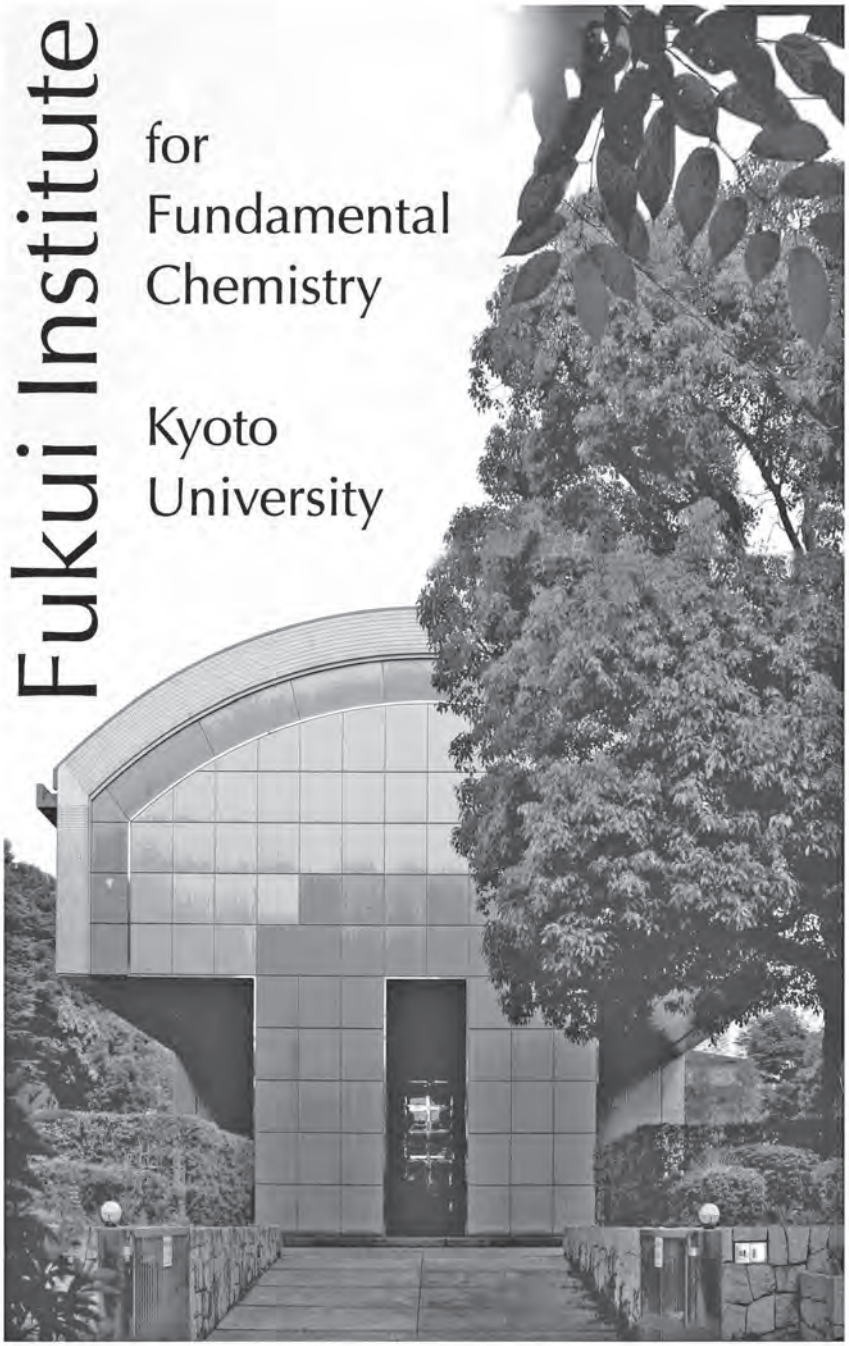
京都大学
福井謙一記念研究センター

Annual Report 2013

Fukui Institute for Fundamental Chemistry Kyoto University

年　報
2013



京都大学
福井謙一記念研究センター

はじめに

2013年度(平成25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。専任教員定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、センター長のほか副センター長と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11名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。そして世界中からの公募による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り、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2006年～2012年(平成18年～24年)の間、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専念されました。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として転出されました。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、2014年(平成26年)3月に日本化学会賞を受賞されました。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、センターが博士学位を取得した若手研究者のさらなる切磋琢磨の場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を終えられた多くの方々が、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)にアジア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、九州大学、分子科学研究所、北京師範大学の教授になり、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。

本センターで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。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、一層の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～初冬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。

また、現在本センターのシニアリサーチフェローである諸熊奎治先生は、複雑分子系の理論研究の発展に多大な貢献をしたとして、2012 年(平成 24 年)11 月に文化功労者の顕彰を受けられました。これは先生ご自身の栄誉はもとより、本センターの名をさらに高めて頂いたことでもあり、大変喜ばしいことであります。

本センターは、上述のように規模は大きくありませんが、研究活動はきわめて活発です。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 26 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

Ⅴ　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/AnnualReport2013.pdf）

Ⅰ　専任教員・スーパーバイザー

１．教員組織

平成２５年度

職　　名		氏　名	備　考
センター長		田 中　一 義	工学研究科分子工学専攻
総合研究部門	副センター長	（欠員中）	
理論研究部門	副センター長	赤 木　和 夫	工学研究科高分子化学専攻
協　議　員	工学研究科長	北 野　正 雄	工学研究科電子工学専攻
	理学研究科長	有 賀　哲 也	理学研究科化学専攻
	化学研究所長	佐 藤　直 樹	化学研究所複合基盤化学研究系
総合研究部門 スーパーバイザー	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	田 中　勝 久	工学研究科材料化学専攻
	教　　授	田 中 耕一郎	理学研究科物理学・宇宙物理学専攻
	教　　授	時 任　宣 博	化学研究所物質創製化学研究系
	教　　授	八 尾　　誠	理学研究科物理学第一教室
理論研究部門 スーパーバイザー	教　　授	田 中　　功	工学研究科材料工学専攻
	教　　授	田 中　庸 裕	工学研究科分子工学専攻
	教　　授	谷 村　吉 隆	理学研究科化学専攻
	教　　授	山 本　量 一	工学研究科化学工学専攻
	教　　授	高 田　彰 二	理学研究科生物科学専攻
	教　　授	林　　重 彦	理学研究科化学専攻
総合研究部門	准 教 授	池 田 昌 司	専任
理論研究部門	准 教 授	（欠員中）	
永瀬グループ	シニアリサーチ フェロー	永 瀬　　茂	研究員（学術研究奨励）
諸熊グループ	シニアリサーチ フェロー	諸 熊　奎 治	研究員（学術研究奨励）
榊グループ	リサーチ リーダー	榊　　茂 好	研究員（学術研究奨励）

2．教員プロフィール

⑴ 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
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【研究分野】	物理化学・量子化学
【現在の研究課題】	量子機能化学、物理化学
【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. 物理化学（化学マスター講座）（共著 , 丸善 , 2010） 2. 炭素学（共編著 , 化学同人 , 2011） 3. 統計力学入門　化学者の視点から（単著 , 化学同人 , 2014） （以上著書） 1. A Stable Germanone as the First Isolated Heavy Ketone with a Terminal Oxygen Atom (L. Li, T. Fukawa, T. Matsuo, D. Hashizume, H. Fueno, K. Tanaka, and K. Tamao) *Nature Chem*., **4**, 361-365 (2012). 2. 1,3,5-Benzenetriamine Double- and Triple-Decker Molecules (D. Sakamaki, A. Ito, K. Tanaka, K. Furukawa, T. Kato, and M. Shiro) *Angew. Chem. Int. Ed*., **51**, 8281-8285 (2012). 3. Electronic Spectra of Cycl[3.3.2]azine and Related Compounds: Solvent Effect on Vibronic Couplings (Y. Shigemitsu, M. Uejima, T. Sato, K. Tanaka, and Y. Tominaga) *J. Phys. Chem. A*, **116**, 9100-9109 (2012). 4. A Triphenylamine Double-Decker: From a Delocalized Radical Cation to a Diradical Dication with an Excited Triplet State (Y. Yokoyama, D. Sakamaki, A. Ito, K. Tanaka, and M. Shiro) *Angew. Chem. Int. Ed*., **51**, 9403-9406 (2012). 5. Mechanisms of Localization in Isotope-Substitutes Dynamical Jahn-Teller Systems (N. Iwahara, T. Sato, K. Tanaka, and L. F. Chibotaru) *Eur. Phys. Lett*., **100**, 43001 1-6 (2012).

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7. A Polymacrocyclic Oligoarylamine with a Pseudobeltane Motif: Towards a Cylindrical Multispin System (D. Sakamaki, A. Ito, K. Furukawa, T. Kato, M. Shiro, and K. Tanaka) *Angew. Chem. Int. Ed.*, **51**, 12776-12781 (2012).

8. Meta-Para-Linked Octaaza[18]cyclophanes and Their Polycationic States (D. Sakamaki, A. Ito, K. Furukawa, T. Kato, and K. Tanaka) *J. Org. Chem.*, **78**, 2947-2956 (2013).

9. Vibronic Couplings in Cycloadditions to Fullerenes (N. Haruta, T. Sato, N. Iwahara, and K. Tanaka) *J. Phys. C: Conf. Ser.*, **428**, 012003 1-7 (2013).

10. Vibronic Coupling Density and Related Concepts (T. Sato, M. Uejima, N. Iwahara, N. Haruta, K. Shizu, and K. Tanaka) *J. Phys. C: Conf. Ser.*, **428**, 012010 1-19 (2013).

11. Vibronically Induced Activation Mechanism in Photocatalysis of Highly Dispersed Vanadium Oxide Supported on Silica, V_2O_5/SiO_2: Evidence in Phosphorescence Spectra (N. Iwahara, T. Sato, K. Tanaka, and T. Tanaka) *Chem. Phys. Lett.*, **584**, 63-66 (2013).

12. Reaction Mechanism in the Mechanochemical Synthesis of Dibenzophenazine: Application of Vibronic Coupling Density Analysis (N. Haruta, T. Sato, K. Tanaka, and M. Baron) *Tetrahedron Lett.*, **54**, 5920-5923 (2013).

13. Redox Modulation of *para*-Phenylenediamine by Substituted Nitronyl Nitroxide Groups and Their Spin States (A. Ito, R. Kurata, D. Sakamaki, S. Yano, Y. Kono, Y. Nakano, K. Furukawa, T. Kato, and K. Tanaka) *J. Phys. Chem. A*, **117**, 12858-12867 (2013).

14. Vibronic Couplings in C_{60} Derivatives for Organic Photovoltaics (N. Iwahara, T. Sato, K. Tanaka, and H. Kaji) *Chem. Phys. Lett.*, **590**, 169-174 (2013).

15. Preparation of D-A Polymer with Disilanobithiophene as New Donor Component and Application to High-voltage Bulk Heterojunction Polymer Solar Cell (J. Ohshita, M. Nakashima, D. Tanaka, Y. Morihara, H. Fueno, and K. Tanaka) *Polym. Chem.*, **5**, 346-349 (2014).

16. Enhancement of Fluorescence in Anthracene by Chlorination: Vibronic Coupling and Transition Dipole Moment Density Analysis (M. Uejima, T. Sato, K. Tanaka, and H. Kaji) *Chem. Phys.*, **430**, 47-55 (2014).

17. Pseudo Jahn-Teller Origin of Distortion in [6]Cycloparaphenylene (Y. Kameoka, T. Sato, T. Koyama, K. Tanaka, and T. Kato) *Chem. Phys. Lett.*, **598**, 69-74 (2014).

18. Highly Coplanar (*E*)-1,2-Di(1-naphthyl)disilene Involving a Distinct CH-π Interaction with the Perpendicularly Oriented Protecting Eind Group (M. Kobayashi, N. Hayakawa, K. Nakabayashi, T. Matsuo, D. Hashizume, H. Fueno, K. Tanaka, and K. Tamao) *Chem. Lett.*, **43**, 432-434 (2014).

（以上学術論文）

⑵ 副センター長

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【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】	カリフォルニア大サンタバーバラ校交換研究員、コーネル大客員研究員
【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 International Conference on Science and Technology of Synthetic Metals (2010).
【主な著書、学術論文】（過去 5 年以内）	1. J. Bu, K. Watanabe, H. Hayasaka, K. Akagi, “Photochemically Colour-Tuneable White Fluorescence Illuminants consisting of Conjugated Polymer Nanospheres”, *Nat. Commun.* **5**, 3799 (2014). 2. S. Matsushita, B. Yan, S. Yamamoto, Y. S. Jeong, K. Akagi, “Helical Carbon and Graphite Films Prepared from Helical Poly(3,4-ethylenedioxythiophene) Films Synthesized by Electrochemical Polymerization in Chiral Nematic Liquid Crystals”, *Angew. Chem., Int. Ed.*, **53**, 1659 (2014). 3. B. A. San Jose, S. Matsushita, K. Akagi, “Lyotropic Chiral Nematic Liquid Crystalline Aliphatic Conjugated Polymers Based on Di-Substituted Polyacetylene Derivatives that Exhibit High Dissymmetry Factors in Circularly Polarized Luminescence”, *J. Am. Chem. Soc.*, **134**, 19895 (2012). 4. K. Watanabe, H. Iida, K. Akagi, “Circularly Polarized Blue Luminescent Spherulites Consisting of Hierarchically Assembled Ionic Conjugated Polymers with a Helically π-Stacked Structure”, *Adv. Mater.*, **24**, 6451 (2012). 5. H. Hayasaka, T. Miyashita, M. Nakayama, K. Kuwada, K. Akagi, “Dynamic Photoswitching of Helical Inversion in Liquid Crystals Containing Photoresponsive Axially Chiral Dopants”, *J. Am. Chem. Soc.*, **134**, 3758 (2012).
【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）

⑶ スーパーバイザー

【氏名（ふりがな）】	北川　進　（きたがわ　すすむ）
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【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】	多孔性配位高分子の化学とその応用
【研究内容キーワード】	配位空間の化学、メゾスコピック化学、多孔性配位高分子
【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. “Mesoscopic architectures of porous coordination polymers fabricated by pseudomorphic replication”, J. Reboul, S. Furukawa, N. Horike, M. Tsotsalas, K. Hirai, H. Uehara, M. Kondo, N. Louvain, O. Sakata and S. Kitagawa, *Nature Materials*, **2012**, 11,717-723. (Cover Picture) 2. “Shape-Memory Nanopores Induced in Coordination Frameworks by Crystal Downsizing”, Y. Sakata, S. Furukawa, M. Kondo, K. Hirai, N. Horike, Y. Takashima, H. Uehara, N. Louvain, M. Meilikhov, T. Tsuruoka, S. Isoda, W. Kosaka, O. Sakata, and S. Kitagawa, *Science*, **2013**, 339, 193. 3. “Self-Accelerating CO Sorption in a Soft Nanoporous Crystal”, H. Sato, W. Kosaka, R. Matsuda, A. Hori, Y. Hijikata, R.V. Belosludov, S. Sakaki, M. Takata, and S. Kitagawa, *Science*, **2014**, 343, 167-170.
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【学会活動】	粉体粉末冶金協会
【主な著書、学術論文】（過去 5 年以内）	1. 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. 2. 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. 3. H. Akamatsu, K. Fujita, H. Hayashi, T. Kawamoto, Y. Kumagai, Y. Zong, K. Iwata, F. Oba, I. Tanaka, and K. Tanaka, “Crystal and electronic structure and magnetic properties of divalent europium perovskite oxides $EuMO^3$ (M=Ti, Zr, and Hf): Experimental and first-principles approaches”, *Inorganic Chemistry* **51** (2012) 4560-4567. 4. X. Meng, U. Guler, A. V. Kildishev, K. Fujita, K. Tanaka, and V. M. Shalaev, “Breaking symmetry of plasmonic nanostructures: an efficient route towards unidirectional spaser”, *Scientific Reports* **3** (2013) 1241-1-5. 5. Y. Hasegawa, M. Maeda, T. Nakanishi, Y. Doi, Y. Hinatsu, K. Fujita, K. Tanaka, H. Koizumi, and K. Fushimi, “Effective optical Faraday rotations of semiconductor EuS nanocrystals with paramagnetic transition-metal ions”, *Journal of the American Chemical Society* **135** (2013) 2659-2666. 6. X. Meng, A. V. Kildishev, K. Fujita, K. Tanaka, and V. M. Shalaev, “Wavelength-tunable spasing in the visible”, *Nano Letters* **13** (2013) 4106–4112. 7. H. Akamatsu, K. Fujita, T. Kuge, A. S. Gupta, A. Togo, S. Lei, F. Xue, G. Stone, J. M Rondinelli, L. Chen, I. Tanaka, V. Gopalan, and K. Tanaka, “Inversion symmetry breaking by oxygen octahedral rotations in Ruddlesden-Popper $NaRETiO_4$ family”, *Physical Review Letters* **112** (2014).187602-1-5.
【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)、Award of the Outstanding Papers Published in the JCerSJ in 2013（2013 年）

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【主な著書、学術論文】 （過去 5 年以内）	1. Tobias Kampfrath, Koichiro Tanaka and Keith A. Nelson, “Resonant and nonresonant control over matter and light by intense terahertz transients”, *Nature Photonics* **7**,680–690 (2013) 2. K. Shinokita, H. Hirori, K. Tanaka, T. Mochizuki, C. Kim, H. Akiyama, L. N. Pfeiffer and K. W. West, “Terahertz-Induced Optical Emission of Photoexcited Undoped GaAs Quantum Wells”, *Phys. Rev. Lett.* **111**, 067401 (2013) 3. F. Blanchard, A. Doi, T. Tanaka, and K. Tanaka, “Real-Time, Subwavelength Terahertz Imaging”, *Annu. Rev. Mater. Res.* **43**:11.1–11.23 (2013) 4. Shuntaro Tani, Francois Blanchard, and Koichiro Tanaka “Ultrafast Carrier Dynamics Under High Electric Field in Graphene”, *Phys. Rev. Lett.* **109**, 166603 (2012) 5. E. Collet, H. Watanabe, N. Bréfuel, L. Palatinus, L. Roudaut, L. Toupet, K. Tanaka, J.-P. Tuchagues, P. Fertey, S. Ravy, B. Toudic, H. Cailleau, “Aperiodic spin state ordering of bi-stable molecules and its photoinduced erasing”, *Phys. Rev. Lett.* **109**, 257206 (2012) 6. H. Hirori, K. Shinokita, M. Shirai, S. Tani, Y. Kadoya, K. Tanaka, “Extraordinary carrier multiplication gated by a picosecond electric field pulse”, *Nature Communications* **2**, 594/1-594/6, (2011)
【学術関係の受賞など】	○平成 26 年度文部科学大臣表彰 科学技術賞 研究部門 2014,4/7 ○平成 26 年度レーザー学会 業績賞・論文賞（研究部門）2014,4/18

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【所属学会】	Chemical Society of Japan, American Chemical Society, The Society of Physical Organic Chemistry, Japan, The Society of Silicon Chemistry, Japan, Kinki Kagaku Kyokai, The Society of Synthetic Organic Chemistry, Japan.
【学会活動】	1996- The Society of Silicon Chemistry, Japan, Standing Board Member; 2006- International Symposium on Inorganic Ring Systems, IAB Member; 2006- International Conference on Heteroatom Chemistry, IAB Member; 2009-2011 The Chemical Society of Japan, a Member of Board of Directors; 1998-2006 Journal of Physical Organic Chemistry, Associate Editor for Asia; 2006-2009 Organometallics, Advisory Board Member; 2011- The Society of Physical Organic Chemistry, Japan, Standing Board Member; 2012 10th International Conference on Heteroatom Chemistry, Chairman; 2012- International Symposium on Silicon Chemistry, IAB Member; 2013- International Conference on Organometallic and Coordination Chemistry of Germanium, Tin and Lead (ICCOC-GTL), IAB Member; 2013- Bulletin of the Chemical Society of Japan (CSJ), Editor-in-Chief
【主な著書、学術論文】（過去 5 年以内）	1. Syntheses and Structures of an “Alumole” and Its Dianion, Agou, T.: Wasano, T.; Jin, P; Nagase, S.; Tokitoh, N. *Angew. Chem. Int. Ed.* **2013**, *125*, 10215–10218. 2. Synthesis and Properties of 4,5,6-Triphospha[3]radialene, Miyake, H.; Sasamori, T.; Tokitoh, N. *Angew. Chem. Int. Ed.* **2012**, *51*, 3458-3461. 3. Synthesis of Kinetically Stabilized 1,2-Dihydrodisilenes, Agou, T.; Sugiyama, Y.; Sasamori, T.; Sakai, H.; Furukawa, Y.; Takagi, N.; Guo, J. D.; Nagase, S.; Hashizume, D.; Tokitoh, N. *J. Am. Chem. Soc.* **2012**, *134*, 4120-4123. 4. Fluorination Reaction of a Ditelluride Bearing Bulky Aryl Substituents: Formation of Mixed-Valent Te(IV)-Te(II) Ditelluride Difluoride, Sasamori, T.; Sugamata, K.; Tokitoh, N. *Chem-Asian J.* **2011**, *6*, 2301-2303. 5. Reactivity of an aryl-substituted silicon-silicon triple bond: 1,2-disilabenzenes from the reactions of a 1,2-diaryldisilyne with alkynes, Han, J. S.; Sasamori, T.; Mizuhata, Y.; Tokitoh, N. *Dalton Trans.* **2010**, *39*, 9238-9240.
【学術関係の受賞】	1992 Incentive Award of the Society of the Synthetic Organic Chemistry, Japan 1996 Incentive Award of the Society of Silicon Chemistry, Japan 1998 Japan IBM Science Award 2003 Chemical Society of Japan Award for Creative Work (CSJ) 2003 Alexander von Humboldt Research Award 2002, 2005, 2007, 2009, 2010 and 2013 BCSJ Awards (CSJ) 2007 Lectureship Award of National Science Council, Republic of China 2010 The 3rd Kim Yong Hae Lectureship Award (KAIST, Korea) 2010 Best Reviewer Commendation (Japan Society for the Promotion of Science) 2013 Alexander von Humboldt Research Award Reinvitation

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【主な著書、学術論文】（過去 5 年以内）	1. A. Togo and I. Tanaka, “Evolution of crystal structures in metallic elements”, *Physical Review B*, **87** 184104 1-6 (2013). 2. H. Akamatsu, Y. Kumagai, F. Oba, K. Fujita, K. Tanaka, and I. Tanaka, “Strong Spin-Lattice Coupling Through Oxygen Octahedral Rotation in Divalent Europium Perovskites,” *Advanced Functional Materials*, **23**[15] 1864-72 (2013). 3. M. Choi, F. Oba, Y. Kumagai, and I. Tanaka, “Anti-ferrodistortive-Like Oxygen-Octahedron Rotation Induced by the Oxygen Vacancy in Cubic SrTiO3,” *Advanced Materials*, **25**[1] 86-90 (2013). 4. R. Ishikawa, N. Shibata, F. Oba, T. Taniguchi, S. D. Findlay, I. Tanaka, and Y. Ikuhara, “Functional Complex Point-Defect Structure in a Huge-Size-Mismatch System,” *Physical Review Letters*, **110**[6] (2013). 5. D. Han, T. Uda, Y. Nose, T. Okajima, H. Murata, I. Tanaka, and K. Shinoda, “Tetravalent Dysprosium in a Perovskite-Type Oxide,” *Advanced Materials*, **24**[15] 2051-53 (2012). 6. Y. Koyama, H. Arai, Z. Ogumi, I. Tanaka, and Y. Uchimoto, “Co K-edge XANES of LiCoO2 and CoO2 with a variety of structures by supercell density functional calculations with a core hole,” *Physical Review B*, **85**[7] (2012). 7. Y. Kumagai, A. Seko, F. Oba, and I. Tanaka, “Ground-state search in multicomponent magnetic systems,” *Physical Review B*, **85**[1] (2012). 8. B. Liu, A. Seko, and I. Tanaka, “Cluster expansion with controlled accuracy for the MgO/ZnO pseudobinary system via first-principles calculations,” *Physical Review B*, **86**[24] (2012).
【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・ｼﾞｰﾎﾞﾙﾄ賞（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）

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【主な著書、学術論文】 （過去 5 年以内）	1. A Doping Technique Suppressing Undesirable H_2 Evolution Derived from Overall Water Splitting in Highly Selective Photocatalytic Conversion of CO_2 in and by Water, Kentaro Teramura, Zheng Wang, Saburo Hosokawa, Yoshihisa Sakata, Tsunehiro Tanaka, *Chemistry –A European Journal,* 2014, in press. 2. Effect of High-Temperature Calcination on the Generation of Brønsted Acid Sites on WO_3/Al_2O_3, Tomoyuki Kitano, Tomohiro Hayashi, Toshio Uesaka, Tetsuya Shishido, Kentaro Teramura, and Tsunehiro Tanaka, *Chem.Cat.Chem*., 2014, in press. 3. Local Structure and La L_1, and L_3-edge XANES Spectra of Lanthanum Complex Oxides, Hiroyuki Asakura, HideoTetsuya Shishido, Kentaro Teramura, Tsunehiro Tanaka, *Inorg. Chem*., 2014, in press 4. Ultrathin Rhodium Nanosheets, Haohong Duan, Ning Yan, Rong Yu, Chun-Ran Chang, Gang Zhou, Jie Zhang, Han-Shi Hu, Hongpan Rong, Junjie Mao, Zhiqiang Niu, Yuen Wu, Shuo Zhang, Liwei Chen, Hiroyuki Asakura, Tsunehiro Tanaka, Paul Joseph Dyson, Jun Li, Yadong Li, *Nature Commun*., 2014, 5:3093. 5. Vibronically Induced Activation Mechanism in Photocatalysis of Highly Dispersed Vanadium Oxide Supported on Silica, V_2O_5/SiO_2: Evidence in Phosphorescence Spectra, Tohru Sato, Naoya Iwahara, Kazuyoshi Tanaka and Tsunehiro Tanaka, *Chem. Phys.Lett*., 2013, **584**, 63-66. 6. Characterization of Thermally Stable Brønsted Acid Sites on Alumina-Supported Niobium Oxide Calcined at High Temperature Tomoyuki Kitano, Tetsuya Shishido, Kentaro Teramura, and Tsunehiro Tanaka, *Chem. Phys. Chem*., 2013, **14**(11), 2560-2564. 7. Development of Palladium Surface-Enriched Heteronuclear Au–Pd Nanoparticle Dehalogenation Catalysts in an Ionic Liquid, Xiao Yuan, Geng Sun, Hiroyuki Asakura, Tsunehiro Tanaka, Xi Chen, Dr. Yuan Yuan, Gabor Laurenczy, Yuan Kou, Paul J. Dyson, Ning Yan, *Chemistry –A European Journal*., 2013, **19**(4), 1227-1234. 8. Reaction Mechanism of Selective Photooxidation of Amines over Niobium Oxide: Visible Light-Induced Electron Transfer Between Adsorbed Amine and Nb_2O_5, Shinya Furukawa, Yasuhiro Ohno, Tetsuya Shishido, Kentaro Teramura, and Tsunehiro Tanaka, *J. Phys. Chem. C*., 2013, **117**(1), 442-450.

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【主な著書、学術論文】（過去 5 年以内）	1. A. Kato and Y. Tanimura, *Quantum Suppression of Ratchet Rectification in a Brownian System Driven by a Biharmonic Force*, J. Phys. Chem. B **117**, 13132-13144 (2013). 2. A. Sakurai and Y. Tanimura, *Self-excited current oscillations in a resonant tunneling diode described by a model based on the Caldeira-Leggett Hamiltonian*, New J. of Phys. **16**, 015002 [24 pages] (2014) 3. M. F. Gelin, Y. Tanimura, and W. Domcke, *Simulation of femtosecond‘ double slit” experiments for a chromophore in a dissipative environment*, J. Chem. Phys. **139**, 214302 (2013). 4. Y. Tanimura, *Reduced hierarchy equations of motion approach with Drude plus Brownian spectral distribution: Probing electron transfer processes by means of two-dimensional correlation spectroscopy*, J. Chem, Phys **137**, 22A550 [9 pages] (2012). 5. A. Sakurai and Y. Tanimura, *An approach to quantum transport based on reduced hierarchy equations of motion: Application to a resonant tunneling diode*, J. Phys. Soc. Jpn **82**, 033707 [4 pages] (2013).
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【所属学会】	分子科学会、生物物理学会
【主な著書、学術論文】（過去 5 年以内）	1. A blue-shifted light-driven proton pump for neural silencing. Yuki Sudo*, Ayako Okazaki, Hikaru Ono, Jin Yagasaki, Seiya Sugo, Motoshi Kamiya, Louisa Reissig, Keiichi Inoue, Kunio Ihara, Hideki Kandori, Shin Takagi and Shigehiko Hayashi, *J. Biol. Chem.* **288**, 20624-20632 (2013). 2. Structural and spectral characterizations of C1C2 channelrhodopsin and its mutants by molecular simulations. Motoshi Kamiya, Hideaki E. Kato, Ryuichiro Ishitani, Osamu Nureki, and Shigehiko Hayashi*, *Chem. Phys. Lett.* **556**, 266-271 (2013). 3. Molecular mechanism of ATP hydrolysis in F1-ATPase revealed by molecular simulations and single molecule observations. Shigehiko Hayashi*, Hiroshi Ueno, Abdul Rajjak Shaikh, Myco Umemura, Motoshi Kamiya, Yuko Ito, Mitsunori Ikeguchi, Yoshihito Komoriya, Ryota Iino, and Hiroyuki Noji. *J. Am. Chem. Soc.* **134**, 8447-8454 (2012). 4. Crucial role of protein flexibility in formation of a stable reaction transition state in an a-amylase catalysis. Kosugi Takahiro and Shigehiko Hayashi*. *J. Am. Chem. Soc.* **134**, 7045-7055 (2012). 5. QM/MM reweighting free energy SCF for geometry optimization on extensive free energy surface of enzymatic reaction. Takahiro Kosugi and Shigehiko Hayashi*. *J. Chem. Theory Comput.* **8**, 322-334 (2012). 6. Protein collective motions coupled to ligand migration in myoglobin. Yasutaka Nishihara, Shigeki Kato, and Shigehiko Hayashi*, *Biophys. J.* **98**, 1649-1657 (2010).

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【主な著書、学術論文】（過去 5 年以内）	1. Atsushi Ikeda and Kunimasa Miyazaki, “Mode-coupling theory as a mean-field description of the glass transition” *Phys. Rev. Lett.* **104**, 255704 (2010). 2. Atsushi Ikeda and Kunimasa Miyazaki “Glass transition of the monodisperse gaussian core model” *Phys. Rev. Lett.* (Editors’ Suggestion) **106**, 015701 (2011). 3. Atsushi Ikeda and Kunimasa Miyazaki “Slow Dynamics of the High Density Gaussian Core Model” *J. Chem. Phys.* **135**, 054901 (2011). 4. Patrick Charbonneau, Atsushi Ikeda, Giorgio Parisi and Francesco Zamponi “Glass Transition and Random Close Packing above Three Dimensions” *Phys. Rev. Lett.* **107**, 185702 (2011). 5. Atsushi Ikeda, Ludovic Berthier and Peter Sollich ”Unified study of glass and jamming rheology in soft particle systems” *Phys. Rev. Lett.* (Editors’ Suggestion) **109**, 018301 (2012). 6. Atsushi Ikeda, Ludovic Berthier and Giulio Biroli “Dynamic criticality at the jamming transition” *J. Chem. Phys.* **138**, 12A507 (2013). 7. Atsushi Ikeda, Ludovic Berthier and Peter Sollich “Disentangling glass and jamming physics in the rheology of soft materials” *Soft Matter* (Highlight Article) **9**, 7669 (2013).
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【主な著書、学術論文】（過去 5 年以内）	過去 5 年間に約 140 報 1. M. Isegawa, S. Maeda, D. J. Tantillo and K. Morokuma, Predicting Pathways for Terpene Formation from First Principles – Routes to Known and New Sesquiterpenes, *Chem. Sci.* **5**, 1555-1560 (2014). 2. T. V. Harris, Y. Kurashige, T. Yanai, and K. Morokuma, Ab Initio Density Matrix Renormalization Group Study of Magnetic Coupling in Dinuclear Iron and Chromium Complexes, *J. Chem. Phys.* **140**, 054303/1-10 (2014). 3. L. Ding, N. Ishida, M. Murakami, and K. Morokuma, sp^3–sp^2 vs sp^3–sp^3 C-C Site-Selectivity in Rh-Catalyzed Ring Opening of Benzocyclobutenol: A DFT Study, *J. Am. Chem. Soc.* **136**, 169–178 (2014). 4. S. Maeda, T. Taketsugu, and K. Morokuma, Exploring Transition State Structures for Intramolecular Pathways by the Artificial Force Induced Reaction (AFIR) Method. *J. Comp. Chem.* **35**, 166-173 (2014). 5. S. Komagawa, C. Wang, K. Morokuma, S. Saito and M. Uchiyama, Mechanistic Origin of Chemo- and Regioselectivity of Nickel-Catalyzed [3+2+2] Cyclization Reaction. *J. Am. Chem. Soc.* **135**, 14508–14511 (2013). 6. H.-B. Li, A. J. Page, S. Irle, and K. Morokuma, Temperature Dependence of Catalyst-Free Chirality-Controlled Single-Walled Carbon Nanotube Growth from Organic Templates, *J. Phys. Chem. Lett.* **4**. 3176-3180 (2013). 7. F. Liu, Y, Kurashige, T. Yanai, and K. Morokuma, Multireference Ab Initio Density Matrix Renormalization Group (DMRG)-CASSCF and -CASPT2 Study on the Photochromic Ring-Opening of Spiropyran, *J. Chem. Theo. Comp.* **9**, 4462–4469 (2013). 8. M. Hatanaka and K. Morokuma, Theoretical Study of Mukaiyama-Aldol Reaction Catalyzed by Water-Tolerant Lanthanide Lewis Acid, *J. Am. Chem. Soc.* **135**, 13972–13979 (2013). 9. F. Liu and K. Morokuma, Multiple Pathways for Primary Step of Spiropyran Photochromic Reaction: a CASPT2//CASSCF Study, *J. Am. Chem. Soc.* **135**, 10693–10702 (2013).
【学術関係の受賞など】	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; 文化功労者 , 2012

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【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
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【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
【主な著書、学術論文】（過去 5 年以内）	1. 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). 2. 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). 3. Two-step evaluation of binding energy and potential energy surface of van der Waals complexes, Milind Deshmukh, Shigeyoshi Sakaki, *J. Compt. Chem.*, **33**, 617-628 (2012). 4. A Theoretical Study of an Unusual Y-Shaped Three-Coordinate Pt Complex: Pt(0) sigma-Disilane Complex or Pt(II) Disilyl Complex?, N. Takagi, S. Sakaki, *J. Am. Chem. Soc.*, **134**, 11749-11759 (2012). 14. 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, S. Aono and S. Sakaki, *Chem. Phys. Lett.* **544**, 77-82 (2012). 15. Evaluation Procedure of Electrostatic Potential in 3D-RISM-SCF Method and Its Application to Hydrolyses of Cis- and Transplatin Complexes, S. Aono and S. Sakaki, *J. Phys. Chem. B*, **116**, 13045-13062 (2012). 16. Absorption of CO_2 and CS_2 into the Hofmann-Type Porous Coordination Polymer: Electrostatic versus Dispersion Interactions, M. M. Deshmukh, M. Ohba, S. Kitagawa, and S. Sakaki, *J. Am. Chem. Soc.*, **135**, 4840-4849 (2013). 17. Theoretical Study of Reactivity of Ge(II)-hydride Compound: Comparison with Rh(I)- Hydride Complex and Prediction of Full Catalytic Cycle by Ge(II)-hydride, N. Takagi, S. Sakaki, *J. Am. Chem. Soc.*, **135**, 8955-8965 (2013). 18. Unexpected Electronic Process of H_2 Activation by a New Nickel Borane Complex: Comparison with the Usual Homolytic and Heterolytic Activations, G. Zeng and S. Sakaki, *Inorg. Chem.*, **52**, 2844-2853 (2013). 19. Theoretical Study of Mononuclear Nickel(I), Nickel(0), Copper(I), and Cobalt(I) Dioxygen Complexes: New Insight into Differences and Similarities in Geometry and Bonding Nature, Y. Chen and S. Sakaki, Inorg. Chem., 52, 13146-13159 (2013). 20. Theoretical Study of One-Electron Oxidized Mn(III)- and Ni(II)-Salen Complexes: Localized vs Delocalized Ground and Excited States in Solution, S. Aono, M. Nakagaki, T. Kurahashi, H. Fujii, and S. Sakaki, *J. Chem. Theory Comput.*, **10,** 1062-1073 (2014).
【学術関係の受賞など】	第 1 回分子科学会賞（2009 年 9 月）　第 66 回日本化学会賞（2014 年 3 月）

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【研究内容キーワード】	Polyelectrolyte, DNA folding transition, Thermofluid, Photophoresis
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【主な著書、学術論文】（過去 5 年以内）	1. T. Iwaki, “Effect of internal flow on the photophoresis of a micron-sized liquid droplet”, *Physical Review E* **81**, 066315 (13 pages) (2010) 2. 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 3. 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* **view l a, T. gedena, PEMS for polymer folding 84**, 021924 (5 pages) 4. Shun N. Watanabe, Takafumi Iwaki, Masahiro I. Kohira, Nobuyuki Magome, and Kenichi Yoshikawa, “Negative photophoresis of smoke particles observed under microgravity”, *Chemical Physics Letters* **511**, 447–451 (2011) 5. Masatoshi Ichikawa, Fumi Takabatake, Keitaro Miura, Takafumi Iwaki, Nobuyuki Magome, and Kenichi Yoshikawa, “Controlling negative and positive photothermal migration of centimeter-sized droplets”, *Phys. Rev. E* **88**, 012403 (2013)

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【現在の研究課題】	時間依存密度汎関数法を用いた溶液における光化学反応の解析
【研究内容キーワード】	時間依存密度汎関数法・積分方程式・円錐交差・自由エネルギー
【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
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【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. N. Minezawa, “Excited-state free energy surfaces in solution: Time-dependent density functional theory/reference interaction site model self-consistent field method”, *J. Chem. Phys.* **138**, article No. 244101 [8 pages] (2013). 2. Y. Harabuchi, S. Maeda, T. Taketsugu, N. Minezawa, and K. Morokuma, “Automated search for minimum energy conical intersection geometries between the lowest two singlet states S_0/S_1-MECIs by the spin-flip TDDFT method”, *J. Chem. Theory Comput.* **9**, 4116-4123 (2013). 3. N. De Silva, N. Minezawa, and M. S. Gordon, “Excited-state hydrogen atom transfer reaction in solvated 7-hydroxy-4-methylcoumarin”, *J. Phys. Chem. B* **117**, 15386-15394 (2013). 4. K. R. Brorsen, N. Minezawa, F. Xu, T. L. Windus, and M. S. Gordon, “Fragment molecular orbital molecular dynamics with the fully analytic energy gradient”, *J. Chem. Theory Comput.* **8**, 5008-5012 (2012). 5. 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.* **137**, article No. 034116 [12 pages] (2012).

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【現在の研究課題】	ソフトマターにおける溶媒和効果、臨界溶液中の物体間相互作用
【研究内容キーワード】	Soft matter, Phase transition, Wetting, Critical phenomena, Colloid
【学歴】	2007 年３月　慶應義塾大学基礎理工学専攻後期博士課程修了
【学位】	博士（理学）
【略歴】	2007 年 4 月 - 2012 年 3 月 京都大学理学研究科博士研究員 2012 年 4 月 - 2014 年 3 月 京都大学福井謙一研究センター FIFC フェロー 2014 年 4 月 - 首都大学東京理工学研究科　特任助教 現在に至る
【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. R. Okamoto and A. Onuki: “Precipitation in aqueous mixtures with addition of strongly hydrophilic or hydrophobic solute”, *Phys. Rev. E* **82**, 051501 (2010). (Also in Virtual Journal of Nanoscale Science and Technology, November 22, 2010). 2. R. Okamoto and A. Onuki: “Charged Colloids in an aqueous mixture with a salt”, *Phys. Rev. E* **84**, 051401 (2011). 3. R. Okamoto and A. Onuki: “Casimir amplitudes and capillary condensation of near-critical fluids between parallel plates: Renormalized local functional theory”, *J. Chem. Phys.* **136**, 114704 (2012). 4. R. Okamoto, Y. Fujitani and S. Komura: “Drag coefficient of a rigid spherical particle in a near-cirtical binary fluid mixture”, *J. Phys. Soc. Jpn.* **82**, 084003 (2013). (Selected as an editors’ choice paper.) 5. R. Okamoto and A. Onuki: “Attractive interaction and bridging transition between between neutral colloidal particles due to preferential adsorption in a near-critical binary mixture”, *Phys. Rev. E* **88**, 022309 (2013)

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【所属学会】	The Physical Society of Japan
【主な著書、学術論文】（過去 5 年以内）	1. Takuya Saito, Takahiro Sakaue, “Cis-trans dynamical asymmetry in driven polymer translocation”, *Phys. Rev. E*, **88**, 042606 (5 pages total) (2013). 2. Takuya Saito, Takahiro Sakaue, “Process time distribution of driven polymer transport”, *Phys. Rev. E*, **85**, 061803 (7 pages total) (2012). 3. Takahiro Sakaue, Takuya Saito, Hirofumi Wada, “Dragging a polymer in a viscous fluid: steady state and transient”, *Phys. Rev. E*, **86**, 011804 (8 pages total) (2012). 4. 坂上貴洋、齋藤拓也, 日本物理學會誌 **67**(10), 705-709, 2012-10-05.「紐状分子の非平衡ダイナミクス：細孔通過現象を中心に」
【学術関係の受賞など】	JSPS Research Fellowships for Young Scientists(DC2) 2005.4-2007.3

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【研究内容キーワード】	Excited state, Spectroscopy, Photo-reaction, ,TDDFT, MCSCF
【学歴】	Jun. 2004, B.S. Major in Chemistry, College of Chemistry, Jilin University Jun. 2009, Ph.D. Major in Theoretical and Computational Chemistry, Institute of Theoretical Chemistry, State Key Laboratory of Theoretical and Computational Chemistry, Jilin University
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【略歴】	Jul. 2009, Research assistant, Jilin University Apr. 2012- Apr. 2013, FIFC Fellow, Kyoto University
【所属学会】	Chinese Chemical Society
【主な著書、学術論文】（過去 5 年以内）	1. Juan Jin, Fu-Quan Bai, Ming-Jun Jia, Yan-Ning Wang, Hong-Li Jia, Jie-Hui Yu, Ji-Qing Xu, “New Cd2+, Pb2+ complexes with acylhydrazidate molecules from in situ acylation reactions”, *Dalton Transactions*, **42**(24), 8771-8780. (2013). 2. Jie Chen, Jian Wang, Fu-Quan Bai, Li Hao, Qing-Jiang Pan*, Hong-Xing Zhang*, “Connection style and spectroscopic properties: Theoretical understanding of the interface between N749 and TiO2 in DSSCs”, *Dyes and Pigments*, **99**(1), 201-208, (2013). 3. Qi Cao, Jing Wang, Zhao-Shuo Tian*, Zai-Feng Xie*, Fu-Quan Bai*, “Theoretical investigation on the photophysical properties of N-heterocyclic carbene Ir (III) complexes (fpmb)xIr(bptz)3-x (x=1-2)”, *Journal of Computational Chemistry*, **33**(10), 1038-1046, (2012). 4. Fu-Quan Bai, Jian Wang, Bao-Hui Xia, Qing-Jiang Pan, Hong-Xing Zhang*, “DFTand TD-DFT study on the electronic structures and phosphorescent properties of 6-phenyl-2,2 '-bipyridine tridentate iridium(III) complexes and their isomer”. *Dalton Transactions*, **41**(27), 8441-8446, (2012). 5. Jian Wang, Fu-Quan Bai, Bao-Hui Xia, Hong-Xing Zhang*, “Efficient blueemitting ir(iii) complexes with phosphine carbanion-based ancillary ligand: a DFT study”. *Journal of Physical Chemistry A*, **115**(42), 11689-11695, (2011).
【学術関係の受賞など】	NSFC Young Scholar, 2010

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【主な著書、学術論文】（過去 5 年以内）	1. Vladimir Ya. Lee, Shinji Aoki, Taka Yokoyama, Satoru Horiguchi, Akira Sekiguchi, Heinz Gornitzka, Jing-Dong Guo, and Shigeru Nagase, “Toward a Silicon Version of Metathesis: From Schrock-Type Titanium Silylidenes to Silatitanacyclobutenes”, *J. Am. Chem. Soc.*, **135**, 2987-2990 (2013) 2. Satoru Sato, Yutaka Maeda, Jing-Dong Guo, Michio Yamada, Naomi Mizorogi, Shigeru Nagase, and Takeshi Akasaka, “Mechanistic Study of the Diels-Alder Reaction of Paramagnetic Endohedral Metallofullerene: Reaction of La@C82 with 1,2,3,4,5-Pentamethylcyclopentadiene”, *J. Am. Chem. Soc.*, **135**, 5582-5587 (2013) 3. Takuya Kuwabara, Masaichi Saito, Jing-Dong Guo, Shigeru Nagase, “Unexpected Formation of Ru2Sn2 Bicyclic Four-Membered Ring Complexes with Butterfly and Inverse-Sandwich Structures”, *Inorg. Chem.*, **52**, 3585-3587 (2013) 4. Chun-Yi Lin, Jing-Dong Guo, James C. Fettinger, Shigeru Nagase, Fernande Grandjean, Gary J. Long, Nicholas F. Chilton, and Philip P. Power, “Dispersion Force Stabilized Two-Coordinate Transition Metal–Amido Complexes of the –N(SiMe3)Dipp (Dipp = C6H3-2,6-Pri Structural, Spectroscopic, Magnetic, and Computational Studie”, *Inorg. Chem.*, **52**, 13584-13593 (2013) 5. Jessica N. Boynton, Jing-Dong Guo, James C. Fettinger, Christopher E. Melton, Shigeru Nagase, and Philip P. Power, “Linear and Nonlinear Two-Coordinate Vanadium Complexes: Synthesis, Characterization, and Magnetic Properties of V(II) Amides”, *J. Am. Chem. Soc.*, **135**, 10720-10728, (2013)

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【学歴】	Jun. 2007, B. Sc. in Applied Chemistry, Xi'an Jiaotong University, China Dec. 2012, Ph, D. in Materials Physics and Chemistry, Xi'an Jiaotong University, China
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【主な著書、学術論文】（過去 5 年以内）	1. W. W. Wang, J. S. Dang, J. J. Zheng, X. Zhao, E. Ōsawa and S. Nagase, "Metal-Promoted Restoration of Defective Graphene" *J. Mater. Chem.* **2012**, *22*, 16370. 2. W. W. Wang, J. S. Dang, J. J. Zheng, X. Zhao, "Heptagons in C_{68}: Impact on Stabilities, Growth, and Exohedral Derivatization of Fullerenes" *J. Phys. Chem. C.* **2012**, *116*, 17288. 3. W. W. Wang, J. S. Dang, X. Zhao, "Role of Four-Membered Rings in C_{32} Fullerene Stability and Mechanisms of Generalized Stone-Wales Transformation: a Density Functional Theory Investigation" *Phys. Chem. Chem. Phys.* **2011**, *13*, 14629. 4. W. W. Wang, J. S. Dang, X. Zhao, "Impact of Tetragonal Rings on the Stability of Small Fullerenes Encapsulated with Noble Gas: a Density Functional Theory Survey" *Chem. Phys. Lett.* **2012**, *536*, 77. 5. W. W. Wang, J. S. Dang, J. J. Zheng, X. Zhao, S. Nagase, "Selective Growth of Fullerenes from C_{60} to C_{70}: Inherent Geometrical Connectivity Hidden in Discrete Experimental Evidence" *J. Phys. Chem. C*, **2013**, *117*, 2349.

