公開している。問い合わせは同センター（075・711・7708）。



京大広報　2012年2月号（No.675）から転載

福井謙一記念研究センターの展示コーナー（福井夫人の話に聴き入る参加者たち）
—関連記事　本文3586ページ—

福井謙一記念研究センターに展示コーナーを開設し，シンポジウムを開催

福井謙一記念研究センターでは，１階エントランスホールに福井謙一博士の展示コーナーを開設し，１月６日（金）に除幕式とシンポジウムを開催した。

この展示コーナーは，福井博士のノーベル化学賞受賞30周年を機会に，博士にゆかりの文物やその複製を収集し，公開したものである。ノーベル賞のメダルや賞状のレプリカなど受賞に関連する品々をはじめ，博士の愛読書，学位論文など受賞に至る軌跡を辿ることができる。福井博士がノーベル賞受賞時に使用されていた机には，愛用のタイプライター，分子軌道をまとめた書籍，辞書，鉛筆などが並べられ，博士が研究された当時の様子を再現している。

これらの展示物は，福井博士の門下生でもある田中一義副センター長（工学研究科教授）が福井家をはじめ本学大学文書館などの関係者を訪れ，協力をお願いし，収集したものである。

コーナーには，博士が逝去される前年に書かれた絶筆研究メモが展示されており，博士のたゆみなき科学への情熱を示す貴重な資料となっている。

式典では，江﨑信芳理事・副学長と小森　悟工学研究科長からの挨拶があり，江﨑理事は「若い学生の刺激となり，京都大学から次のノーベル賞につながること」への期待を述べた。引き続いて，福井友榮夫人と田中　功センター長を加えて，テープカットが行われた。

式典の後，学内外からの多数の研究者，一般参加者が展示物を見学し，研究者としての博士の姿に思いをはせた。友榮夫人は，博士が「技術の進化をコントロールする知恵が大切だ」と述べておられたことを振り返るなど，参加者と歓談された。

引き続き行われたシンポジウムでは，理化学研究所基幹研究所の玉尾皓平所長，当センターの諸熊奎治リサーチリーダー，理化学研究所計算科学研究機構の平尾公彦機構長による講演が行われた。これらの貴重な講演に対して，参加者からは多くの質問が寄せられ，盛会のうちに終了した。

テープカットの様子

シンポジウムの様子

（福井謙一記念研究センター）

京都大学福井謙一記念研究センター　年報　2011

2012 年 12 月発行

発行人　　田 中 一 義

編　者　　石 田 俊 正

発行所　　京都大学福井謙一記念研究センター
（京都市左京区高野西開町 34-4）

印刷所　　株式会社 エヌジーピー
（京都市右京区太秦森ヶ東町 21-10）

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Annual Report 2011