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【研究分野】	理論化学　計算化学
【現在の研究課題】	・ 柔らかなランタノイド不斉触媒を用いる向山アルドール反応の立体選択性発現機構の解明及び触媒設計 ・ Y3+ 触媒を用いるイソプロペン重合反応のレジオ選択性の理論的研究 ・ 4fN エネルギーシフト法を用いる感温性ランタノイド発光プローブの励起エネルギー移動の機構解明 ・ Gd3+ を含む MRI コントラスト剤の構造分布と水交換反応の理論的研究 ・ 星間空間における炭化水素アニオンの生成機構の解明
【研究内容キーワード】	ランタノイド・自動反応経路探索 (GRRM)・触媒反応・発光プローブ
【学歴】	2011 年 3 月　慶應義塾大学大学院理工学研究科 基礎理工学専攻後期博士課程修了
【学位】	2011 年 3 月　博士（理学）　慶應義塾大学
【略歴】	2009 年 4 月　慶應義塾大学大学院理工学研究科助教（有期・研究奨励） 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、分子科学会
【主な著書、学術論文】 （過去 5 年以内）	1. M. Hatanaka, M. Saito, M. Fujita, K. Morokuma, “σ-Aromaticity in Hexa-Group 16 Atom Substituted Benzene Dications. A Theoretical Study”, *J. Org. Chem.* **79**, pp 2640-2646 (2014). 2. M. Hatanaka, K. Morokuma, “Role of Water in Mukaiyama-Aldol Reaction Catalyzed by Lanthanide Lewis Acid: A Computational Study” *J. Am. Chem. Soc.* **135**, pp 13972-13979 (2013). ※*Spotlights on Recent JACS Publications*, **135**, pp. 13999-13999 (2013)に掲載 3. M. Hatanaka, S. Maeda, K. Morokuma, “Sampling of Transition States for Predicting Diastereoselectivity Using Automated Search Method —Aqueous Lanthanide-Catalyzed Mukaiyama Aldol Reaction” *J. Chem. Theory. Comput.* **9**, pp 2882-2886 (2013). 4. S. Maeda, E. Abe, M. Hatanaka, T. Taketsugu, K. Morokuma, “Exploring Potential Energy Surfaces of Large Systems with Artificial Force Induced Reaction Method in Combination with ONIOM and Microiteration” *J. Chem. Theory Comput.* **8**, pp 5058-5063 (2012). 5. M. Hatanaka, S. Yabushita, “Mechanisms of f-f hypersensitive transition intensities of lanthanide trihalide molecules: a spin-orbit configuration interaction study” *Theor Chem Acc* (in press) 6. 前田理, 畑中美穂, 植松遼平, 武次徹也, 諸熊奎治, “人工力誘起反応法による化学反応経路の自動探索：有機合成化学への応用と展望”, 有機合成化学協会誌 **72**, pp567-579 (2014)（総説）
【学術関係の受賞など】	2013 年 9 月　第 7 回分子科学討論会 (京都)2013 分子科学会優秀講演賞 2013 年 6 月　The Best Poster Award in “The 6th Asia Pacific Conference of Theoretical and Computational Chemistry” 2011 年 4 月　京都大学福井謙一記念研究センターフェロー

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【現在の研究課題】	Theoretical calculation of molecular motor and switch
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【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
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【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. F.Y. Liu, K. Morokuma, Multiple Pathways for Primary Step of Spiropyran Photochromic Reaction: A CASPT2//CASSCF Study, *J. Am. Chem. Soc.*, 2013, **135**, 10693–10702 2. F.Y.Liu, K.Yuki, T. Yanai, K. Morokuma, Multireference Ab Initio Density Matrix renormalization Group (DMRG)-CASSCF and -CASPT2 Study on the Photochromic Ring-Opening of Spiropyran, *J. Chem. Theory Comput.*, 2013, **9**, 4462–4469. 3. W. Piao, S. Tsuda, Y. Tanaka, S. Maeda, F.Y. Liu, S. Takahashi, Y. Kushida, T. Komatsu, T. Ueno, T. Terai, T. Nakazawa, M. Uchiyama, K. Morokuma, T. Nagano, and K. Hanaoka, Development of a New Class of Azo-based Fluorescence Probes to Detect Different Levels of Hypoxia. *Angew. Chem. Int. Ed.*, 2013, **52**, 13028–13032. 4. 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.

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【主な著書、学術論文】（過去 5 年以内）	1. Lina Ding, Lung Wa, Chung, Keiji Morokuma*, "Excited-State Proton Transfer Controls Irreversibility of Photoisomerization in Mononuclear Ruthenium(II) Monoaquo Complexes: A DFT Study", *J. Chem. Theory Comput.,* **2014**, *10*, 668–675 2. Lina Ding, Naoki Ishida, Masahiro Murakami, and Keiji Morokuma*, "sp^3–sp^2 vs sp^3–sp^3 C–C Activation in Rh-Catalyzed Ring Opening of Benzocyclobutenol: A DFT Study", *J. Am. Chem. Soc.,* **2014**, *136*, 169–178. 3. Lina Ding, Lung Wa Chung, Keiji Morokuma*, “Reaction Mechanism of Photoinduced Decarboxylation of the Photoactivatable Green Fluorescent Protein: An ONIOM(QM:MM) Study”, *J. Phys. Chem. B,* **2013**, *117*, 1075–1084. 4. Ganglong Cui, Lina Ding, Feng Feng, Yajun Liu, and Weihai Fang, “Insights into Mechanistic Photochemistry of Urea”, *J. Chem. Phys.* **2010**, *132*, 194308; 5. 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. 6. 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. 7. 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.
【学術関係の受賞など】	Beijing Normal University, Academic Excellence Award, 2009. Beijing Normal University, Scientific Achievement Award, 2010.

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【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, Alister J. Page, Christian Hettich, Bálint Aradi, Christof Köhler, Thomas Frauenheim, Stephan Irle, and Keiji Morokuma, Graphene Nucleation on a Surface-Molten Copper Catalyst: Quantum Chemical Molecular Dynamics Simulations. *Chem. Sci.* accepted, 2014 2. Hai-Bei Li, Alister J Page, Stephan Irle*, Keiji Morokuma*, “The Dual Role of Hydrogen Atoms during Polycyclic Aromatic Hydrocarbon Formation” *J. Phys. Chem. Lett.*, **4**(14), 2323-2327, 2013 3. Hai-Bei Li, Alister J Page, Stephan Irle*, Keiji Morokuma*, “Temperature Dependence of the Catalyst-free Growth of Single-Walled Carbon Nanotubes” *J. Phys. Chem. Lett.*, **4**(18), 3176-3180, 2013 4. Hai-Bei Li, Alister J Page, Ying Wang, Stephan Irle*, Keiji Morokuma*, “Sub-surface nucleation of graphene precursors near a Ni(111) step-edge” *Chem. Comm.*, **48**(64), 7937-7939, 2012 5. Hai-Bei Li, Alister J Page, Stephan Irle*, Keiji Morokuma*, “Single-walled Carbon Nanotube Growth from Chiral Carbon Nanorings: Prediction of Chirality and Diameter Influence on Growth Rates” *J. Am. Chem. Soc.*, **134**(38), 15887-15896, 2012
【学術関係の受賞など】	Qiu Shi Graduate Student Scholarship (2009) Supported by the Scientific Research Foundation of Shandong University (2014)

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【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; strongly-correlated systems
【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. 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. 2. 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 3. 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. 4. 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. 5. 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. 6. 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. 7. 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. 8. 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. 9. Ding, L.; Chung, L. W.; Morokuma, K. “Reaction Mechanism of Photoinduced Decarboxylation of the Photoactivatable Green Fluorescent Protein: An ONIOM(QM:MM) Study” *J. Phys. Chem. B* **2013**, *117*, 1075. 10. Ding, S.; Song, L.-J.; Chung, L. W.; Zhang, X.; Sun, J.; Wu, Y.-D. “Ligand-Controlled Remarkable Regio- and Stereodivergence in Intermolecular Hydrosilylation of Internal Alkynes: Experimental and Theoretical Studies”, *J. Am. Chem. Soc.* **2013**, *135*, 13835.

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【現在の研究課題】	Hetero- and homogeneous catalysis
【研究内容キーワード】	Asymmetric catalysis, Phase-transfer catalysts, DNA based catalysts, 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】	06/2013-02/2014, Postdoctoral Scholar at FIFC, Kyoto University, Kyoto, Japan 05/2012-05/2013, JSPS Fellow at FIFC, Kyoto University, Kyoto, Japan 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. P. Petrova, H.-B. Li, K. Maruoka, K. Morokuma, “Asymmetric Phase-Transfer Catalysis with Homo- and Heterochiral Quaternary Ammonium Salts: A Theoretical Study”, *J. Phys. Chem. B*, 2014, **118** (19), pp 5154–5167. 2. G. P. Petrova, Z. Ke, S. Park, H. Sugiyama, K. Morokuma, “The origin of enantioselectivity for intramolecular Friedel–Crafts reaction catalyzed by supramolecular Cu/DNA catalyst complex”, *Chem. Phys. Lett.*, 2014, **600**, pp 87–95. 3. 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.*, 2012, **14**, pp 5879-5890. 4. 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”, *Nat. Mater.*, 2011, **10**, pp 310–315. 5. G. P. Petrova, G. N. Vayssilov, N. Rösch, “Interaction of ethene and ethyne with bare and hydrogenated Ir4 clusters. A density functional study”, *Catal. Sci. Tech.* 2011, **1**, pp 958-970.
【学術関係の受賞など】	JSPS Research Fellowship, 2013-2014 Student award for high academic achievements of the Foundation for support of the Bulgarian Higher Education named after Prof. Michael Klett (2003)

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【現在の研究課題】	Computational studies of transition metal homogeneous catalysis, and properties of metallocofactors and molecular magnets
【研究内容キーワード】	Rh(I)-catalyzed hydroboration, DMRG, magnetic exchange coupling, [Fe-S] clusters
【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.; Kurashige, Y.; Yanai, T.; Morokuma, K. Ab Initio Density Matrix Renormalization Group Study of Magnetic Coupling in Dinuclear Iron and Chromium Complexes. *J. Chem. Phys.* **2014**, *140* (5), 054303. 2. Harris, T. V.; Szilagyi, R. K. Iron-Sulfur Bond Covalency from Electronic Structure Calculations for Classical Iron-Sulfur Clusters. *J. Comput. Chem.* **2014**, *35* (7), 540. 3. Harris, T. V.; Morokuma, K. QM/MM Structural and Spectroscopic Analysis of the Di-iron(II) and Di-iron(III) Ferroxidase Site in M Ferritin *Inorg. Chem.*, **2013**, *52* (15), 8551. 4. Harris, T. V.; Szilagyi, R. K. Comparative Assessment of the Composition and Charge State of Nitrogenase FeMo-Cofactor. *Inorg. Chem.*, **2011**, *50* (11), 4811. 5. 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.
【学術関係の受賞など】	JSPS Fellowship, 2012 NSF Materials Computation Center Travel Grant, 2011 Kopriva Graduate Student Fellowship, 2009 Molecular Biosciences Fellowship, 2007–2011 Mildred Livingston Grant, 2007–2008

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【研究内容キーワード】	励起状態、反応経路、DFT、分子スイッチ
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【略歴】	2009- 博士号取得（理学、京都大学） 2010- 米国ミネソタ大学博士研究員 2013- 福井謙一記念研究センター研究員
【学会活動】	(1) 分子科学討論会2013京都 (2) 京都大学福井謙一記念センターシンポジウム2014
【主な著書、学術論文】（過去 5 年以内）	1. Incorporation of charge transfer into the explicit polarization fragment method by grand canonical density functional theory, M. Isegawa, J. Gao, and D. G. Truhlar, *J. Chem. Phys.* **135**, 084107 (2011). 2. Performance of Recent Approximation Density functional for Time-Dependent Density Functional Theory Calculations of Valence and Rydberg Electronic Transition Energies, M. Isegawa, R. Peverati, and D. G. Truhlar, *J. Chem. Phys.* **137**, 244104 (2012). 3. Electrostatically Embedded Molecular Tailoring Approach and Validation for Peptide, M. Isegawa, B. Wang, and D. G. Truhlar, *J. Chem. Theory Comput.* **9**, 1381 (2013). 4. Predicting pathways for terpene from first principles-routes to known and new sesquiterpenes, M. Isegawa, S. Maeda, D. J. Tantillo, and K. Morokuma, *Chemical Science*, **5**, 1555 (2014).

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【所属学会】	Marie Curie Fellowship, University of Gothenburg, Sweden (2013)
【学会活動】	Member, Royal Society of Chemistry, United Kingdom. Member, American Chemical Society.
【主な著書、学術論文】 （過去 5 年以内）	1. J. Llaveria, Á. Beltrán, W. M. C. Sameera, A. Locati, M. M. Díaz-Requejo, M. I. Matheu, S. Castillón, F. Maseras, P. J. Pérez, “Regio- and Stereoselective Silver-catalyzed aziridination of dienes: scope, mechanistic studies and ring-opening reactions”, *J. Am. Chem. Soc.* **136**, 14, 5342-5350. 2. L. Maestre, W. M. C. Sameera, M. M. Díaz-Requejo, F. Maseras, P. J. Pérez. “A General Mechanism for the Copper- and Silver-Catalyzed olefin aziridination reactions: concomitant involvement of the singlet and triplet pathways”, *J. Am. Chem. Soc.* 2013, **135**, 1338-1348. 3. W. M. C. Sameera, F. Maseras, “Transition metal catalysis by density functional theory and density functional theory molecular mechanics”, *WIREs Comput. Mol. Sci.,* Wiley-VCH, 2012, **2,** 375-380. 4. W. M. C. Sameera, D. A. Pantazis, “A hierarchy of methods for the energetically accurate modelling of isomerism in aldohexoses”, *J. Chem. Theory Comput.*, 2012, **8**, 2630-2645. 5. W. M. C. Sameera, F. Maseras, “Quantum mechanics/molecular mechanics methods can be more accurate than full quantum mechanics in system involving dispersion correlations”, *Phys. Chem. Chem. Phys.*, 2011, **13**, 10520-10526.
【学術関係の受賞など】	Postdoctoral fellowship, Kyoto University. (2013) Marie Curie fellowship, University of Gothenburg, Sweden. (2012) WATOC poster prize, WATOC conference, Santiago de Compostela. (2011) Postdoctoral fellowship, ICIQ foundation, Spain. (2010) EPSRC postdoctoral fellowship, University of Oxford (2009) CRC press award for the best poster, the seventh Canadian computational chemistry meeting, Canada. (2009) The Jim Gatheral Scholarship, University of Glasgow. (2008) WestCHEM postgraduate scholarship, University of Glasgow. (2006)

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【現在の研究課題】	C-H activation in organic synthesis
【研究内容キーワード】	Homogeneous Catalysis, Radical Reaction, Asymmetric Synthesis
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【学位】	Ph.D, University of Sheffield, UK
【略歴】	From March, 2014, Fukui Institute for Fundamental Chemistry
【主な著書、学術論文】（過去 5 年以内）	1. Steven J. Edeson, Julong Jiang, Stephen Swanson, Panayiotis A. Procopiou, Harry Adams, Anthony J. H. M. Meijer and Joseph P. A. Harrity, “Studies on the stereochemical assignment of 3-acylidene 2-oxindoles”, *Org. Biomol. Chem.,* **2014**, *12*, 3201-3210. 2. Damien F.P. Crépin , Joseph P. A. Harrity , Julong Jiang , Anthony J. H. M. Meijer , Anne-Chloé M. A. Nassoy , and Piotr Raubo, “A Mechanistic Study of the Lewis Base Directed Cycloaddition of 2-Pyrones and Alkynylboranes”, *J. Am. Chem. Soc.*, **2014**, ASAP. (Authorship sequence in the alphabetical order with respect to the surnames)
【学術関係の受賞など】	Faculty of Science Scholarship, University of Sheffield, 2010-2013

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【現在の研究課題】	有機化学反応における水素結合の役割
【研究内容キーワード】	反応経路、 軌道相互作用、 水素結合、プロトン移動
【学歴】	1969年3月　　京都大学　工学部燃料化学科　卒業、 1974年3月末　京都大学　工学研究科　燃料化学専攻　博士課程　終了。
【学位】	工学博士
【略歴】	1974年4月-1975年9月末　米国　Rochester大学　博士研究員、 1975年10月-2012年3月末　奈良教育大学　教員。
【所属学会】	日本化学会
【主な著書、学術論文】 （過去 5 年以内）	1. “Presence or absence of a novel charge-transfer complex in the base-catalyzed hydrolysis of N-ethylbenzamide or ethyl benzoate”, Shinichi Yamabe, Wei Guan and Shigeyoshi Sakaki, *Beilstein J. Org. Chem.* 2013, **9**, 185-196. 2. “Three Competitive Transition States at the Glycosidic Bond of Sucrose in Its Acid-Catalyzed Hydrolysis”, Shinichi Yamabe, Wei Guan and Shigeyoshi Sakaki, *J. Org. Chem.*, 2013, **78** (6), pp 2527-2533. DOI: 10.1021/jo3027565 3. “An aniline dication-like transition state in the Bamberger rearrangement”, Shinichi Yamabe, Guixiang Zeng, Wei Guan and Shigeyoshi Sakaki, *Beilstein J. Org. Chem.* 2013, **9,** 1073-1082.doi:10.3762/bjoc.9.119 4. “Substrate dependent reaction channels of the Wolff-Kishner reduction reaction: A theoretical study”, Shinichi Yamabe, Guixiang Zeng, Wei Guan, Shigeyoshi Sakaki, *Beilstein Journal of Organic Chemistry* 2014, **10,** 259-270. 5. “SN1-SN2 and SN2-SN3 mechanistic changes revealed by transition states of the hydrolyses of benzyl chlorides and benzenesulfonyl chlorides”, Shinichi Yamabe, Guixiang Zeng, Wei Guan and Shigeyoshi Sakaki, *Journal of Computational Chemistry*, vol.**35**, issue 15, pages 1140-1148 (2014), DOI: 10.1002/jcc.23607.

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【現在の研究課題】	Gas Adsorption, Proton Conductivity
【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
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【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. Yuh HIJIKATA and Shigeyoshi SAKAKI, “Interaction of various gas molecules with paddle-wheel-type open metal sites of porous coordination polymers: theoretical investigation”, *Inorg. Chem.*, **53** 2417-2426 (2014) 2. Hiroshi SATO, Wataru KOSAKA, Ryotaro MATSUDA, Akihiro HORI, Yuh HIJIKATA, Shigeyoshi SAKAKI, Masaki TAKATA, and Susumu KITAGAWA, “Self-accelerating CO sorption in a soft nanoporous crystal”, *Science*, **343**, 167-170 (2014) 3. Yuh HIJIKATA, Satoshi HORIKE, Masayuki SUGIMOTO, Munehiro INUKAI, Tomohiro FUKUSHIMA, and Susumu KITAGAWA, “Pore design of two-dimensional coordination polymers toward selective adsorption”, *Inorg. Chem.*, **52**, 3634-3642 (2013) 4. 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) 5. 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)
【学術関係の受賞など】	JSPS Research Fellowships for Young Scientists (DC1) 2008-2011

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【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）
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【所属学会】	日本分子化学会
【主な著書、学術論文】（過去 5 年以内）	1. Aono S., Nakagaki M., Kurahashi T., Fujii H., and Sakaki S., “Theoretical Study of One-Electron Oxidized Mn(III)– and Ni(II)–Salen Complexes: Localized vs Delocalized Ground and Excited States in Solution”, *J. Chem. Theory Comput.* **10** 1062 (2014). 2. Aono S., Hosoya T., and Sakaki S., “A 3D-RISM-SCF method with dual solvent boxes for a highly polarized system: application to 1,6-anhydrosugar formation reaction of phenyl alpha- and beta-D-glucosides under basic conditions”, *Phys. Chem. Chem. Phys.* **17** 6368 (2013) 3. Aono S. and Sakaki S., “Evaluation Procedure of Electrostatic Potential in 3D-RISM-SCF Method and Its Application to Hydrolyses of Cis- and Transplatin Complexes”, *J. Phys. Chem. B* **116** 13045 (2012) 4. Aono S. and 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.* **544** 77 (2012). 5. 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). 6. Aono S. and Kato S. “Proton Transfer in Phenol-Amine Complexes: Phenol Electronic Effect on Free Energy Profile in Solution”, *J. Comput. Chem.* **31** 2924-2931 (2010). 7. 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).

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【研究分野】	Theoretical and Computational Chemistry
【現在の研究課題】	Gas Absorption in Metal Organic Framework, Non covalent Interactions and Activation of small molecule by transition metal complexes.
【研究内容キーワード】	Metal-Organic Framework, Potential Energy Surface, Catalysis
【学歴】	March 2001, Master of Sci., University of Pune, India October 2008, Doctor of Philosophy, 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 Nov. 2013: Postdoctoral Research Fellow, Kyoto University, Japan
【主な著書、学術論文】 （過去 5 年以内）	1. Milind M. Deshmukh, Sakaki Shigeyoshi “Generation of Dihydrogen Molecule and Hydrosiliylation of Carbon Dioxide Catalyzed by Zinc Hydride Complex: Theoretical Understanding and Prediction, *Inorg. Chem.* (Under Revision 2014). 2. Milind M. Deshmukh, Masaaki Ohba, Susumu Kitagawa, and Shigeyoshi Sakaki “Absorption of CO_2 and CS_2 into the Hofmann-Type Porous Coordination Polymer: Electrostatic versus Dispersion Interactions” *J. Am. Chem. Soc.* **135**, 4840 (2013). 3. 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). 4. 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). 5. 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). 6. 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).
【学術関係の受賞など】	Senior Research Fellowship of CSIR, India, (2005-2008). Senior Research Fellowship of C-DAC, Pune, India (2004-2005).

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【現在の研究課題】	1. Cooperative catalysis through new metal-Ligand cooperation modes 2. H-H and C-H bond activations 3. Dehydrogeanation and hydrogenation reactions
【研究内容キーワード】	Cooperation catalysis, C-H bond, H-H bond, main group catalyst
【学歴】	2005~2010, Ph. D. education, School of Chemistry & Chemical Engineering, Nanjing University
【学位】	Ph. D. in Physical Chemistry, 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. G. Zeng, Y. Guo, and S. 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. G. Zeng and S. 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. G. Zeng and S. 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. G. Zeng, and S. 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. G. Zeng and S. 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). 6. G. Zeng and S. Sakaki, “Unexpected Electronic Process of H_2 Activation by a New Nickel Borane Complex: Comparison with the Usual Homolytic and Heterolytic Activations” *Inorg. Chem.*, **52**, 2844 (2013). 7. S. Yamabe, G. Zeng, W. Guan, and S. Sakaki, “An Aniline Di-cation like Transition State in the Bamberger Rearrangement” *Org. Biomol. Chem.* **9**, 1073-1082 (2013). 8. S. Yamabe, G. Zeng, W. Guan, and S. Sakaki, “Substrate Dependent Reaction Channels of the Wolff-Kishner reduction reaction: A Theoretical Study” *Beilstein J. Org. Chem.,* **10**, 259–270 (2014). 9. G. Zeng, S. Sakaki, K.-I. Fujita, H. Sano, and R. Yamaguchi, “Efficient Catalyst for Acceptorless Alcohol Dehydrogenation: Interplay of Theoretical and Experimental Studies” *ACS Catal.*, **4**, 1010–1020 (2014). 10. G. Zeng, S. Maeda, T. Taketsugu, and S. Sakaki, “Catalytic Transfer Hydrogenation by a Trivalent Phosphorus Compound: Phosphorus-Ligand Cooperation Pathway or P^{III}/P^{V} Redox Pathway?” *Angew. Chem. Int. Ed.*, **53**, 4633–4637(2014). 11. S. Yamabe, G. Zeng, W. Guan, and S. Sakaki, “S_N1-S_N2 and S_N2-S_N3 Mechanistic Changes Revealed by Transition States of the Hydrolyses of Benzyl Chlorides and Benzenesulfonyl Chlorides” *J Comput. Chem.*, **35**, 1140-1148(2014). 12. W. Guan, F. B. Sayyed, G. Zeng, and S. Sakaki, (common authors) “σ–Bond Activation of Small Molecules and Reactions Catalyzed by Transition-Metal Complexes: Theoretical Understanding of Electronic Processes” *Inorg. Chem.* DOI 10.1021/ic5003429.

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【現在の研究課題】	d- 電子複合系および高周期典型元素化合物の理論化学
【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
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【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）
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【主な著書、学術論文】（過去 5 年以内）	1. “Theoretical Study of Reactivity of Ge(II)-hydride Compound: Comparison with Rh(I)-hydride Complex and Prediction of Full Catalytic Cycle by Ge(II)-hydride” N. Takagi, S. Sakaki, *J. Am. Chem. Soc.*, **135**, 8955-8965 (2013). 2. “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.*, **134**, 11749-11759 (2012). 3. “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). 4. “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). 5. “Divalent Pb(0) Compounds” N. Takagi, G. Frenking, *Theor. Chem. Acc.*, **129**, 615-623 (2011). 6. “Bonding Analysis for Metal-Metal Multiple bonds in $R_3M\text{-}M'R_3$ (M, M’ = Cr, Mo, W; R = Cl, NMe_2)” N. Takagi, A. Krapp, G. Frenking, *Inorg. Chem.*, **50**, 819-826 (2010). 7. “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). 8. “Divalent E(0) Compounds (E = Si - Sn)” N Takagi, T. Shimizu, G. Frenking, *Chem. Eur. J.*, **15**, 8593-8604 (2009). 9. “Divalent Si(0) Compounds” N Takagi, T. Shimizu, G. Frenking, *Chem. Eur. J.*, **15**, 3448-3456 (2009).
【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）

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【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
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【所属学会】	Japan Society for Molecular Science The Chemical Society of Japan
【主な著書、学術論文】 （過去 5 年以内）	1. Masayuki Nakagaki and Shigeyoshi Sakaki “CASPT2 Study of Inverse Sandwich-Type Dinuclear Cr(I) and Fe(I) Complexes of the Dinitrogen Molecule: Significant Differences in Spin Multiplicity and Coordination Structure between These Two Complexes” *J. Phys. Chem. A*, **118**, 1247-1257 (2014) 2. Shinji Aono, Masayuki Nakagaki, Takuya Kurahashi, Hiroshi Fujii, and Shigeyoshi Sakaki “Theoretical Study of One-Electron Oxidized Mn(III)– and Ni(II)–Salen Complexes: Localized vs Delocalized Ground and Excited States in Solution” *J. Chem. Theory Comput.*, **10** 1062-1073 (2014)

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【現在の研究課題】	Nickel-Catalyzed Inert Bond Activation
【研究内容キーワード】	C − C Bond Activation, Cooperative Catalysis, Lewis Acid, Nickel
【学歴】	June 2008, Faculty of Chemistry, Northeast Normal University, P.R. China
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【略歴】	July 2009 - Jan. 2012: State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, P.R. China. Postdoc fellow in Prof. Zhijian Wu's group. July 2008 – Present: Faculty of Chemistry, Northeast Normal University, Changchun, P.R. China. Research Associate in Prof. Zhongmin Su's group. (On Study Leave)
【所属学会】	Chinese Chemical Society membership
【主な著書、学術論文】（過去 5 年以内）	1. Guan, W.; Sayyed, F. B.; Zeng, G. X.; Sakaki, S. *Inorg. Chem.* **2014**, *ic5003429*. 2. Guan, W.; Sakaki, S.; Kurahashi, T.; Matsubara, S. *Organometallics* **2013**, *32*, 7564−7574. 3. Guan, W.; Yamabe, S.; Sakaki, S. *Dalton Trans.* **2013**, *42*, 8717−8728. 4. Yamabe, S.; Guan, W.; Sakaki, S. *J. Org. Chem.* **2013**, *78*, 2527−2533. 5. Yamabe, S.; Zeng, G. X.; Guan, W.; Sakaki, S. *J. Comput. Chem.* **2014**, *35*, 1140–1148.
【学術関係の受賞など】	China Postdoctoral Science Special Foundation 2010-2011

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【研究分野】	Computational Chemistry
【現在の研究課題】	Theoretical Study of Benzene formation from Alkyne catalyzed by Mo-Mo Quintuple Bond.
【研究内容キーワード】	Electronic Structure of Transition Metal and Lanthanide Complexes
【学歴】	June 2012, College of Chemistry, Beijing Normal University
【学位】	Doctor of Physical Chemistry from Beijing Normal University
【略歴】	July. 2012, Postdoctoral Fellow, Kyoto University
【主な著書、学術論文】（過去 5 年以内）	1. Chen, Yue; Fang, Wei-Hai "Mechanism for the Light-Induced O_2 Evolution from H_2O Promoted by Ru(II) PNN Complex: A DFT Study" *J. Phys. Chem. A*, **114**, 10334-10338 (2010) 2. Juan Han, Xuebo Chen, Lin Shen, Yue Chen, Weihai Fang, Haobin Wang "Energy Transfer Tunes Phosphorescent color if single-Dopant White OLED" *Chem. -Eur. J.*, **17**, 13971-13977 (2011) 3. Yue Chen, Juan Han, Wei-Hai Fang "Mechanism of Water Oxidation to Molecular Oxygen with Osmocene as Photocatalyst: A Theoretical Study" *Inorg. Chem.*, **51**, 4938–4946 (2012) 4. Yue Chen, Shigeyoshi Sakaki "Theoretical Study of Mononuclear Nickel(I), Nickel(0), Copper(I), and Cobalt(I) Dioxygen Complexes: New Insight into Differences and Similarities in Geometry and Bonding Nature." *Inorg. Chem.,* **52**, 13146-13159 (2013). 5. Yue Chen, Shigeyoshi Sakaki The important role of the Mo-Mo quintuple bond in catalytic synthesis of benzene from alkynes. A theoretical study. *Dalton Trans.*, 2014, Advance Article. DOI: 10.1039/C4DT00595C

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【現在の研究課題】	Organometallic reactions
【研究内容キーワード】	Nickel catalysis, Carboxylation, Carbon dioxide activation
【学歴】	January 2008, Master of Science, University of Pune August 2013, Doctor of Science, University of Kerala
【学位】	Doctor of Science from University of Kerala
【主な著書、学術論文】 （過去 5 年以内）	1. Suresh, C. H.; Sayyed, F. B. “Resonance Enhancement via Imidazole Substitution Predicts New Cation Receptors”. *J. Phys. Chem. A, 2013,* **117**, 10455–10461. 2. Sayyed, F. B.; Suresh, C. H. “Accurate Prediction of Cation-π Interaction Energy Using Substituent Effects”. *J. Phys. Chem. A 2012*, **116**, 5723–5732. 3. Sayyed, F. B.; Suresh, C. H. “Quantitative Assessment of Substituent Effects on Cation-π Interactions Using Molecular Electrostatic Potential Topography”. *J. Phys. Chem. A 2011*, **115**, 9300–9307. 4. Sayyed, F. B.; Suresh, C. H. “Substituent Effects in Cation-π Interactions: A Unified View from Inductive, Resonance, and Through-Space Effects”. *J. Phys. Chem. A 2011*, **115**, 5660–5664. 5. Sayyed, F. B.; Suresh, C. H.; Gadre, S. R. “Appraisal of Through-Bond and Through-Space Substituent Effects via Molecular Electrostatic Potential Topography”. *J. Phys. Chem. A 2010*, **114**, 12330–12333.

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【研究分野】	計算化学、理論化学
【現在の研究課題】	水素発生活性をもつ遷移金属錯体に関する理論研究
【研究内容キーワード】	遷移金属錯体、分子構造、水素発生、触媒活性
【最終学歴】	2011年 3月 名古屋大学大学院博士課程 単位取得済満期退学
【学位】	2012年 4月 学位 博士(情報科学)（名古屋大学）
【略歴】	2012年 5月 横浜市立大学 大学院生命ナノシステム科学研究科 特任助手 2012年 12月横浜市立大学 大学院生命ナノシステム科学研究科 特任助教 2013年 4月 京都大学福井謙一記念研究センター 特推研究フェロー
【所属学会】	日本化学会
【主な著書、学術論文】（過去 5 年以内）	1. Okamoto, T.; Yamada, K.; Koyano, Y.; Asada, T.; Koga, N.; Nagaoka, M. “A Minimal Implementation of the AMBER–GAUSSIAN Interface for Ab Initio QM/MM-MD Simulation” *J. Comput. Chem. 32*, 932–942, **2011**. 2. Yamada, K.; Koyano, Y.; Okamoto, T.; Asada, T.; Koga, N.; Nagaoka, M. “Toward a New Approach for Determination of Solute’s Charge Distribution to Analyze Interatomic Electrostatic Interactions in QM/MM Simulations” *J. Comput. Chem. 32*, 3092–3104, **2011**. 3. Yamada, K.; Koga, N. “Variationally determined electronic states for the theoretical analysis of intramolecular interaction: I. Resonance energy and rotational barrier of the C–N bond in formamide and its analogs” *Theor. Chem. Acc. 131*, 1178–1195, **2012**. 4. Yamada, K.; Koga, N. “Variationally Determined Electronic States for the Theoretical Analysis of Intramolecular Interaction. II. Qualitative Nature of the P–O Bond in Phosphine Oxides” *J. Comput. Chem. 34*, 149–161, **2012**. 5. Yamada, K.; Kawashima, Y.; Tachikawa, M. “Muon-electron hyperfine coupling constants of muoniated ethyl radical: a path integral simulations study with semiempirical molecular orbital method” *Chin. J. Phys. 52*, 126–137, **2014**. 6. Mashiko, T.; Yamada, K.; Kojima, T.; Nagashima, U.; Hiraoka, S.; Tachikawa, M. “Molecular dynamics and principal component analysis for a self-assembled nanocube in aqueous solution” *Chem. Lett. 40*, 366–368, **2014**. 7. Hiyama, M.; Akiyama, H.; Mochizuki, T.; Yamada, K.; Koga, N. “Analysis of Photoexcitation Energy Dependence in the Photo Luminescence of Firefly Luciferin” *Photochem. Photobio.* Accepted. **2014**
【学術関係の受賞など】	日本学術振興会 特別研究員 (DC2) 2008-2010, 日本学術振興会 特別研究員 (PD) 2011-2013, 日本化学会第93春季年会　優秀講演賞(学術)

Ⅲ　研究広報活動

１．福井謙一記念研究センターシンポジウム

第１１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　2014 年（平成 26 年）1 月 23 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　谷口　正輝（大阪大学産業科学研究所 教授）
「１分子接合の物性」
10:15―11:15

永瀬　茂（京都大学福井謙一記念研究センター シニアリサーチフェロー）
「高周期元素を骨格にもつ分子とフラーレン 」
11:30―12:30

時任　宣博（京都大学化学研究所 教授）
「高周期典型元素を含む新規なπ電子系の創出」
14:00―15:00

ポスターセッション　15:15―17:15

― コーヒーブレイク ―

懇親会（１F 多目的ルーム）　17:30―19:00

２．センターセミナー

第 11 回福井センターセミナー

日　　時　2013 年（平成 25 年）7 月 24 日　14:00－17:30

場　　所　京都大学福井謙一記念研究センター（1F　多目的室）

14:00～14:05　Opening by Professor Kazuyoshi Tanaka
(Director, Fukui Institute for Fundamental Chemistry)

14:05～15:05　Professor Shin-ichi Yamabe
(Fukui Institute for Fundamental Chemistry)
“Proton transfers in some organic reaction pathways”

15:05 ～16:05　Professor Mitsutaka Okumura　(Osaka University)
“Theoretical study for the characteristics and catalytic reactions of Au clusters”

Break

16:20～17:30　Professor Odile Eisentein　(Université Montpellier 2, France)
“ Computational studies and chemical complexity: A half　full/half empty glass story illustrated by the computational studies of the olefin metathesis catalysis with the Schrock alkylidene complexes ”

３．社会へのアウトリーチ活動

高等学校への出張講義

（1）畑中美穂 特定研究員

兵庫県立北摂三田高等学校	2013 年（平成 25 年）9 月 12 日
〃	2013 年（平成 25 年）12 月 18 日
京都府立城南菱創高等学校	2013 年（平成 25 年）12 月 17 日

(2) 榊 茂好リサーチリーダー
京都府立洛北高等学校　2013 年(平成 25 年) 11 月 15 日

(3) 諸熊　奎治シニアリサーチフェロー
京都府立南陽高等学校　2013 年(平成 25 年) 11 月 7 日

４．その他（報告）

諸熊　奎治シニアリサーチフェローは、２０１３年ノーベル化学賞の受賞者の授賞研究の業績説明で、重要な貢献をした７人の中に含まれていることが判った。
（資料編６を参照）

Ⅳ　研究業績

1．専任教員

池田　昌司

総合研究部門　准教授

1. 今年度の研究の要約

ガラス転移・ジャミング転移の統計力学研究

【始めに】液体を急冷すると、分子の運動が劇的にスローダウンし、ついにはアモルファス状に凍結してしまう。これがガラス転移である。一方、このガラス転移とよく似た現象として、ジャミング転移が知られている。ジャミング転移とは、泡や粉体などで見られる、流動相から非流動相への転移現象である。ガラス転移とジャミング転移の違いは、後者の場合、粒子が十分大きく、その熱運動が無視できることである。しかしそれ以外では、共にアモルファス固体相への転移現象であり、非常に似通っていることから、その関係は近年のガラス研究のホットトピックとなっている。10 年程前に、現象論的に両転移を同一視する相図（図 1a）が提案され[1]、当該分野で重要視されてきた。

私はここ数年、この両転移の関係解明に集中的に取り組んできた。昨年度には、シミュレーションを用いてガラス転移とジャミング転移を分離することに成功した。具体的には、有限温度ではガラス転移を、ゼロ温度ではジャミング転移を起こすモデルに注目し、両者の統一的研究を行ったところ、両者を明確に分離することに成功した[2]。得た相図を図 1b に示す。これは、幅広い温度・応力・密度領域において、固体相と液体相のありかを示す相図である。図 1a と図 1b の違いは明らかだ。図 1a では、ガラス転移とジャミング転移が混同されていたのだ。

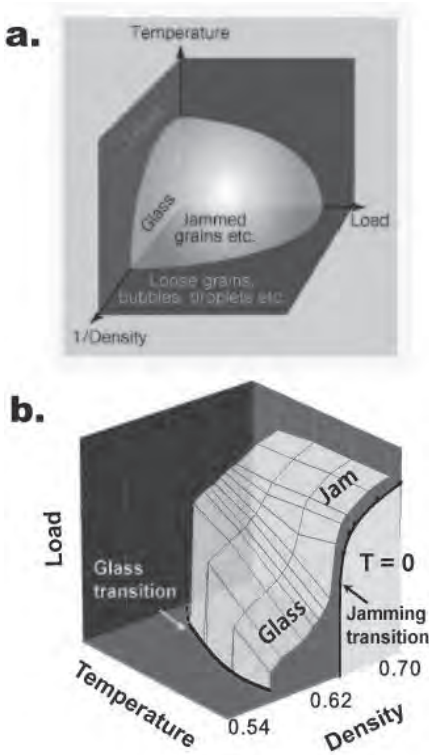

図1 a）ガラス転移とジャミング転移に関する従来の現象論的相図。両転移は区別されていない。b）シミュレーションで決定した相図。両転移は明確に分離される。

本年度は、(1)この成果に基づいて多種多様な実験を説明する試み、(2)この成果をモード結合理論で再現できるかを検討する試み、を行った。また付加的に、(3)これまで研究してきたガウスコア模型のガラス転移の研究を拡張する試み、を行った。以下でこれらを詳述する。

【レオロジー実験の見せるガラス転移とジャミング転移を分離する】以上のシミュレーションで得た知見をもとに、様々な分散系のレオロジー実験を解析した。まず、シミュレーションの結果と実験結果を整合的に記述する新しい現象論モデルを構築した。

分散系の粒子は、周りの液体分子に衝突されるために、熱運動しうる。一方で、粒子が別の粒子と接触するとき、粒子間には直接的な力が働く。つまり系は二つのエネルギースケールをもつ。一

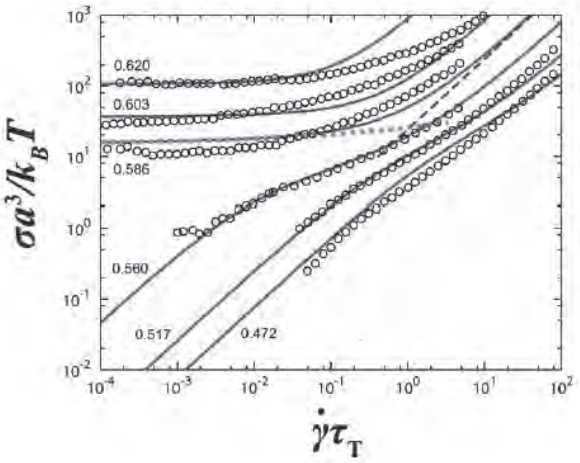

図2 PMMA コロイドの流動曲線（シンボル）を、開発したレオロジー模型（線）で解析した。

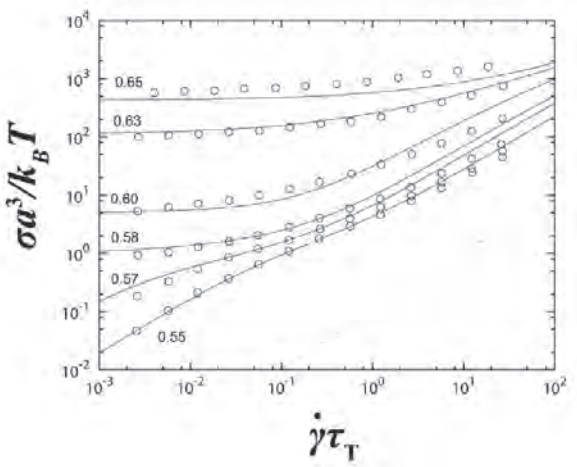

図3 Oil in Water エマルジョンの流動曲線（シンボル）を、開発したレオロジー模型（線）で解析した。

つはブラウン運動の駆動力である「熱的なエネルギースケール k_BT」であり、もう一つは粒子の硬さに対応する「非熱的なエネルギースケール（ここでは ε と置く）」である。そして、二つのエネルギースケールに付随して、二つの微視的時間スケールが現れる。散逸の時間スケール $\tau_0 = \xi a^2/\varepsilon$ と、ブラウン運動の時間スケール $\tau_T = \xi a^2/k_BT$ である。ここで ξ を液体の粘性に由来する散逸として導入した。さらに，せん断流速 γ が，第三の時間スケールを与える．そこで重要な無次元量として，$\gamma\tau_T$ を導入する．$\gamma\tau_T \ll 1$ は，粒子が，せん断流よりずっと速く，ブラウン運動している状態であり，$\gamma\tau_T \gg 1$ は，ブラウン運動よりずっと速く，せん断流が粒子を押し流している状態である．そして、応力についても、非熱的な応力スケール $\sigma_0 = \varepsilon/a^3$ と、熱的な応力スケール $\sigma_T = k_BT/a^3$ が現れる。

我々のシミュレーション研究は、ガラス転移は熱的な時間領域で見られる転移であり、そこで発生する応力は熱的なスケール σ_T にコントロールされており、ジャミング転移は非熱的な時間スケールで起こる転移であり応力は非熱的なスケール σ_0 にコントロールされていることを示した。そこで、この効果を取り込んだ現象論的なレオロジー模型を導入する：

$$\sigma(\varphi, \dot{\gamma}) = S_g(\varphi, \dot{\gamma})\sigma_T + S_j(\varphi, \dot{\gamma})\sigma_0$$

この模型の基本的な哲学は、ガラス転移とジャミング転移は別々であり、全応力は両者の寄与の和として表されるというものだ。*Sg* と *Sj* の具体形は、ガラス転移とジャミング転移の物理からそれぞれ別々に決まる。この模型を用いて、コロイド分散系、マイクロジェル、エマルション、泡、さらに調和粒子系のシミュレーションを解析した（図２、図３）。これらの実験系が、構築した現象論モデルで極めてうまく記述できることがわかった。この解析を用いると、これらの実験系のどの部分がガラス転移の物理にコントロールされており、どの部分がジャミング転移に対応しているかを解析することができる。その結果コロイド分散系は、完全にガラス転移の物理によりコントロールされていること、一方で泡はジャミング転移の物理によりコントロールされていることを示した。さらに、エマルションの理解には、ガラス転移とジャミング転移の両方の寄与をバランスよく取り込む必要があることが明らかとなった。最後にマイクロジェルの解析をしたところ、この系は

しばしばジャミング転移のモデルとして研究されているにもかかわらず、ほぼガラス転移だけで解析できることが明らかとなった。上述の知見をまとめるために、図４に、様々な実験系のパラメータ領域を動的相図上にプロットした。各実験系が、ガラス転移を示すのか、ジャミング転移を示すのかは、極めて明確である。

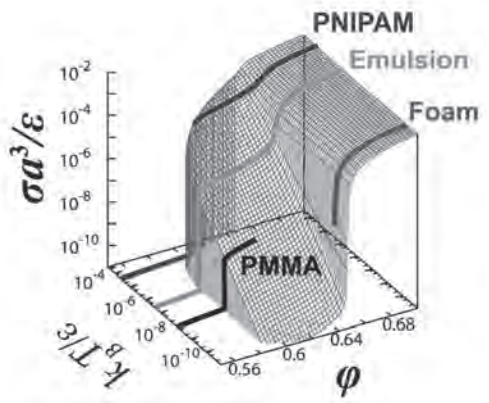

図4 ガラス・ジャミング相図上に、様々な実験系のパラメータ領域をプロットした。

【ガラス転移・ジャミング転移をモード結合理論で解析する】次に、これらのシミュレーションや実験の結果を、現在のガラス転移の微視的理論は説明できるかを検討した。具体的には、モード結合理論により、図１の相図が再現できるかに注目した。

ここではシア流中に拡張されたモード結合理論に注目する。この理論は、ガラス的な系の応力を微視的に計算する理論である。この理論では、系の応力は

$$\sigma = \frac{\dot{\gamma} k_B T \rho^2}{60\pi^2} \int_0^\infty dt \int_0^\infty dk \, \frac{k^5 c'(k) c'(k(t))}{k(t)} F_l(k(t),t)^2$$

と表される。ここで c(k)は直接相関関数であり、Ft(k,t)はシア流中での中間散乱関数、すなわち密度場の時間相関関数である。MCT に従って中間散乱関数を評価し、この表式を通じて系の応力を求めた。この計算を様々な密度と温度とシア流速の場合について繰り返し、モード結合理論による相図を得た。その結果をまとめると、(1)ガラス相において σ_T に比例する応力が発生する。(2)ジャミング相に向かい、応力が密度差の 4 乗で発散挙動を示す。(3)ジャミング相内部では、密度の増加とともに応力が減少する。このうち、(1)はシミュレーションの結果を正しく再現している。(2)は定性的には正しいが、定量的には大きく異なる。シミュレーションの場合、応力発散の指数は 1 である。(3)はシミュレーションの結果を全く捕らえられていない。

従って、図１におけるガラス相の部分と、ガラス相からジャミング相への臨界的な挙動については、定性的にはモード結合理論で記述できることが分かった。一方でジャミング相の応力の再現には、さらなるガラス転移理論の深化が必要である。

【ガウスコア模型に非常に近い模型の研究】柔らかいコロイド系のモデルとして、ガウスコア模型(GCM)が研究されてきた。ガウスコア模型は、系の粒子がガウス型の相互作用 $v(r) = \exp(-r^2)$をする液体モデルである。我々の先行研究により、ガウスコア模型のガラス転移は、極度に平均場的になり、モード結合理論と極めて相性がよくなることがわかっている [3]。一方で、ガウス関数の指数を２から４に変えた模型を一般化指数関数模型(n=4)と呼ぶ。近年、一般化指数関数模型(n=4)のガラス転移が調べられ、その低温領域には、クラスターガラスという全く新しいガラス相があることが分かった [4]。クラスターガラスとは、多数の粒子が一つのサイトに集まりクラスターを形成し、そしてそのサイトの空間分布がガラス状にアモルファスに分布する相である。

では、この指数の変更は、系の統計力学をどのようにして変えているのだろうか？我々は、ガウス関数の指数を２から 2.01、2.02 と連続的に大きくし、まず、その結晶化挙動を詳しく解析した。このような模型は、単なる理論家のおもちゃではない。実際に、両親媒性を有するデンドリマーの相互作用は、このような２よりわずかに大きいガウス関数でうまくモデル化できることが知られている。

我々はまず、HNC 理論と MSA 理論という液体の統計力学の手法を用いて、この系の相図の概略を検討した（図５）。すると、指数が２からわずかに大きくなると、低密度での相図はほぼガウスコア模型と同様であるが、高密度側で指数４の場合と同種のクラスター相が現れることが分かった。さらに指数を大きくすると、このクロスオーバ密度が徐々に低下し、最終的に、クラスター相が、結晶相全体を占めるようになることがわかった。さらにこの結果を、シミュレーションで確認し、その変化をポテンシャルエネルギー地形の観点からも解析した。すると、ポテンシャルエネルギー地形そのものにおいても、クラスター状態が極めて安定に存在していることが分かった。

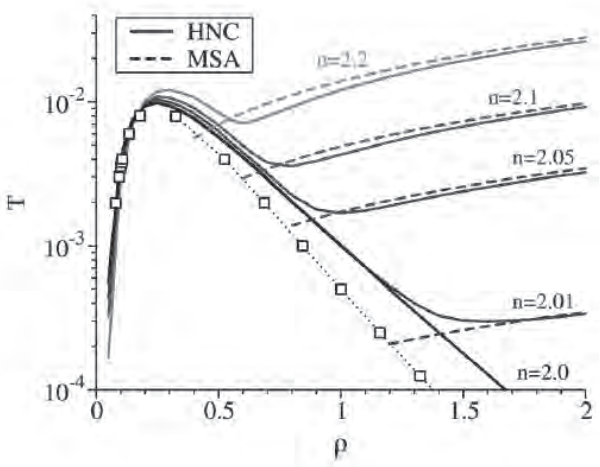

図５ 様々な指数での、一般化指数模型 v(r) = exp(-r^n)の相図を HNC 理論と MSA 理論に基づいて予測した。実線より下の部分が結晶相である。n=2 から大きくすると、ガウスコア模型の場合からのずれが、高密度側で現れることが分かる。このリエントラント的振る舞いを見せる結晶相こそ、クラスター相だ。

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"Unified study of glass and jamming rheology in soft particle systems"
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２．シニアリサーチフェロー

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1. Summary of the research of the year

(a) Development of RI-MP2Auxiliary Basis Functions for 6-31G** and 6-311G** Basis Sets

Electron correlation plays an important role in the accurate description of energies, structures, and properties of molecules. Density functional theory (DFT) is widely used to take account of electron correlation because of its low computational cost. However, generally used DFT methods present several shortcomings. For example, they fail to describe non-covalent interactions and reaction barriers. Second-order Møller–Plesset perturbation (MP2) theory is the simplest method to include electron correlation at an *ab initio* level, which is important for non-covalent interactions and reaction barriers. However, the computational cost of MP2 calculations is considerably high and practical applications are limited to molecules of moderate size. The resolution-of-identity (RI) approximation for MP2 is a promising approach to reduce the computational cost and resources used for MP2 calculations without sacrificing accuracy. The accuracy of RI-MP2 calculations, considering error from conventional MP2 calculations, depends on the quality of the auxiliary basis functions, while the computational cost of RI-MP2 calculations depends on the size of auxiliary basis functions. Consequently, various RI-MP2 auxiliary basis functions are developed to obtain appropriate accuracy with reasonable size.

Pople-type basis sets represented by 6-31G** and 6-311G** are widely used as standard basis sets for calculations of large systems because of their reasonable accuracy and computational cost. However, the auxiliary basis functions are not developed up to date. Therefore, we have developed the auxiliary basis functions that are suitable for RI-MP2/6-31G** and RI-MP2/6-311G** calculations in terms of accuracy and computational costs. In the development of the auxiliary basis functions, the strategy for adding *g*-type auxiliary functions is proposed to improve the accuracy of the RI approximation with low computational cost. The performance of the developed auxiliary basis functions is assessed for 114 small and 23 large molecules (Fig. 1). It is remarkable that the developed auxiliary basis functions shows much smaller RI errors than other auxiliary basis functions used for 6-31G** and 6-311G** basis sets with similar computations costs. This fact suggests that the developed 6-31G** and 6-311G* auxiliary basis functions are widely applicable to the RI-MP2 calculations of large molecules with high accuracy and low computational cost.

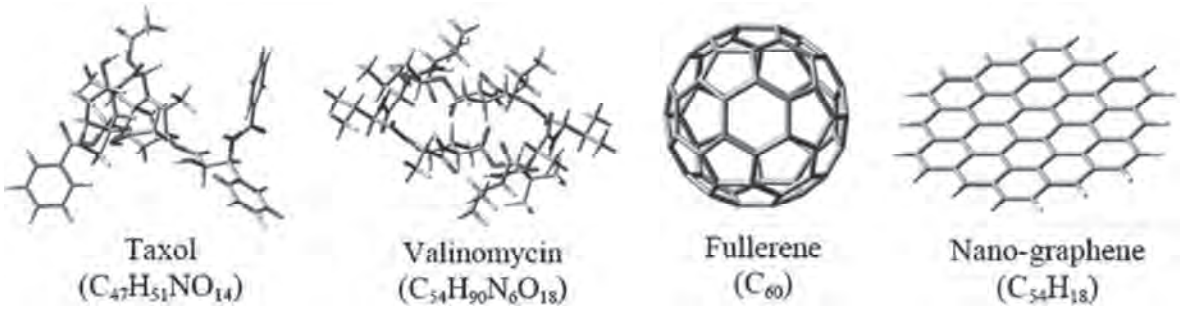

Fig. 1. Examples of large molecules tested for RI-MP2 calculations.

(b) Carbide Cluster Metallofullertenes: Structures, Properties, and Possible Origin

Endohedral metallofullerenes (EMFs) are hybrid molecules with different metallic species encapsulated inside hollow fullerene cages. In addition to conventional EMFs that contain merely metal ions, novel compounds encapsulating a metallic cluster of, for instance, nitride, carbide, oxide, cyanide, and sulfide have all been obtained. Among them, carbide cluster metallofullerenes (CCMFs) are quite unique because their synthetic processes require no extra element except graphite and the metal sources, which results in the intractable situation that the molecular structures of CCMFs are particularly difficult to identify because exactly two carbon atoms are encapsulated inside the cage, but they do not participate in constructing the cage framework. Because of recent achievements in the theoretical and X-ray crystallographic studies of EMFs, several new CCMFs (e.g. $M_xC_2@C_{2n}$) have been assigned unambiguously, most of which were previously proposed as conventional EMFs $M_x@C_{2n+2}$. Such species are mainly scandium-containing compounds such as $Sc_3C_2@I_h(7)$-C_{80} [not $Sc_3@C_{3v}(7)$-C_{82}] (see: Fig.2), $Sc_2C_2@C_{2v}(5)$-C_{80} [not $Sc_2@C_{82}$], $Sc_2C_2@C_s(6)$-C_{82} [not $Sc_2@C_s(10)$-C_{84}], $Sc_2C_2@C_{2v}(9)$-C_{82} [not $Sc_2@C_{2v}(17)$-C_{84}], $Sc_2C_2@C_{3v}(8)$-C_{82} [not $Sc_2@D_{2d}(23)$-C_{84}], and $Sc_2C_2@D_{2d}(23)$-C_{84} [not $Sc_2@C_{86}$]. Additional examples of CCMFs include $Gd_2C_2@D_3(85)$-C_{92}, $Sc_2C_2@C_{2v}(6073)$-C_{68}, $Ti_2C_2@D_{3h}(5)$-C_{78}, $M_2C_2@C_{3v}(8)$-C_{82}, $M_2C_2@C_s(6)$-C_{82} (M = Y, Er etc.), $Y_2C_2@C_{84}$, $Y_2C_2@D_3(85)$-C_{92}, $Y_2C_2@D_5(450)$-C_{100}, and $Lu_3C_2@D_2(35)$-C_{88}. We present a detailed summary of all aspects of CCMFs, including historically erroneous assignments and corrected structural characterizations, along with their intrinsic properties such as electrochemical and chemical properties. Emphasis is given to the structural issues which are fundamental aspects for understanding their intrinsic properties. Finally, discussion related to the formation mechanism and possible origin of cluster EMFs, not only related to CCMFs, is presented.

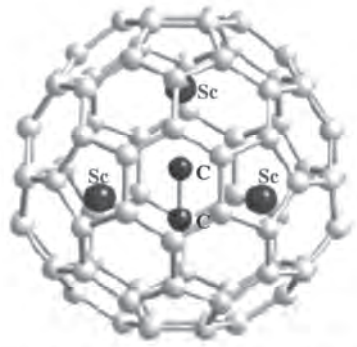

Fig. 2. An example of $Sc_3C_2@C_{80}$ (not $Sc_3@C_{82}$)

(c) Mechanistic Study of the Diels-Alder Reaction of La@C_{82}

The Diels-Alder reaction is an extremely valuable type of cycloaddition in organic chemistry. In recent year, much attention has been focused on the Diels-Alder reaction of fullerenes because it can be a useful method for introducing functionality to fullerene cages. The fact that fullerenes such as C_{60} and C_{70} act as polyalkenes and possess reactive dienophile character derived from their electron-deficient properties has prompted the development of numerous efficient Diels-Alder reactions of fullerenes.

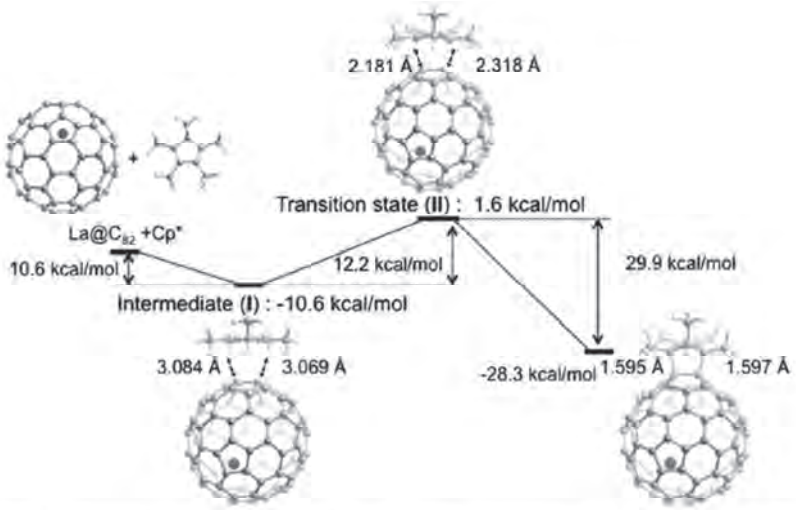

Fig. 3. Reaction profile for the Diels-Alder Reaction of La@C_{82} and Cp*

The reaction mechanism of the Diels-Alder reaction of paramagnetic endohedral metallofullertene, La@C_{82}, and 1,2,3,4,5-pentamethylcyclopentadiene (Cp*) was investigated theoretically and experimentally. Density functional theory calculations reveal that the reaction proceeds via a concerted mechanism that includes formation of a stable intermediate (Fig. 3). The activation energy of a retro-Diels-Alder reaction is also investigated experimentally, which agrees well with the results of density functional theory calculations.

(d) Structural, Electronic, and Optical Properties of Bulk Graphdiyne

Graphdiyne is a newly discovered two-dimensional carbon allotrope with many special features. The structural, electronic, and optical properties of several bulk graphdiyne structures were investigated using density functional theory with van der Waals correction (Fig. 4). It is found that bulk graphdiyne can be either semiconductive or metallic, depending on its stacking configuration. The interlayer van der Waals force red-shifts the optical absorption peaks of bulk graphdiyne relative to those of monolayer; the spectra of different stacking structures display notable differences in the energy range below 1 eV. Finally, the structure of the recently synthesized graphdiyne film is identified combining with previous electronic and optical experiments.

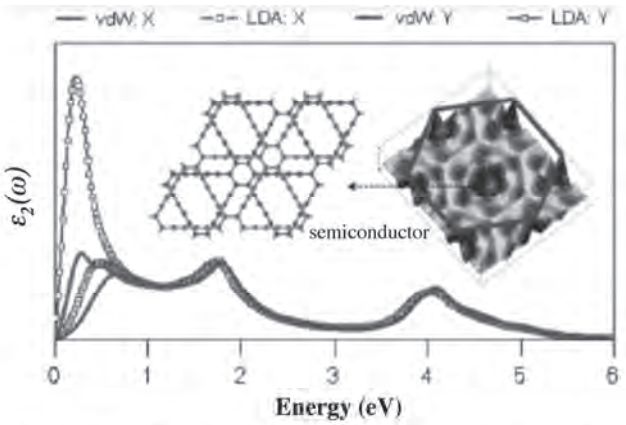

Fig. 4. Optical absorption spectra of stacked graphdiyne

(e) Several Other Research Subjects

(1) Unexpected Formation of Ru_2Sn_2 Bicyclic Four-Membered Ring Complexes with Butterfly and Inverse-Sandwich Structures. (2) Density Functional Theory Study of Fullerene-Carbene Lewis Acid-Base Adducts: Critical Role of Dispersion Interactions. (3) Hellicity-selective photoreaction of single-walled carbon nanotubes with organosulfur compounds in the presence of oxygen. (4) Regiochemistry of Nonclassical C_{62} Fullerene: Role of Tetragonal Carbocyclic Ring in Cycloadditions and Thermal/Photoinduced Interconversions of Fulleroid Derivatives. (5) Intramolecular versus Intermolecular Electronic Interactions between [5,6]-Open and [6,6]-Closed Adducts with exTTF. (6) Linear and Nonlinear Two-Coordinate Vanadium Complexes: Synthesis, Characterization, and Magnetic Properties of V(II) Amides. (7) A Metallofullerene Electron Donor that Powers an Efficient Spin Flip in a Linear Electron Donor- Acceptor Conjugate. (8) Enhanced Many-Body Effects in One-Dimensional Linear Atomic Chains. (9) 1,3-Dipolar Cycloadditions of Stone-Wales Defective Single-Walled Carbon Nanotubes: A Theoretical Study. (10) Dispersion Force Stabilized Two-Coordinate Transition Metal-Amido Complexes of the -N($SiMe_3$)Dipp (Dipp = C_6H_3-2,6-Pr^i_2) Ligand: Structural, Spectroscopic, Magnetic, and Computational Studies. (11) Cycloaddition of Benzyne to Armchair Single-Walled Carbon Nanotubes: [2+2] or [4+2]? (12) Diversity of the Structures in a Distannene Complex and its Reduction to Generate a Six-Membered Ti_2Sn_4 Ring Complex. (13) Regioselective Derivatization of C_{84} by Diels-Alder Reactions: Applications to Photovoltaic Solar Cells and Fullerene Polymerization.

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3. Review articles

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(2) M. Yamada, T. Akasaka, and S. Nagase, "Carbene Additions to Fullerenes", *Chem. Rev.,* **113**, 7209-7264 (2013).

(3) S. Nagase, "Theory and Calculations of Molecules Containing Heavier Main Group Elements and Fullerenes Encaging Transition Metals: Interplay with Experiment", *Bull. Chem. Soc. Jpn. (Award Accounts)*, **87**, 167-195 (2014).

4. Books

(1) M. Yamada, X. Lu, L. Feng, S. Sato, Y. Takano, S. Nagase, and T. Akasaka, "Fundamental and Applied Aspects of Endohedral Metallofullerenes as Promissing Carbon Nanomaterials", In *Organic Nanomaterials: Synthesis, Chracterization, and Device Appilcations* (Eds. T. Torres and G. Bottarti), John Wiley & Sons, Chapter 12, pp. 241-258 (2013).

(2) 土屋敬広、溝呂木直美、永瀬 茂、赤阪 健、"□空間に閉じ込められた物質系の創製と機能"、*高次□空間の創発と機能開発*、(赤阪 健、大須賀篤弘、福住俊一、神取秀樹 監修)、シーエムシー出版、pp. 5-9 (2013).

Keiji MOROKUMA

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1. Summary of the Research of the Year

Theoretical and Computational Studies of Complex Molecular Systems

The goals of the research of this group are 1. to develop theoretical methods (such as ONIOM, GRRM) for complex systems, 2. to demonstrate that such methods can be used for simulations of structures, reactions and dynamics of complex systems and 3. to solve some of the important problems in each field. Of the FIFC team members who have contributed to the development of our program, five postdoctoral fellows (Fukui, JSPS and CREST) from abroad left our group in FY 2013, and all of them found excellent faculty positions in their respective native countries. We have welcomed to our group one JSPS foreign postdoctoral fellow (from France) and three postdoctoral fellows (from China, Sri Lanka and Japan) supported mainly by Kakenhi (grants from the Minister of Education, Culture, Sports, Science and Technology) as well as one visiting research fellow (PhD student from Thailand). We continued to have a strong team of theoretical/computational chemists at FIFC and at Emory University working together toward a common goal. Since detailed description on individual projects at FIFC can be found in the reports of postdoctoral fellows, here the areas of studies and titles of individual projects are summarized.

I. Theoretical Studies of Reactions of Complex and Biomolecular Systems

In this area, in recent years we have studied structures and reactions of organic and organocatalytic systems, and inorganic and homogenous metal catalytic systems as well as biomolecular systems. Our emphasis has been on catalyses, both transition metal catalysis and organic catalysis, with special attention to selectivity. In addition to the standard TS optimization method, we extensively used the GRRM strategy (see research area III below) to find reaction pathways.

Another research topic in complex systems is chemical reactions in excited electronic states. We have studied potential energy surfaces of low-lying excited states for some organic and inorganic photochemical reactions, and elucidated rather complex reaction mechanisms involving different electronic states. Recently a most advanced multiconfigurational ab initio method called DMRG (density matrix renormalization group) method, has been used in collaboration with its developer, Prof. Yanai of Institute of Molecular Science, for calculations of potential energy surfaces of multiple states of complex molecular systems.

IA. Organic and Organocatalytic Reaction Systems

a. The mechanism of the Ugi reaction, a four-component organic reaction (See research activities of R. Ramozzi)

b. Theoretical study of the Biginelli reaction, a three-component organic reaction (See research activities of M. Puripat)

c. Heavy-atom tunneling in cyclobutadiene (See research activities of L. W. Chung)

d. Asymmetric phase-transfer catalysis with homo- and heterochiral quaternary ammonium salts (See research activities of G. P. Petrova)

e. Mechanistic study on the metal-free C-H activation by using a hypervalent iodine(III) reagent (See research activities of J. Jiang)

f. σ–aromaticity of hexa-group 16 atom-substituted benzene dications (See research activities of M. Hatanaka. Paper 1)

g. Multiple pathways for primary step of spiropyran photochromic reaction: a CASPT2//CASSCF study (see paper 18)

h. Multireference ab initio density matrix renormalization group (DMRG)-CASSCF and -CASPT2 study on the photochromic ring-opening of spiropyran (see paper 11).

IB. Inorganic and Organometallic Reaction Systems

a. Theoretical study of aqueous Mukaiyama-Aldol reaction catalyzed by lanthanide complexes (See research activities of M. Hatanaka, Papers 12 and 22)

b. Asymmetric Mukaiyama-Aldol reaction of silicon enolates with aldehydes catalyzed by chiral Fe(II) complex (See research activities of W. M. C. Sameera)

c. QM/MM structural and spectroscopic analysis of the di-iron(II) and di-iron(III) ferroxidase site in M ferritin (Paper 15)

d. sp^3–sp^2 vs sp^3–sp^3 C–C activation in Rh-catalyzed ring opening of benzocyclobutenol: A DFT study (See research activities of L. Ding. Paper 6)

e. Mechanistic origin of chemo- and regioselectivity of nickel-catalyzed [3+2+2] cyclization reaction (See paper 9)

f. Hydroboration mechanism revisited: alkene addition partner depends on ligand and substrate (See research activities of T. Harris)

g. The origin of enantioselectivity for intramolecular Friedel-Crafts reaction catalyzed by supramolecular Cu / DNA catalyst complex (See research activities of G. P. Petrova)

h. Theoretical investigation on the Pd-catalyzed C(sp^3)-H activation in the synthesis of unnatural amino acids (See research activities of J. Jiang)

i. Density matrix renormalization group (DMRG) calculations of magnetic exchange coupling in dinuclear transition metal complexes (See research activities of T. Harris. Paper 4)

j. Application of ab initio density matrix renormalization group (DMRG) on the simplest Fe(IV)-oxo complex. (See research activities of L. W. Chung)

k. Excited-state proton transfer controls irreversibility of photoisomerization in mononuclear ruthenium(II) monoaquo complexes: a DFT study (See research activities of L. Ding. Paper 3).

IC. Biomolecular Reaction Systems

a. A theoretical study on the UVR8 photoreceptor (See research activities of L. W. 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 nanostructure formation based on density functional tight binding (DFTB). Our focus in the last few years has been on the growth dynamics of single-walled carbon nanotube (SWCNT) and graphene, for which the growth mechanism is still poorly understood. The chirality control in the CNT growth is one of the most important pending issues. We addressed on the chirality control in the CNT growth from organic templates. The nucleation and growth of graphenes on transition metal surfaces have also been studied using a variety of model systems. The research activity in this area is slightly slowed down, as we feel that we have accomplished what we can hope for using the present methodology and techniques.

a. Quantum chemical simulations reveal acetylene-based growth mechanisms in the chemical vapor

deposition synthesis of carbon nanotubes (See paper 5)

b. Temperature dependence of catalyst-free chirality-controlled single-walled carbon nanotube growth from organic templates (See paper 10)

c. Revealing the dual role of hydrogen for defect healing and growth inhibition in polycyclic aromatic hydrocarbon formation with QM/MD simulations (see paper 19)

d. Nucleation of graphene precursors on transition metal surfaces: insights from theoretical simulations (See paper 21)

e. Step-edge self-assembly during graphene nucleation on a Ni surface: QM/MD simulations (See paper 7)

f. Graphene nucleation on a surface-molten copper catalyst (See research activities of H.-B. Li)

III. Method Developments and Applications

In collaboration with Profs. Koichi Ohno and Satoshi Maeda, combining the two methods of potential energy search, the ADDF (adiabatic downward distortion following) method and the AFIR (artificial force-induced reaction (AFIR) method, we have developed the Global Reaction Route Mapping (GRRM) strategy**.** These methods allow determination of all the reaction pathways, including intermediates and transition states as well as minimum energy conical intersections and seam of crossing, of complex reaction systems without any guess. The strategy includes expanding the applicability to complex molecular systems by using micro-iteration techniques. The GRRM strategy has been actively applied to homogenous catalysis systems such as transition metal catalysts and metal-free organocatalysts, for which the research area I above should also be referred to. The GRRM strategy has been particularly powerful in finding reaction pathways of photo-activated molecules, in which multiple pathways involving various electronically excited states and crossings between them can efficeintly be located using the GRRM strategy.

IiIA. Development of the GRRM Strategy

a. Exploring pathways of photoaddition reactions by artificial force induced reaction (AFIR) method: A case study on the Paternò-Büchi reaction (See paper 17)

b. Exploring transition state structures for intramolecular pathways by the artificial force induced reaction (AFIR) method (See paper 8)

c. Automated search for minimum energy conical intersection geometries between the lowest two singlet states S_0/S_1-MECIs by the spin-flip TDDFT method (See paper 14)

IIB. Applications of the GRRM Strategy

a. Theoretical study on the photodissociation of methylamine involving S_1, T_1, and S_0 states (See paper 20)

b. A CASPT2 study of photodissociation pathways of ketene (See paper 16)

c. Theoretical studies of photodissociation of nitromethane (See research activities of M. Isegawa)

d. CASPT2 study of reaction paths starting from $N(^2D) + H_2NO$ (See research activities of M. Isegawa)

e. Mechanism of $C_nH^{\square}$ (n = 2, 4, 6) generation in the interstellar media (See research activities of M. Hatanaka)

f. Predicting pathways for terpene formation from first principles – routes to known and new sesquiterpenes (See research activities of M. Isegawa. Paper 2)

g. Development of a new class of azo-based fluorescence probes to detect different levels of hypoxia (See paper 13)

h. Computational studies of fluorescent probes, Tokyo Green and Tokyo Magenta (See research activities of W. M. C. Sameera)

i. Ring opening-closing mechanism of diarylethene induced by UV-visible photon: potential energy surface mapping by spin-flip time dependent DFT (See research activities of M. Isegawa)

IIIC. Others

a. Development of Gau_mopac2012 algorithm (See research activities of W. M. C. Sameera)

Original papers

1. M. Hatanaka, M. Saito, M. Fujita and K. Morokuma, □-Aromaticity in Hexa-Group 16 Atom-Substituted Benzenes Dications. A Theoretical Study. J. Org. Chem. *79*, 2640–2646 (2014).
2. M. Isegawa, S. Maeda, D. J. Tantillo and K. Morokuma, Predicting Pathways for Terpene Formation from First Principles – Routes to Known and New Sesquiterpenes, Chem. Sci. 5, 1555-1560 (2014).
3. L. Ding, L. W. Chung, and K. Morokuma, Excited-State Proton Transfer Controls Irreversibility of Photoisomerization in Mononuclear Ruthenium(II) Monoaquo Complexes: A DFT Study. J. Chem. Theory Comput. 10, 668–675 (2014).
4. T. V. Harris, Y. Kurashige, T. Yanai, and K. Morokuma, Ab Initio Density Matrix Renormalization Group Study of Magnetic Coupling in Dinuclear Iron and Chromium Complexes, J. Chem. Phys. 140, 054303/1-10 (2014).
5. Y. Wang, X. Gao, H.-J. Qian, Y. Ohta, X. Wu, G. Eres, K. Morokuma, and S. Irle, Quantum Chemical Simulations Reveal Acetylene-Based Growth Mechanisms in the Chemical Vapor Deposition Synthesis of Carbon Nanotubes. Carbon 72, 22-37 (2014).
6. L. Ding, N. Ishida, M. Murakami, and K. Morokuma, sp^3–sp^2 vs sp^3–sp^3 C-C Site-Selectivity in Rh-Catalyzed Ring Opening of Benzocyclobutenol: A DFT Study, J. Am. Chem. Soc. J. Am. Chem. Soc. 136, 169–178 (2014).
7. Y. Wang, A. J. Page, H.-B. Li, H.-J. Qian, M.-G, Jiao, Z.-J. Wu, K. Morokuma, and S. Irle, Step-Edge Self-Assembly During Graphene Nucleation on a Ni Surface: QM/MD Simulations, Nanoscale 6, 140-144 (2014).
8. S. Maeda, T. Taketsugu, and K. Morokuma, Exploring Transition State Structures for Intramolecular Pathways by the Artificial Force Induced Reaction (AFIR) Method. J. Comput. Chem. 35, 166-173 (2014).
9. S. Komagawa, C. Wang, K. Morokuma, S. Saito and M. Uchiyama, Mechanistic Origin of Chemo- and Regioselectivity of Nickel-Catalyzed [3+2+2] Cyclization Reaction. J. Am. Chem. Soc. 135, 14508–14511 (2013).
10. H.-B. Li, A. J. Page, S. Irle, and K. Morokuma, Temperature Dependence of Catalyst-Free Chirality-Controlled Single-Walled Carbon Nanotube Growth from Organic Templates, J. Phys. Chem. Lett. 4. 3176-3180 (2013).
11. F. Liu, Y, Kurashige, T. Yanai, and K. Morokuma, Multireference Ab Initio Density Matrix Renormalization Group (DMRG)-CASSCF and -CASPT2 Study on the Photochromic Ring-Opening of Spiropyran, J. Chem. Theory Comput. 9, 4462–4469 (2013).
12. M. Hatanaka and K. Morokuma, Theoretical Study of Mukaiyama-Aldol Reaction Catalyzed by Water-Tolerant Lanthanide Lewis Acid, J. Am. Chem. Soc. 135, 13972–13979 (2013).
13. W. Piao, S. Tsuda, Y. Tanaka, S. Maeda, F. Liu, S. Takahashi, Y. Kushida, T. Komatsu, T. Ueno, T. Terai, T. Nakazawa, M. Uchiyama, K. Morokuma, T. Nagano, and K. Hanaoka, Development of a New Class of Azo-based Fluorescence Probes to Detect Different Levels of Hypoxia. Angew. Chem. Int. Ed. 52, 13028-13032 (2013).
14. Y. Harabuchi, S. Maeda, T. Taketsugu, N. Minezawa, and K. Morokuma, Automated search for minimum energy conical intersection geometries between the lowest two singlet states S_0/S_1-MECIs by the spin-flip TDDFT method. J. Chem. Theory Comput. 9, 4116–4123 (2013).
15 T. V. Harris and K. Morokuma, QM/MM Structural and Spectroscopic Analysis of the Di-iron(II) and Di-iron(III) Ferroxidase Site in M Ferritin, Inorg. Chem. 52, 8551-8563 (2013).
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18. F. Liu and K. Morokuma, Multiple Pathways for Primary Step of Spiropyran Photochromic Reaction: a CASPT2//CASSCF Study, J. Am. Chem. Soc. 135, 10693–10702 (2013).
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20. H. Xiao, S. Maeda and K. Morokuma, Theoretical Study on the Photodissociation of Methylamine Involving S_1, T_1, and S_0 States, J. Phys. Chem. A 117, 5757–5764 (2013).
21. A. J. Page, Y. Wang, H.-.B Li, K. Morokuma, and S. Irle, Nucleation of Graphene Precursors on Transition Metal Surfaces: Insights from Theoretical Simulations. J. Phys. Chem. C, 117, 14858–14864 (2013).
22. M. Hatanaka, S. Maeda and K. Morokuma, Sampling of Transition States for Predicting Diastereoselectivity Using Automated Search Method – Aqueous Lanthanide-Catalyzed Mukaiyama-Aldol Reaction, J. Chem. Theory Comput. 9, 2882–2886 (2013).

4. Presentation at academic conferences and universities

1. Keiji Morokuma, Exploring potential energy surfaces with GRRM automatic search strategy, International Symposium on Organic Reaction Mechanism, Shenzhen, China, May 8-9, 2013.
2. Keiji Morokuma, Development of Advanced Approaches to Potential Energy Landscaping for Fuel Cracking and Oxidation, US AFOSR symposium on combustion, Arlington, VA, USA, June 3-6, 2013.
3. Keiji Morokuma, Exciting World of Theoretical Studies of Chemical Reactions -- From Gas Phase Reactions to Catalysts, and Enzymatic Reactions, Asian Pacific Conference of Theoretical and Computational Chemistry (APCTCC6), Gyeonju, Korea, July 10-13, 2013.
4. Keiji Morokuma, Theory Can Provide Insights Unavailable from Experiments in Catalysis, A, The Sixteenth International Symposium on Relations between Homogeneous and Heterogeneous Catalysis, Sapporo, Japan, August 4-9, 2013.
5. Keiji Morokuma, Theory Provides Insights Unavailable from Experiments in Chemical Reactions, The CRC symposium of post ISHHC-16 “Advanced Synthesis and Characterization Techniques for the Atomic-level Understanding and Control of Chemical Reactions” and The 4th CSE Summer School. Jozankei, Sapporo, Japan, August 10-11, 2013.
6. Keiji Morokuma, Theory Provides Insights Unavailable from Experiments in Chemical Reactions, Department of Chemistry, California Institute of Technology, Pasadena, CA, USA, August 26, 2013.
7. Keiji Morokuma, Automatic exploration of potential energy surfaces for catalysis and other complex chemical reactions, DOE Symposium on New Theoretical Concepts and Directions in Catalysis, Santa Barbara, CA, USA, August 27-30, 2013.
8. Keiji Morokuma, Automatic exploration of reaction pathways in complex environments, CAMM Forum, Tokyo, October 3, 2013.
9. Keiji Morokuma, Exciting World of Theoretical/Computational Studies of Chemical Reactions of Complex Chemical Systems, CMSI International Symposium “Extending the power of computational materials sciences with K-computer”, Tokyo, October 21-22, 2013.
10. Keiji Morokuma, Automatic exploration of reaction pathways in complex environments, Symposium on "Electronic Structure in Complex Environments”, Southeast Regional Meeting of the American Chemical Society, Atlanta, GA, USA, November 13-14, 2013.
11. Keiji Morokuma, Complex Chemical Reaction Pathways Explored by Automatic Search Strategy, 5th

Japan-Czech-Slovakia International Symposium on Theoretical Chemistry, Nara, , December 2-6, 2013.

12. Keiji Morokuma, Chemical Theory of Complex Molecular Systems: Discovery and Insights from Computational Studies of Chemical Reactions, CRC□EC Joint International Symposium on Chemical Theory for Complex Systems, Atlanta, GA, USA, January 9-10, 2014.

5. Public talks

1. Let's Explore the World of Chemical Reactions Using Computer (in Japanese), Career Orientation Forum, Nanyo High School, Kyoto, November 7, 2013.
2. The Root of My Science (Chemistry): Izumisano, Presentation Ceremony of Honorary Citizenship, City of Izumisano, Osaka, March 19, 2014.

３．リサーチリーダー

Shigeyoshi SAKAKI

Research Leader, Kenichi Fukui Memorial Research Groups II

1. Summary of the research of 2013

Molecules and molecular systems which consist of transition metal element, organic moiety, non-transition metal element, and hypervalent species are attractive research targets in wide areas of chemistry. This is because those molecules play important roles as metal enzymes, molecular catalysts, and molecular devices such as photo-sensitizer, molecular switch, luminescence material etc. Also, they exhibit a variety of geometry, molecular property, and bonding nature, which attract a lot of interest in theoretical and computational chemistry. All these features deeply relate to their electronic structures. In this regard, the theoretical knowledge of the electronic structure of the complex system including transition metal element is indispensable in wide areas of chemistry.

At the same time, those complex systems are interesting and challenging research targets from the point of view of theoretical/computational chemistry, because their electronic structures are not simple but complicated in many cases. In particular, transition metal complexes bearing large correlation effects are challenging research targets even nowadays. Also, the post Hartree-Fock calculations of very big systems like metal-organic-framework and molecular crystal are challenging. Our group is theoretically investigating those complex systems bearing complicated electronic structure.

This year, we theoretically investigated (i) gas absorption into the Hofmann-type metal-organic-framework (MOF), (ii) RASPT2 study of unusual Ni(I) and Co(I) dioxygen complexes, (iii) luminescent vapochromic compounds including an $AuCu_2(NHC)_2$ core, (iv) interest in new heterodinuclear transition-metal/main-group-metal complexes: electronic structure and mechanism of fluoride sensing function, and (v) 3D-RISM-SCF method with dual solvent boxes for a highly polarized system: application to 1,6-anhydrosugar formation reaction of phenyl α- and β-D-glucosides under basic conditions, (vi) Theoretical Study of Reactivity of Ge(II)-hydride Compound:Comparison with Rh(I)-Hydride Complex and Prediction of Full Catalytic Cycle by Ge(II)-hydride, (vii) Novel Ni(0)-Catalyzed [6 − 2 + 2] Cycloaddition Reactions of Isatoic Anhydrides with Alkynes: Origin of Facile Decarboxylation and (viii) The crucial role of a Ni(I) intermediate in Ni-catalyzed carboxylation of aryl chloride with CO_2.

. We wish to report summary of them.

(i) Gas Absorption into the Hofmann-type Metal-Organic-Framework (MOF)

Porous coordination polymers (PCPs) or metal-organic frameworks (MOFs) recently attract a lot of attentions because of their potential application to gas storage,[1,2] gas separation,[2,3] catalysis,[4] and nanospace engineering.[5] The flexibility in the use of a variety of organic linkers and/or metals leads to syntheses of many kinds of PCP with required properties. Among the desired properties, selective uptake[6] and storage[1,2] of gas molecule have been investigated well. However, theoretical understanding of the gas absorption and gas storage has been reported well. One reason is that the dispersion interaction plays important role in gas absorption and gas storage but the evaluation of dispersion interaction in big system is not easy even nowadays. In this regard, we have started theoretical study of gas absorption and gas storage into MOF, recently.

This year, absorption of CO_2 and CS_2 molecules into the Hofmann-type three-dimensional porous coordination polymer (PCP) $\{Fe(Pz)[Pt(CN)_4]\}_n$ (Pz = pyrazine) was theoretically explored with the ONIOM (MP2.5 or SCS-MP2:DFT) method, where the M06-2X functional was employed in the DFT calculation. The binding energies of CS_2 and CO_2 are evaluated to be -17.3 kcal mol^{-1} and -5.2 kcal mol^{-1}, respectively at

the ONIOM(MP2.5:M06-2X) level and -16.9 kcal mol^{-1} and -4.4 kcal mol^{-1} at the ONIOM(SCS-MP2:M06-2X) level. It is concluded that CS_2 is strongly absorbed in this PCP but CO_2 is weakly. The absorption position is completely different between these two molecules; CO_2 exists between two Pt atoms. To the contrary, one S atom of CS_2 exists between two Pz ligands and the other S atom is between two Pt atoms, as shown in Figure 1. The optimized position of CS_2 agrees with experimentally reported X-ray structure. To elucidate the reasons of these differences, we performed the energy decomposition analysis and found that (i) both of the large binding energy and the absorption position of CS_2 arise from a large dispersion interaction between CS_2 and the PCP, (ii) the absorption position of CO_2 is mainly determined by the electrostatic interaction between CO_2 and the Pt moiety, and (iii) the small binding energy of CO_2 comes from the weak dispersion interaction between CO_2 and the PCP. Important molecular properties relating to the dispersion and electrostatic interactions are discussed in detail, which are useful for understanding and predicting gas absorption into PCP.

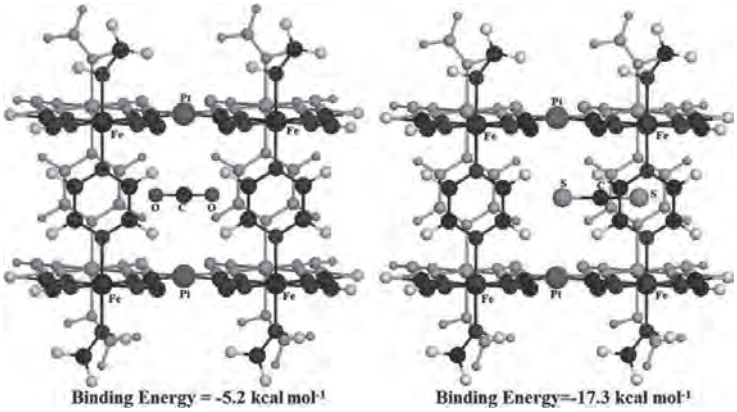
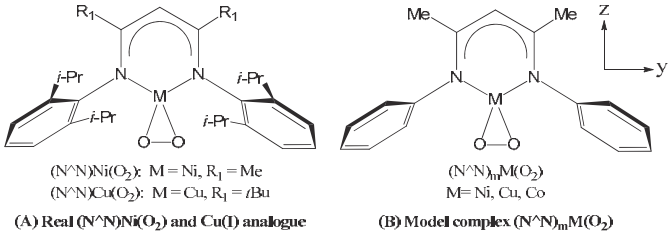


Figure 1. Absorption positions of CO_2 and CS_2 in the Hofmann-type MOF

(ii) Theoretical Study of Mononuclear Nickel(I), Nickel(0), Copper(I), and Cobalt(I) Dioxygen Complexes: New Insight into Differences and Similarities in Geometry and Bonding Nature
Theoretical Study of Mononuclear Nickel(I), Nickel(0), Copper(I), and Cobalt(I) Dioxygen Complexes: New Insight into Differences and

Activation of dioxygen by such first row transition metals as Mn, Fe, Co, Ni, and Cu plays crucial roles in biological oxidation. For instance, the importance of copper dioxygen complex is well recognized in bioinorganic chemistry. In this regard, a lot of efforts have been made to characterize the geometry, the electronic structure, the physicochemical property, and the nature of metal-dioxygen interaction of those dioxygen complexes. However, the nickel-dioxygen interaction and the role of the nickel center in the relevant dioxygen complexes have been much less investigated than those of copper-dioxygen complexes despite the importance of the nickel-dioxygen species in superoxide dismutase. It is of considerable importance to know how much and why the electronic structure and bonding interaction of the nickel dioxygen complex are different from and/or similar to those of the copper dioxygen complex. Such knowledge is indispensable for understanding the various metal dioxygen complexes in biological systems.

Geometries, bonding nature, and electronic structures of (N^N)Ni(O_2) (N^N = β-diketiminate), its cobalt(I) and copper(I) analogues, and $(Ph_3P)_2Ni(O_2)$ were investigated by DFT and MS-RASPT2 methods. Only (N^N)Ni(O_2) takes a C_S symmetrical structure due to the pseudo-Jahn-Teller effect, while all other complexes take a C_{2V} structure. The symmetry lowering in (N^N)Ni(O_2) is induced

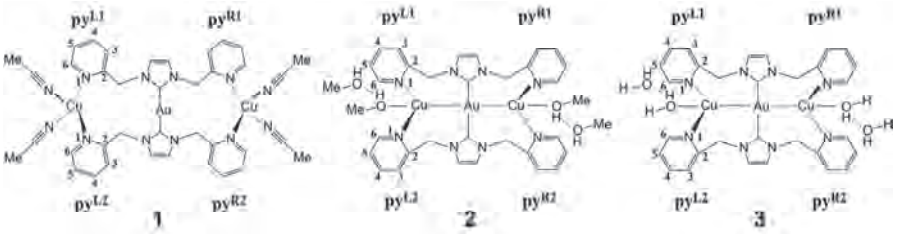


Scheme 1. Ni(I), Co(I), and Cu(I) dioxygen complexes investigated here.

by the presence of the singly occupied $\delta_{d_{xy}-\pi_x^*}$ orbital. In all these complexes, significant superoxo (O_2^-) character is found from the occupation numbers of natural orbitals and the O-O π^* bond order, which is independent on the number of d electrons and the oxidation state of metal center. However, this is not a typical superoxo species because spin density is not found on the O_2 moiety even in open-shell complexes, (N^N)Ni(O_2) and (N^N)Co(O_2). The M-O and O-O distances are considerably different from each other in spite of the similar superoxo character. The M-O distance and the interaction energy between the metal and O_2 moieties are determined by the d_{yz} orbital energy of the metal moiety taking the valence state. The binding energy of the O_2 moiety is understood in terms of the d_{yz} orbital energy in the valence state and the promotion energy of the metal moiety from the ground state to the valence state. Because of the participations of various charge transfer (CT) interactions between the metal and O_2 moieties, the d_{yz} orbital energy and the electron population of the O_2 moiety both do not clearly relate to the O-O bond length. Here, the π bond order of the O_2 moiety is proposed as a good measure for discussing the O-O bond length. Because the d electron configuration is different among these complexes, the CT interactions are different, leading to the differences in the π bond order and hence the O-O distance among these complexes. The reactivity of dioxygen complex is discussed with the d_{yz} orbital energy.

(iii) A Theoretical Study of Luminescent Vapochromic Compounds Including an $AuCu_2(NHC)_2$ Core

Vapochromic complexes $[Au(im(CH_2py)_2)_2(Cu(MeCN)_2)_2]^{3+}$ **1**, $[Au(im(CH_2py)_2)_2(Cu(MeOH))_2]^{3+}$ **2** and $[Au(im(CH_2py)_2)_2(Cu(H_2O))_2]^{3+}$ **3** were theoretically investigated with DFT and MP2 methods. The Au–Cu distances of **1** and **2** (4.631 Å and 2.767 Å, respectively) optimized by the SCS-MP2 method in this work agree with the literature experimental values (4.591 Å and 2.792 Å). Their structural features are explained by computational results: (i) in **1**, two MeCN molecules coordinate with the Cu center, because of the strong coordination ability of MeCN, to afford a four-coordinate tetrahedral-like Cu center. This geometry needs a long Au–Cu distance. (ii) In **2** and **3**, only one MeOH or H_2O molecule coordinates with the Cu center because of their weak coordination abilities, to afford a three-coordinate planar Cu center. Because the threecoordinate Cu center is flexible, the Au–Cu distance becomes short due to the Au–Cu metallophilic interaction, the strength of which is 5.3 kcal mol^{-1} at the SCS-MP2 level. The emission energies of **1**, **2** and **3** (2.62, 2.40 and 2.38 eV, respectively) calculated here by the B3PW91 agree with their literature experimental values (2.68, 2.47, and 2.39 eV). The lowest energy triplet excited state (T1) is assigned as the excitation from the Cu d to the pyridine π* orbital in **1** and that from the Au–Cu 5d–3d anti-bonding MO to the Au–Cu 6p–4sp bonding MO in **2** and **3**. As a result, the emission energy from the T1 to the ground state is different between these compounds. The difference in Au–Cu distance is one of the important factors for the differences in emission energy and assignment between **1** and others (**2** and **3**). The vapochromism of these compounds arises from the difference in Au–Cu distance which is determined by the balance between the strengths of the coordination of a gas molecule and the Au–Cu metallophilic interaction; in other words, the Au–Cu heterometallophilic interaction is important for the vapochromic activity of the complex.

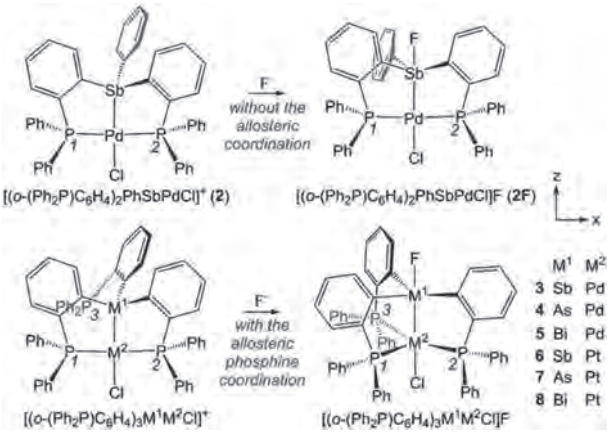


Scheme 2. Vapochromic complexes including $AuCu_2$ core

(iv) Interest in New Heterodinuclear Transition-metal/main-group-metal Complexes: Electronic

Structure and Mechanism of Fluoride Sensing Function

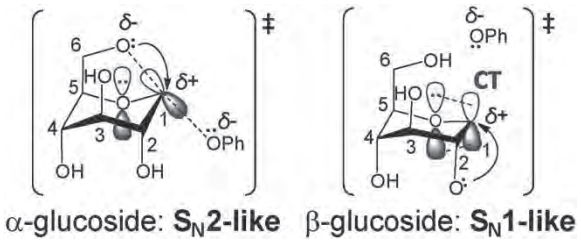
Systematic DFT calculations were carried out on a series of heterodinuclear complexes $[(o\text{-}(Ph_2P)C_6H_4)_3M1M_2Cl]^+$ (M1 = As, Sb, or Bi; M2 = Pd or Pt) to investigate the mechanism of colorimetric sensing function for the fluoride anion. The fluoride anion binds with the M1 center to afford a hypervalent M1 species with large stabilization energy. For instance, the stabilization energy by the fluoride adduct formation is −15.5 kcal mol−1 for **3** (M1 = Sb; M2 = Pd) and −16.2 kcal mol−1 for **6** (M1 = Sb; M2 = Pt), where a negative value represents stabilization. Interestingly, the allosteric coordination of the third phosphine with the M2 center is induced by the fluoride adduct formation. For chloride, bromide, and thiocyanide anions, the binding energies are positive (<4.5 kcal mol−1), and the allosteric coordination does not occur. The allosteric coordination plays a crucial role in the absorption spectrum change induced by the fluoride adduct formation. For instance, the fluoride adduct formation quenches the absorption band of 3 around 400 nm and newly exhibits two absorption peaks at longer wavelength, 475 and 451 nm. These two peaks are assigned to ligand-field transitions (dxy → dz2 and dx2−y2 → dz2) including metal-toligand charge transfer character. We discussed the reasons why the allosteric coordination can occur only in the fluoride adduct and induces these two absorptions in the longer wavelength region. In addition, the Bi–Pd combination is also recommended for a fluoride sensing material, while the Sb–Pt combination is recommended for cyanide sensing.



Scheme 3. Transition metal/heavy main group element hybrid complexes.

(v) A 3D-RISM-SCF method with dual solvent boxes for a highly polarized system: application to 1,6-anhydrosugar formation reaction of phenyl α- and β-D-glucosides under basic conditions

One of the difficulties in application of the usual reference interaction site model self-consistent field (RISM-SCF) method to a highly polarized and bulky system arises from the approximate evaluation of electrostatic potential (ESP) with pure point charges. To improve this ESP evaluation, the ESP near a solute is directly calculated with a solute electronic wavefunction, that distant from a solute is approximately calculated with solute point charges, and they are connected with a switching function. To evaluate the fine solvation structure near the solute by incorporating the long-range solute–solvent Coulombic interaction with low computational cost, we introduced the dual solvent box protocol; one small box with the fine spacing is employed for the first and the second solvation shells and the other large box with the normal spacing is employed for long-range solute–solvent interaction. The levoglucosan formation from phenyl a- and b-D-glucosides under basic conditions is successfully inspected by this 3D-RISM-SCF method at the MP2 and SCS-MP2 levels, though the 1D-RISM-SCF could not be applied to this reaction due to the presence of highly polarized and bulky species. This 3D-RISMSCF calculation reproduces the

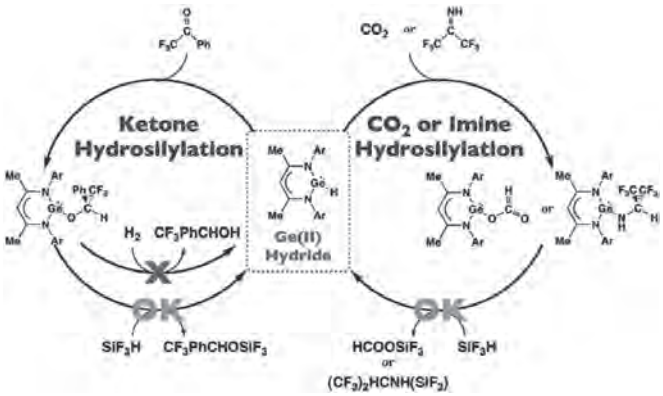


Scheme 4. Stereoelectronic effect in transition states in the rate-determining step of levoglucosan formation reaction

experimentally reported higher reactivity of the b-anomer. The 3D-RISMSCF-calculated activation free energy for the b-anomer is closer to the experimental value than the PCM-calculated one. Interestingly, the solvation effect increases the difference in reactivity between these two anomers. The reason is successfully elucidated with 3D-RISM-SCF-calculated microscopic solvation structure and decomposition analysis of solute–solvent interaction.

(vi) Theoretical Study of Reactivity of Ge(II)-hydride Compound:Comparison with Rh(I)-Hydride Complex and Prediction of Full Catalytic Cycle by Ge(II)-hydride

The reaction of a Ge(II) hydride compound HC{CMeArN}2GeH (Ar = 2,6-iPr2C6H3) 1 with 2,2,2-trifluoroacetophenone (CF_3PhCO) is theoretically investigated with density functional theory and spin-component-scaled secondorder Møller–Plesset methods. This reaction easily occurs with moderate activation barrier and considerably large exothermicity, to afford a Ge(II) alkoxide 2 through a four-membered transition state. In the transition state, the charge transfer from the Ge–H σ-bonding molecular orbital (MO) to the C=O π*-antibonding MO of CF_3PhCO plays an important role. Acetone ($(CH_3)_2CO$) and benzophenone (Ph_2CO) are not reactive for 1, because their π*-antibonding MOs exist at higher energy than that of CF_3PhCO. Though 2 is easily formed, the catalytic hydrogenation of CF3PhCO by 1 is difficult because the reaction of 2 with a dihydrogen molecule needs a large activation energy. On the other hand, our calculations clearly show that the catalytic hydrogenation of ketone by cis-$RhH(PPh_3)_2$ 4 easily occurs, as expected. The comparison of catalytic cycle between 1 and 4 suggests that the strong Ge–O bond of 2 is the reason of the very large activation energy for the hydrogenation by 1. To overcome this defect, we investigated various reagents and found that the catalytic cycle can be completed with the use of SiF_3H. The product is silylether $CF_3PhCHOSiF_3$, which is equivalent to alcohol because it easily undergoes hydrolysis to afford $F_3PhCHOH$. The similar catalytic cycles are also theoretically predicted for hydrosilylations of CO_2 and imine. This is the first theoretical prediction of the full catalytic cycle with a heavier main-group element compound.



Scheme 6. Theoretically proposed catalytic cycles by Ge-H compound

(vii) Novel Ni(0)-Catalyzed [6 − 2 + 2] Cycloaddition Reactions of Isatoic Anhydrides with Alkynes: Origin of Facile Decarboxylation

A thorough theoretical analysis was carried out on the novel Ni-catalyzed decarboxylative [6 − 2 + 2] cycloaddition reactions of isatoic anhydrides with alkynes. This is the first theoretical analysis of this new kind of decarboxylative coupling reaction, which has attracted recent attention. The

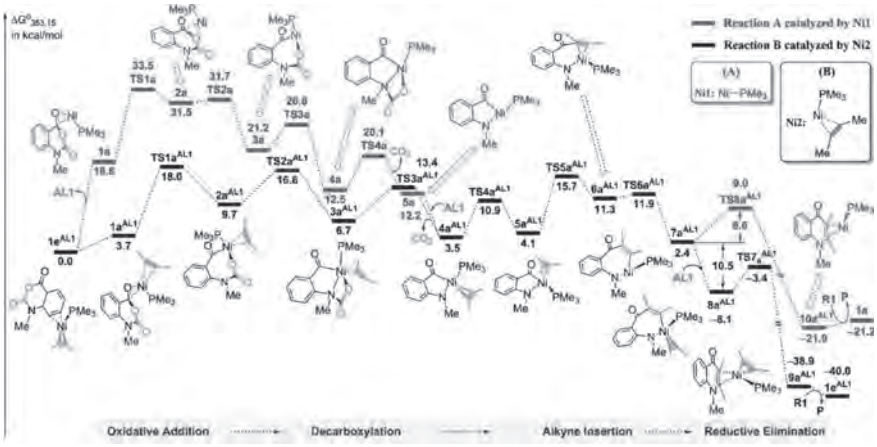
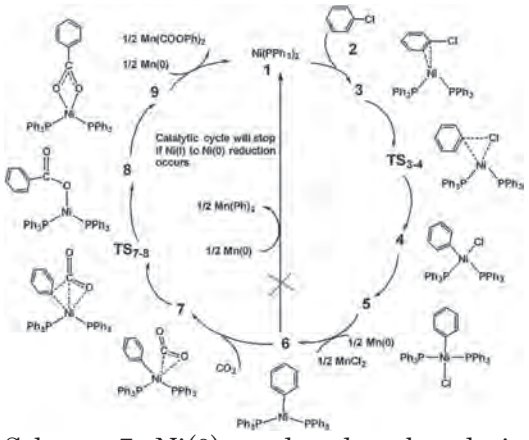


Figure 2. Gibbs energy changes in the [6-2+2] cycloaddition reaction

active species is a two-coordinate Ni0(phosphine)(alkyne) complex. The catalytic cycle consists of the four elementary processes: oxidative addition, decarboxylation, alkyne insertion, and reductive elimination. The oxidative addition of the C(=O)−O bond of isatoic anhydride to Ni(phosphine)(alkyne) proceeds with a moderate Gibbs activation energy ($\Delta G^{\circ\ddagger}$) of 18.0 kcal/mol. In the transition state, the charge transfer from the Ni 3dπ orbital to the antibonding LUMO of isatoic anhydride plays an important role in the weakening of the anhydride C(=O)−O bond, which determines the regioselectivity of the oxidative addition. Then, the decarboxylation proceeds in a stepwise manner through Ni−N bond formation and CO_2 elimination. In this decarboxylation, the Ni−N bond formation is crucial for a moderate $\Delta G^{\circ\ddagger}$ value of 6.7 kcal/mol. After this step, alkyne and phosphine change their positions around the Ni center, followed by alkyne insertion into the nickel−acyl (Ni−C(=O)R) bond and reductive elimination. All of these steps occur easily with moderate $\Delta G^{\circ\ddagger}$ values. The facile decarboxylation is the origin of this successful catalytic reaction. This is because the N atom in isatoic anhydride plays an important role by coordinating with the Ni center to accelerate the decarboxylation. The electronic processes of decarboxylation as well as other important elementary steps are discussed in detail.

(viii) **The crucial role of a Ni(I) intermediate in Ni-catalyzed carboxylation of aryl chloride with CO_2**

Over the past few years, significantly large growth has been achieved in CO_2 conversion to useful chemicals with catalysts.1,2 Transition metal complexes are promising catalysts for the CO_2 conversion. Actually, many catalysts have been developed for the syntheses of a variety of useful chemicals. In particular, syntheses of carboxylic acids and their derivatives from CO_2 are of recent interest because they are important starting materials of organic syntheses. However, the successful results have been very limited. Recently, Tsuji and coworkers reported interesting synthesis of benzoic acid from chlorobenzene with CO_2 using Ni(0) complex as a catalyst. In this catalytic system, the Mn metal powder was employed. We theoretically investigated this catalytic reaction to elucidate the reason why Mn metal powder is indispensable in this catalytic reaction. DFT calculations show the important features of this reaction; the active species is Ni(0) complex and the first step is the oxidative addition of Ph-Cl to the Ni(0) complex to afford a Ni(II) phenyl chloride species. The next step is one-electron reduction of the Ni(II) phenyl species to a Ni(I)-phenyl species with the Mn metal powder. This one-electron reduction is indispensable to perform the CO_2 insertion into the Ni(I)-Ph bond. This is because the CO2 insertion into the Ni(II)-Ph bond is difficult but easy into the Ni(I)-Ph bond. The final is one-electron reduction of the Ni(I)-h2-benzoate species. It is clearly shown that the one-electron reduction of the Ni(II)-phenyl complex is necessary to perform the next CO2 insertion. The reason was clearly elucidated by considering the charge-transfer from the Ni(I)-Ph moiety to CO_2.



Scheme 7. Ni(0)-catalyzed carboxylation of phenyl chloride

Original Papers

(1) Toru Matsui, Yasutake Kitagawa, Mitsutaka Okumura, Yasuteru Shigeta, Shigeyoshi Sakaki, "Consistent scheme for computing standard hydrogen electrode and redox potentials" *J. Comp. Chem.*, *34*, 21-26 (2013).

(2) Shinji Aono, Takashi Hosoya, and Shigeyoshi Sakaki " A 3D-RISM-SCF method with dual solvent boxes for a highly polarized system: application to

1,6-anhydrosugar formation reaction of phenyl α- and β-D-glucosides under basic conditions"
Phys. CHem. Chem. Phys., 15, 6368-6381 (2013).

(3) Milind Madhusudan Deshmukh, Masaaki Ohba, Susumu Kitagawa, and Shigeyoshi Sakaki
"Absorption of CO_2 and CS_2 into the Hofmann-Type Porous Coordination Polymer: Electrostatic versus Dispersion Interactions"
J. Am. Chem. Soc., 135, 4840−4849 (2013).

(4) Guixiang Zeng and Shigeyoshi Sakaki,
"Unexpected Electronic Process of H_2 Activation by a New Nickel Borane Complex: Comparison with the Usual Homolytic and Heterolytic Activations"
Inorg. Chem., 52, 2844−2853 (2013)..

(5) Shinya Tsukamoto and Shigeyoshi Sakaki,
"A theoretical study of luminescent vapochromic compounds including an AuCu2(NHC)2 core"
Dalton Trans., 42, 4809-4821 (2013).

(6) Terutaka Yoshizawa, Shigeyoshi 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"
J. Compt. Chem., 34, 1013-1023 (2013).

(7) Wei Guan, Shinichi Yamabe and Shigeyoshi Sakaki,
"Interests in new heterodinuclear transition-metal/main-group-metal complexes: DFT study of electronic structure and mechanism of fluoride sensing function"
Dalton Trans., 42, 8717 – 8728 (2013).

(8) Nozomi Takagi and Shigeyoshi Sakaki,,
"Theoretical Study of Reactivity of Ge(II)-hydride Compound: Comparison with Rh(I)- Hydride Complex and Prediction of Full Catalytic Cycle by Ge(II)-hydride"
J. Am. Chem. Soc., 135, 8955−8965 (2013).

(9) Wakioka, M.; Nakamura, Y.; Hihara, Y.; Ozawa, F.; Sakaki, S. ,
"Factors Controlling the Reactivity of Heteroarenes in Direct Arylation with Arylpalladium Acetate Complexes"
Organometallics, 32, 4423 4430 (2013).

(10) Guan, W.; Sakaki, S.; Kurahashi, T.; Matsubara, S.
"Theoretical Mechanistic Study of Novel Ni(0)-Catalyzed [6-2+2] Cycloaddition Reactions of Isatoic Anhydrides with Alkynes: Origin of Facile Decarboxylation,"
Organometallics, 32, 7564-7574 (2013).

(11) Yue Chen and Shigeyoshi Sakaki,
"Theoretical Study of Mononuclear Nickel(I), Nickel(0), Copper(I), and Cobalt(I) Dioxygen Complexes: New Insight into Differences and Similarities in Geometry and Bonding Nature"
Inorg. Chem., 52, 13146−13159 (2013).

(12) Fareed Bhasha Sayyed,[a] Yasushi Tsuji[b] and Shigeyoshi Sakaki
"Crucial Role of Ni(I) Intermediate in Ni-Catalyzed Direct Carboxylation of Aryl Chloride with CO_2: A Theoretical Study"
Chem. Comm., 49, 10715 – 10717 (2013).

(13) Takashi Hosoya and Shigeyoshi Sakaki,
"Levoglucosan Formation from Crystalline Cellulose: Importance of a Hydrogen Bonding Network in the Reaction"
ChemSusChem, 6, 2356 – 2368 (2013). .

3. Presentation at academic conferences

(1) Shigeyoshi Sakaki,
"Theoretical Study of Complex Systems From Small Transition Metal Complex to Big Systems such as Metal Organic Framework and Infinite Molecular Crystal", 6th APCTCC Asian Pacific Congress for Theoretical and Computational Chemsitry, Gyeongju, Korea, July 10-13. (keynote)

(2) Shigeyoshi Sakaki
"Gas Absorption and Spin Transition of the Hofmann-type Porous Coordination Polymer Theoretical Study", UK-Japan Workshop on Organic-Inorganic Framework Materials, Kyoto, Japan, Oct. 10-11. (Invited)

(3) Shigeyoshi Sakaki
"Gas Absorption and Spin Transition of the Hofman-type Metal Organic Framework: Theoretical Study", The 5th Japan-Checz-Slovaria Joint-Symposium for Theoretical and Computational Chemistry, Nara, Japan, Dec. 2-6. (Invited)

4. Others

(1) 榊　茂好
"遷移金属元素を含む複合系の理論的研究: 反応の電子的過程に注目して"
反応経路探索のニューフロンテイア2013、2013年9月　京都（京大　福井謙一記念研セ）

(2) 榊　茂好
"二核金属錯体の構造と電子状態：理論的研究"
第３回分子アーキテクトシンポジウム　2013 年 10 月　大阪(大阪市中央公会堂)

(3) 榊　茂好
"ｄ電子複合系の構造と機能の理論化学"　産総研ナノシステム連携促進フォーラム　2014 年 2 月　東京（秋葉原ダイビル）

(4) 榊　茂好
"理論化学・計算化学と触媒・電池元素戦略研究"　触媒・電池元素戦略研究拠点　第 4 回公開シンポジウム　2014 年 3 月　東京（東大武田先端知ビル）

(5) 榊　茂好
"遷移金属複合系の構造と反応の理論および計算化学研究"　日本化学会第９４回春季年会 2014 年 2
3 月　名古屋（名古屋大学）

４．博士研究員

Takafumi IWAKI

FIFC Fellow

1. Summary of the research of the year

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 was published in The Journal of Chemical Physics.

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 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.

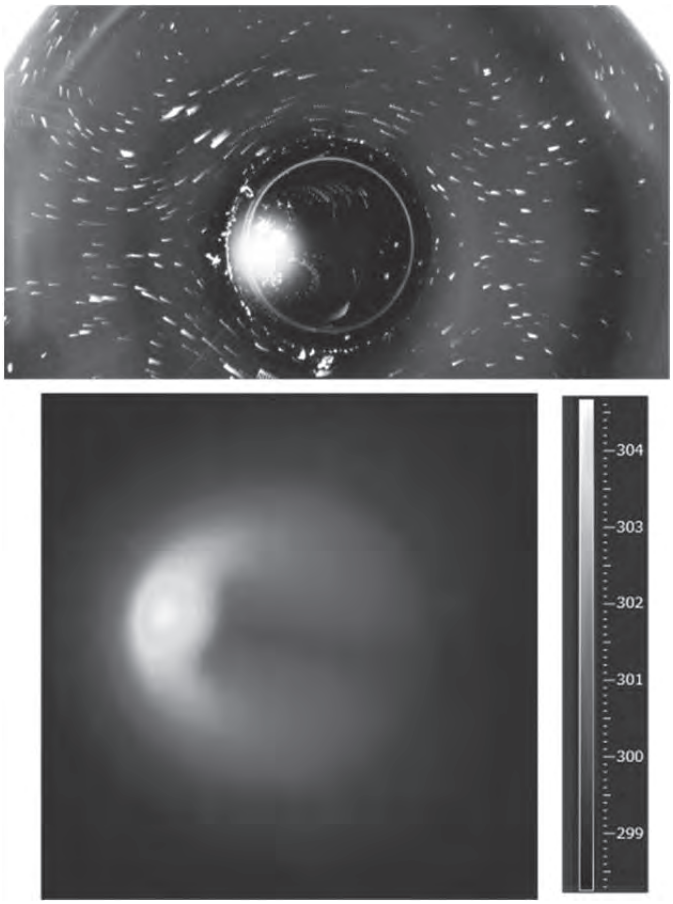


Figure 2: Flow pattern and temperature distribution of a paraffin droplet on pure water heated by a laser irradiation.

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 was published in Physical Review E.

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 submitted to a scientific journal.

Study of the radius of gyration for circular and linear DNA

The radius of gyration for polymer material is a historical problem. While the radius of gyration itself is frequently measured, its distribution (standard deviation etc.) has been not argued in experimental study in detail. In this study, we measured a time series of major-axis length of BAC DNA for linear and circular architectures by means of fluorescent microscopy. In the result, we found that both DNA chains exhibit considerably small standard deviations for major-axis length. The standard deviation for a circular chain is particularly inhibited. Moreover, we found that the major-axis lengths for two types of molecules take very similar values rather than the expected. We considered the radius of gyration of interacting semiflexible polymer, and compared it with the present experimental result. Though the radius of gyration and the major-axis length is not identical, additional simulations illustrate that this two variables are highly correlated, and they can be equated with each other as a matter of fact. In this argument, we found that the traditional equation of end-to-end distance of a segment in a circular chain leads to a result totally dislocated from experimental observations. Thus we proposed a new equation on the basis of the mean-field theory, and compared it with experiments. They well agree with each other except for the standard deviation for a circular chain. For the standard deviation for a circular chain, we may need to consider other factors such as an effect of twisting and a transient topological constraint. This work is now being summarized as a manuscript, which is to be submitted to a scientific journal.

Study of two-dimensional convectional flows in two-phase mixtures

Recently, it was found that a stable interfacial wave appears when one pours ethanol on hot water in a thin cuboid container. This phenomenon seems to derive from the coupled convectional flows in upper and lower fluids which lead to an oscillatory hydrodynamic pressure on the interface. To testify this explanation with a simple model, we devise and examine several toy models. While this process is still developing, this concept should be more rationalized with the further experimental tests. It is planned to advance a theoretical consideration to lead to some

phenomenological prediction, which will be examined by an actual experimental test.

2. Original papers

(1) Shunsuke F. Shimobayashi1, Takafumi Iwaki, Toshiaki Mori, and Kenichi Yoshikawa "Probability of double-strand breaks in genome-sized DNA by g-ray decreases markedly as the DNA concentration increases", The Journal of Chemical Physics **138**, 174907 (2013).

(2) Masatoshi Ichikawa, Fumi Takabatake, Keitaro Miura, Takafumi Iwaki, Nobuyuki Magome, and Kenichi Yoshikawa, "Controlling negative and positive photothermal migration of centimeter-sized droplets", Phys. Rev. E 88, 012403 (2013).

3. Presentation at academic conferences

(1) 岩城 貴史、"非等方粘性系を用いた上皮細胞増殖による形態形成のモデル"、 日本物理学会 2013 年秋季大会、Tokushima, Sep. 28, 2013

(2) 岩城 貴史、"ライデンフロスト効果とベナール対流の協奏： 水-エタノール系の自発的界面振動"、 日本物理学会第 67 回年次大会、Kanagawa, March 30, 2014

4. Others

We cooperated with an online encyclopedia project developed by Springer. We provided the following article to the *Encyclopedia of Polymeric Nanomaterials* edited by S. Kobayashi and K. Muellen: "DNA as Polymer and Polyelectrolyte" by Takafumi Iwaki and Kenichi Yoshikawa (containing about 3400 words and 2 figures).

嶺澤　範行

センターフェロー

1. 今年度の研究の要約

今年度は昨年度に引き続き、溶液内における光化学反応を自由エネルギーの観点から解析した。

【始めに】

溶液における光化学反応を理解するためには、電子励起状態の詳細な記述と溶媒効果の適切な評価を取り入れる必要がある。過去の研究において、時間依存密度汎関数法 (TDDFT) と積分方程式を組み合わせた手法を導入した[1]。TDDFT 法は、動的電子相関の取り扱いに優れ、計算コストも小さい。さらに、解析的なエネルギー微分も得られるため、励起状態のポテンシャル面の構築には適当な方法である。溶媒効果は、溶媒和構造を分子論的に記述できる積分方程式 (RISM) で取り入れ、電子状態計算と組み合わせた (RISM-SCF)。この方法は、溶媒分子の配置空間について統計サンプリングを必要とせず、溶液における自由エネルギーを効率よく決定できる。今年度は、電子励起状態の自由エネルギー面をこの手法で構築し、光化学反応への応用を目指した。

【状態依存と線形応答の溶媒和モデルの比較】

まず、TDDFT 法と RISM-SCF 法を組み合わせた計算手法[1]の精度について検証した。電子励起状態の平衡溶媒和自由エネルギー面を構築するためには、励起状態の電子密度と溶媒和構造が平衡でなければならない。しかしながら、TDDFT 法は多配置関数の方法とは異なり容易ではない。これは、線形応答を仮定しているためである。すなわち、電子基底状態を参照系として、時間依存の摂動を加えた時の分子の密度変化に着目している。励起エネルギーは参照系の情報のみで記述することができ、励起状態の情報を一切必要としない。これは、長所であると同時に短所でもある。

実際、RISM-TDDFT 法における自由エネルギーは

$$A \simeq A_0 + \Omega_0 + \mathrm{Tr}[(\mathbf{X}+\mathbf{Y})\hat{\mathbf{Q}}]\cdot\left(\frac{\partial \mathbf{V}}{\partial \mathbf{Q}}\right)\cdot \mathrm{Tr}[(\mathbf{X}+\mathbf{Y})\hat{\mathbf{Q}}]$$

ここで、A_0 は基底状態の自由エネルギー、Ω_0 は溶媒を凍結した時の励起エネルギー、$\mathbf{X}+\mathbf{Y}$ は transition amplitude、$\hat{\mathbf{Q}}$ は電荷生成演算子である。第 3 項から明らかなように、溶媒の再配向エネル

ギーの寄与は、遷移に伴う電荷の変化とそれに伴う静電ポテンシャル $\mathbf{V}$ の変化の積であらわされる。電子励起状態の電子密度はあらわに含まれないため、基底状態と励起状態で電子密度が大きく変化する場合、再配向の効果が適切に表現される保証はない。

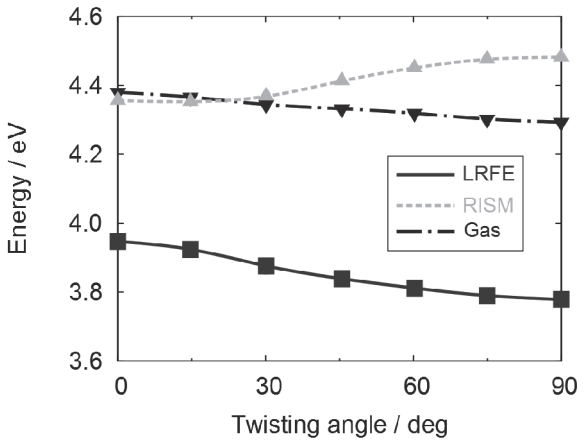


図 1: PBN の自由エネルギープロファイル

今回、励起状態の電子密度を反映させるため、非平衡自由エネルギーの表式 (LRFE) [2,3]を TDDFT 法と組み合わせた。LRFE-TDDFT 法における自由エネルギーは

$$A \approx A_0 + \Omega_0 + \frac{1}{2}\Delta\mathbf{Q}\cdot\Delta\mathbf{V}$$

ここで、$\Delta\mathbf{Q} \equiv \mathbf{Q}_{\mathrm{ex}} - \mathbf{Q}_{\mathrm{gs}}$ は、基底状態と励起状態の電荷の差をあらわに含んでおり、励起状態の電子密度が自由エネルギーに反映されている。

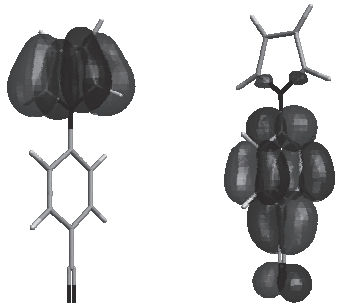


図 2: PBN の分子軌道 (左) HOMO (右) LUMO

この 2 つの溶媒和モデルの比較を分子内電荷移動反応 (ICT) の記述で検証した。ICT 反応では基底状態 (DA) と励起状態 (D+A−) で電荷分布が大きく異なるため、適当な計算例である。(*N*-pyrrolo)benzonitrile (PBN) のアセトニトリル溶液を分子系として選択した。図 1 から明らかなように、反応座標に対して、線形応答溶媒和モデル (RISM-TDDFT) と状態依存溶媒和モデル (LRFE-TDDFT) では、定性的に異なる描像を与えた。これは、生成物が twisted-ICT であり、HOMO-LUMO 励起における、分子軌道間の重なりが小さい (図 2)。その結果として $\mathrm{Tr}\left[(\mathbf{X}+\mathbf{Y})\hat{\mathbf{Q}}\right]$ の寄与も非常に小さい。したがって線形応答溶媒和モデル (RISM-TDDFT) では、緩和による安定化を過小評価してしまう。このような場合、あらわに励起状態の電子密度の溶媒和への寄与を考慮した LRFE-TDDFT 法を適用しなければならない。本研究の結果は近日中に公開予定である[4]。

【GFP 発色団水溶液の円錐交差の記述】

昨年度、溶液における円錐交差を決定する方法を開発した。それは、2 つの非平衡自由エネルギー

面を定義し、その交差を求めることである[2,3]。非平衡自由エネルギーは、核座標だけでなく溶媒和座標にも依存するため、両方の座標について構造最適化を行う。アルゴリズムは非断熱カップリングの計算を必要としない分岐面更新法[5]を採用している。

本研究では、緑色蛍光タンパク質 (GFP) の発色団である *p*-hydroxybenzylideneimidazolinone (HBI) (図 3) の水溶液について考察した。発色団分子はタンパク質に囲まれた状態では、非常に良い蛍光物質である。一方、この分子だけを水に溶解させた場合、蛍光の量子収率が著しく減少し、蛍光が消失する。これは、タンパク質残基の阻害を受けない自由な分子内振動により無輻射遷移が優位になることを示唆している。そこで、励起状態の自由エネルギー面の解析により、その HBI 分子の水溶液における光化学を明らかにすることを目標とする。

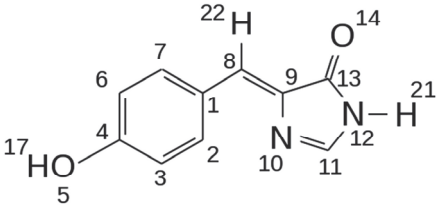


図 3: HBI の分子構造

その第一歩として、spin-flip TDDFT 法[6]を用いて円錐交差の構造を孤立分子と水溶液で決定した (図 4)。エチレン分子で見られた傾向と同様に、C9 における面外角が減少した。これは、溶質 - 溶媒間の相互作用により、分子内の構造変化をそれほど必要としないことと対応する。現在、電子励起状態の自由エネルギー面の構築を進めており、詳細は発表予定である[7]。

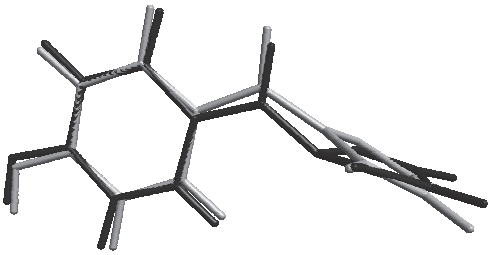


図 4: HBI の円錐交差 (黒) 気相 (グレー) 水溶液

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Linear-response free energy/spin-flip time-dependent density functional theory approach", in preparation.

2. 論文

(1) N. Minezawa, "Excited-state free energy surfaces in solution: Time-dependent density functional theory/reference interaction site model self-consistent field method", J. Chem. Phys. **138**, article No. 244101 [8 pages] (2013).

(2) Y. Harabuchi, S. Maeda, T. Taketsugu, N. Minezawa, and K. Morokuma, "Automated search for minimum energy conical intersection geometries between the lowest two singlet states S_0/S_1-MECIs by the spin-flip TDDFT method", J. Chem. Theory Comput. **9**, 4116-4123 (2013).

(3) N. De Silva, N. Minezawa, and M. S. Gordon, "Excited-state hydrogen atom transfer reaction in solvated 7-hydroxy-4-methylcoumarin", J. Phys. Chem. B **117**, 15386-15394 (2013).

3. 学会発表

(1) 嶺澤　範行

「SF-TDDFT法による溶液内分子の最小自由エネルギー交差点の探索」

第7回分子化学討論会　京都 09/25/2013 2P116

Ryuichi OKAMOTO

Project Assistant Professor, Tokyo Metropolitan University, Tokyo

1. Summary of the research of the year (3-5 pages, includes appropriate figures and tables)

Attractive interaction and bridging transition between neutral colloidal particles due to preferential adsorption in a near-critical binary mixture

We study solvent mediated interaction between uncharged colloidal particles in a near-critical binary fluid mixture. The surface of the particles preferentially attracts one of the fluid components, which results in composition gradient (adsorption layer) near the surface. The overlap of the composition gradient around each particle induces attractive force between the particles. Particularly, near the critical point of the mixture, the composition gradient becomes long-ranged and exhibits universal behavior in the sense that it does not depend on the microscopic details of the surface and the solvent molecules. Correspondingly, the solvent mediated interaction becomes universal, strong and long-ranged near the critical point.

In order to investigate the universal, strong and long-ranged interaction, we take into account the renormalization effect due to the critical fluctuations using our local functional theory [Okamoto and Onuki, J. Chem. Phys. 136, 114704 (2012)]. We find the interaction become strong when the mixture is poor in the component preferred by the surface. Especially, in one phase state near the coexistence curve below the critical temperature T_c, the adsorption layer bridges the particles when the separation distance is smaller than a threshold value (Fig. 1). In the bridged state, the adsorption layer induces strong attractive force between the particles.

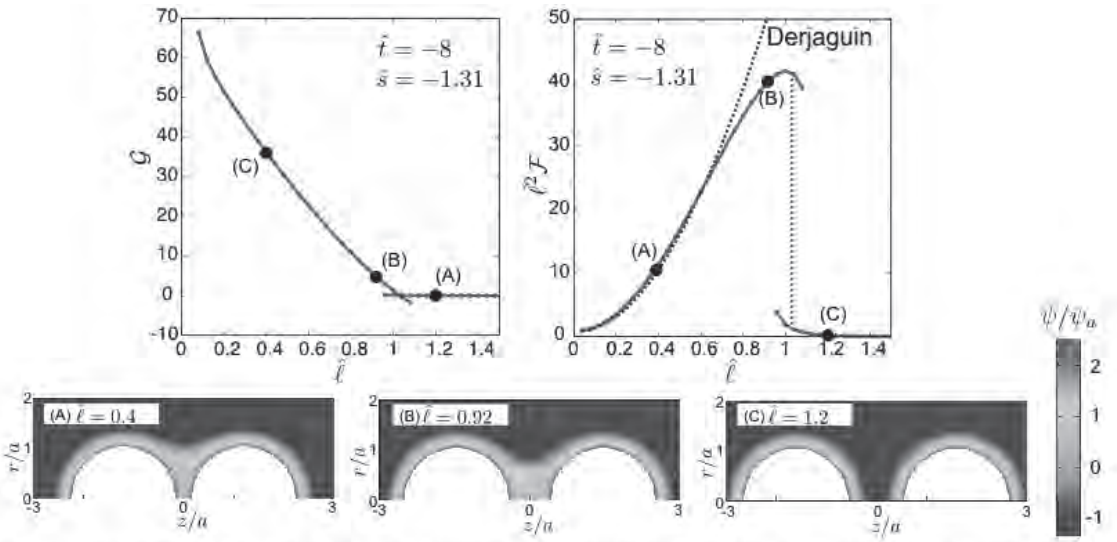


Fig. 1 Normalized free energy $\mathcal{G}$ vs normalized separation distance $\hat{\ell}$ (upper left) and normalized attractive force $\mathcal{F}$ vs normalized separation distance $\hat{\ell}$ (upper right) outside the coexistence curve below Tc. In the bottom composition proliles $\psi(r,z)$ are shown at (A) $\hat{\ell} = 0.4$, (B) 0.92 and (C) 1.2. At (A) and (B), the adsorption layer bridges the particles, while particles are separated at (C). At $\hat{\ell} = 1.04$ the particles undergo discontinuous change between bridged- and separated-state.

Drag coefficient of a rigid spherical particle in a binary fluid mixture: Effect of preferential adsorption on the particle surface

We calculate the drag coefficient of a rigid spherical particle in an incompressible binary fluid mixture. A weak preferential attraction is assumed between the particle surface and one of the fluid components, and the difference in the viscosity between the two components is neglected. Using the Gaussian free-energy functional, we solve the hydrodynamic equation explicitly under the condition that the particle moves with constant velocity. Near the particle surface, there appears an adsorption layer of the preferred component of the mixture due to the preferential attraction. We find that the adsorption layer reduces the hydrodynamic flow near the particle from that in a one-component fluid having the same viscosity. As a result, the drag coefficient becomes larger in a binary fluid mixture. Furthermore, we can show that the preferential adsorption makes the drag coefficient larger as the bulk correlation length becomes longer. The dependence of the deviation from the Stokes law on the correlation length, when it is short, turns out to be much steeper than the previous estimates.

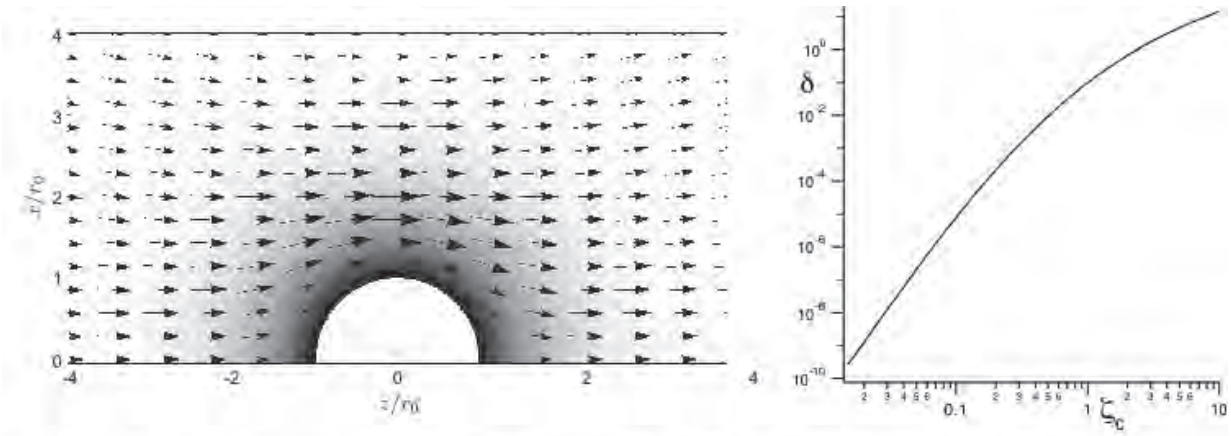


Fig. 2 The order paramter profile (gray gradation) and the deviation of the flow field from that in one-component fluid (arrows) on x-z plane (left). The spherical particle moves along the z-axis in negative direction. The deviation of the drag coefficient from that in one component fluid is plotted as a function of normalized correlation length ζ_c.

2. Original papers

(1) Ryuichi Okamoto and Akira Onuki
"Attractive interaction and bridging transition between between neutral colloidal particles due to preferential adsorption in a near-critical binary mixture", Phys. Rev. E **88**, 022309 (2013)

(2) Ryuichi Okamoto, Youhei Fujitani and Shigeyuki Komura
"Drag coefficient of a rigid spherical particle in a near-critical binary fluid mixture"
J. Phys. Soc. Jpn. **82**, 084003 (2013)

3. Presentation at academic conferences

(1) Ryuichi Okamoto and Akira Onuki
”Wetting on ionizable surfaces: Statics and dynamics”(powter)
International soft matter conference 2013, Rome, Italy, September 15-19, 2013

(2) Ryuichi Okamoto and Akira Onuki
“Wetting on an ionizable surface: Statics and dynamics” (oral)
Physical society of Japan autumn meeting 2013, Tokushima, September 25-28, 2013

Takuya SAITO

FIFC Fellow

1. Summary of the research of the year

Fluctuation in polymer stretching

Pulling of a polymeric chain is a basic operation to investigate a physical characteristics. A linear polymeric chain is largely stretched to an inhomogeneous shape by pulling the one end. The deformed shape is described by the relation of the tension with thermal agitation. The fluctuation of each monomer should have the information about the interaction among monomers such as the excluded volume effect as well as the string-like chain connectivity, but the better description of the dynamical fluctuation on the large deformation still remains elusive.

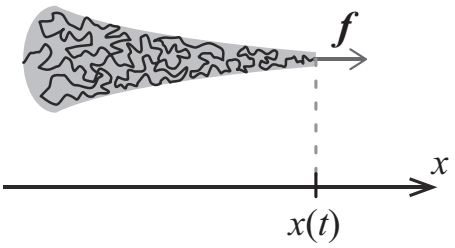


Fig. 1 Schematic representation of the polymer stretching under steady state.

We proposed the theoretical approach of the fluctuation in the polymer stretching. The stochastic dynamics is described by the pre-averaged non-linear Langevin equation, in which the transversal monomer fluctuation is casted on the pulling direction.

We furthermore apply the homogeneous approximation by the head spatial fluctuation. The Langevin eq. then becomes linear so that it enables us to analytically handle the fluctuation on the stretching. On the basis of the approximated Langevin equation, we theoretically obtained the variance of the head monomer position as well as the average under stretching steady state. We found two regimes; (i) the relaxation of internal configuration; (ii) the translational diffusion. The former shows the anomalous (sub-) diffusion, while the latter is the normal diffusion.

To verify the theory, we carried out the molecular dynamics (MD) simulation. In the steady state, the predicted scaling laws are in agreement with the MD results.

Effects of cis-/trans-sides in the driven polymer translocation

Polymer translocation is a polymer passage through the small pore and has been intensively investigated for various purposes. Especially, in experiment, the electric potential difference across the pore has been used in the translocation of DNA or RNA and it allows us to measure the passage time, the scaling laws of which has been experimentally reported. Establishing the scaling theory of the driven translocation is then considered to be an attractive subject in single chain dynamics.

In translocation, a membrane or a thin plate separate the system and the polymer passes across cis- to trans-sides. In cis-side, polymer is pulled and the tension is transmitted along the polymeric chain. The

moving domain, in which the tension is propagated, is stretched and grows with time. On the other hand, in trans-side, the polymer is pushed and compressed in the vicinity of the pore, and then the part is decompressed outward. Previous studies can deal with each side, separately, but lacks the understanding of the large deformations in cis- and trans-sides on even ground.

To evaluate both sides in the same framework, we describe the cis- and trans-side effect by fast and slow diffusion equations, respectively. Both are described by the same type of non-linear partial differential equation, but physical characteristics is completely different. The lower line (the higher volume) density is, the higher current is in cis-(trans-)sides. Moreover, to give the time evolution at the scaling levels, the cis dynamics needs the global information (extension), but the trans-side only requires the local quantities around pore.

On the basis of them, we established the scaling theory of the passage time. The scaling exponents are suggested to be determined by the cis-side in the long chain limit.

Dynamical efficiency in template-directed polymer synthesis

Many of biopolymers like DNA, RNA have sequence information in one dimensional structure. In the synthesis, a catalyst reads a sequence along the template and incorporates the substrates into the product. However, mismatches between template and product elements sometimes occurs, since the synthesis takes place in the presence of thermal random force.

The substrates serve as the energy sources as well as the materials, which drive the catalyst. The catalyst moving at the high effective speed achieves the high production rate. However, we may imagine, in a lot of situations, the high speed is not compatible with the accuracy. The accuracy and speed are usually measured by different scales, and then the qualitative discussion about a balance between the accuracy and speed is difficult.

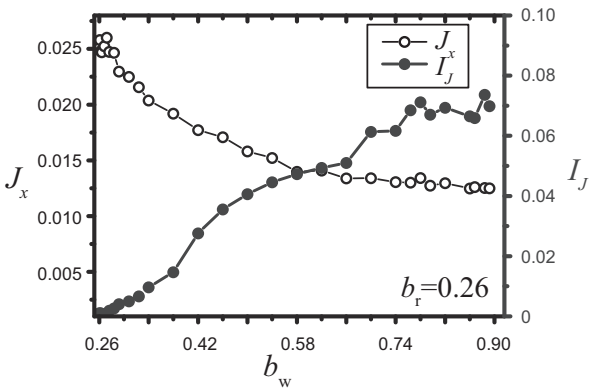


Fig. 3 Numerical results of TDS rate and total probability flow on the sequential switching potential model.

In this study, we propose a rate of the template-directed synthesis (TDS) to evaluate the balance of the speed with the accuracy on the same scale. First we define the order of the correct sequences. In our criterion, if the amount of the products is larger, the products are more correct. Developing this arguments, we can define the TDS rate, which evaluates the TDS system. The TDS rate contains a function form analogous to the Shannon entropy. The high speed basically increases the TDS rate, but, if the sequences of the products are diversified, the TDS rate decreases.

We discuss how the system conditions affects the TDS rate in two different models. Even if the synthesis speed is enhanced, the TDS rate does not necessarily increases.

2. Original papers

(1) Takuya Saito, and Takahiro Sakaue,
"Cis-trans dynamical asymmetry in driven polymer translocation"
Phys. Rev. E 88, 042606(2013).

3. Presentation at academic conferences

(1) 齋藤拓也, 坂上貴洋,
"Crumpled Globule における標識されたモノマーの異常拡散"
日本物理学会 2013 秋季大会, 徳島大学 常三島キャンパス, Sep 28, 2013

(2) 齋藤拓也、坂上貴洋
"Crumpled Globule の異常拡散現象"
第３１回染色体ワークショップ, 第１２回核ダイナミクス研究会 足柄下郡箱根町ホテルおかだ, Nov 26, 2013

(3) 齋藤拓也、坂上貴洋
"伸張される高分子鎖の過渡的過程における揺らぎ"
日本物理学会第６９回年次大会　東海大学 湘南キャンパス, Mar 27, 2014

4. Others

(1) Takuya Saito and Takahiro Sakaue
"Crumpled Globuleにおける標識されたモノマーの異常拡散現象"
The 11th symposium of Fukui Institute for Fundamental Chemistry, Kyoto, Jan. 23, 2014.

Fu-Quan BAI

FIFC Fellow

1. Summary of the research of the year

Excited States of a Significantly Ruffled Porphyrin: Computational Study on the Structure-Induced Rapid Decay Mechanism via Intersystem Crossing

The out-of-plane macrocycle distortion in a series of sterically-crowded porphyrins results in unusual optical properties. Their enhanced radiationless decay of the 1(π, π*) excited state is comparable to those of the DNA bases. Not only ruffled metalloporphyrins but also ruffled free-base porphyrins reduce excited-state life time by a factor of 200, which indicates that the origin of the rapid decay is not only in the metal d-d deactivation but also in the excited state of the distorted porphyrin ring. This raises the possibility that the excited-state properties of the porphyrin are able to adjust step by step through introducing distortions into this tetrapyrroles skeleton. It is, therefore, important to understand how the structural distortion is linked with the photochemical and photophysical consequences.

In the last decade, there have been significant progresses particularly in quantitative computational study on the excited states of porphyrins. Concerning the excited state decay via intersystem crossing (ISC), Marian and co-workers performed DFT/MRCI calculations for unsubstituted planer free-base porphin and found two possible decay pathways from S_1 to T_1 state. Spin-orbit coupling (SOC) increases by out-of-plane vibrations of the porphyrin ring. Concerning ruffled porphyrins, there was a controversy on the origin of the bathochromic shift of the Q band (the lowest-energy absorption) in the absorption spectrum; out-of-plane distortion of the ring versus the electronic effect of substituents On the origin of the fast deactivation, however, we have found no report on the excited-state potential surface to explain the course of the relaxation process.

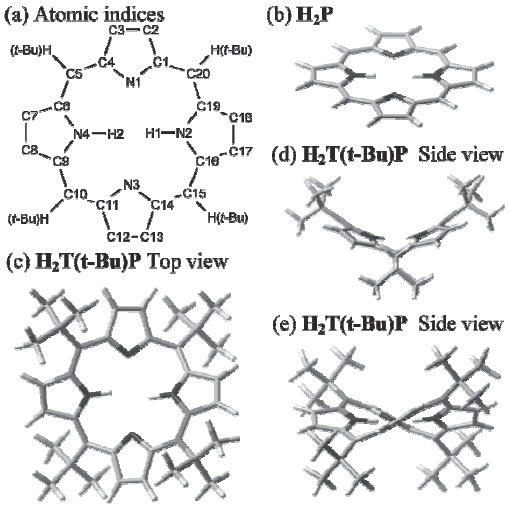


Figure 1 (a) Chemical structures of free-base porphyrin (**H_2P**) and meso-tetra-*tert*-butylporphyrin (**H_2T(t-Bu)P**). (b) and (c) Ground-state optimized structures of **H_2P** and **H_2T(t-Bu)P**, respectively.

The green area denotes the dihedral angles C4-C5-C6-N4 and C14-C15-C16-N2 (see (a) for atomic indices). (d) and (e) The side view of (c) along C10-C20 axis and N1-N3 axis, respectively.

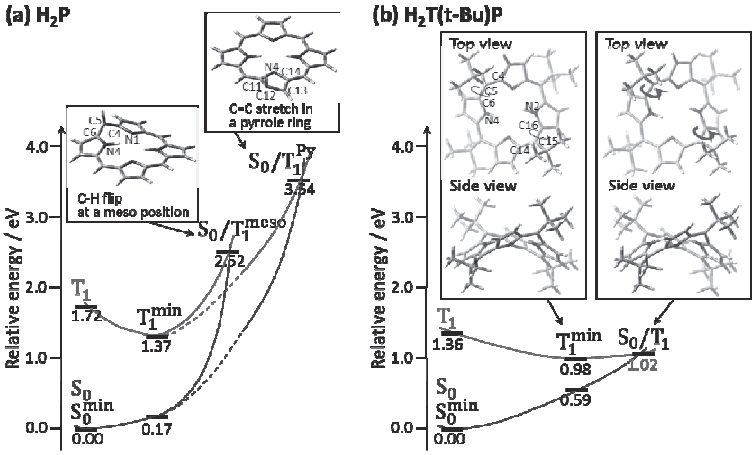


Figure 2. Potential energy profiles of the singlet and triplet excited states of (a) **H_2P** and (b) **H_2T(t-Bu)P** at equilibrium and intersystem crossing points. Calculations were performed at B3LYP/6-31+G(d,p) level.

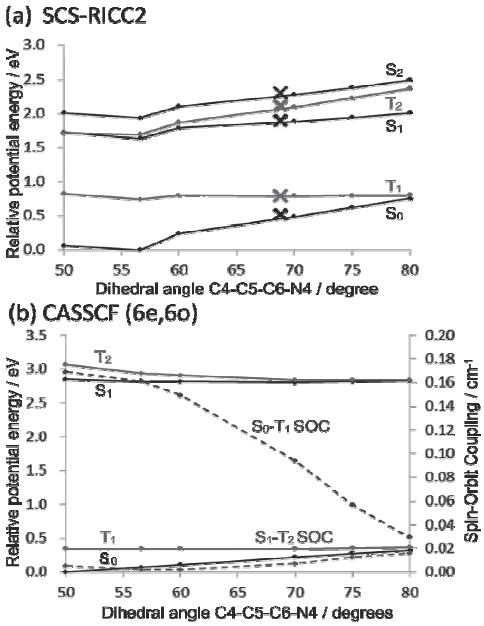


Figure 3. Potential energy curves of singlet and triplet states of **H_2T(t-Bu)P** along the C4-C5-C6-N4 angles. Calculations were performed at the (a) SCC-RICC2/def-SV(P) and (b) CASSCF/ANO-RCC-VDZP levels. Structure was optimized for T_1 state at each angle. Cross marks denote potential energies at S_0/T_1 structure that was optimized at the B3LYP/6-31+G** level. Spin-Orbit Coupling between the S_0 and T_1 states and between the S_1 and T_2 states were obtained with the CASSI method.

Ruffled porphyrins show by 100 times more rapid decay from electronic excited states. This photophysical property is in contrast with the ordinary planer porphyrins that are often used for photosensitization and transportation medium for excitation energy transfer in biology and photochemistry. As nature shows, stabilization of the chemical system against photo irradiation is achieved by introducing a good quencher molecule that can release extra electronic energy to

thermal bath. In the present study, we study potential energy surface of a ruffled porphyrin, **H_2T(t-Bu)P**, to understand the rapid non-radiative decay mechanism**.**

On the basis of the SCS-RICC2 calculations, which is an approximated coupled-cluster method, we investigated potential energy surfaces of **H_2T(t-Bu)P**. We found that the S_1 and T_2 states lie close in energy from the S_1 minima point to a wide range of structures with distortion angles. There should be many chances for ISC to the T_2 surface and then to the T_1 surface (Kasha rule). Regarding the S_0/T_1 ISC, we located MEISC point at the B3LYP/6-31+G(d,p) level. The MEISC structure is similar to that of T_1 minimum but with more distorted dihedral angles. We also found that the T_1 surface along the distortion is surprisingly flat. The reason of the flatness is interpreted by the nodal structure of HSOMO in which the distortion helps to avoid destabilization due to the anti-bonding interactions at the twisting bond. This result indicates that the trajectory can easily reach to the ISC crossing point after relaxing into the T_1 surface. We also performed CASSCF(6e, 6o) calculations and obtained similar results. CASSI calculations were also performed for calculating SOCs between S_1-T_2 states and between T_1-S_0 states. From these results, in addition to the vibronic SOC mechanism as has been proposed for the planer porphyrin, ISC through the T_1-S_0 intersection could also be a possible mechanism for the distorted porphyrin case. We also investigated excited state potential surfaces of **H_2P** and located two MEISC points. In contrast to the **H_2T(t-Bu)P** case, there are significant energy barrier in the T_1 surface to reach the minimum energy ISC points.

2. Original papers

(1) Jie Chen, Jian Wang, Fu-Quan Bai, Li Hao, Qing-Jiang Pan*, Hong-Xing Zhang*,
"Connection style and spectroscopic properties: Theoretical understanding of the interface between N749 and TiO2 in DSSCs".
Dyes and Pigments, 99(1), 201-208, (2013). DOI: 10.1016/j.dyepig.2013.04.008

(2) Jie Chen, Jian Wang, Fu-Quan Bai, Qing-Jiang Pan, Hong-Xing Zhang*,
"Theoretical Studies on Structural and Spectroscopic Properties of Photoelectrochemical Cell Ruthenium Sensitizers, Derivatives of AR20".
International Journal of Quantum Chemistry, 113(7), 891-901, (2013).

(3) Juan Jin, Fu-Quan Bai, Ming-Jun Jia, Yan-Ning Wang, Hong-Li Jia, Jie-Hui Yu*, Ji-Qing Xu*,
"New Cd2+, Pb2+ complexes with acylhydrazidate molecules from in situ acylation reactions".
Dalton Transactions, 42(24), 8771-8780, (2013). DOI: 10.1039/c3dt50411e.

3. Presentation at academic conferences

(1) Fu-Quan Bai, The 12th National Symposium of Computational Chemistry, Suzhou, China, Oct. 21-24, 2013.

Jing-Dong GUO

SPR Fellow

1. Summary of the research of the year

I. Theoretical study of the Diels−Alder reaction of La@C82 with 1,2,3,4,5-Pentamethylcyclopentadiene.

The Diels-Alder (DA) reaction is an extremely valuable type of cycloaddition in organic chemistry. The DA reaction of pure C60 with CpH was explored and published. (Osuna, et.al, J. Phys. Chem. A, 2009, 113, 9721) In our paper, we investigated the mechanism and regioselectivity of the reaction of paramagnetic metallofullerene (La@C82) with Cp*H by using density functional theory at spin-unrestricted M06-2x level.

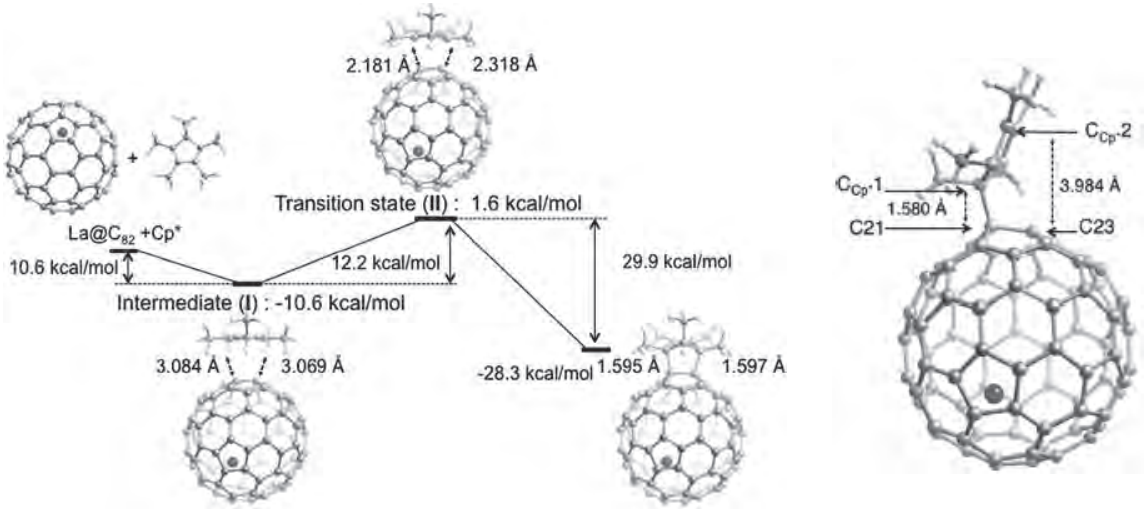


Figure 1a) Reaction profile for the DA reaction of La@C82 and Cp*. 1b) Singly linked intermediate (III) for the stepwise cycloadditionreaction between La@C82 and Cp*H.

§1. It is shown in Figure 1a that the reaction proceeds via a concerted mechanism.

In the initial step for the cycloaddition reaction, a complex of La@C82 and Cp* (intermediate I) was formed, which is more stable by 10.6 kcal/mol than the reactants (La@C82 + Cp*). The shortest carbon-carbon distances between La@C82 and Cp* for I with addition carbon sites are 3.069 and 3.084 Å. The slight differences of these two distances are derived from the asymmetric structure of I. The energy

barrier from I to the final adduct via a transition state (II) is 12.2 kcal/mol. The geometry of II closely resembles the reported transition structure for the DA reaction of C60 with CpH. The closest carbon−carbon distances between La@C82 and Cp* are 2.318 and 2.181 Å, which are similar to the distances reported for the transition states of C60−Cp and C60−quinodimethane reactions.

§2. The located singly linked intermediate exhibits that stepwise way is much less favorable than the concerted way.

For the case of the stepwise addition, the singly linked intermediate between La@C82 and Cp* at addition carbon site C21 or C23 was searched in detail. As a result, the formation of one singly linked intermediate shown in Figure 1b was found. It is notable that the Intermediate is 19.3 kcal/mol higher in energy than reactants. This result suggests that the energy barrier for the stepwise path is considerably larger than that for the concerted path in the reaction of La@C82 and Cp*H.

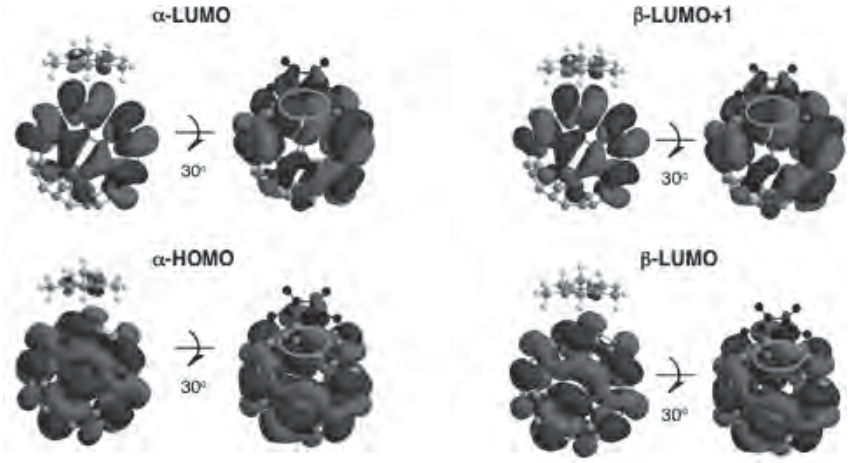


Figure 2. The α-HOMO, β-LUMO,α-LUMO, and β-LUMO+1 of I. Orange circles show the addition site.

§3. Molecular orbitals analysis suggests that the DA reaction proceeds via a concerted mechanism.

According to the Woodward−Hoffmann rule and Frontier Molecular Orbital theory, the LUMO of La@C82 is expected to play a key role in the interaction with the HOMO of Cp*H because the smaller HOMO−LUMO gap between the HOMO of diene and the LUMO of dienophile results in the decreasing of the energy barrier. Furthermore, In the initial step for this reaction, we found that the α-LUMO and β-LUMO+1 of La@C82 have large orbital coefficients on the addition site carbons (C21 and C23) (Figure 2). This indicates that the α-LUMO and β-LUMO+1 of La@C82 can play a main role in interaction with

the HOMO of Cp*H. The fact that the α-LUMO and β-LUMO+1 of La@C82 present a favorable orbital at the addition site to react with Cp*H suggests that the DA reaction proceeds via a concerted mechanism.

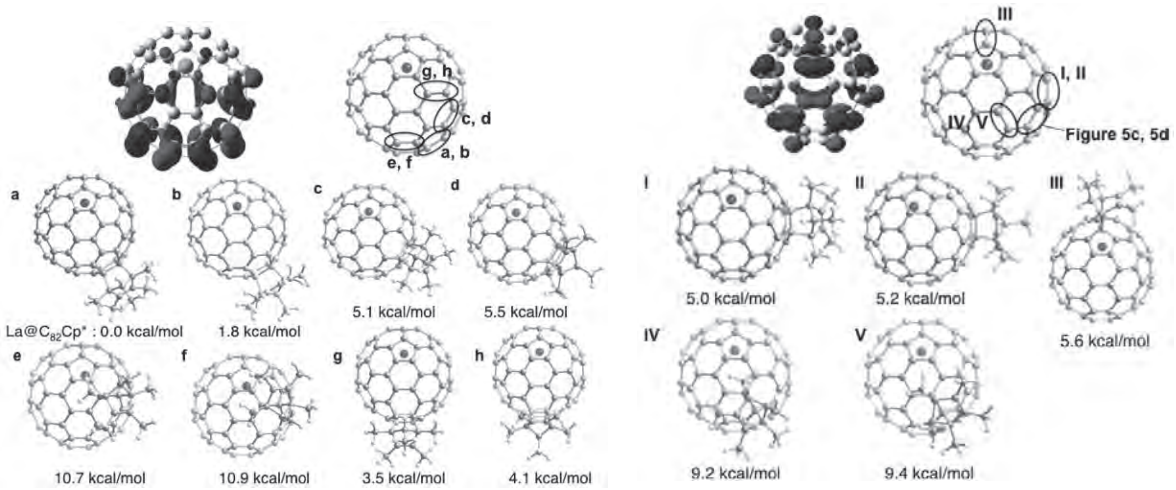


Figure 3. Relative energies calculated for La@C82Cp* isomers.

§4. The relative stability of regioisomer confirms that isomer a with addition C21/23 sites is probably the monoadduct.

Experimentally, the DA reaction between La@C82 and Cp* afforded only one isomer. To confirm the experimental result, the addition site of 13 isomers in Figure 3 was selected by the orbital coefficients in the LUMO of La@C82. It is noted that the most stable on is isomer a which is determined using X−ray crystallographic analysis. These results confirm that isomer a is not only kinetically but also thermodynamically the most conceivable monoadduct.

§5. The retro-DA reaction data verify that the utilized M06-2x functional is reliable.

The activation energy for the retro-DA reaction of La@C82Cp* was determined as 27.0 kcal/mol, which is 3.1 kcal/mol higher in energy than the retro-DA reaction of La@C82Cp. This higher activation energy is mainly attributable to the substituent effect of electron donation derived from five methyl groups of Cp*H, increasing the stability of La@C82Cp* similarly in the case of C60Cp*. In addition, the experimental value of 27.0 kcal/mol agrees reasonably well with the calculated values of 29.9 kcal/mol, suggesting that the M06-2x functional is suitable for the exploration of such DA reaction.

In conclusion, results of this study show that the DA cycloaddition reaction of Cp*H and paramagnetic

La@C82 proceed via a concerted bond formation mechanism, through an intermediate formation of La@C82 and Cp*H. The experimentally obtained results related to the retro-DA reaction of La@C82Cp* exhibit the activation energy, which is in good agreement with the theoretical predicted one. Using the M06-2X method therefore enables the analysis of endohedral metallofullerene DA cycloaddition reactions, in spite of the fact that La@C82 has a radical character. This approach is therefore also promising for further investigation of the reaction mechanism of functionalization of endohedral metallofullerenes.

1. Original papers:

(1) Satoru Sato, Yutaka Maeda, Jing-Dong Guo, Michio Yamada, Naomi Mizorogi, Shigeru Nagase, Takeshi Akasaka,
"Mechanistic Study of the Diels−Alder Reaction of Paramagnetic Endohedral Metallofullerene: Reaction of La@C82 with 1,2,3,4,5-Pentamethylcyclopentadiene"
J. Am. Chem. Soc. 135, 5582-5587 (2013).

Wei-Wei WANG

SPR Fellow

1. Summary of the research of the year

I. Oxygen Reduction and Nitrogen Doping Mechanisms of Graphene Oxides

Ever since its isolation in 2004, graphene has attracted tremendous attention due to its exceptional characteristics. To date, great achievements have been made on graphene-based nanomaterials in the fields of chemistry, physics, and life science. Besides the pristine graphene structure, both experimental and theoretical efforts were made to design and synthesize heteroatom-doped graphene materials to tailor the physicochemical properties for extending applications. For example, because of the unique electronic properties, nitrogen-doped graphene (NG), in which one or more carbon atoms are substituted by nitrogen atoms, is expected to utilize in fuel cells and other electrochemical devices. Structurally, there are three types of bonding configurations for a doped nitrogen atom in graphene, including graphitic N, pyridinic N, and pyrrolic N (Figure 1). The pyridinic N and pyrrolic N are formed at the edge or defective sites. The graphitic N, which bond with three carbon atoms, is formed inside the continuous network of graphene.

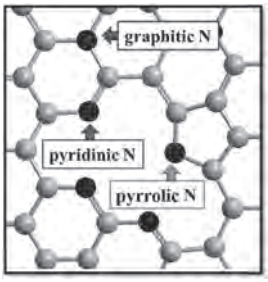


Figure 1. Bonding types of nitrogen atoms in nitrogen-doped graphene

In 2009, Li et al reported a simple chemical method to obtain NG in bulk quantities. By annealing the graphene oxides (GO) in NH_3, they synthesized NG materials at evaluated temperatures. XPS spectra revealed that the nitrogen atoms were embedded into the carbon skeleton and the graphitic N exhibited a more prevailing role than pyridinic N and pyrrolic N over 900°. So far as we know that nearly all the theoretical studies of GO focus on the oxygen reduction reactions and there is no explanation on the nitrogen-doping mechanisms. In this context, our objectives is to elucidate the interactions between ammonia and various oxygen groups (epoxide, hydroxyl and carbonyl), and to uncover the formation mechanisms of graphitic N from NH_3 and GO.

We modeled the structures of graphene oxides as finite fragmental carbon sheets with various oxygen groups (Figure 2). Such finite structures have been extensively used for theoretical calculations. All computations were performed with the M06-2X density functional in conjunction with the basis sets of 6-31G(d) by using the Gaussian 09 program.

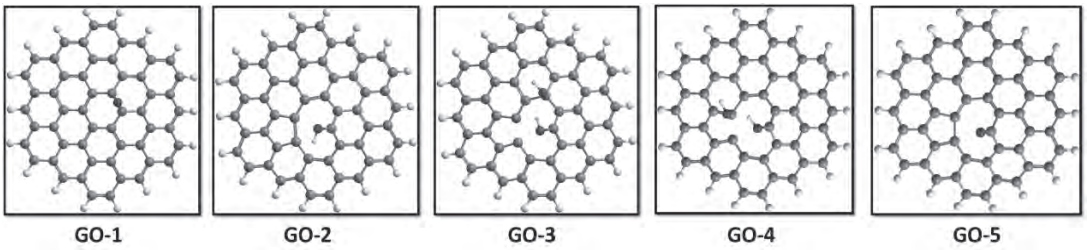


Figure 2. Structures of graphene oxides.

In general, our calculations suggest that chemically reduction on perfect carbon skeleton of GO with ammonia is facilitated at evaluated temperature, but the following doping process is kinetically impossible because of the high energy requirement. Accordingly, direct doping from flawless graphene network seems unpractical. To put the nitrogen atom into carbon network, graphene vacancies is indispensible and the reactions between NH_3 and defective GO with hydroxyl or carboxyl groups have been calculated. All possible mechanisms are explored in detail. The formation of hexagonal graphitic N from NH_3 and GO with vacancies is proved to be a feasible process at high temperature and the interaction between NH_3 and oxygen groups is found to play a fundamental role in assisting the nitrogen doping and the oxygen removal processes. The results provide insight into hetero-graphene formation and may useful for the design of functionalized carbon-based hybrid materials in the future.

II. Theoretical Study of Atomic Carbon Participated Fullerene Growth Mechanisms

Ever since the discovery of fullerene C_{60}, numerous hypothetical models were proposed around its formation. Among various theoretical predictions, the “bottom-up” growth is well-accepted because of experimental supports. As illustrated in the hypothesis, the enlargement of fullerenes is achieved by capturing and assembling the ambient small carbon clusters (e.g. C_2 dimer). The C_2 addition was firstly proposed by Endo and Kroto in 1992 to explain the fullerene growth (Figure 1). Subsequently, this Endo-Kroto model was proved as a stepwise pathway and widely used to interpret the topological connection between carbon cages.

However, in some cases, structural relations among special carbon cages (such as the formation of C_{70} from C_{68}) indicate that direct C_2 insertion cannot always accomplish the growth and structural reconstruction is unavoidable. For instance, the Stone-Wales transformation (SWT, Figure 1) is a common reaction to describe the rearrangement between fullerene species, although the process needs to overcome a huge energy barrier (5-7 eV).

Figure 1. Endo-Kroto C_2 addition (left) and Stone−Wales transformation (right)

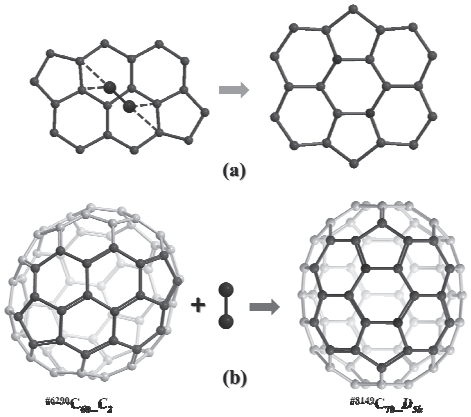


Figure 2. (a) Saito C_2 addition model and (b) structural connection between $^{\#6290}C_{68}\_C_2$ and $^{\#8149}C_{70}\_D_{5h}$.

Besides the classical Endo-Kroto model, another C_2 addition model (Figure 2 (a)) which was proposed by Saito *et al*., has long been dismissed as "chemically unacceptable" because of the large energy requirements for the dissociation of the C_2 dimer. Nevertheless, it is undeniable that the Saito model can accomplish special connections among fullerenes which can not be constructed by the Endo-Kroto model. For example, existing theoretical investigations have suggested that there is still no direct C_2 growth route among stable C_{68} and C_{70} cages. However, based on our geometrical analysis, $^{\#6290}C_{68}\_C_2$ and $^{\#8149}C_{70}\_D_{5h}$, the lowest energy isomers of C_{68} and C_{70}, can be topologically connected *via* the Saito C_2 addition model (see Figure 2 (b)). Therefore, if a reasonable mechanism can be offered to explain the kinetic process, a direct growth channel toward the formation of C_{70} can be uncovered.

Energetically, the "Saito addition" is not approbated because the hypothesized overlapping C_2 insertion seems unrealistic. However, such a C_2 addition which leaps over two carbocyclic rings can be considered as stepwise atomic carbon additions on two respective carbon segments, since it was proved that besides the C_2 group, other addition reagents (such as C_1 or C_3) can assist the growth of fullerenes as well. Moreover, since the odd-numbered fullerenes were reported recently in experiments, the atomic carbon addition can serve as another significant fullerene growth route while using the odd-numbered cages as intermediates. Therefore, we proposed that the "Saito addition" can be chemically treated as two sequential atomic carbon additions combining with the migration and reconstruction of the unsaturated *sp*-hybridized carbon. Worthwhile to note that though the reconstruction is unavoidable after the single atom injection, the rearrangement which occurs on the active odd-numbered fullerene clusters can be assisted by the unsaturated carbon, and consequently, a considerably lower energy barrier can be predicted.

In the present study, we proposed an atomic carbon growth mechanism to explicate the SWT-involved growth procedure for some special fullerenes (e.g. $^{\#6290}C_{68}\_C_2 \rightarrow {}^{\#8149}C_{70}\_D_{5h}$). The DFT calculation results (at the level of B3LYP/6-311G(d)) suggest that the energy barrier of single carbon addition mechanism (2-3 eV) is much lower than that of the traditional Stone-Wales rearrangement (5-7 eV). Our work will supply a new interpretation on fullerene formation mechanisms.

2. Original papers

(1) J. –S. Dang, W. –W. Wang, S. Nagase, and X. Zhao
"Regiochemistry of Nonclassical C_{62} Fullerene: Role of Tetragonal Carbocyclic Ring in Cycloadditions and Thermal/Photoinduced Interconversions of Fulleroid"
J. Phys. Chem. C 117, 12882-12889 (2013).

(2) H. Zheng, X. Zhao, W. –W, Wang, J. –S. Dang, and S. Nagase
"Quantum Chemical Insight into Metallofullerenes M_2C_{98}: $M_2C_2@C_{96}$ or $M_2@C_{98}$, Which Will Survive?"
J. Phys. Chem. C 117, 25195-25204 (2013).

(3) J. –S. Dang, W. –W. Wang, X. Zhao, and S. Nagase
"Regioselective Derivatization of C_{84} by Diels-Alder Reactions: Applications to Photovoltaic Solar Cells and Fullerene Polymerization"
Org. Lett. 16, 170-173 (2014).

(4) W. –W. Wang, and S. Nagase
"Oxygen Reduction and Nitrogen Doping Mechanisms of Graphene Oxides"
Manuscript in preparation

(5) W. –W. Wang, S. Nagase, J. –S. Dang, and X. Zhao
"Theoretical Study of Atomic Carbon Participated Fullerene Growth Mechanisms"
Manuscript in preparation

Miho HATANAKA

FIFC Fellow

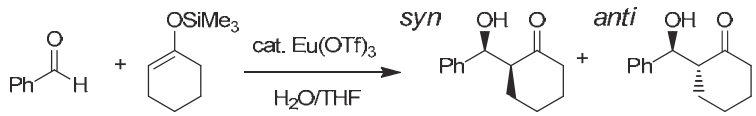
1. Summary of the research of the year

1.1. Theoretical study of aqueous Mukaiyama-Aldol reaction catalyzed by lanthanide complexes

Highly stereoselective reactions have been achieved by using chiral catalysts, and the computational chemistry contributed to better understanding of the mechanism of such reactions. Conventional chiral catalysts usually have rigid structures, and only a few transition states of stereo-determining step need to be computed to elucidate the origin of stereoselectivity. Recently, many catalytic systems having flexible structures have been reported for highly stereoselective C-C bond formations in aqueous media. These catalysts are quite different from conventional rigid chiral catalysts which were used for various reactions in organic solvent. Here, three questions arise in the following way; [1] How do the flexible chiral catalysts control the stereoselectivities? [2] Is it an appropriate way to compute one or few transition states for studying the stereo-selectivity of flexible reaction systems? [3] What role does water play, just solvent or an important key for the reactions?

To discuss the stereoselectivity of such flexible catalytic systems, it might not be enough to compare only few TSs of stereo- determining step because there should be a number of TSs whose structures are slightly different because of the structural fluctuation. To overcome this problem, an automated explore method, called the Global Reaction Root Mapping (GRRM) strategy was applied to predicting the ratios of stereoisomers quantitatively. In this study, I focus on two flexible reaction systems, such as the Kobayashi-modification of Mukaiyama-Aldol reactions catalyzed by two kinds of lanthanide (Ln) Lewis acid catalysts in aqueous solution and discuss their stereoselectivity.

【Topic 1】Ln^{3+} catalysts are drawing attention because they are active as Lewis acid catalysts even in aqueous media. Though the first report about the aqueous Mukaiyama-Aldol reaction catalyzed by Ln^{3+} (Scheme 1) was published 20 years before by Kobayashi, there are still unsolved questions concerning the role of water. One question is why the product yield of this reaction catalyzed by $Ln(OTf)_3$ in organic solvent dramatically increased upon addition of water. Another is why the diastereoselectivity of this aqueous reaction shows *syn*-preference.



Scheme 1. Aqueous Mukaiyama-Aldol reaction catalyzed by $Eu(OTf)_3$.

To answer these questions, we applied one of the GRRM strategy, the artificial force induced reaction (AFIR) method with the B3LYP-D3 theory and clarified the most favorable reaction pathway. This reaction proceeds via a stepwise mechanism, first C-C bond formation, followed by proton transfer from water to benzaldehyde and then trimethylsilyl (TMS) dissociation caused by nucleophilic attack by bulk water molecules. The answer of the first question can be found by the nature of the Gibbs free energy surface of this reaction. Without water, this reaction should stop after the first C-C bond formation step because the remaining steps need water molecules. Focusing on the first step, the rate of backward reaction is much faster than that of the forward one, which results in low yield under anhydrous condition. Next, to discuss the diastereoselectivity, the structural sampling of TSs of stereo-determining C-C bond formation step was obtained exhaustively. We used the AFIR method and found 91 *syn*-TSs and 73 *anti*-TSs whose coordination structures around Eu^{3+} and orientation between two substrates are slightly different. Among them 17 TSs contributed greatly to the diastereomeric ratio and I succeeded in reproducing the ratio quantitatively by considering all the obtained TSs. The second question was explained by the comparison of the lowest *syn*- and *anti*-TSs. The *anti*-TS for C−C bond formation in water is entropically less favored relative to the *syn*-TS because of the existence of a rigid hydrogen bond between the TMS part and coordination water around Eu^{3+} in the former. As shown above, considering only a few TSs for the rate-determining step is not enough to reproduce the experimental ratio, the exhaustive sampling of TSs can be obtained by the AFIR method, and water was not just a solvent but contributed to promote the reaction.

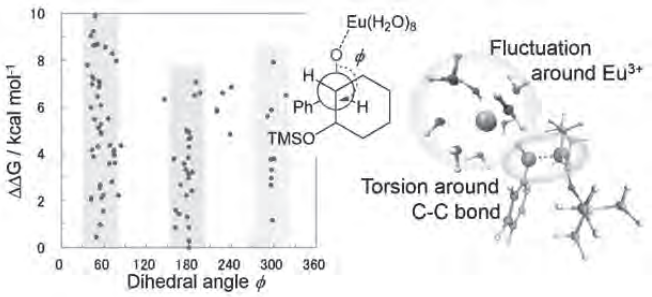
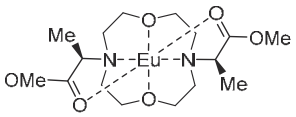


Figure 1. Obtained TSs for C-C bond formation step producing the *syn*-structures

【Topic 2】One may think that Ln^{3+} complex seems to be unsuitable for highly stereoselective reactions because of its flexible coordination structure. However, this problem can be solved by removing coordination water molecules around Ln^{3+} by using a ligand. For example, Allen *et al*. reported the highly enantio- and diastereo-selective aqueous Mukaiyama-Aldol reaction catalyzed by chiral Eu-DOTA derivative (Scheme 2). However, Ln-DOTA and its derivatives are known to have a number of conformers and flexible structures. How does this flexible catalyst control the stereoselectivity? To answer this question, the possible conformations of the catalyst were explored by using the anharmonic downward distortion following (ADDF) method which is the second method in the GRRM strategy and it was found that



Scheme 2. Chiral Eu-DOTA derivative

three conformers (A, B, and C shown in Figure 2) coexisted in the reaction system.

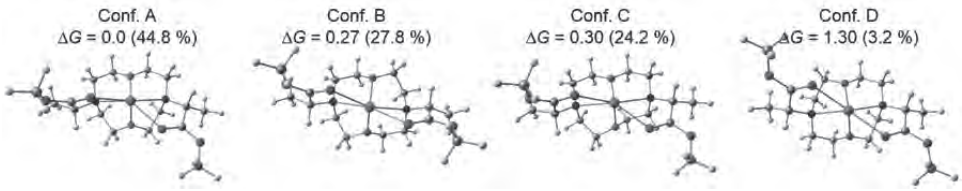


Figure 2. Four stable conformers of the chiral Eu-DOTA derivative. Gibbs free energies at -25°C are in kcal/mol. Numbers in parentheses are the existing probabilities.

Next, to discuss the stereoselectivity, the AFIR calculations were performed for gathering the TSs of C-C bond formation step. By considering all the obtained TSs, both diastereomeric ratio and enantio excess were evaluated very quantitatively. The most stable TS which produced the major (*R*,*R*) product had Conf. B structure, that was not the most stable conformer, for the catalyst part. The structure of catalyst part of the most stable TS producing the enantiomer (*S*,*S*) was not Confs. A and B but Conf. C. What we can say from here is that if Conf. C does not exist in the reaction system, the enantioselectivity should be higher. Therefore, to improve the enentio-selectivity, we need to control the stability of each conformer to reduce the amount of Conf. C. The easiest way to change the stability of each conformer is changing the lanthanide cations. Figure 3 shows the existing probabilities of four conformers in each Ln-DOTA derivative. By using lighter Ln, the existing probability of Confs. A and C can be reduced dramatically. This result is consistent with the experimental study that the highest enantioselectivity was shown in Nd catalyst and the second in Pr catalyst. Therefore, we can say that for flexible catalytic systems, the most important point to improve the stereoselectivity is not to use bulky catalysts but to reduce the conformers which produce the minor products.

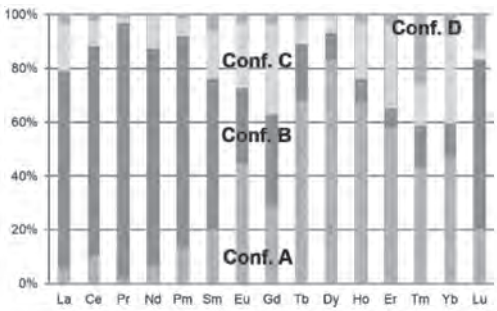


Figure 3. Existing probabilities of Ln-DOTA derivatives at -25°C condition

1.2. Mechanism of C_nH^- (n = 2, 4, 6) generation in the interstellar media

In the past few decades, a number of cations and neutral molecules were detected in the interstellar media (ISM) and the mechanism of generation and reactivity of these molecules have been investigated by experimental and computational methods. However, there are still remaining questions. One of them is the generation mechanism of anions. Until now, only six anions, such as C_nH^- (n = 4, 6, 8) and C_nN^- (n = 1, 3, 5) have been detected and the existence probability of C_nH^- increases as the number of carbon (n) increases. However, the reason of the

low abundance of anions and the abundance dependency on carbon chain have not clarified. In this study, to clarify the reason of the questions above, three reaction systems $C_nH + e^- \rightarrow C_nH^-$ (n = 2, 4, 6) were focused on and the critical points on potential energy surfaces (PESs) of C_nH and C_nH^- were explored by using the ADDF method.

Although the numbers of carbons are different, there were many similarities for C_nH/C_nH^- (n = 2, 4, 6) systems. The GMs on neutral doublet ground states (**D0**) and anionic singlet ground states (**S0**) had linear structures for n = 2, 4, 6. To form anions from neutral C_nH, their PESs must have crossing points. However, the difference between PESs of **D0** and **S0** were too large and they did not cross each other. Therefore, the formation of anions from neutral C_nH should proceed through excited states of anions. Crossing points between **D0** and anionic excited states were found nearby the GM structures. However, the characters of anionic excited states depended on the number of carbon atoms.

For n = 2, the closest anionic state from **D0** was the lowest triplet state. However, the MSX between **D0** and the triplet state was 17 kcal/mol higher than the GM on **D0**, and so the electron attachment process cannot occur in the ISM. For n = 4, the closest anionic state from **D0** was also the triplet state and the energy of their MSX was close to the GM on **D0**. Though the reaction barrier for electron attachment is enough small, the following radiative stabilization to reach the **S0** state rarely proceeds because of the spin-forbidden transition. For n = 6, on the other hand, the closest anionic state from **D0** was not triplet but singlet excited state. Therefore the radiative stabilization after the electron attachment can proceed easier than that for n = 4. The singlet excited state had the Rydberg state character where 2s orbital of H atom was singly occupied. Therefore, the electron attachment process for n = 6 is the same as those for typical molecules where electrons are trapped on Rydberg states first and then relaxed to the ground states. As shown above, the reason of anion abundance dependency on the number of carbon can be explained.

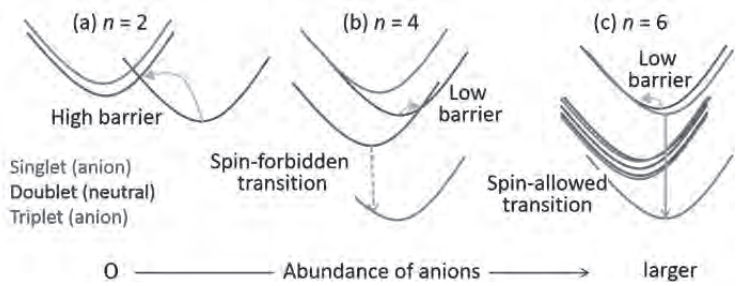


Figure 4. Schematic explanation about the reaction pathways for the C_nH^- (n = 2, 4, 6) formations.

1.3. σ-aromaticity of hexa-Group 16 atom-substituted benzene dications

Nowadays many systems that show aromaticity caused by σ, δ, and ϕ electrons have been reported, though the typical aromaticity is shown in π-electron delocalized systems. One of the well-known candidates that show σ-aromaticity is $C_6I_6^{2+}$ in which removal of two σ anti-bonding electrons localized on I_6 from neutral C_6I_6 results in fulfilling the Hückel (4n+2) rules for I_6^{2+} as well as C_6 parts. Such σ-aromaticity is not shown in $C_6Br_6^{2+}$ and $C_6Cl_6^{2+}$ because

smaller overlaps of in-plane valence p orbitals of halogens cause smaller destabilization of σ anti-bonding orbital and result in removal of two electrons not from the anti-bonding σ orbital but from a delocalized π orbital. Hexa-group 16 atom-substituted benzene dications can be also candidates because of the similarity of electronic states between halogens and group 16 atoms capped by hydrogens or substituents. One of the advantages of hexa-group 16 atom-substituted benzenes is that geometries and electronic structures can be controlled by modifying substituents on the group 16 atoms. If the magnitude of overlap of valence p orbitals, which determines the stability of the σ anti-bonding orbital, can be controlled by changing geometry and electronic structures with different substituents, hexa-group 16 atom-substituted benzene derivatives can have strong σ-aromatic character.

To investigate the aromaticity of dicationic benzene derivatives, the isotropic nucleus independent chemical shift ($NICS_{iso}$) and its zz component ($NICS_{zz}$) were evaluated by B3LYP theory. NICS is a magnetic index of aromaticity and negative NICS values indicate aromaticity, whereas positive NICS values indicate anti-aromaticity. Figure 5 shows the Kohn-Sham orbitals and $NICS_{zz}(1)$ values of dicationic benzene derivatives. (b) and (c) in Figure 5 are different conformers of $C_6(SH)_6^{2+}$ and the directions of H atoms are perpendicular to the C_6 plane for (b) and four of them are in-plane and two are perpendicular for (c). Only the conformer with D_{3d} symmetry (b) has a similar LUMO to $C_6I_6^{2+}$ which results in fulfilling Hückel ($4n$+2) rules for S_6^{2+} and C_6 parts and having aromatic character. The other conformer with C_{2h} symmetry (c) has a delocalized LUMO and anti-aromaticity. Therefore, to find a molecule that shows σ-aromaticity, we should find a molecule whose most stable conformer has the singlet state and the geometry where all of the substituents are directed perpendicular to the C_6 plane.

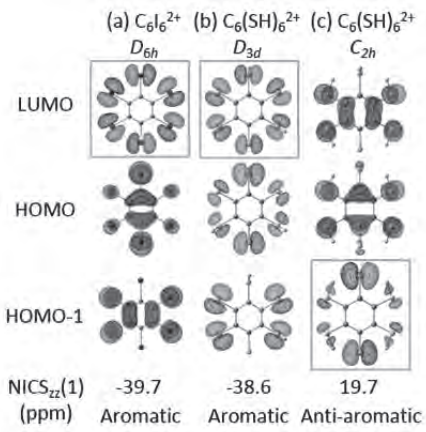


Figure 5. Molecular orbitals and $NICS_{zz}$ values of singlet dications

To find such molecules, a number of derivatives were examined and several candidates were found, such as $C_6(SeH)_6^{2+}$, $C_6(TeH)_6^{2+}$, and their derivatives, which have larger aromatic characters than neutral benzene. To clarify the origin of larger aromatic characters, the NICS values were dissected into contributions from canonical molecular orbitals and from localized natural bonding orbitals. Both analyses showed the existence of contributions to aromaticity from π orbitals of C_6 and in-plane σ orbitals of Se_6 and Te_6. To clarify the substituent dependency on aromaticity, their derivatives were examined. However, the NICS values were almost independent of the substituents, because the charge transfer between group 16 atoms and substituents takes place only through p_z orbitals that are orthogonal to the in-plane σ orbitals. In addition, the aromaticity of hexa-groups 14 and 15 atom-substituted benzene dications were

examined and it was found that only $C_6(SbH_2)_6^{2+}$ had a large negative NICS value.

2. Original papers

(1) M. Hatanaka, M. Saito, M. Fujita, K. Morokuma, "σ-Aromaticity in Hexa-Group 16 Atom Substituted Benzene Dications. A Theoretical Study", *J. Org. Chem.* **79**, pp 2640-2646 (2014).

(2) M. Hatanaka, K. Morokuma, "Role of Water in Mukaiyama-Aldol Reaction Catalyzed by Lanthanide Lewis Acid: A Computational Study" *J. Am. Chem. Soc.* **135**, pp 13972-13979 (2013).
※Spotlights on Recent JACS Publications, **135**, pp. 13999-13999 (2013)

(3) M. Hatanaka, S. Maeda, K. Morokuma, "Sampling of Transition States for Predicting Diastereoselectivity Using Automated Search Method —Aqueous Lanthanide-Catalyzed Mukaiyama Aldol Reaction" *J. Chem. Theory. Comput.* **9**, pp 2882-2886 (2013).

(4) 前田 理, 畑中 美穂, 植松 遼平, 武次 徹也, 諸熊 奎治, "人工力誘起反応法による化学反応経路の自動探索：有機合成化学への応用と展望", 有機合成化学協会誌 **72**, pp567-579 (2014). (総説:査読なし)

3. Presentations at academic conferences

(1) ○M. Hatanaka, "Theoretical study of highly stereoselective Mukaiyama-Aldol reaction in aqueous media", Asian International Symposium – Theoretical Chemistry, Chemo-informatics, Computational Chemistry – in The 94th Annual Meeting of the Chemical Society of Japan, Nagoya, Japan, March, 2014 (Invited Talk)

(2) ○M. Hatanaka, K. Morokuma, "Theoretical study on Aqueous Lanthanide-Catalyzed Mukaiyama-Aldol Reaction", 5th JCS International Symposium on Theoretical Chemistry, Nara, Japan, December, 2013. (Invited Poster)

(3) ○畑中美穂, 諸熊奎治, "ランタノイドキレート触媒を用いる向山アルドール反応の配位構造と立体選択性の理論的研究",第 7 回分子科学討論会 2013, 京都, 2013 年 9 月. (優秀講演賞受賞)

(4) ○畑中美穂, 前田理, 諸熊奎治, "ランタノイド触媒を用いる水中向山アルドール反応の機構と立体選択性", 第 16 回理論化学討論会 2013, 福岡, 2013 年 5 月. (口頭)

(5) ○M. Hatanaka, S. Maeda, K. Morokuma, "The role of water in aqueous Mukaiyama-Aldol reaction catalyzed by lanthanide Lewis acid", The 6th Asia Pacific Conference of Theoretical and Computational Chemistry, Gyeongju, Korea, June, 2013. (Best poster award)

4. Others

4.1. Presentations at symposiums

(1) ○ M. Hatanaka, K. Morokuma, "Theoretical Study of Highly Stereoselective

Mukaiyama-Aldol Reaction in Aqueous Media", the 11th symposium of FIFC, Kyoto, January, 2014 (Poster).

(2) ○畑中美穂, 諸熊奎治, "ランタノイド DOTA 誘導体の構造揺らぎーキラル触媒・MRI コントラスト剤を例にー", 化学反応経路探索のニューフロンティア 2013, 京都, 2013 年 9 月. (Poster)

(3) ○M. Hatanaka, "Mechanism of Mukaiyama Aldol Reaction Catalyzed by Water-Tolerant Lanthanide Lewis Acid – An Artificial Force Induced Reaction Study", The 10th Fukui Center Seminar, Kyoto, Japan, March 2013. (Invited Talk)

4.2. Lectures for high school students

(1) 畑中美穂, "新薬ができるまで―化学はこんなふうに新薬開発に関わっていますー", 人間科学類型特別授業, 兵庫県立北摂三田高等学校, 2013 年 12 月. (高校 1 年生(約 30 人)対象)

(2) 畑中美穂, "コンピュータで見る化学反応の世界", 子どもの知的好奇心をくすぐる体験授業, 京都府立城南菱創高等学校, 2013 年 12 月. (高校 1 年生(約 160 人)対象)

(3) 畑中美穂, "コンピュータで見る化学反応の世界",理系インスパイアー講演会, 兵庫県立北摂三田高等学校, 2013 年 9 月. (高校 2 年生(理系限定約 120 人)対象)

Fengyi LIU

Postdoctoral Fellow

1. Summary of the research of the year

Exploring the Deactivation Path of Fluorescent Dyes by SF-TDDFT

The quantum yields for fluorescent dyes are critical, while theoretical predictions of radiationless decay channel are often difficult due to the known issues. Recently, the global reaction route mapping (GRRM) method has successfully been applied to automatically explore multiple PESs and tested to be a powerful tool to discovery nonadiabatic pathways. We employed the GRRM MSX searching algorithm, in combination with spin-flipping (SF) TDDFT, to locate the minimal-energy crossing points (MECP) between the excited and ground states of the fluorescent dyes. Taking the open-shell, triplet ground state as reference, the SF-TDDFT can describe the S_1 and S_0 state balancedly, therefore is capable of describing the conical intersection region. The influences of the reference function, i.e., unrestricted or restricted open-shell DFT, different Kohn-Sham wave functions, etc., have been systematically evaluated. The results are useful in explaining experimental findings as well as designing new high-yield fluorescent materials.

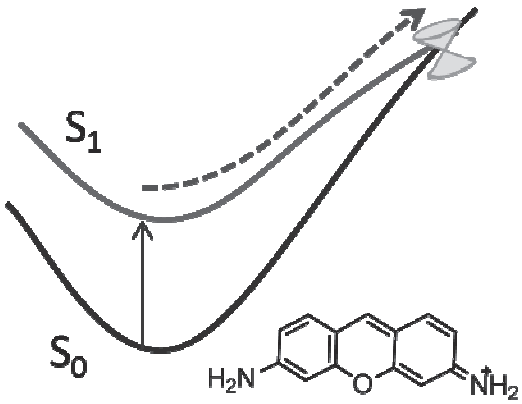


Figure 1. Schematic radiationless decay channel for a fluorescent dye.

Reaction 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. In this project, CASSCF and CASPT2 studies on the reaction mechanism of the photochromic ring-opening process of a spiropyran (SP) (1′,3′,3′-trimethylspiro-[2*H*-1-benzopyran-2,2′-indoline], also known as BIPS) have been performed and

possible excited-state C–O (and C–N) bond cleavage pathways and S_1-to-S_0 nonadiabatic transition channels have been explored. (1) The C–O bond dissociation in SP does not follow a conical-intersection mechanism that has been proposed in a model study with a simplified benzopyran. The CASSCF-optimized crossing points are actually avoided crossings with a large S_1–S_0 energy gap at the CASPT2 level; thus, they could not act as efficient S_1-to-S_0 funnels. (2) C–O bond cleavage paths on S_1 leading to both the CCC (cis–cis–cis with respect to the configuration around α, β, γ) and TCC (trans–cis–cis) intermediates of merocyanine (MC) are barrierless, in line with the experimentally observed ultrafast formation of MC. (3) An unexpected low-energy hydrogen-out-of-plane (HOOP) valley on the (π→σ*) surface was located not far from the C–O bond cleavage path and was suggested to be an efficient S_1-to-S_0 nonadiabatic decay channel. Triggered by the active HOOP mode, the molecule can easily access the S_1–HOOP valley and then make a transition to the S_0 surface through the narrow S_1–S_0 gap that exists in an extended region. Nonadiabatic decay through a conical intersection on C–N dissociation path as well as the HOOP funnel is responsible for high internal conversion yields of SP. These findings shedding light on the complex mechanism of SP–MC interconversion provide fundamental information for design spiropyran-based photochromic devices.

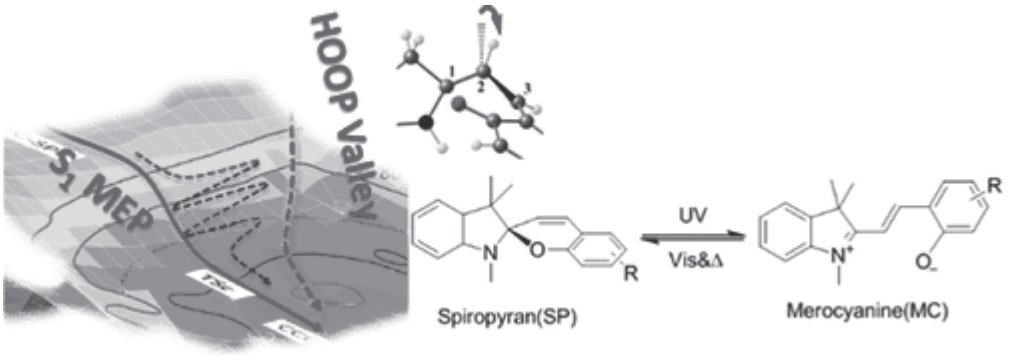


Figure 2. Multiple pathways for the primary step of the spiropyran photochromic reaction.

The photochromic ring-opening reaction of spiropyran has been revisited at the multireference CASSCF and CASPT2 level with a CAS(22e,20o) active space, in combination with density matrix renormalization group (DMRG) methods. The accuracy of the DMRG-CASSCF and DMRG-CASPT2 calculations, with respect to the number of renormalized states, the number of roots in state-averaged wave functions, and the number basis functions, was examined. For the current system, chemically accurate results can be obtained with a relatively small number of renormalized states. The nature and vertical excitation energies of the excited (S_1 and S_2) states are consistent with conventional CAS(or RAS)PT2 with medium active spaces. The capability of the DMRG-CASSCF method in the optimization of molecular geometry is demonstrated for the first time. The computation costs (several hours per optimization cycle) are comparable with that of the conventional CASSCF geometry optimization with small active space. Finally, the DMRG-PT2 computed

S_1-MEP for the C–O and C–N bond-cleavage processes show good agreement with our previous calculations with a CAS(12e,10o) active space [Liu, F.; Morokuma, K. *J. Am. Chem. Soc.* **2013**, *135*, 10693–10702]. Especially, the role of the HOOP valleys in the $S_1 \rightarrow S_0$ nonadiabatic decay has been confirmed.

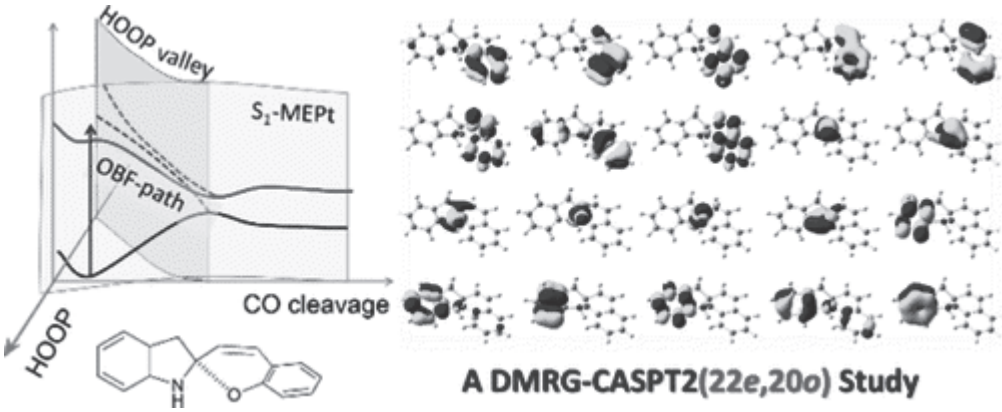


Figure 3. Multireference Ab initio DMRG-CASSCF and DMRG-CASPT2 study on the photochromic ring opening of Spiropyran.

2. Original papers

(1) Fengyi Liu and Keiji Morokuma

Multiple Pathways for the Primary Step of the Spiropyran Photochromic Reaction: A CASPT2//CASSCF Study

J. Am. Chem. Soc., **2013**, *135* (29), pp 10693–10702.

(2) Fengyi Liu, Yuki Kurashige, Takeshi Yanai, and Keiji Morokuma

Multireference Ab Initio Density Matrix Renormalization Group (DMRG)-CASSCF and DMRG-CASPT2 Study on the Photochromic Ring Opening of Spiropyran

J. Chem. Theory Comput., **2013**, *9* (10), pp 4462–4469.

(3) Piao, W., Tsuda, S., Tanaka, Y., Maeda, S., Liu, F., Takahashi, S., Kushida, Y., Komatsu, T., Ueno, T., Terai, T., Nakazawa, T., Uchiyama, M., Morokuma, K., Nagano, T. and Hanaoka, K.

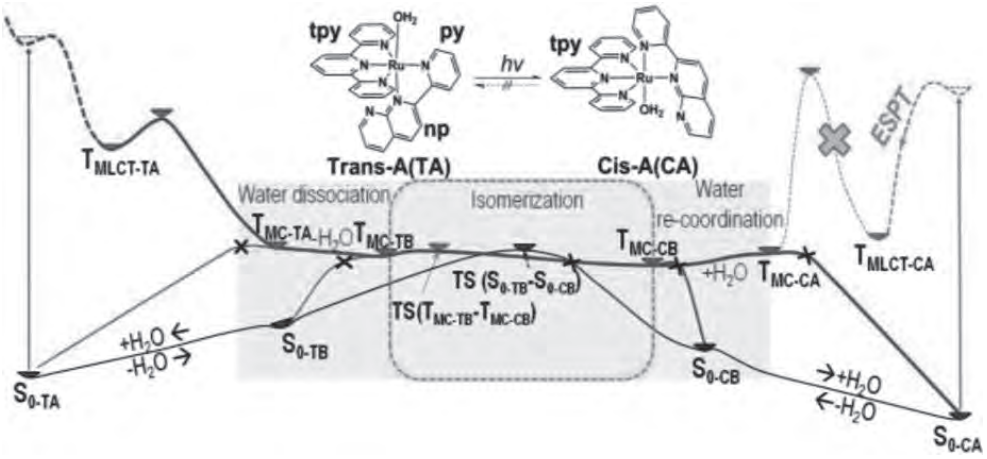
Development of Azo-Based Fluorescent Probes to Detect Different Levels of Hypoxia. *Angew. Chem. Int. Ed.*, **2013**, *52*: 13028–13032.

Lina DING

Research Fellow

1. Summary of the research of the year

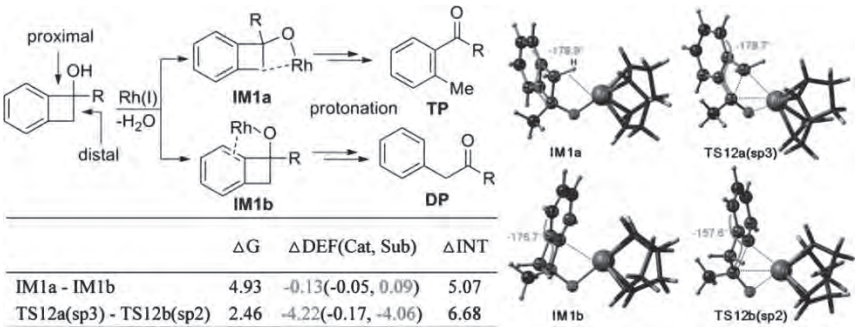
P1. Excited-State Proton Transfer Controls Irreversibility of Photoisomerization in Mononuclear Ruthenium(II) Monoaquo Complexes: A DFT Study



The detailed DFT investigation clears the working mechanism of the irreversible photoisomerization of *trans*-[Ru(tpy)(pynp)(OH_2)]$^{2+}$ (TA) and *cis*-[Ru(tpy)(pynp)(OH_2)]$^{2+}$ (CA) complexes. Both TA and CA complexes present two types of low lying triplet states, one resulting from a triplet metal–ligand charge-transfer (T_{MLCT}) and the other from a triplet metal-centered d–d transition (T_{MC}). The vertical excitation of the singlet ground state of the complexes leads to a singlet excited state, which undergoes ultrafast decay to the corresponding T_{MLCT}. For TA, this T_{MLCT} transforms with a low barrier to a T_{MC} state. The dissociative nature of the T_{MC} state leads to easy water removal to produce a five-coordinate intermediate that can isomerize via rotation of a pynp ligand and proceed towards the CA product. For CA, however, during this excitation and intersystem crossing process, an excited-state proton transfer (ESPT) occurs and the resultant T_{MLCT} is very much stabilized with a very strong Ru(II)–OH bond; the high barrier from this T_{MLCT} blocks conversion to a T_{MC} state and thus prevents isomerization from the *cis* to the *trans* isomer. This high barrier also prevents the possibility of the isomerization process

from TA to CA solely on the adiabatic triplet pathway. Instead, crossing points ($X_{MC\text{-}CB}$, $X_{MC\text{-}CA}$) near the minimum of the triplet metal-centered state of the *cis* isomer provide nonadiabatic decay channels to the ground-state $S_{0\text{--}CA}$, which completes the photoisomerization pathway from TA to CA.

P2. sp^3–sp^2 vs sp^3–sp^3 C–C Activation in Rh-Catalyzed Ring Opening of Benzocyclobutenol: A DFT Study



	ΔG	ΔDEF(Cat, Sub)	ΔINT
IM1a - IM1b	4.93	-0.13(-0.05, 0.09)	5.07
TS12a(sp3) - TS12b(sp2)	2.46	-4.22(-0.17, -4.06)	6.68

The C_{sp^3}–C_{sp^2} vs C_{sp^3}–C_{sp^3} site selectivity in the C–C bond activation in Rh-catalyzed ring opening of benzocyclobutenol was systematically investigated using density functional theory (DFT). The catalytic cycle includes three elementary steps: the proton transfer from the substrate to a rhodium hydroxide, the C–C cleavage, and the proton transfer from water onto a carbon forming the final product with regeneration of the rhodium hydroxide. The site selectivity is determined by the C–C cleavage step; the C_{sp^3}–C_{sp^2} cleavage is favored over the C_{sp^3}–C_{sp^3} cleavage because the former transition state is stabilized by an interaction between the benzene ring of the substrate and Rh. DMSO, a more polar solvent, reduces the site selectivity as the more polar C_{sp^3}–C_{sp^3} transition state (TS) is stabilized more than the C_{sp^3}–C_{sp^2} TS and decreases the advantage of the latter TS. DPPF ligand is bulky, and the steric repulsion on the tighter C_{sp^3}–C_{sp^2} TS causes the loss of the site selectivity. For the even more crowded $Rh(P(t\text{-}Bu)_3)_2$ catalyst, one phosphine has to dissociate before the C–C cleavage reaction takes place, and the advantage of the C_{sp^3}–C_{sp^2} TS is regained for the less crowded $RhP(t\text{-}Bu)_3$ active catalyst.

2. Original Papers

(1) **Lina Ding**, Lung Wa, Chung, Keiji Morokuma*,
Excited-State Proton Transfer Controls Irreversibility of Photoisomerization in Mononuclear Ruthenium(II) Monoaquo Complexes: A DFT Study, *J. Chem. Theory Comput.*, **2014**, *10* (2), 668–675.

(2) **Lina Ding**, Naoki Ishida, Masahiro Murakami, and Keiji Morokuma*,
sp^3–sp^2 vs sp^3–sp^3 C–C Activation in Rh-Catalyzed Ring Opening of Benzocyclobut--enol: A DFT Study, *J. Am. Chem. Soc.*, **2014**, *136* (1), 169–178.

(3) **Lina Ding**, Lung Wa Chung, Keiji Morokuma
"Reaction Mechanism of Photoinduced Decarboxylation of the Photoactivatable Green Fluorescent Protein: An ONIOM(QM:MM) Study", *J. Phys. Chem. B,* ***2013****, 117 (4), 1075–1084.*

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

(3) Lina Ding, Naoki Ishida, Masahiro Murakami, and Keiji Morokuma*,
"Ligands and Solvent Effects on the Site-Selectivity of Rh-Catalyzed-Ring-Opening of Benzocyclobutenol: A Computational Study,"
The 10th FIFC Symposium, 2012, Nov. 30.

Hai-Bei LI

Postdoctoral Fellow, Fukui Kenichi Memorial Research Group 1

1. Summary of the Research of the Year

Graphene Nucleation on a Surface-Molten Copper Catalyst

CVD has been the most preferred method of producing graphene, due to its ability to produce graphene films with large-domains and high-quality. Of particular importance in this respect are Ni and more recently Cu catalysts, which are the most widely used for graphene formation. One limitation of Ni catalysts for CVD graphene growth is their propensity to form multi-layered graphene sheets, as opposed to single layer graphene, and this presumably arises from a metastable Ni-carbide phase at CVD-relevant temperatures. Ni exhibits both high carbon solubility and bulk carbon diffusivity. Cu, as opposed to Ni, predominantly forms single-layer graphene exclusively via surface catalytic reactions and processes, and this can be explained by its ultralow carbon solubility. This, combined with the lower market price of copper, have made it perhaps the most preferred catalyst for CVD graphene production. Large-size, spatially self-aligned, and single-crystalline hexagonal graphene flakes have been produced on *liquid* Cu surfaces, implicating remarkable surface atom mobility in the formation of high-quality graphene. However, the role of surface morphology on graphene formation with Cu catalysts therefore remains an important question.

In this work, we present quantum chemical simulations towards this end. We provide the first comprehensive atomistic picture of nucleation and growth of graphene on the Cu(111) surface. We demonstrate here that the physical state of the Cu surface region plays a key role on graphene growth. In particular, we reveal a potential mechanism that explains copper's intrinsic ability to form higher quality graphene structures compared with Ni and Fe catalysts, and attribute this phenomenon to the healing role provided by highly mobile Cu surface atoms.

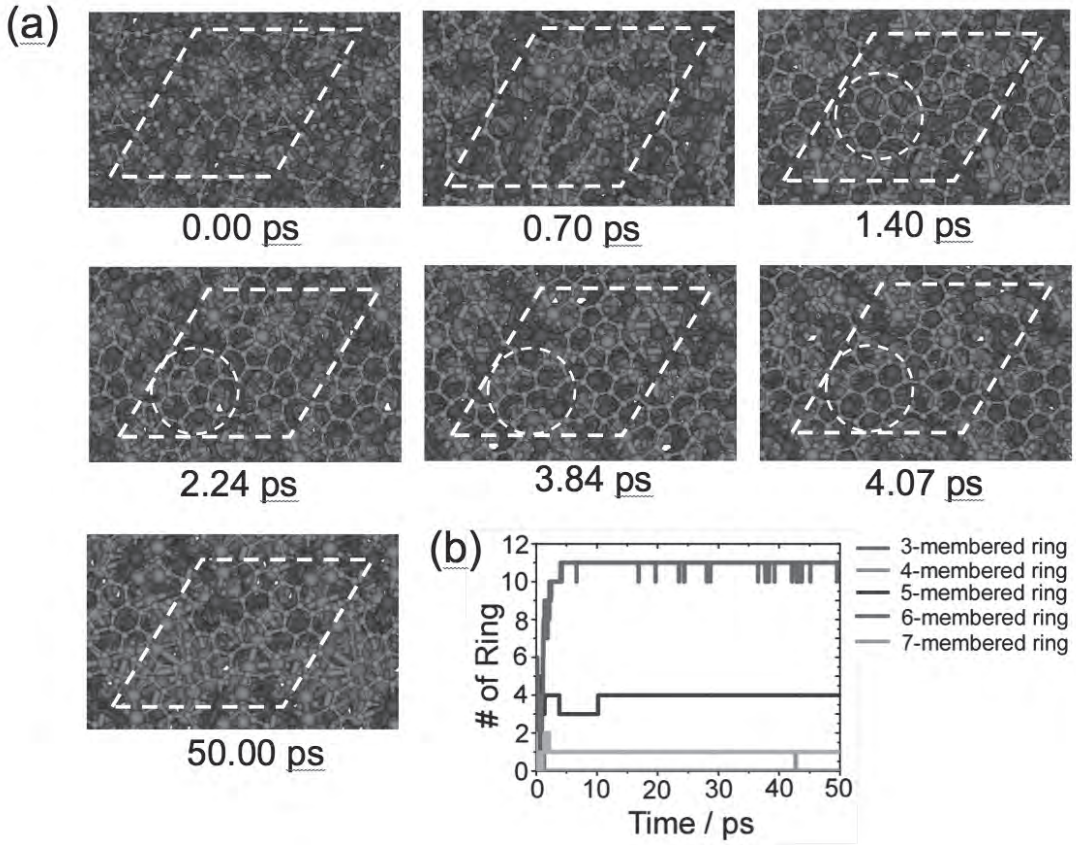


Figure 1. (a) Evolution of trajectory 6, depicting graphene nucleation and defect rings healing on Cu(111). Defect healing mechanisms discussed in the text (white circle) are included in supporting information. (b) Formation statistics polygonal carbon rings as a function of simulation time for trajectory 6.

Snapshots depicted in Figure 1(a) typify the dynamics of graphene nucleation observed on the surface-molten Cu(111) surface. As predicted, the basic chemical reaction observed here is similar to that observed on Ni(111). The formation of extended polyyne chains and Y-junction precursors were common and immediate following the deposition of a high density of C_2 fragments. Following the formation of these polyyne chains, subsequent ring condensation and the formation of sp^2-hybridized islands is rapid. This simulation provides the first evidence of defect healing during graphene growth, which potentially underpins the high structural quality observed in graphene grown on Cu catalysts. Figure 1(a) shows a structure (1.4 ps) consisting of approximately 50% structural defects *i.e.* pentagonal and heptagonal rings. Following a further 50 ps, this highly defective structure – reminiscent of Haeckelite – was transformed into an essentially pristine graphene

structure, *i.e.* one composed almost completely from carbon hexagons. This is confirmed in Figure 1(b), which quantifies the population of different polygonal carbon rings in the structure during the course of the trajectory. The transformation of this originally defective structure took place via a number of chemical pathways, yet in all cases was driven by the mobility of the Cu atoms in the underlying catalyst surface. For example, the pentagon-heptagon defect (indicated by the circle in Figure 1(a)) observed at 1.4 ps was healed by 2.67 ps. This process is driven by the diffusion of a single Cu atom in the surface layer which opens a vacancy in the Cu(111) surface, and consequently forces the cleavage of a C-C bond in the heptagon. The terminal carbon in the polyyne chain thus formed then resides in the surface vacancy, due to attractive forces between it and the Cu surface, and this facilitates the formation of the hexagon in place of the original heptagon defect. The attraction between this terminal carbon atom and the Cu surface is sufficiently strong so that it is cleaved from the hexagon and diffuses into the subsurface region of the catalyst. The neighboring pentagon defect was subsequently healed into a hexagon via a comparable chemical route – first C-C bond cleavage and then ring closure, both being driven by the dynamics of the underlying substrate.

The formation of polygonal carbon rings on the molten Cu(111) is remarkably different compared to that observed using Ni(111). Ring formation in the latter case is essentially instantaneous (due to the artificial nature of the initial conditions employed), with the final structure obtained essentially within *ca*. 2.5 ps (Figure 2). Conversely, using Cu(111), the ring formation statistics evolve over a much longer period. Initially increasing sharply (*ca* 5 ps), it takes a further 30 ps for the ultimate populations of pentagons, hexagons and heptagons to be obtained on Cu(111). This is because the nucleating graphene structure is constantly being reorganized by the underlying catalyst atoms towards the most thermodynamically favorable configuration (one consisting entirely of hexagons). Consequently, the population of hexagons observed using graphene becomes maximized compared to heptagons and, more importantly, pentagons. This is not the case on Ni(111), for which approximately equal populations of pentagons and hexagons are formed.

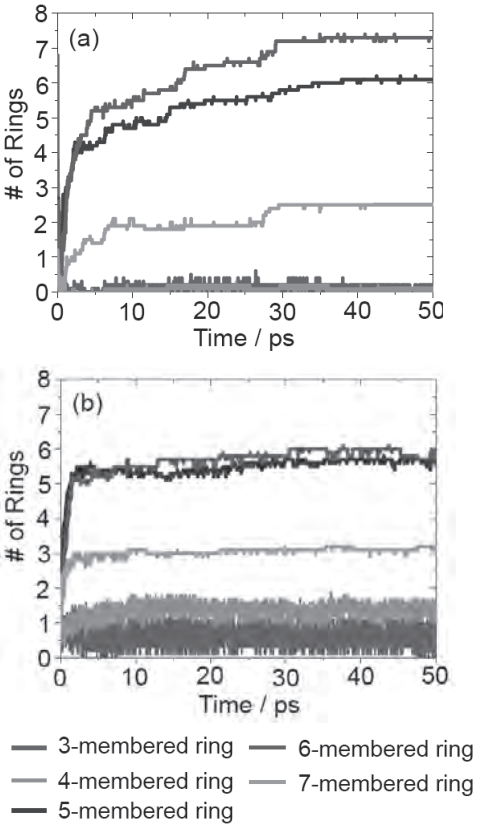


Figure 2. Average polygonal carbon ring populations observed during graphene nucleation on (a) Cu(111) and (b) Ni(111) surfaces. The final graphene structures observed on Cu(111) take an order of magnitude longer to be achieved than for Ni(111), as the atomic configuration of the structure is constantly rearranged by defect healing mechanisms. By contrast, the final graphene structure on Ni(111) is obtained almost immediately, within *ca*. 5 ps. All data averaged over 10 trajectories.

2. Original papers

(1) H-B. Li, A. J. Page, A. M. Mebel, S. Irle, and K. Morokuma, "Graphene Nucleation on a Surface-Molten Copper Catalyst: Quantum Chemical Molecular Dynamics Simulations", *Chem. Sci.* accepted, 2014.

3. Oral Presentations at Academic Conferences

(1) H-B. Li, A. J. Page, S. Irle and K. Morokuma, "SWCNT Growth from Organic Precursors without a Catalyst: Possibility and Limitations Revealed by Theoretical Simulations", *NT14*, USC, University of Sourthern California (June. 1, 2014)

(2) H-B. Li, A. J. Page, S. Irle and K. Morokuma, "Graphene Nucleation on a Surface-Molten Copper Catalyst: QM/MD Simulations", *NT14*, University of Sourthern California, USA (June. 7, 2014)

Lung Wa CHUNG

Postdoctoral Fellow

1. Summary of the research of the year

1. Application of Ab Initio Density Matrix Renormalization Group (DMRG) on the Simplest Fe(IV)-Oxo Complex. Iron-containing oxygenases catalyze many important biochemical oxidations. High-valent Fe(IV)-oxo species has been observed or proposed as an active oxidant in many of these oxygenases. Previous studies on Fe(IV)-oxo species were mostly based on single-reference DFT method. Recent rapid development of ab initio density matrix renormalization group (DMRG), e.g. DMRG-CASSCF and DMRG-CASPT2, allows us to use a much larger active space than the conventional CASSCF method. Through collaboration with Drs. Kurashige and Yanai, I studied the state order of the simplest Fe(IV)-oxo complex and its reactivity towards CH_4 by using various QM methods (e.g. DFT, DMRG-CASSCF, DMRG-CASPT2, RASSCF, RASPT2) (Figure 1). PES computed by DMRG-CASPT2 is qualitatively similar to that evaluated by the B3LYP method, esp. significant dynamic correlation observed in the product side.

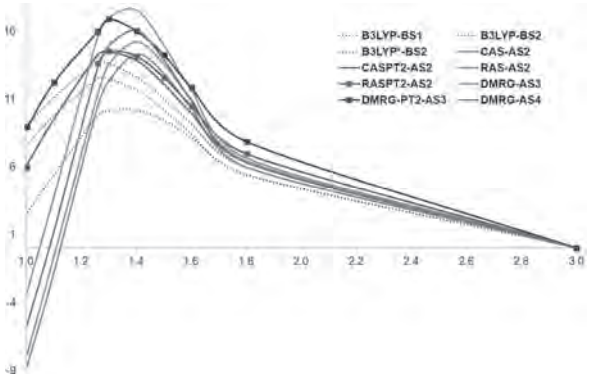


Figure 1.

2. Heavy-atom Tunneling in Cyclobutadiene: Quantum mechanical tunneling plays an important role in enhanced reactivity of some organic and enzymatic reactions. Generally, tunneling probability increases with smaller masses of atoms involved, as well as a lower reaction height and narrow barrier width. Thus, tunneling involving electron or hydrogen was commonly observed. Besides, more reactions mediated by heavy-atom tunneling have been suggested or observed by experimental and computational means. For instance, Carpenter proposed that automerization of cyclobutadiene (CBD) involves dominant heavy-atom tunneling below 0 ^{o}C. I carried out high-level QM (QM = CASSCF, CASPT2 and MRCI) calculations and variational transition state theory (VTST) with multidimensional tunneling simulations to elucidate realistic and detailed heavy-atom tunneling of cyclobutadiene (Figure 2). These semi-classical results suggest that the heavy-atom tunneling dominates the reaction rate, even around the room temperature.

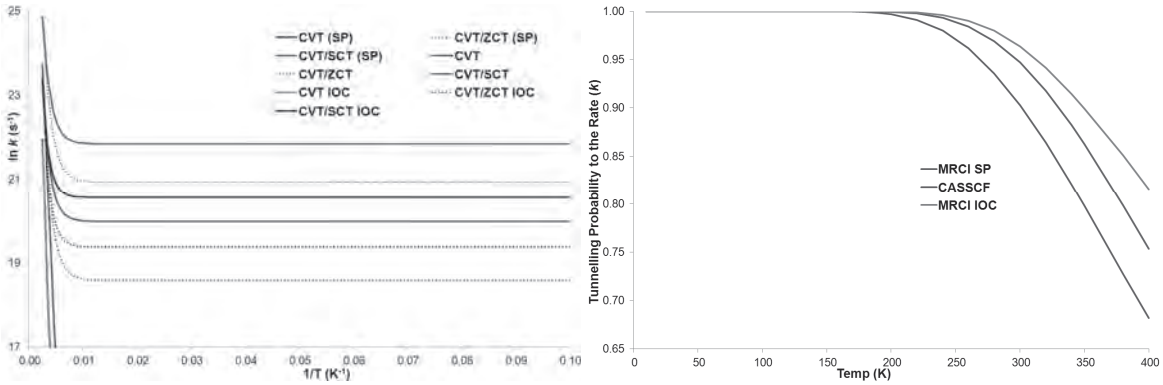


Figure 2.

3. A Theoretical Study on the UVR8 Photoreceptor: By the irradiation of ultraviolet-B (UV-B) light, UVR8 photoreceptor can undergo dissociation of the protein homodimer and regulate gene expression in plants. We have carried out high-level quantum mechanics (QM) and ONIOM(QM:MM) calculations to study spectra of key tryptophan residues in UVR8 homodimer. Benchmark calculations on the absorption and emission of 3-methylindole in the gas phase have been performed by different QM methods (TD-DFT, CASSCF, MS-CASPT2, and SAC-CI). Twenty different DFT functionals, including double hybrid and Minnesota functionals, were tested, but all these functionals failed to give satisfactory description of two key transitions. In comparison, SAC-CI and CASPT2 methods can give reliable transition energies and a correct order of 1La and 1Lb excited states. Furthermore, the vertical absorption and emission energies of tryptophan in UVR8 have been investigated by the ONIOM method (Figure 3). Our results supported that W285 is the major chromophore of UVR8, while W233 can also sense the UV-B light. Geometrical effects as well as electrostatic and polarization interactions with the protein matrix were found to influence optical properties of these tryptophan residues in UVR8.

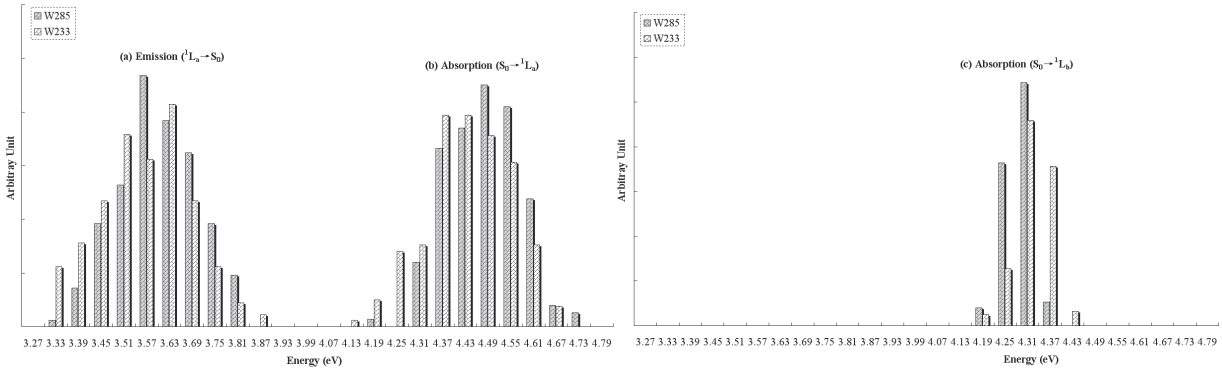


Figure 3. Histograms of distribution of the ONIOM computed (a) $^1L_a \rightarrow S_0$ emission, (b) $S_0 \rightarrow {}^1L_a$ absorption and (c) $S_0 \rightarrow {}^1L_b$ absorption for W285 and W233 in UVR8.

2. Original papers

(1) Ding, L.; Chung, L. W.; Morokuma, K. "Reaction Mechanism of Photoinduced Decarboxylation of the Photoactivatable Green Fluorescent Protein: An ONIOM(QM:MM) Study" *J. Phys. Chem. B* **2013**, *117*, 1075.

(2) Ding, L.; Chung, L. W.; Morokuma, K.* "Excited-State Proton Transfer Controls Irreversibility of Photoisomerization in Mononuclear Ruthenium(II) Monoaquo Complexes: A DFT Study", *J. Chem. Theory Comput.* **2014**, *10*, 668.

(3) Li, X.;* Chung, L. W.; Morokuma, K.;* Li, G. "A Theoretical Study on the UVR8 Photoreceptor: Sensing Ultraviolet-B by Tryptophan and Dissociation of Homodimer", *J. Chem. Theory Comput.* **2014**, DOI: 10.1021/ct5003362.

(4) Chung, L. W.; Hrovat, D. A.; Morokuma, K.; Borden, W. T. "Dominant Heavy-Atom Tunneling from the Vibrational Ground State in Automerization of Cyclobutadiene Below Room Temperature", Manuscript in preparation.

(5) Chung, L. W.; Kurashige, Y.; Yanai, T.; Morokuma, K.; "Ab Initio Density Matrix Renormalization Group Study of Hydrogen Atom Transfer with an Iron(IV)-Oxo Complex", Manuscript in preparation.

3. Presentation at academic conferences

(1) Lung Wa Chung, Xin Li, Keiji Morokuma, "A Recent Mechanistic Insight and Comparative Reactivity of Fe(III)-Superoxo and Fe(IV)-Oxo: DFT, QM/MM and Multi-Reference Methods", The 4th Asian Conference on Coordination Chemistry (ACCC4), Jeju, November 5, 2013 ("invited lecture").

Galina PETROVA

JST Fellow, Fukui Kenichi Memorial Research Group I

1. Summary of the research of the year

Our research in the last year was concentrated on the theoretical modeling of experimentally studied asymmetric organic reactions catalyzed by different homogeneous catalysts: a Cu/DNA supramolecular catalyst [Sugiyama et al. Chem. Commun. 2012], phase-transfer catalysts [Maruoka, Tetrahedron 2006], or asymmetric counteranion directed catalysis [List et al. Angew. Chem. Int. Ed. 2013; Chem. Eur. J. 2012]. The aim of the theoretical investigations was to gain better knowledge on the reaction mechanisms and the nature of the enantio(stereo) selectivity which may allow further modifications of the catalysts and the experimental conditions. In modeling the reaction mechanisms we applied the artificial force induced reaction (AFIR) method [Maeda, Ohno, Morokuma, Phys. Chem. Chem. Phys. 2013], in order to find all possible conformations of the transition state (TS) structures without prejudice.

The origin of enantioselectivity for intramolecular Friedel-Crafts reaction catalyzed by supramolecular Cu / DNA catalyst complex

As a first stage of our investigation, we performed a combined MD and QM/MM theoretical study on the binding of L-Cu(II)-R complex to d(CAAAAATTTTTG)$_2$ dodecamer. The L-Cu(II)-R complex consisted of bipyridine (L) and the reactant (R) that undergoes the unimolecular FC reaction. The main goal was to find the preferred conformation of the L-Cu(II)-R / DNA reactant complex and to explain the influence of DNA micro-environment on the enantioselectivity of the reaction. We modeled 28 structures of the Cu / DNA supramolecular catalyst with different initial conformation of L-Cu(II)-R, two pro-*S* and two pro-*R*, and different intercalation position in the DNA strand considering all symmetrically unique base pairs layers (BP layers). In the comparison of different Cu / DNA complexes, several important features were taken into account: energetic characteristics of the system as binding energy and energy of deformation, deformation of the DNA strand, and deformation of the metal complex.

Intercalation of the metal complex at the edge of the DNA strand, BP layers C1/A2, was found least favorable and hardly induced any distortion of the DNA structure from the standard B type DNA. Structures with intercalation of L-Cu(II)-R in the central part of the DNA dodecamer (BP layers A4/A5, A5/A6, A6/T7) showed higher binding energy BE^{MD} as well as higher energy of interaction $Eint^{QM/MM}$. These complexes showed slight DNA distortion towards A type DNA and more pronounced axis bending. As a result of the interaction with the DNA strand, the metal complex itself was also deformed as loss of the indole-imidazol π-π stacking of the reactant and the electrostatic interaction between the π-electrons and the Cu(II) center was observed. Some of the complexes exhibited conformation with the indole moiety enveloped in the DNA minor groove.

On the base of the obtained results and energetic and structural analyses, the preferred formation of the *S* product in the experimental studies could be explained on the base of several characteristics of the system:

(*i*) Stability of the supramolecular complexes: pro-*S* structures showed higher binding energy to the

DNA strand, and the formation of pro-*S* Cu / DNA complexes should be preferred to the formation of pro-*R* reactant complexes (Fig. 1a).

(*ii*) Short C3-C2' distance in the supramolecular complexes: the C3-C2' distances in the pro-*S* complexes are shorter in comparison to the pro-*R* structures and closer to the expected TS structures (Fig. 1b). This feature also suggests the reaction to occur more easily for the pro-*S* structure. The pro-*S* structures are usually only shallowly intercalated in the DNA strand, which would also facilitate TS formation decreasing the energy required for conformational changes.

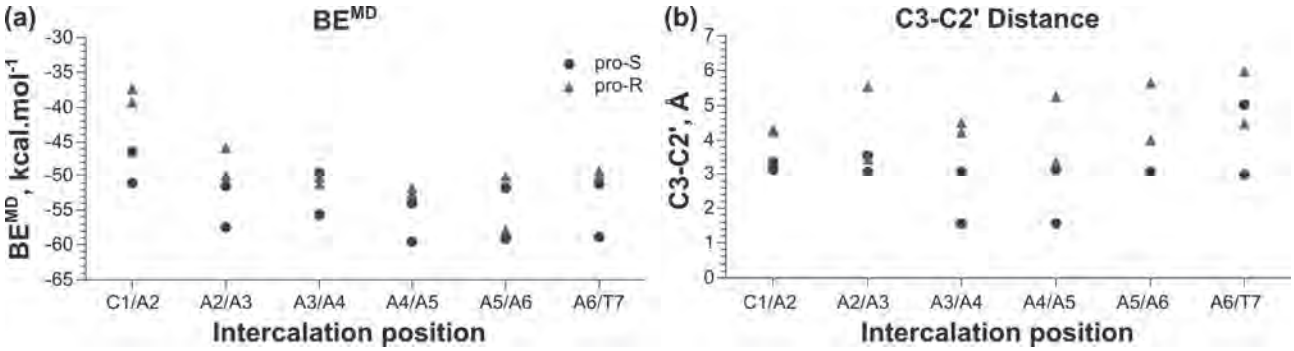


Figure 1. (a) Binding energy of L-Cu(II)-R to DNA1, BE^{MD}, estimated at MD level; (b) C3-C2' distances in the supramolecular L-Cu(II)-R / DNA1 structures optimized at level M. Red triangles represent pro-R (R1 & R2) structures, blue circles are used for pro-S (S1 & S2) structures.

The next stage of our study was focused on modeling the mechanism of the intramolecular Friedel-Crafts reaction. The simulations were performed with 12 initial L-Cu(II)-R / DNA supramolecular complexes, featuring the 4 conformations of the L-Cu(II)-R complex and 3 intercalating positions, DNA_56, DNA_67, and DNA_67maj with L-Cu(II)-R intercalated between BP layers 56 (AT-AT) and 67 (AT-TA) with R on the minor groove side and 67 (AT-TA) but with reactant on the major groove side of DNA. All initial L-Cu(II)-R / DNA supramolecular complexes were subjected to C3-C2' bond formation TS search within the AFIR approach.

The first C3-C2' bond formation stage of the reaction involving L-Cu(II)-R / DNA_56 complex with pro-*S* conformation of the reactant was the most favorable within the whole set of data. It was characterized by a very low C3-C2' bond formation TSII32' (DNA_56_*S*2_$TSII_{32'}$, 2.6 kcal.mol^{-1}) leading to formation of a very stable intermediate (i.e. reverse reaction would not be favored or expected to occur). The following hydrogen transfer stage was found somewhat high in energy even through a water molecule (Fig. 2). If two water molecules were considered to take part in this stage, the barrier for proton abstraction from C2' (through TS DNA_56_*S*2_$TSIV_{32'}$ww, 25.3 kcal.mol^{-1}) was decreased by 10.1 kcal.mol^{-1}. This TS, however, was found to connect to the relatively unstable intermediate structure DNA_56_*S*2_$V_{32'}$ww (24.5 kcal.mol^{-1}) in which the abstracted proton remained in the H_3O^+ moiety instead of being transferred to C2. Our attempts to locate the TS for the next HT (from H_3O^+ to C2 or the carbonyl O) failed which may mean that the process was spontaneous or close to barrierless.

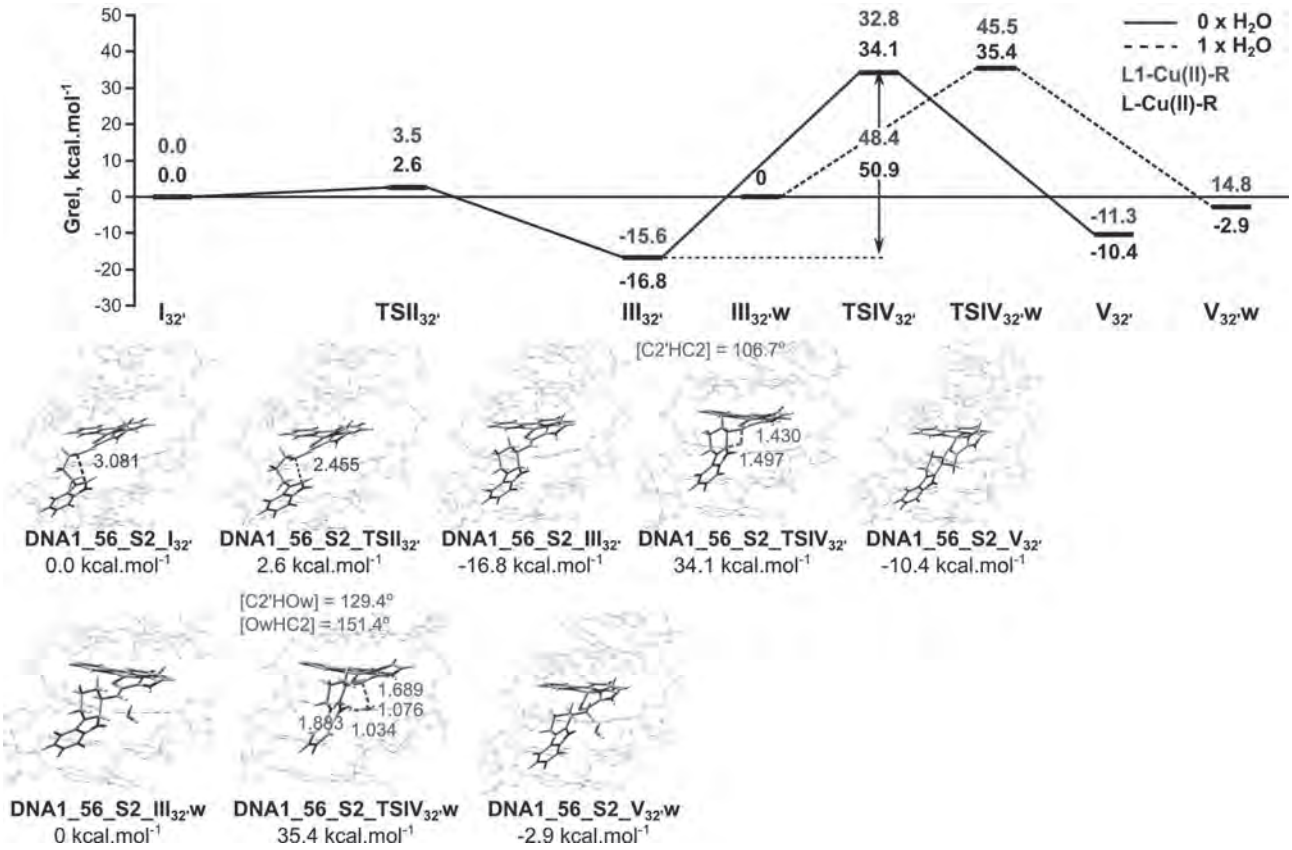


Figure 2. Energy diagram and intermediate and TS structures for the intramolecular Friedel-Crafts reaction in the case of the pro-*S* L-Cu(II)-R(*S*2) / DNA_56 supramolecular complex: L = bipyridine, L1 = 5,6-dimethylphenantroline. Important interatomic distances (in Å) are provided; blue color is used for the C-C bond formation distances, red color for H-bonds. Solvating water molecules and charge compensating Na^+ are not shown for simplicity.

Asymmetric phase-transfer catalysis with homo- and heterochiral quaternary ammonium salts

We also performed a thorough theoretical study of phase transfer quaternary ammonium catalysts designed in Maruoka group in attempt to gain better understanding in the properties and catalytic behavior of the homo- and heterochiral forms of these systems. For this pupose, we modeled the interconversion of the homo / heterochiral forms of conformationally flexible catalysts, simulated and analyzed the ^{1}H NMR spectra of chiral forms of several different quaternary ammonium salts as well as their performance in asymmetric catalysis for the interaction of the imine ester of glycine ester and benzyl bromide. Considering the complexity of the system and its flexibility as well as the fact that the catalyst does not participate actively in the catalyzed process but only provides the local asymmetric environment via electrostatic and short-range interactions, we used AFIR method for automated TSs search.

The conformationally flexible analog was found to easily undergo interconversion from the homo- to the heterochiral form driven by the higher thermodynamic stability of the heterochiral isomer and resulting in alternation in catalytic behavior. Theoretical calculations of ^{1}H NMR spectra of the two isomers for different model systems are in good agreement with the experimental data, allowing us to conclude that the up-field shift of

signals for the benzylic protons in the heterochiral form could be explained by increase in the shielding effect of the aromatic parts of the system around these protons due to the conformational changes.

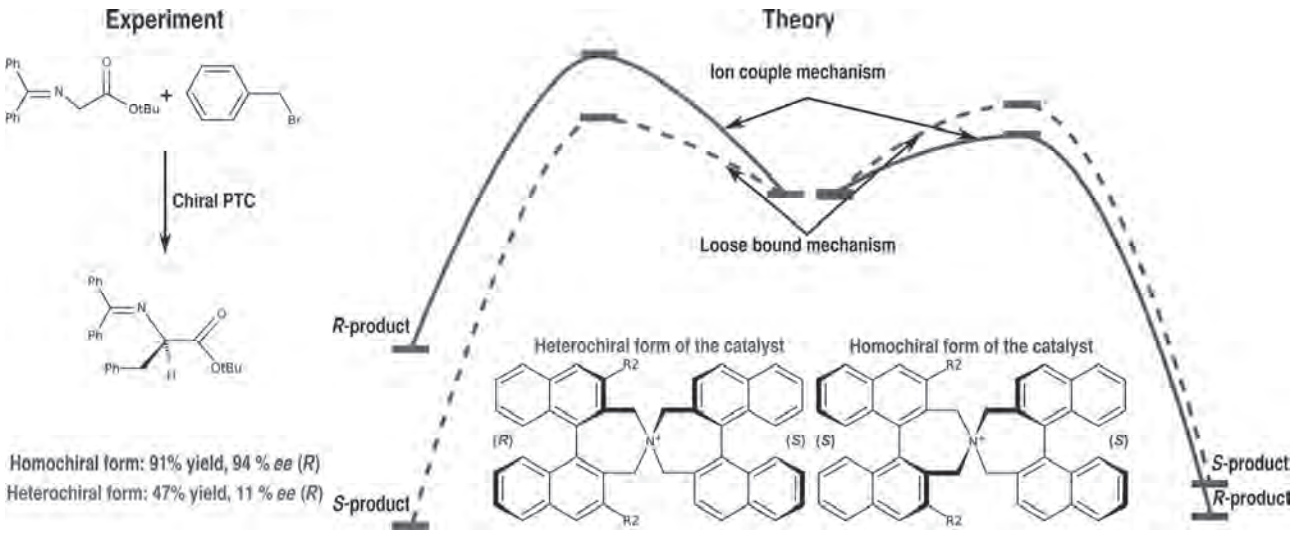


Figure 3. Summary of the experimental and theoretical results for asymmetric alkylation of glycine Schiff base under phase-transfer catalytic conditions.

By applying the automated TS search procedure for the alkylation of glycine derivatives catalyzed by the homo- / heterochiral form of a conformationally rigid analog (Fig. 3), we were able to locate more than 40 configurations of possible TS structures. The homochiral form was theoretically confirmed to catalyze the formation of predominantly *R*-product of the reaction, while for the heterochiral form the catalytic activity was found to depend on two factors: (*i*) formation of a tight ion pair between the catalyst and the glycine derivative, which resulted in decrease in the reaction rate, in agreement with the experimental data, and formation of only the *R*-product; and (*ii*) the possibility that the reaction occured without the initial formation of the ion pair or after its dissociation, in which case the formation of *S*-product was predominant. The combined effects of both factors could explain the lower reaction rate and the poor enantioselectivity observed experimentally for the heterochiral form.

2. Original papers

(1) G. P. Petrova, H.-B. Li, K. Maruoka, K. Morokuma, “Asymmetric Phase-Transfer Catalysis with Homo- and Heterochiral Quaternary Ammonium Salts: A Theoretical Study”
J. Phys. Chem. B, 2014, 118 (19), pp 5154–5167

(2) G. P. Petrova, Z. Ke, S. Park, H. Sugiyama, K. Morokuma, “The origin of enantioselectivity for intramolecular Friedel–Crafts reaction catalyzed by supramolecular Cu/DNA catalyst complex”
Chem. Phys. Lett., 2014, 600, pp 87–95.

3. Presentation at academic conferences

4. Others

Travis HARRIS

Research Fellow, Fukui Kenichi Memorial Research Group 1

1. Summary of the research of the year

I. Density Matrix Renormalization Group Calculations of Magnetic Exchange Coupling in Dinuclear Transition Metal Complexes

The applicability of *ab initio* multireference wavefunction-based methods to the study of magnetic complexes has been restricted by the quickly rising active-space requirements of oligonuclear systems and dinuclear complexes with $S > 1$ spin centers. *Ab initio* density matrix renormalization group (DMRG) methods built upon an efficient parameterization of the correlation network enable the use of much larger active spaces, and therefore may offer a way forward. In this research, we applied DMRG-CASSCF to the dinuclear complexes $[Fe_2OCl_6]^{2-}$ and $[Cr_2O(NH_3)_{10}]^{4+}$. After developing the methodology through systematic basis set and DMRG M testing, we explored the effects of extended active spaces that are beyond the limit of conventional methods. The calculated exchange coupling constants (J of the Heisenberg spin-Hamiltonian $H = -2JS_AS_B$) for $[Fe_2OCl_6]^{2-}$ from various methods with a triple-ζ ANO-RCC basis set are shown in Table 1. The J values were derived from the lowest spin states, $S = 0$ and 1, because the higher spin states were not significantly populated in the temperature-dependent magnetic susceptibility experiments from which the J value was derived. We find that CASSCF with the minimal active space, (10,10), gives the weakest magnetic coupling of −39.7 cm^{-1}, just 34% of the experimental value (-117 cm^{-1}). Including O(2*p*) orbitals in (16,13) considerably strengthens the interaction to −58.6 cm^{-1}. Further inclusion of the virtual double shell orbitals for Fe(*d*) and O(*p*) in DMRG(16,26) captures a major portion of the dynamic correlation effects, leading to an accurate reproduction of the experimental value. The analogous active space for $[Cr_2O(NH_3)_{10}]^{4+}$ (12,32) also considerably improves upon the small active space results. For comparison, we performed conventional MRCI+Q calculations and the J values are consistent with those from DMRG-CASSCF. We also examined the full Heisenberg spin ladder and found that, in contrast to previous studies, the two studied complexes behave similarly, with weaker magnetic coupling at higher spin states, regardless of the computational method.

Table 1. J values for $[Fe_2OCl_6]^{2-}$ from various methods

method	J (cm^{-1})
CAS(10,10)SCF	-39.7
CAS(16,13)SCF	-58.6
MRCI(10,10)	-61.3
MRCI(16,13)	-96.3
MRCI+Q(10,10)	-75.6
MRCI+Q(16,13)	-115.3
DMRG(16,16)[1000]	-57.7
DMRG(10,20)[256]	-49.0
DMRG(16,26)[∞]	-117.4
exp	-117

[a] M values are given in brackets, but they can all be considered as saturated for the respective active spaces; thus they are not responsible for the differences in the listed DMRG J values.

II. Hydroboration Mechanism Revisited: Alkene Addition Partner Depends on Ligand and Substrate

This investigation of Rh(I)-catalyzed hydroboration with pinacolborane (HBPin) was prompted by an experimental finding that norbornene reacts faster than 1-octene, both yielding alkyl boranes. The catalytic cycle is shown in Figure 1. Addition of the alkene can occur through either an H migration or a B migration path followed by reductive elimination with C-B or C-H bond formation, respectively. The alkene addition partner (the migrating species) is typically considered to be the hydride, which leads to C-B reductive elimination. This reductive elimination step is expected to be rate limiting, and to have a lower barrier for the primary alkyl (octyl) than the secondary alkyl (norbornyl); thus, the hydroboration of norbornene may proceed through a different mechanistic pathway.

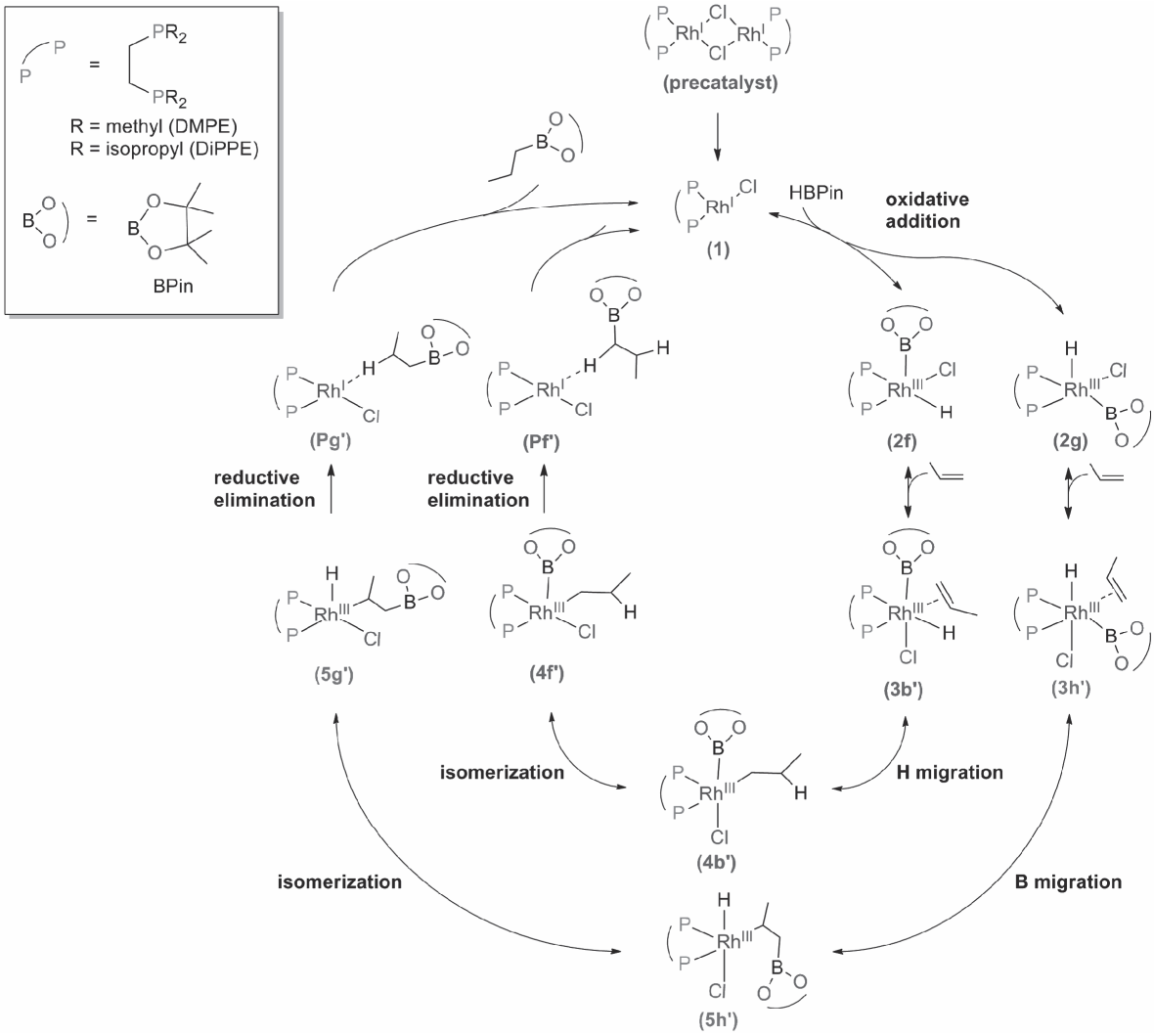


Figure 1. Catalytic cycle for Rh(I)-catalyzed hydroboration.

To determine why the hydroboration reaction is faster for norbornene than 1-octene, the catalytic cycles for RhCl(DiPPE) (DiPPE = 1,2-bis(diisopropylphosphino)ethane) were calculated

at the B3LYP/6-31G(d) level. 1-octene was modeled as propene, whereas norbornene was not truncated. For propene, H migration was rate limiting with a 20.2 kcal/mol barrier. The alternative pathway was less favorable with a B migration barrier of 23.3 kcal/mol followed by a rate-limiting reductive elimination step (23.6 kcal/mol). For norbornene, B migration had a lower barrier (18.4 kcal/mol) than H migration (25.1 kcal/mol), and both were the rate limiting steps in their respective paths. Thus, the addition partner is the hydride for propene, and BPin for norbornene. These two mechanisms are compared in Figure 2, which shows that norbornene has a lower rate-limiting barrier (18.4 kcal/mol) than propene (20.2 kcal/mol), as expected based on the experimental reaction rates.

In addition to the substrate dependence, the mechanisms are significantly affected by varying the ligand. Calculations with 1,2-bis(dimethylphosphino)ethane (dmpe) showed that the addition partner is the hydride for both substrates, whereas with 1,2-bis(ditertbutylphosphino)ethane (dtbpe) the addition partner is BPin for both. In summary, bulky ligands and norbornene both favor pathways in which BPin is the addition partner.

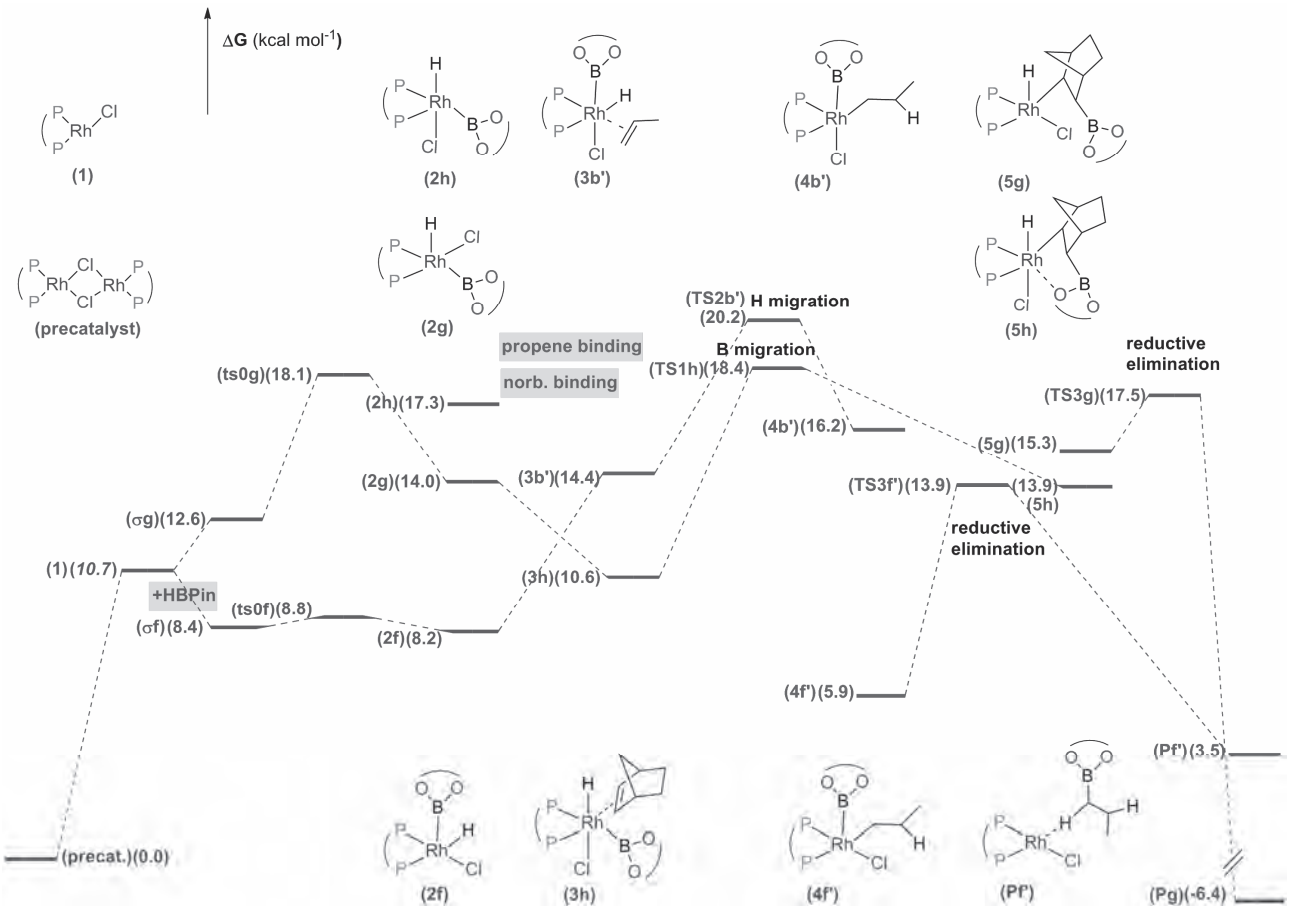


Figure 2. Free energy profiles of Rh-catalyzed hydroboration of propene and norbornene.

III. AFIR Study of [2Fe-2S] Cluster Degradation by NO

[Fe-S] clusters are biological targets of NO that disassemble, producing dinitrosyl iron complexes (DNICs), which are known to affect vasodilation, enzymatic activity, and other biological processes. To investigate the mechanism of [2Fe-2S] cluster degradation by NO, TPSSh/TZVP calculations for all possible reactions after addition of each NO molecule were carried out. The AFIR method was employed for a thorough assessment of the initial NO binding. Figure 3 shows the free energy profile for this initial binding process. The most favorable pathway involves NO insertion into an Fe-S bond, producing the intermediate EQ2. From here, a second NO can bind, resulting in cleavage of the Fe-S(NO) bond, followed by loss of SNO. The formation of two equivalents of DNIC products $[FeCl_2(NO)_2]^-$ thus requires 6NO, as two NO are involved in formation and dissociation of SNO. The full, detailed mechanism is currently in progress.

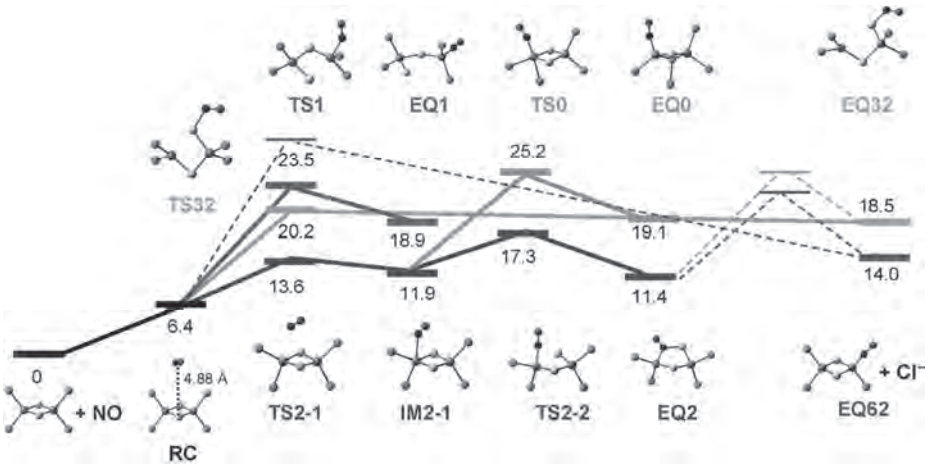


Figure 3. Free energy profile of NO binding to $[Fe_2S_2Cl_4]^{2-}$.

2. Original papers

(1) Harris, T. V.; Kurashige, Y.; Yanai, T.; Morokuma, K.
"*Ab Initio* Density Matrix Renormalization Group Study of Magnetic Coupling in Dinuclear Iron and Chromium Complexes"
J. Chem. Phys. 2014, 140 (5), 054303 (10 pages)

(2) Harris, T. V.; Szilagyi, R. K.
"Iron-Sulfur Bond Covalency from Electronic Structure Calculations for Classical Iron-Sulfur Clusters."
J. Comput. Chem. 2014, 35 (7), 540-552

(3) Harris, T. V.; Morokuma, K.
"QM/MM Structural and Spectroscopic Analysis of the Di-iron(II) and Di-iron(III) Ferroxidase Site in M Ferritin"
Inorg. Chem. 2013, 52 (15), 8551-8563

5. Others

(1) Harris, T. V.; Kurashige, Y.; Yanai, T.; Morokuma, K.
"*Ab Initio* Density Matrix Renormalization Group Study of Magnetic Coupling in Dinuclear Iron and Chromium Complexes" (Poster)
11th FIFC Symposium (2014).

Miho ISEGAWA

Research Fellow

1. Photodissociation of nitromethane

Photodissociation pathways of nitromethane following $\pi \rightarrow \pi^*$ electronic excitation are investigated. The potential energy surfaces for four lowest singlet states are explored, and structures of many intermediates, dissociation limits, transition states and minimum energy conical intersections were determined using the automated searching algorism called the global reaction route mapping (GRRM) strategy. Geometries are finally optimized at CASSCF(14*e*, 11*o*) level and energies are computed at CAS(14*o*,11*e*)PT2 level. The calculated preferable pathways and important products qualitatively explain experimental observations. The major photodissociation product CH_3 and NO_2 ($^2B_2$) is formed by direct dissociation from the S_1 state. Important pathways involving S_1 and S_0 states for production of various dissociation products CH_3NO + O (^1D), $CH_3O(X^2E)$ + NO ($X^2\Pi$), CH_2NO + OH and CH_2O + HNO, as well as various isomerization pathways have been identified. Three roaming processes also have been identified: the O atom roaming in O dissociation from CH_3NO_2, the OH radical roaming in OH dissociation from $CH_2N(O)(OH)$, and the NO roaming in NO dissociation from CH_3ONO.

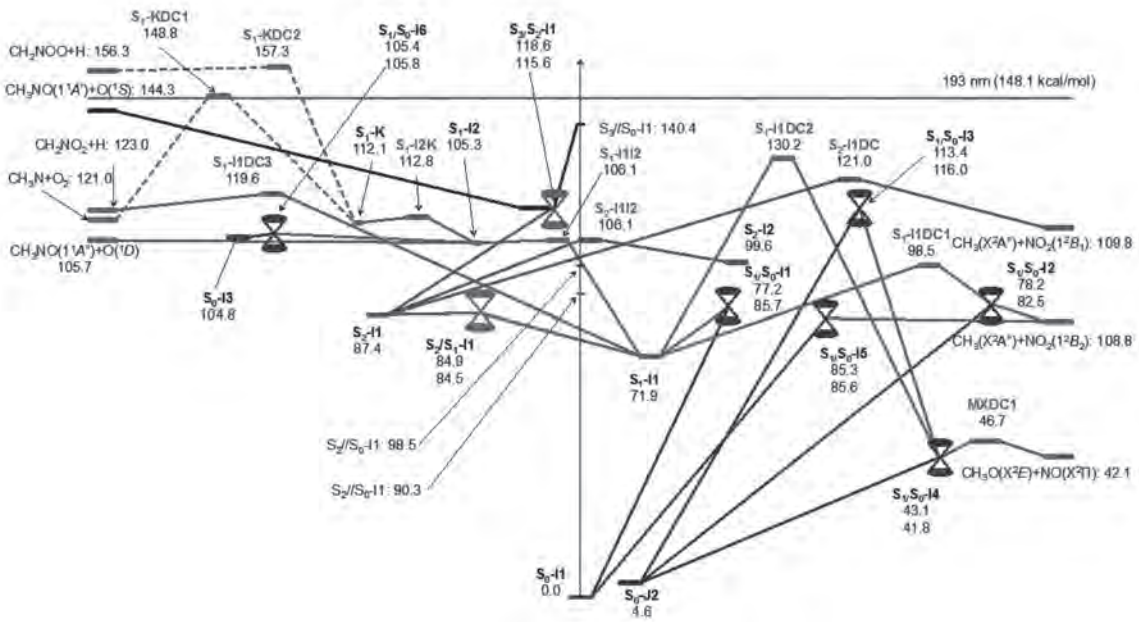


Fig. 1 S_3 (black), S_2 (green), S_1(red), and S_0 (blue) potential energy profiles (in kcal/mol) calculated at the MS-CAS(14*e*,11*o*)PT2/6-311++G**//CASSCF(14*e*,11*o*)/6-31G* level. There are one S_3/S_2 (ocher), one S_2/S_1 (cyan) and five S_1/S_0 (purple) minimum energy conical intersections (MECIs). Two energy values are given for each CI; one for the upper state and the other for the lower state. Label of transition state (TS) is given by red and label of minimum (MIN) is given by black. The horizontal bar in side of S_3/S_2-I1 means S_3 minimum is the same structure as S_3/S_2-I1. The grey lines in the middle show energy of 193nm photon, 148.1 kcal/mol, and calculated vertical excitation energy S_3//S_0-I1. IRC paths given by dotted line are above the energy of 193 nm photon.

2. CASPT2 study of reaction paths starting from $N(^2D) + H_2NO$

We investigated reaction paths staring from $N(^2D) + H_2O$ for doublet spin states, D_0 and D_1. The potential energy surfaces are explored in an_automated fashion using global reaction root mapping method (GRRM). The energy paths are confirmed by intrinsic reaction coordinate at the_CASPT2 level taking full valence electrons in the active space. Three roaming processes, two roaming dissociation and one roaming isomerization; (1) H_2NO → NOH--H → NO + H_2, (2) *cis*-HNOH → HNO--H → H--HNO → H_2 + NO, (3) H_2NO → H--HNO → HNO--H → *cis*-HNOH, are confirmed at the CASPT2 level. Some analogies with H_2CO system are observed for the structure in the roaming. The two roaming dissociations (1) and (2) should play important role to understand the reaction products, $NO(^2\Pi) + H_2$.

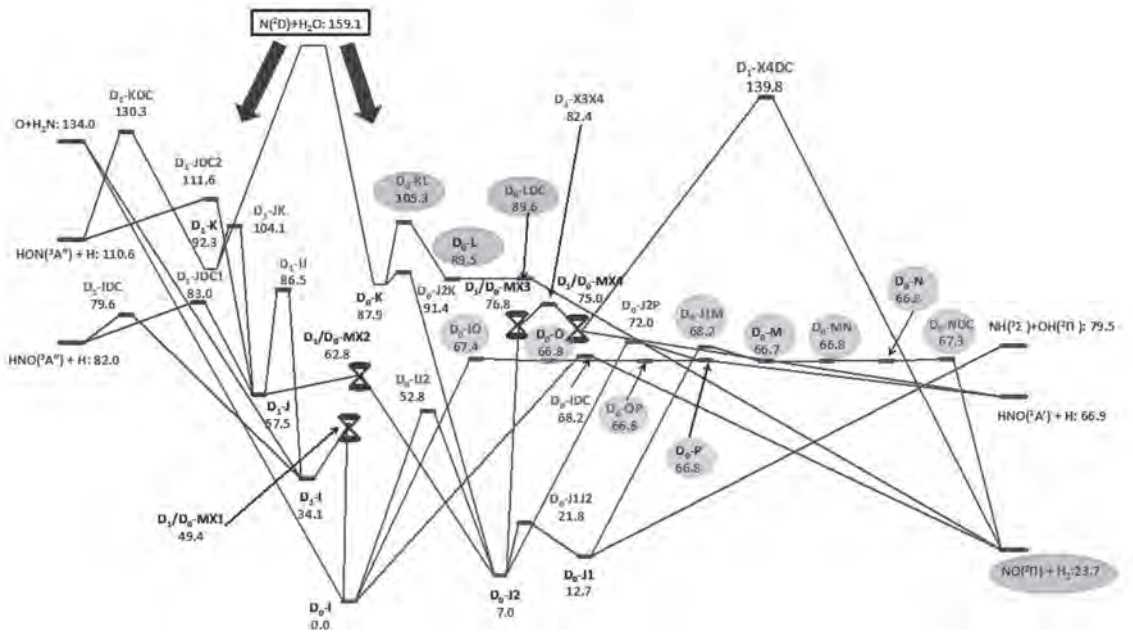


Fig. 2 Potential energy diagram of D_1 and D_0 for reactions starting from $N(_2D) + H_2O$ on D_1 and D_0 PESs. Both of structure and energy are determined at MS-CAS(13*e*,10*o*)PT2/cc-pVTZ level. This diagram includes four D_1/D_0 conical intersections, **D_1/D_0-MX1, MX2, MX3 and MX4**. Label of transition state (TS) is given by red and label of minimum (MIN) and conical intersection (MECI) is given by black. Critical points which relate to roaming process are marked with shadow circle.

3. Predicting pathways for terpene formation from first principles – routes to known and new sesquiterpenes

The Artificial Force Induced Reaction (AFIR) method is applied to predict cyclization/rearrangement pathways for carbocation precursors to sesquiterpenes. This method captures many of the features revealed in previous studies as well as new ones, including a pathway to a sesquiterpene not yet isolated in nature that we suspect will be in time.

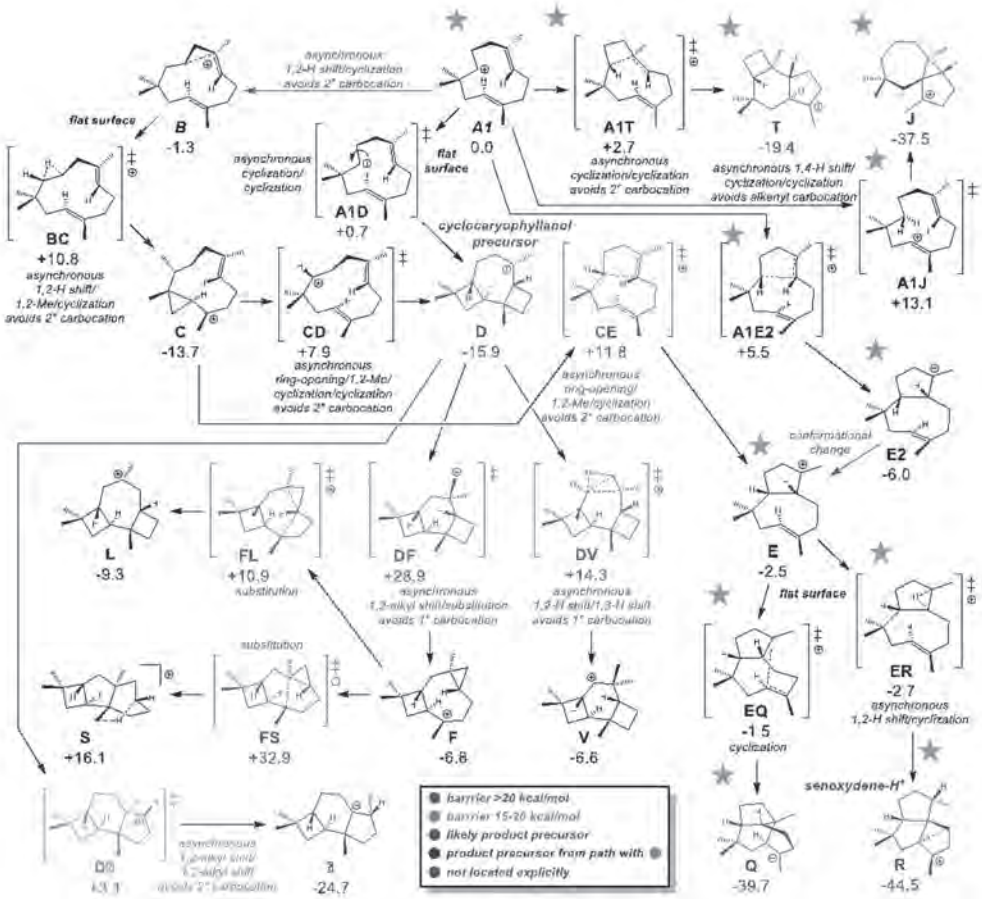


Figure 1. Reaction network arising from **A1** computed by mpW91PW91/6-31+G(d, p). Relative energies are shown in kcal/mol including zero point energy corrections. All of structures shown are newly found in this paper by quantum chemistry method, except for **A1** and **B**, given in italic, that are known previously. The pathways particularly focused in this paper are marked with stars.

4. Ring opening-closing mechanism of diarylethene induced by UV-visible photon: potential energy surface aapping by spin-flip time dependent density functional theory

Reaction mechanisms of laser induced ring opening and closing transformation are investigated for diarylethene (DAE) which works as a molecular switch and photo device. Spin-flip time dependent density functional theory is employed to reveal the reaction mechanism of the model system for three isomers, normal, inverse, and mixed types. The reaction mechanisms we proposed based on potential energy mapping and the intrinsic reaction coordinate (IRC) qualitatively explain the different quantum yields (QYs) for each type reported by Feringa's group.

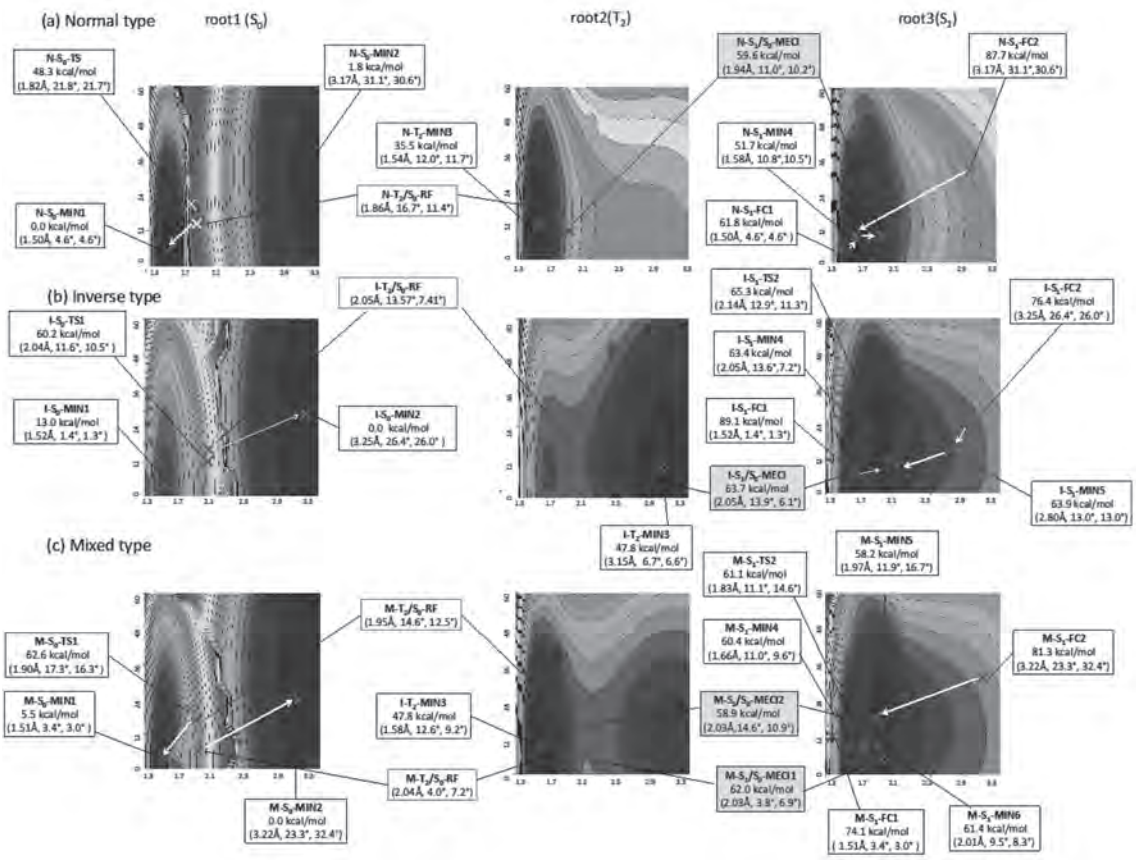


Fig 6 Contour map of S_0(root1) and S_1(root3) for (a) normal, (b) mixed, and (c) inverse type. Root1(mainly S_0), root2(mainly T_2) , and root3 (mainly S_1) from left to right.

5. Original paper

Miho Isegawa, Satoshi Maeda, Dean J. Tantillo, and Keiji Morokuma, “Predicting pathways for terpene formation from first principles – routes to known and new sesquiterpenes”, *Chemical Science*, **5**, 1555 (2014).

6. Presentation at academic conferences

(1) Miho Isegawa, Fengyi Liu, Satoshi Maeda, Keiji Morokuma,
“Ab initio reaction paths of nitromethane”,
The 7th Annual Meeting of Japan Society for Molecular Science, 2013

(2) Miho Isegawa, Satoshi Maeda, Dean J. Tantillo,
“Predicting pathways for terpene formation from first principles -routes to known and new sesquiterpenes”,
The 11th FIFC Symposium, 2014

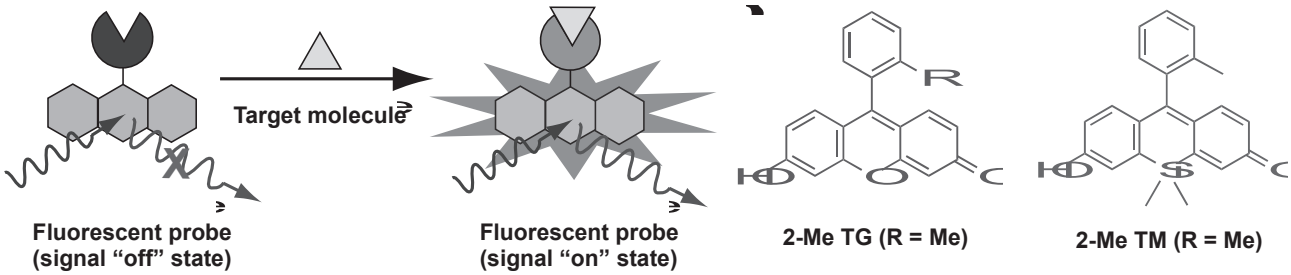
W. M. C. SAMEERA

Research Fellow, Fukui Kenichi Memorial Research Group 1

1. Summary of the research

Computational studies of fluorescent probes

Fluorescent compounds are powerful tools to visualize biological events in living cells and organisms. Small fluorescent compounds can be used as fluorescent probes, and they show a change of fluorescence properties in the presence of their target molecule (Figure 1a). There is a significant interest to design fluorescent probes for biological research, diagnosis, and treatment of diseases. Our focus in this study is two fluorescent compounds, TokyoMagenta (2-Me TM) and TokyoGreen (2-Me TG) (Figure 1b). The 2-Me TM system exhibits a large red-shift of the absorption spectrum upon deprotonation at basic conditions. Fluorescence intensity of the anion form of 2-Me TM is significantly larger than that of the neutral form. Therefore, 2-Me TM can be used as a fluorescence probe. In this study, we use computational methods to understand photophysical behaviours of 2-Me TM and 2-Me TG.

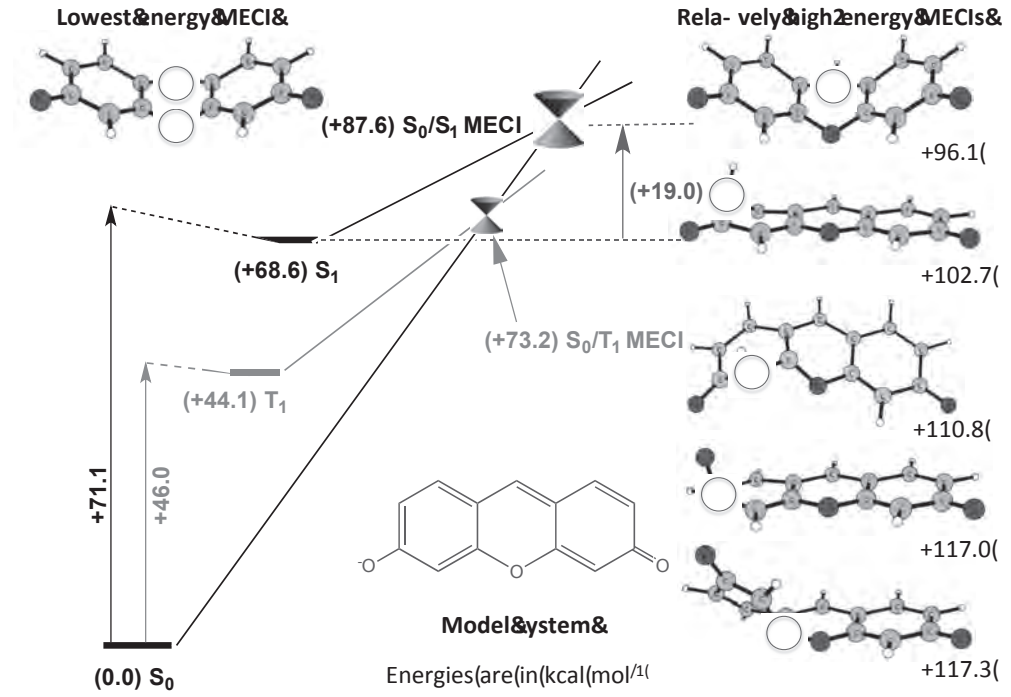


(a) **(b)**

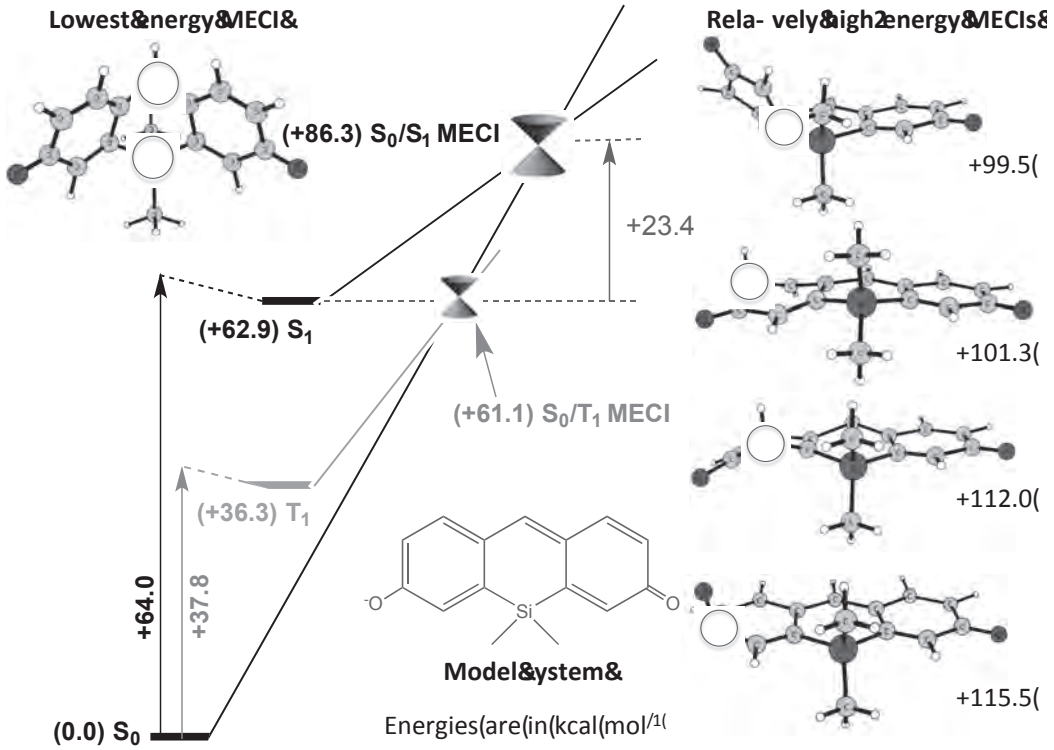
Figure 1. (a) Schematic representation of fluorescent probes. (b) Molecular structures of TokyoGreen (TG) and TokyoMagenta (TM).

In photochemical reactions, nonadiabatic transitions occur through the conical intersections (CIs). A CI is an f-2 dimensional intersection hyperspace between two or more potential energy surfaces of the same spin and space symmetry (f = the number of degrees of freedom). In the absence of low-energy a CI(s), nonradiative decay pathway becomes slower, and exhibits a high fluorescence quantum yield. In this project, I calculate S_0/S_1 minimum energy conical intersections (MECIs) of TM and TG with the spin-flip time-dependent density functional theory (SF-TDDFT) method in combination with the anharmonic downward distortion following (ADDF) method. I have systematically analysed possible S_0/S_1 MECIs of TokyoGreen and TokyoMagenta (model systems), and identified the lowest energy MECIs (Figure 2). Calculated potential energy surfaces are qualitatively similar for the both systems. The most striking difference is the barrier for going from S_1 equilibrium structure to S_0/S_1 MECI. In the case of 2-Me TG model system, S1 equilibrium structure is 68.6 kcal mol^{-1} higher in energy, and S_0/S_1 MECI is further 19 kcal mol^{-1} higher in energy. This barrier becomes 23.4 kcal mol^{-1} for 2-Me TM model system, and therefore

the nonradiative decay pathway is relatively difficult. This is in an agreement with the experimental observations. My future studies of this project will be focused on more complex fluorescent compounds. Our ultimate goal is to design fluorescent probes with very high fluorescence quantum yield.



(a)



(b)

Figure 2. Calculated S_0/S_1 MECIs of (a) TokyoGreen, and (b) TokyoMagenta (model systems). The BHandH functional was used in all calculations.

Computational studies of transition metal homogeneous catalysis

Transition metal homogeneous catalysis is an efficient way to perform catalytic reactions in a selective fashion. Quantitative mechanistic and selectivity details are very important to develop more efficient catalysis. The emergence of computational methods over the past two decades means that these properties can now be computed within the vicinity of chemical accuracy.

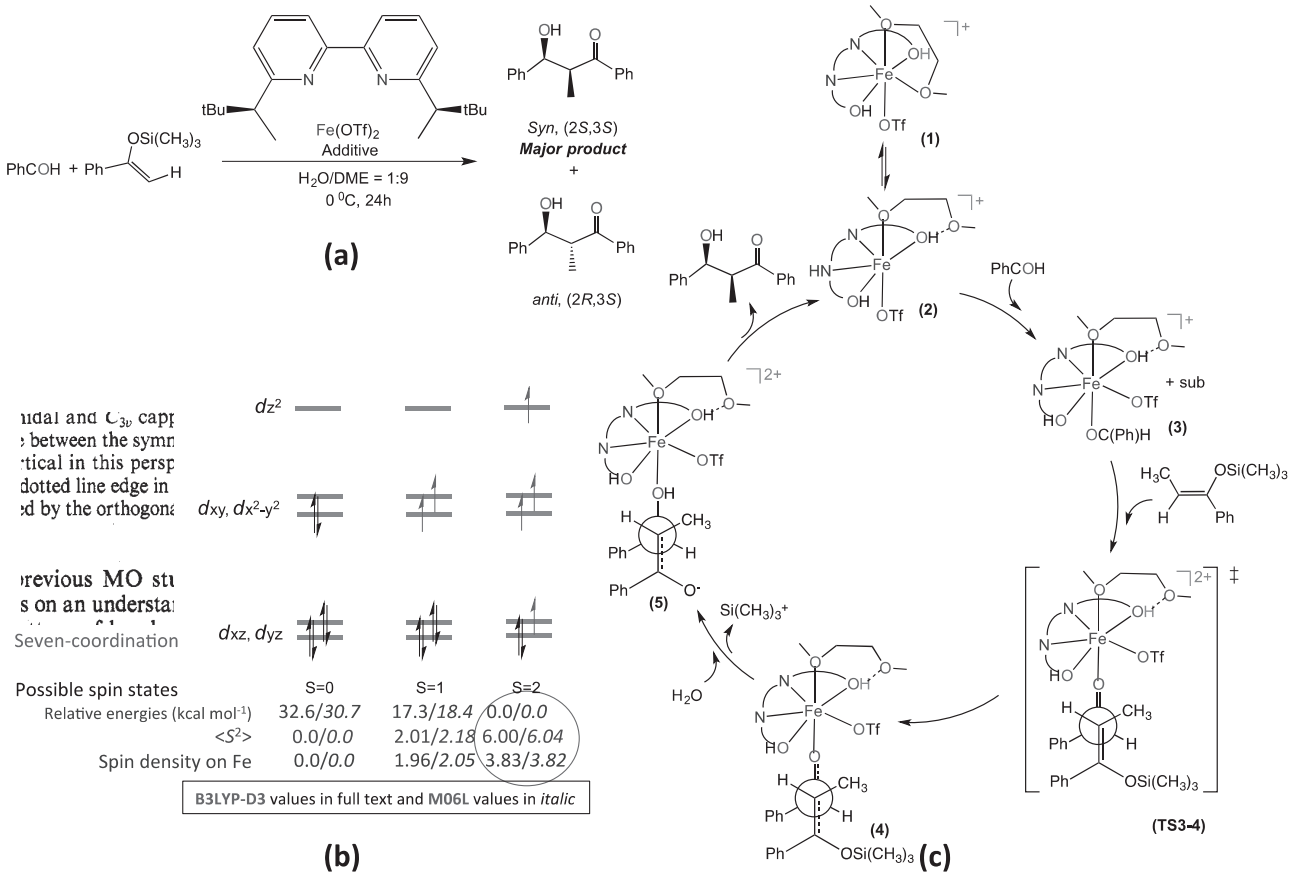


Figure 3. (a) Asymmetric Mukaiyama aldol reaction of silicon enolates with aldehydes catalysed by chiral Fe(II) complex, (b) electronic structure of $[Fe^{II}(L1)(DME)(H_2O)]^{2+}$ complex, (c) computed catalytic cycle [AFIR calculations: ONIOM(B3LYP-D3/LanL2DZ:PM6-D3). Structure optimizations: B3LYP-D3 functional, SDD for Fe, 6-31+G for O and N, 6-31G(d) for other atoms].

I study the asymmetric Mukaiyama aldol reactions of Kobayashi and co-workers. In their approach, reaction of silicon enolates and aldehydes is catalysed by a chiral a Fe(II) complex to afford the desired aldol product in a high yield and high diastereo- and enantioselectivity (Figure 3a). This reaction proceeds in the presence of water at 0 ^{0}C. They have used Brønsted acids and bases as efficient additives to increase the enantioselectivity of the reaction. My objective in this project is to develop a full catalytic cycle for the reaction, and explain the diastereo- and enantioselectivities. Electronic structural analysis of the $[Fe^{II}(L1)(DME)(H_2O)]^{2+}$ complex rationalized three important ligand field states (Figure 3b). Of these, thermodynamically stable electronic state is the quintet, while the triplet and single electronic states are significantly higher in energy. Similar trend can be observed for all seven-coordination Fe(II)-based complexes in this study, which suggests the

single-state reactivity. I have analysed the possible intermediates in the solution, and identified a low-energy pathway leading to the product (Figure 3c). According to the calculated catalytic cycle, selectivity-determining step of the mechanism is the carbon-carbon bond formation step (**TS3-4**).

Development of Gau_mopac2012 algorithm

In this project, I have been implementing the Gau_mopac2012 algorithm to perform ONIOM(QM:QM) calculations in combination with the Gaussian09 and Mopac2012 programmes. The ONIOM(QM:QM) implementation in Gau_mopac2012 supports for various semi-empirical methods available in the mopac2012 program. The Gau_mopac2012 package has three modules, namely *ext_mopac*, *make_inp*, and *make_out* to automate the overall mechanism shown in Figure 4.

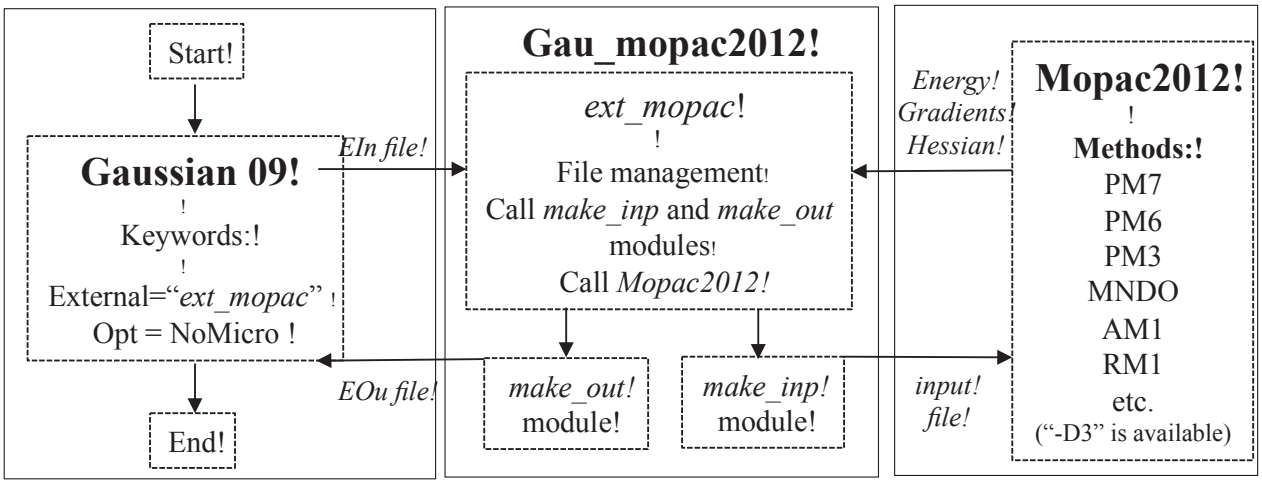


Figure 4. ONIOM(QM:QM) implementation in the Gau_mopac2012 algorithm.

The Gau_mopac2012 algorithm can be activated by using the *external="ext_mopac"* keyword in the Gaussian09 input file. Then the Gaussian09 programme provides text files with the *EIn* extension, and these files contain Cartesian coordinates and connectivity details of the atoms (both *real* and *model* systems). After that, *make_inp* module refers the information in *EIn* files to setup input files for the Mopac2012 and run Mopac2012 program. Finally, the *make_out* module reports energy and derivatives into a standard text file with the *EOu* extension, which can be recovered by the Gaussian09 programme.

2. List of original papers

1. W. M. C. Sameera, F. Lui, S. Maeda, K. Morokuma, "Spin-flip time-dependent density functional theory (SF-TDDFT) study of TokyoMagenta (2-Me TM) and TokyoGreen (2-Me TG)". (In preparation)
2. J. Llaveria, Á. Beltrán, W. M. C. Sameera, A. Locati, M. M. Díaz-Requejo, M. I. Matheu, S. Castillón, F. Maseras, P. J. Pérez, "Regio- and Stereoselective Silver-catalyzed aziridination of dienes: scope, mechanistic studies and ring-opening reactions", *J. Am. Chem. Soc.* 2014,

136, 14, 5342-5350.

3. E. M. Zueva, R. Herchel, S. Borshch, E. V. Govor, W. M. C. Sameera, R. McDonald, J. Singleton, Y. Sanakis, J. Krzystek, J. E. McGrady, and R. G. Raptis. Double exchange in a mixed-valent octanuclear iron cluster, $[Fe_8(\mu_4\text{-}O)_4(\mu\text{-}4\text{-}Cl\text{-}pz)_{12}Cl_4]^-$, *Dalton Trans.* 2014 (In press) [This article is part of themed collection: Synergy between Experiment and Theory]
4. L. Maestre, W. M. C. Sameera, M. M. Díaz-Requejo, F. Maseras, P. J. Pérez. "A General Mechanism for the Copper- and Silver-Catalyzed olefin aziridination reactions: concomitant involvement of the singlet and triplet pathways", *J. Am. Chem. Soc.* 2013, 135, 1338-1348.
5. I. Rivilla, W. M. C. Sameera, E. Alvarez, M. M. Díaz-Requejo, F. Maseras, P. J. Pérez, Catalytic cross-coupling of diazo compounds with coinage metal-based catalysts: an experimental and theoretical study. *Dalton Trans.* 42, 4132-4138, 2013. [This article is part of themed collection: Mechanistic Organometallic Chemistry]

3. List of presentations at meetings.

1. W. M. C. Sameera, F. Maseras, DFT and DFT/MM methods for mechanistic and selectivity studies of transition metal homogeneous catalysis. The 10th FIFC Symposium, Kyoto University. (Poster, 2014)
2. Development of hybrid methods for the study of photon-driven processes of interstellar ices. The chemical cosmos annual meeting, Windsor, United Kingdom. (Talk, 2013)
3. Density functional theory and density functional theory/molecular mechanics methods for modern homogeneous catalysis, University of Gothenburg. (Talk, 2013)

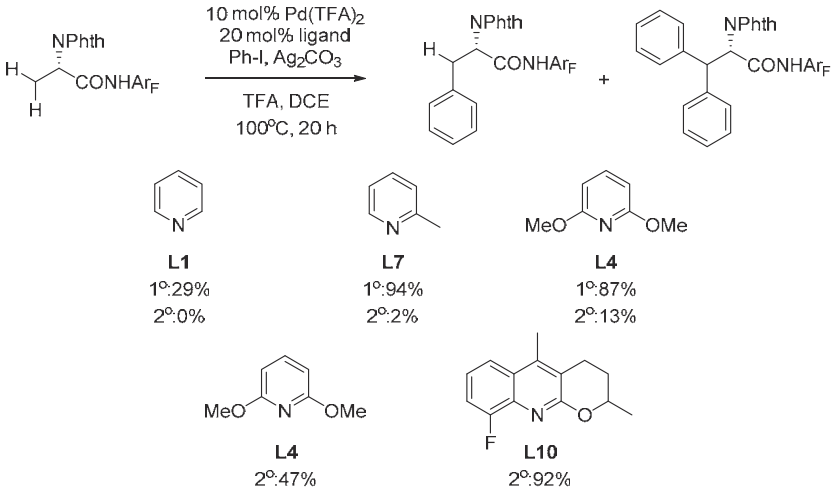
Julong JIANG

SPR Fellow

Research Topics

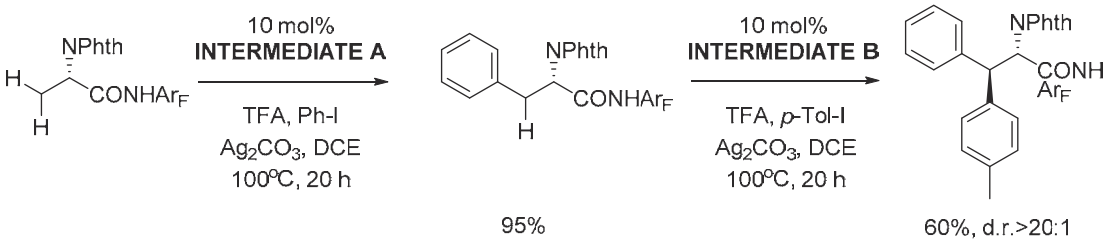
1. Theoretical investigation on the Pd-catalyzed C(sp^3)-H activation in the synthesis of unnatural amino acids

In the past several decades, the dominant strategy in the organic synthesis to form a C-C bond was through the transition metal catalyzed C-C coupling reactions. However, in most cases, a special starting material is required for the coupling reaction, for example, the boronic ester employed in the Suzuki reaction. It is not straightforward to synthesize those precursors and those reactions suffer from the decomposing of the reaction precursors. In recent years, people turned the focus to the direct C-H activation, which has the potential to be a general and powerful tool in the future's organic chemistry. The Yu's group in the Scripps research institute has reported a series of direct C-H activation reactions. Among them, a recent paper, which was published on *Science*, has the most exciting result as a direct C-H activation on sp^3 carbons. (Yu *et al.*, *Science*, **2014**, *343*, 1216).



Scheme 1 The Pd-catalyzed direct C(sp^3)-H activation

Not only for the primary C(sp^3)-H bond, by carefully choosing a ligand, a secondary C(sp^3)-H bond can also be activated for further C-C bond formation in a stereo-selective manner.

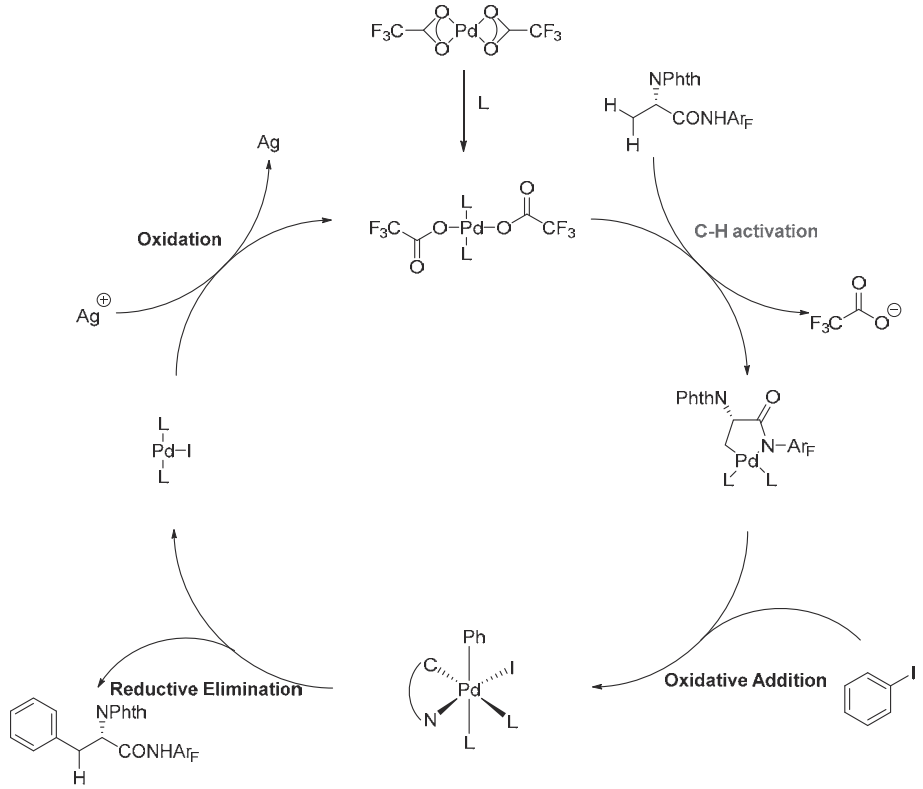


Scheme 2 Asymmetric C-C coupling reaction on the secondary sp3-carbon atom

However, as a pure synthetic publication, no details was given to discuss the mechanism. Thus, we decide to carry out a theoretical investigation on this reaction, in order to reveal the

mechanism for a general improvement of this reaction. Once the mechanism is unveiled, it will helpful to make the reaction as a general and effective strategy to functionalize a sp^3-carbon atom, which is pursued by most of organic chemists.

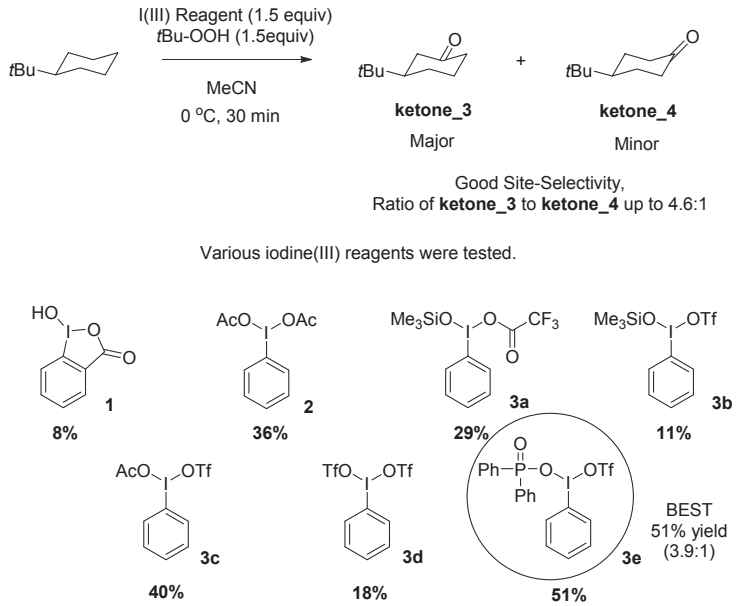
We have already proposed a mechanism as the model for our calculations. It seems that the palladium in this reaction goes through a Pd(II)-Pd(IV)-Pd(II) catalytic cycle, which is uncommon.



Scheme 3 Proposed mechanism for the C(sp^3)-H activation in which a Pd(II)-Pd(IV)-Pd(II) cycle is involved

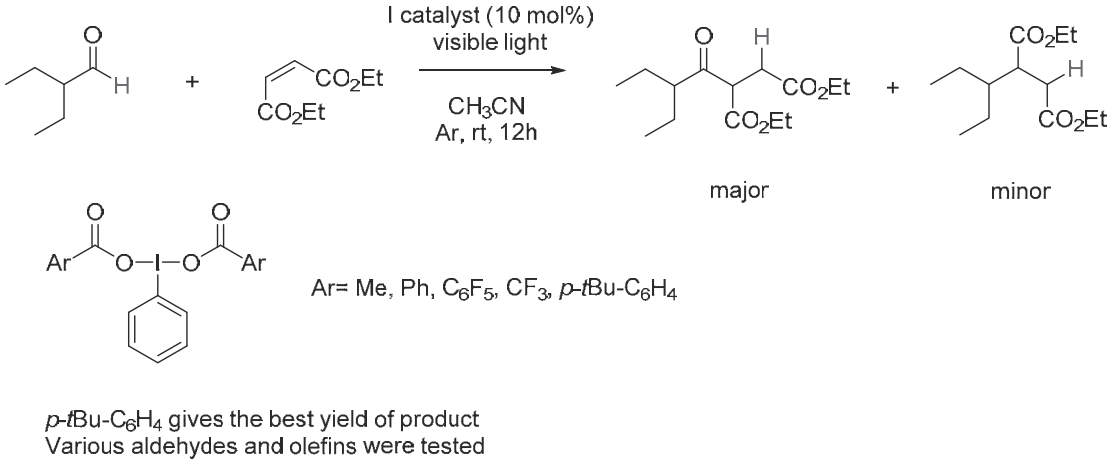
2. Mechanistic study on the metal-free C-H activation by using a hyper-valent iodine(III) reagent

Despite the transition metal catalyzed C-H activation, the organic chemists also started to seek alternative methods to facilitate the C-H bond cleavage in a more economical way. The Maruoka group in Kyoto university recently discovered a metal-free C-H activation which is validated by the using of hyper-valent iodine(III) reagent in a site-selective manner (*Angew. Chem. Int. Ed.,* **2013**, *52*, 8657). The hyper-valent iodine reagent has been employed in organic synthesis for a long period as an oxidant, which is related to the Dess-Martin reaction. However, it is novel to use the hyper-valent iodine reagent for the C-H activation purpose.



Scheme 4 The activation and oxidation of C-H by hyper-valent iodine (III) reagent

Not only for the oxidation of alkane, the hyper-valent iodine reagent is also reported as a reactive catalyst to promote the formation of acyl radicals without decarbonylation (*Nature Chem.,* **2014**, submitted manuscript).



Scheme 5 The hyper-valent iodine (III) promoted formation of acyl radical and the further addition to an alkene

A hypothetical hyper-valent iodine has been proposed by the Maruoka group to rationalize the experimental observations. Therefore, our research will be focus on theoretically testing the proposed mechanism in which a hypothetical iodine radical is involved, and propose alternative mechanism if necessary.

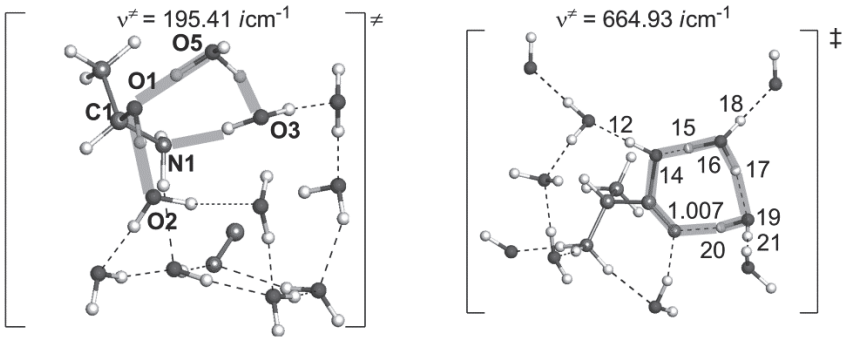
Shinichi YAMABE

FIFC Fellow, Kenichi Fukui Memorial Research group 2

1. Summary of the research of the year

(1-1) Proton Transfers in the Strecker Reaction Revealed by DFT Calculations

The Strecker reaction of acetaldehyde, NH_3, and HCN to afford alanine was studied by DFT calculations for the first time, which involves two reaction stages. In the first reaction stage, the amino-nitrile was formed. The rate-determining step is the deprotonation of the NH_3^+ group in MeCH(OH)-NH_3^+ to form 1-amino-ethanol, which occurs with an activation energy barrier ($\Delta E^{\neq}$) of 9.58 kcal/mol. The stereochemistry (R or S) of the product amino-nitrile is determined at the NH_3 addition to the carbonyl carbon of the aldehyde. While the addition of CN^- to the carbon atom of the protonated imine (**7**) appears to scramble the stereochemistry, the water cluster above the imine plane reinforces the CN^- to attack the imine group below the plane. The reforcement hinders the scrambling. In the second stage, the amino-nitrile transforms to alanine, where an amide Me-CH(NH_2)-C(=O)-NH_2 is the key intermediate. The rate-determining step is the hydrolysis of the cyano group of N(amino)-protonated amino-nitrile which occurs with an $\Delta E^{\neq}$ value of 34.72 kcal/mol. In the Strecker reaction, the proton transfer along hydrogen bonds plays a crucial role.



(1-2) Substrate dependent reaction channels of the Wolff-Kishner reaction; A theoretical study

Wolff-Kishner reduction reactions were investigated by DFT calculations for the first time. B3LYP/6-311+G(d,p) SCRF=(PCM, solvent=1,2-ethanediol) optimizations were carried out. To check the role of the base catalyst the base-free reaction was examined by the use of acetone, hydrazine(H2N-NH2) and (H2O)8. A ready reaction channel ofacetone -> acetone hydrazone(Me2C=N-NH2) was obtained. The channelinvolves two likely proton-transfer routes. However, the base-free reaction was found to be unlikey at the N2 extrusion step from the isopropyl

diimine intermediate(Me2C(H)-N=H-H).

Two base-catalyzed reactions were investigated by models of the ketone, H2N-NH2 and OH-(H2O)7. Here, ketones are acetone and acetophenone. While routes of the ketone -> hydrazone -> diimine aresimilar, those from the diimines are different. From the iso-propyl diimine,the N2 extrusion and the C-H bond formation takes place concomitantly.The concomitance leads to the propane product concertedly. From the(1-phenyl)ethyl substituted diimine, a carbanion intermediate is formed. The para carbon of the phenyl ring of the anion is subject to the protonation, which leads to the a 3-ethylidene-1,4-cyclohexadiene intermediate. Its[1,5]hydrogen migration gives the ethylbenzene product. For both ketonesubstrates, the diimines undergoing E2 reactions were found to be key intermediates.

(1-3) A DFT computational study of SN1-SN2 and SN2-SN3 mechanistic changes in hydrolyses of benzyl chlorides and benzenesulfonyl chlorides

B3LYP/6-311(+)G(d,p) calculations of hydrolysis reactions of benzyl chlorides and benzenesulfonyl chlorides were performed. A reaction of methyl chloride was also examined as a standard of a neutral SN2 reaction. Transition states (TSs) of Ph-CH2Cl + (H2O)n with n= 6, 9, 11, 17, 23 and 29 were obtained under the SCRF=(PCM, solvent=acetone). The variation of n corresponds nearly to that of molar fractions in the water-acetone binary solvent. For benzyl chlorides, the effect of para-substituents (Zs) on those structures was examined with n=17. For Z = O2N, Cl, H and H3C, paths of concerted bond interchanges leading to the benzyl alcohols were obtained. In contrast, for Z=MeO, a stepwise path invloving a carbocation (MeO-C6H4-CH2+) or "solvent separated ion pair" was calculated.
Although the central carbons of benzyl chlorides are primary, the mechanistic change ("SN2-SN1") suggested experimentally was obtained. Same analyses were made for benzenesulfonyl chlorides (para-Z-C6H4-SO2-Cl). For all substituents (Zs) and the number of water molecules (n), concerted paths were found. For the combination of the small n value and the electron-withdrawing group, the general base catalysis by the second H2O molecule is enhanced. The enhancement would correspond to the SN2-SN3 Mechanistic change.

.

2 Original Papers

(1) "Presence or absence of a novel charge-transfer complex in the base-catalyzed hydrolysis of N-ethylbenzamide or ethyl benzoate",
Shinichi Yamabe, Wei Guan and Shigeyoshi Sakaki,
Beilstein J. Org. Chem. 2013, 9, 185-196.

(2) "Three Competitive Transition States at the Glycosidic Bond of Sucrose in Its Acid-Catalyzed Hydrolysis",
Shinichi Yamabe, Wei Guan and Shigeyoshi Sakaki

J. Org. Chem., 2013, 78 (6), 2527-2533.

(3) "An aniline dication-like transition state in the Bamberger rearrangement",
Shinichi Yamabe, Guixiang Zeng, Wei Guan and Shigeyoshi Sakaki
Beilstein J. Org. Chem. 2013, 9, 1073-1082.

(4) "Interest in new heterodinuclear transition-metal/main-group-metal complexes: DFT study of electronic structure and mechanism of fluoride sensing function",
Wei Guan, Shinichi Yamabe and Shigeyoshi Sakaki,
Dalton Trans., 2013, 42, 8717-8728, DOI: 10.1039/C3DT50597A

(5) "Substrate dependent reaction channels of the Wolff-Kishner reduction reaction: A theoretical study",
Shinichi Yamabe, Guixiang Zeng, Wei Guan, Shigeyoshi Sakaki
Beilstein Journal of Organic Chemistry 2014, 10, 259-270.

(5) "A DFT Study of the Triplet Excited States of Iridium(III) Complexes with Terpyridine Ligands",
Naokazu Y., Shinichi Y.,*, Shigeyoshi S., Nobuko K.,
Tsuyoshi I., and Hiroshi T.,
Canadian Chemical Transactions, 2014, vol.2, issue 2, 134-148.

(6) "SN1-SN2 and SN2-SN3 mechanistic changes revealed by transition states of the hydrolyses of benzyl chlorides and benzenesulfonyl chlorides",
Shinichi Yamabe, Guixiang Zeng, Wei Guan and Shigeyoshi Sakaki,
Journal of Computational Chemistry, vol.35, issue 15,
pages 1140-1148 (2014), DOI: 10.1002/jcc.23607.

2. Presentation at academic conference

“Proton transfers in some organic reaction pathways”,
July 24, 2013, The 11-th Fukui Center seminar
At Fukui Institute for Fundamental Chemistry, Kyoto University.

土方　優

FIFC フェロー

1. 今年度の研究の要約

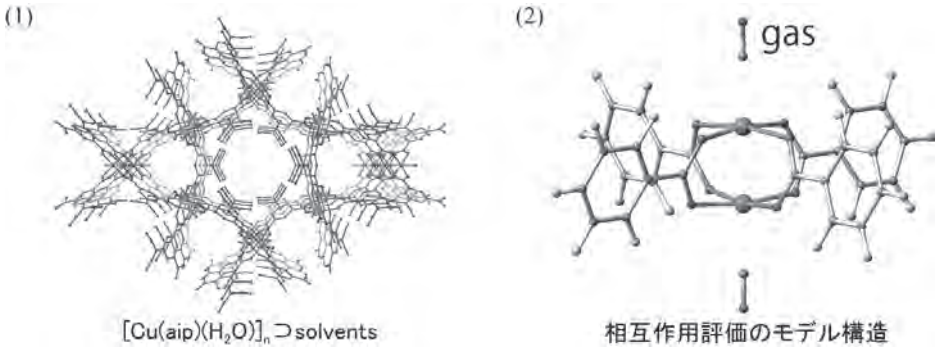
今年度は配位高分子における、配位不飽和サイトと呼ばれる金属部位とガス分子の吸着相互作用に関する研究、およびその相互作用と構造から生み出されるガス分子の選択的吸着機構の解明に関する研究を行った。

【始めに】

多孔性配位高分子（PCPs: Porous coordination polymers）は金属イオンを有機配位子が架橋した無限構造を有した結晶性の物質群であり、生み出される骨格中には規則正しく並んだ空孔が存在している。その骨格や空孔を利用し、ガス貯蔵、ガス分離、触媒、光応答や磁性など様々な機能に関する研究が行われている。貯蔵に関してはガス分子の貯蔵可能な空隙が多く、捕捉されるガス分子と骨格との相互作用が強ければより有望な材料となりうる。一方で分離においては、あるガスに対して骨格からの相互作用が強い場合は、その他のガスに対してもその相互作用は強く働くことが多く、特定のガス分子に対してのみ強い相互作用を発現するような設計は容易ではない。本研究では PCPs の設計性の高さと構造の柔軟性を利用した self-accelerating という新しい分離機構を提案し、さらに PCPs 中における相互作用部位とガス分子が相互作用した際に受ける影響を明らかにすることを目的とし理論計算によるアプローチを試みた。

【計算、結果、考察】

図 1 に示した kagomé 型層状骨格の $[Cu(aip)]_n$（aip = 5-azidoisophthalate）は、相互作用サイトとして paddle-wheel 型の潜在的な銅配位不飽和サイト（Cu-OMS）を有している。この $[Cu(aip)]_n$ は分子物性の似通った CO と N_2 に対し CO の高い選択性を有している事が実験によって見出された。一般に CO と N_2 は分子サイズ、電子数、沸点、臨界温度、臨界圧など多くの性質が似ており、CO/N_2 の分離は容易ではない。結晶構造解析によって CO の Cu-OMS への配位が確認されており、図 1 に示すようなモデルで CO と N_2 の Cu-OMS への相互作用エネルギーの評価を行ったところ、SCS-MP2/TZ//M06L/TZ レベルでそれぞれ-20.4 $kJmol^{-1}$ と-13.0 $kJmol^{-1}$ であった。同様の Cu-OMS ユニットを有する HKUST-1 など他の PCPs では、このような CO/N_2 における CO の選択性が見られないことから、この選択性は相互作用エネルギーの違いによるものではないことが示唆された。

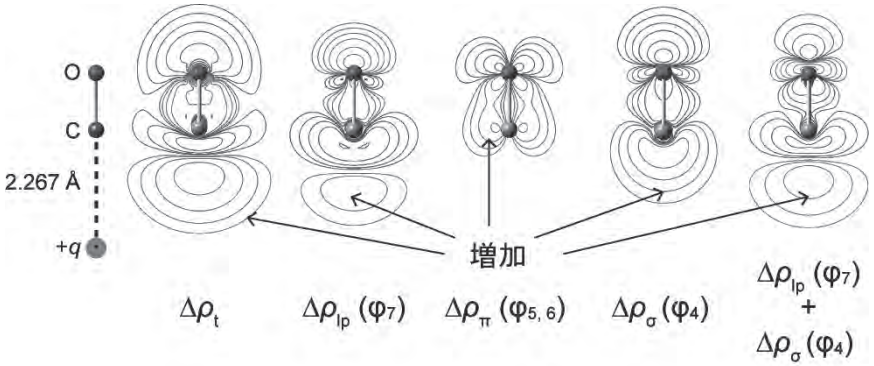


（図 1）対象とした PCP とその計算モデル

この選択性の原因の一つは、ガス分子吸着前の Cu-OMS には隣接層のカルボキシレートの酸素が配位しており、N_2ではこの Cu-O 結合を切断することができない一方で、配位可能な CO の場合にのみ結合開裂を伴った吸着が起きるためと考えられる。CO が配位した後に注目すると、細孔内へのガス分子の拡散における障壁は理論計算から、100kJmol^{-1}以上の障壁であることが明らかとなった。つまり、CO, N_2どちらも拡散が困難である。仮に、非配位 N_2が配位 CO と交換した場合、上に示した相互作用のエネルギー差から不安定化するため、非配位 N_2と配位 CO の交換はやはり困難である。一方で、非配位 CO が配位 CO と交換した場合、エネルギー的損失は無くこの障壁を回避して細孔内への拡散が可能となり、CO のみの選択的な拡散が進行すると考えられる。相互作用部位を骨格中に構築し、PCPs の持つ柔軟性という特徴を組み合わせた PCP における self-accelerating という新しい分離機構を理論計算と組み合わせることで提案した。

さらに、上記の機構において重要となるのは CO が Cu-OMS と穏和な相互作用をするということである。一般に CO が金属に配位したカルボニル錯体では金属-CO 間の相互作用は強いことが知られている。これは Dewar-Chatt-Duncanson モデルおける σ-donation と π-back donation によって説明されており、CO の lone pair の σ-donation による金属への配位と同時に π-back donation によって CO の反結合性 π*軌道への電子の流入が起き、金属-CO 間の結合が補強されるためである。このとき、CO の反結合性 π*軌道への電子の流入によって C-O の結合は弱くなり、低波数シフトする事も知られている。しかし、$[Cu(aip)]_n$では CO 伸縮の高波数シフトが観測され、モデル計算でも同様に高波数シフトを示した。Cu-CO における σ-donation と π-back donation の量はそれぞれ 0.320 e と 0.034e であり、ほとんど π-back donation が起きず適度な結合力によって Cu-OMS は CO を捕捉し CO 同士の交換を可能としていることを明らかにした。

しかし、π-back donation はあくまでも CO の反結合性 π*軌道への電子の流入であり、観測される CO 伸縮は低波数シフトを示すはずである。一方で観測されたのは高波数シフトであり、その高波数シフトの原因を明らかにするため、Cu-OMS によって形成される静電場に注目した。図 2 に示したように、Cu-OMS の Cu の正電荷+q によって CO の電子密度の変化が誘起され、CO の結合領域の電子密度（$\Delta\rho_t$）が増加していることがわかる。この CO 結合領域の電子密度の増加によって高波数シフトが誘起されていることを明らかにした。さらに、各軌道の電子密度の増減をみると、CO の π 軌道の電子密度の変化を示す$\Delta\rho_\pi(\varphi_{5,6})$から π 電子が正電荷側に引き寄せられていることがわかる。一方、σ 軌道の変化の和、$\Delta\rho_{lp}+\Delta\rho_\sigma$は減少しており、π 軌道の電子の結合領域への偏りによって CO の高波数シフトが誘起されているという事を明らかにした。一般に、PCPs の吸着測定では前処理として加熱するため単結晶性を保持するのは難しい。そのため、このような OMSs とガス分子の相互作用に関して、分光スペクトルの解釈において、細孔が形成する場の重要性を示すものと言える。



（図 2）電荷が存在する時の CO の各軌道の電子密度の変化

2. 論文

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"Anion-dependent host-guest properties of porous assemblies of coordination complexes (PACs), $[Cu(A)_2(py)_4]$ (A = PF_6, BF_4, CF_3SO_3, and CH_3SO_3; py = pyridine), based on Werner-type copper (II) complexes in the solid state"
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(5) Hiroshi Sato, Wataru Kosaka, Ryotaro Matsuda, Akihiro Hori, Yuh Hijiakta, Shigeyoshi Sakaki, Masaki Takata, and Susumu Kitagawa
"Self-accelerating CO sorption in a soft nanoporous crystal"
Science, 2014, 343, 167-170 (Science Express, 2013)

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The international symposia on advancing the chemical science 10 (ISACS 10), Kyoto, 2013/6/19

(2) Yuh Hijikata, Shigeyoshi Sakaki
"Theoretical investigation for the interaction of various gas molecules with paddle-wheel type open metal site of porous coordination polymers"
UK-Japan Workshop on Organic-Inorganic Framework Materials, Kyoto, 2013/10/10-11

(3) 土方　優，榊　茂好
「フッ化物アニオンを骨格に持つ PCP の二酸化炭素吸着に関する理論的研究」
錯体化学会第 63 回討論会　沖縄　2013/11/2-4

(4) 野呂真一郎，水谷純也，土方　優，久保和也，中村貴義
「電荷分極型中性配位子を用いた多孔性軽金属錯体の合成と吸着・分離機能」
日本化学会第 94 春季年会　愛知　2014/3/27-30

(5) 土方　優，榊　茂好
「フッ化物アニオンからなる多孔性配位高分子の二酸化炭素吸着に関する理論的研究」
日本化学会第 94 春季年会　愛知　2014/3/27-30

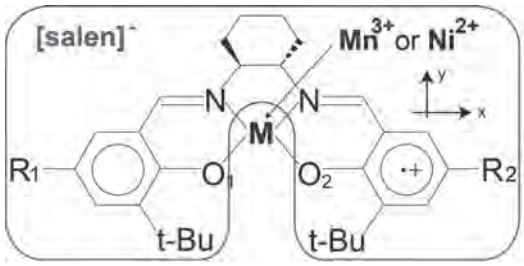
青野　信治

特定研究員

1. 今年度の研究の要約

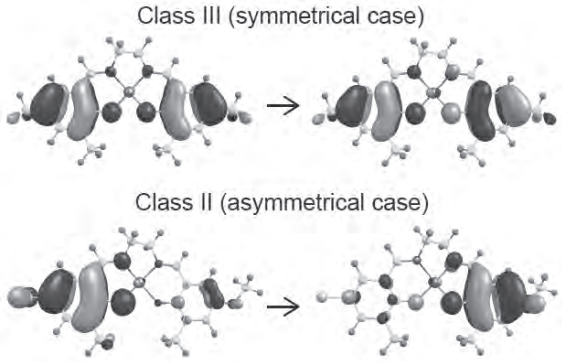
本年度は遷移金属錯体に対する溶媒和効果を中心に研究を行った。

【序】 Mn(III)-および Ni(II)-salen 錯体は一電子酸化状態において、金属および salen 配位子の種類によりラジカル中心が salen 配位子内に局在化もしくは非局在化した原子価異性状態を示し、混合原子価電子状態の観点からも興味深い(Scheme 1)。これらの錯体の吸収スペクトルが実験で測定されており、Mn(III)-salen 錯体の一電子酸化体では強度が弱くブロードなスペクトルが、Ni(II)-salen 錯体では対称的な salen 配位子($R_1 = R_2$)の場合に強度が強くシャープなスペクトルが観測されている。



Scheme 1: 金属 salen 錯体

これらの特徴的な違いに対し、実験分野では Mn(III)-salen 錯体のスペクトルは salen ラジカルが一方の phenolate に局在した状態から他方の phenolate へ電荷移動遷移した一種の原子価間電荷移動吸収(class II に対応)に、Ni(II)-salen 錯体のスペクトルは salen 配位子内の非局在な状態間の電子励起(class III に対応)に帰属し、解釈されている(Scheme 2) [1]。



Scheme 2: 局在的・非局在的な電子励起の違い

本研究では、salen 配位子の(R_1, R_2)が(Me, Me)、(OMe, OMe)、(OMe, Cl)の場合の Mn(III)-および Ni(II)-salen 錯体の 3D-RISM-SCF 研究を行い、金属および配位子による電子状態と

溶媒効果の違いを検討した。また Mn(III)と同じ d^4 金属である Tc(III)-salen 錯体、Ni(II)と同じ d^8 金属である Pd(II)-salen 錯体についても同様の計算を行い、d 軌道の広がりの違いが原子価異性にどう影響するのかを比較・検討した。

【方法】CH_2Cl_2 溶媒中における錯体構造と溶媒和構造は 3D-RISM-DFT/M06 法により求めた。3D-RISM-SCF 計算では、溶質の電子密度から溶媒平衡分布 $g_s(\mathbf{x})$を定める際に、溶質周囲の静電ポテンシャルを求める必要があるが、本研究では式(1)のように溶質周囲の領域では波動関数から静電ポテンシャルを計算し、溶質から遠く離れた領域では点電荷近似計算を行い、この２つを swithing 関数 Sw(**x**)によって滑らかに接続する方法を採用した[2]。

$$V_{es}(\mathbf{x}) = \sum_{\mu,\nu} P_{\mu\nu}\left[\mathrm{Sw}(\mathbf{x})\int d\mathbf{r}'\,\frac{\chi_\mu^*(\mathbf{r}')\chi_\nu(\mathbf{r}')}{|\mathbf{r}'-\mathbf{x}|} + \{1-\mathrm{Sw}(\mathbf{x})\}\sum_a \frac{Q_{\mu\nu}^a}{|\mathbf{R}_a-\mathbf{x}|}\right], \quad (1)$$

これにより得られた電子基底状態に対する溶媒和構造 $g_{\mathrm{gr,s}}(\mathbf{x})$を一電子ハミルトニアン項に平均場近似として含める事で、２状態に対して状態平均を課した 3D-RISM-GMC-QDPT 計算を行い、式(2)と(3)のように溶質の電子エネルギー変化と溶質-溶媒間相互作用の変化からなる励起エネルギー ΔE、それに対応する振動子強度 $f_{\mathrm{gr,ex}}$ を見積もった。

$$\Delta E = \left\langle \underline{\Phi}_{\mathrm{ex}} \middle| \hat{H}_{\mathrm{gas}} + \hat{V}_{\mathrm{int}}(\mathbf{r};\mathbf{R},g_{\mathrm{gr}}) \middle| \underline{\Phi}_{\mathrm{ex}} \right\rangle - \left\langle \underline{\Phi}_{\mathrm{gr}} \middle| \hat{H}_{\mathrm{gas}} + \hat{V}_{\mathrm{int}}(\mathbf{r};\mathbf{R},g_{\mathrm{gr}}) \middle| \underline{\Phi}_{\mathrm{gr}} \right\rangle, \quad (2)$$

$$f_{\mathrm{gr,ex}} = \frac{2m_e}{3\hbar^2}\Delta E \left| \left\langle \underline{\Phi}_{\mathrm{gr}} \middle| \sum_{i\in\mathrm{electron}} \hat{\mathbf{r}}_i \middle| \underline{\Phi}_{\mathrm{ex}} \right\rangle \right|^2, \quad (3)$$

但し、$\hat{V}_{\mathrm{int}}$ は式(4)で定義された演算子である。

$$\hat{V}_{\mathrm{int}}(\mathbf{r};\mathbf{R},g_{\mathrm{gr}}) \equiv \rho \sum_{s\in\mathrm{solvent\ site}} q_s \int d\mathbf{x}\, g_{\mathrm{gr}\,s}(\mathbf{x}) \left\{ \mathrm{Sw}(\mathbf{x}) \sum_{i\in\mathrm{electron}} \frac{1}{|\hat{\mathbf{r}}_i - \mathbf{x}|} + (1-\mathrm{Sw}(\mathbf{x}))\sum_a \frac{\hat{Q}_a}{|\mathbf{R}_a-\mathbf{x}|} \right\}, \quad (4)$$

構造最適化および GMC-QDPT 計算では Mn、Ni には(311111/22111/411/1)基底を、Tc、Pd には(311111/22111/411)基底を用い、内殻電子は Stuttgart ECP に置き換えた。それ以外の原子には cc-pVDZ 基底を用い、O、N、Cl に diffuse 関数を加えた。また Mn、Tc では 22、Ni、Pd では 18 の軌道を active 空間に選び、主に基底状態と励起状態の各々に対応する２つの主配置から二電子励起までを許容する計算を行った。

【結果】 3D-RISM-UDFT(M06)による構造最適化の結果、対称的な salen 配位子(R_1 = R_2)の場合に Mn(III)-と Ni(II)-salen 錯体の違いが見られた。気相中では双方とも C_2 対称構造を持つのに対して、溶媒効果を考慮すると Mn(III)-salen 錯体では対称性が低下し、salen ラジカルが片方の phenolate に局在化した電子状態を持つようになる。一方、Ni(II)-salen 錯体では溶媒効果による対称性の低下が起こらず、ラジカルが salen 配位子内で非局在化したままである（表 1）。

表 1: Mn(III)-および Ni(II)-salen 錯体の最適化構造と溶媒効果

単位			結合長 [Å]				双極子 [Debye]
	溶媒	対称性	C=O_1	C=O_2	M-O_1	M-O_2	x 成分
Mn(III)-salen							
(Me,Me)	gas	C_2-like	1.30	1.30	1.84	1.84	0.5 (非局在)
	CH_2Cl_2	C_1	1.32	1.27	1.80	1.91	9.1 (局在)
(OMe,OMe)	gas	C_2-like	1.30	1.30	1.84	1.84	0.5 (非局在)
	CH_2Cl_2	C_1	1.32	1.28	1.81	1.91	10.5 (局在)
(Cl,OMe)	gas	C_1	1.32	1.28	1.80	1.90	12.8 (局在)
	CH_2Cl_2	C_1	1.32	1.28	1.81	1.90	15.7 (局在)
Ni(II)-salen							
(Me,Me)	gas	C_2-like	1.28	1.28	1.83	1.83	0.0 (非局在)
	CH_2Cl_2	C_2-like	1.28	1.28	1.84	1.84	0.0 (非局在)
(OMe,OMe)	gas	C_2-like	1.28	1.28	1.84	1.84	0.0 (非局在)
	CH_2Cl_2	C_2-like	1.28	1.28	1.84	1.84	0.0 (非局在)
(Cl,OMe)	gas	C_2-like	1.29	1.27	1.82	1.85	9.0 (局在)
	CH_2Cl_2	C_2-like	1.30	1.27	1.82	1.87	15.2 (局在)

これらの錯体構造と溶媒和構造を用いて 3D-RISM-GMC-QDPT 計算を行った結果、実験で観測された吸収スペクトルの傾向が再現された（表 2）。 特に ESP 電荷の変化を調べると Ni(II)-salen 錯体では電子遷移に伴う原子価間電荷移動がなく、Mn(III)-salen 錯体では約 0.9e の原子価間電荷移動が起こる事が示唆された。一方、気相中の計算では、Mn(III)の(Me,Me)および(OMe,OMe)錯体において実験値との相違が大きく、溶媒効果は構造変化およびラジカルの局在化/非局在化に重要な役割を果たしている事が示された。また C_2 対称な構造を調べると金属種の d 軌道エネルギーの違いから、2 つの非局在性π軌道とπ*軌道のエネルギー差を Ni(II)は大きくする一方、Mn(III)は差を小さくする事が分かり、この結果 Mn(III)-salen 錯体の方が非局在性π軌道とπ*軌道が混ざり易く、局在化が起こり易い事で構造の非対称化が進む事が分かった。

表 2: Mn(III)-および Ni(II)-salen 錯体の励起エネルギー ΔE [eV] と振動子強度 $f_{gr,ex}$

	Mn(III)			Ni(II)		
(R_1, R_2)	(Me, Me)	(OMe,OMe)	(OMe, Cl)	(Me, Me)	(OMe,OMe)	(OMe,Cl)
構造/溶媒和	垂直励起エネルギーΔE [eV]					
gas /gas	0.340	0.388	1.314	0.479	0.460	0.812
RISM/MD	1.078	1.112	1.658	0.455	0.457	1.430
RISM/RISM	1.113	1.126	1.699	0.492	0.454	1.465
実験値	0.838	0.976	1.389	0.620	0.579	0.885
構造/溶媒和	振動子強度 $f_{gr,ex}$					
gas /gas	0.349	0.425	0.061	0.404	0.401	0.242
RISM/MD	0.107	0.119	0.044	0.384	0.396	0.129
RISM/RISM	0.103	0.117	0.042	0.414	0.394	0.138

[1] T. Kurahashi and H. Fujii, *J. Am. Chem. Soc.* **2011**, 133, 8307-8316.
[2] S.Aono and S. Sakaki, *J. Phys. Chem. B* **2012**, 116, 13045.

2. 論文

(1) Shinji Aono, Masayuki Nakagaki, Takuya Kurahashi, Hiroshi Fujii, and Shigeyoshi Sakaki, “Theoretical Study of One-Electron Oxidized Mn(III)- and Ni(II)-Salen Complexes: Localized vs Delocalized Ground and Excited States in Solution” J. Chem. Theory Comput. 10 1062 (2014).

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「Localized vs. Delocalized Ground and Excited States of Mn(III) and Ni(II) Salen Complexes: Theoretical Study of Solvation Effects」
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第５回 JCS 理論化学国際会議　奈良　2013/12/3　PIb-19

4. その他

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第11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　2014/1/23　XXXX

Milind Madhusudan DESHMUKH

SPR Fellow

1. Summary of the research carried out during April 2013 to March 2014.

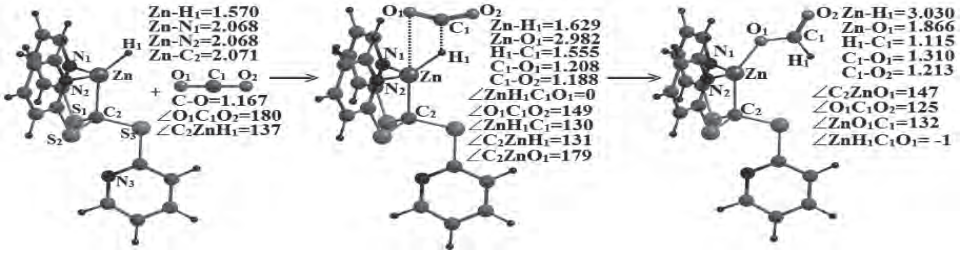
A) Absorption of Gas Molecules into the Porous Coordination Polymer: Understanding of the Determining Factors for Absorption position and Energy

We recently studied absorption/adsorption of CO_2 and CS_2 into porous coordination polymers (PCPs). For details of this work See; published in *J. Am. Chem. Soc.* **2013,** *135*, 4840 and previous annual report.

B) Theoretical study of Molecular Hydrogen and Carbon Dioxide Functionalization with Zinc Hydride: Insights into Interesting Catalytic Cycle

The discovery of catalytic methods is important for (i) the rapid generation of H_2 as use a fuel source and (ii) utilization of CO_2 as an effective C-source. Transition metal complexes are shown by number of studies that they can act as effective catalyst for variety of conversion of chemical entities into desired products. Recent experimental study reported that [tris(2-pyridylthio)methyl] zinc hydride **1** is an effective catalyst for H_2 generation from methanol or water and for CO_2 utilization (*J. Am. Chem. Soc.* **2011**, *133*, 9708). However, no detailed mechanistic insights have been presented.

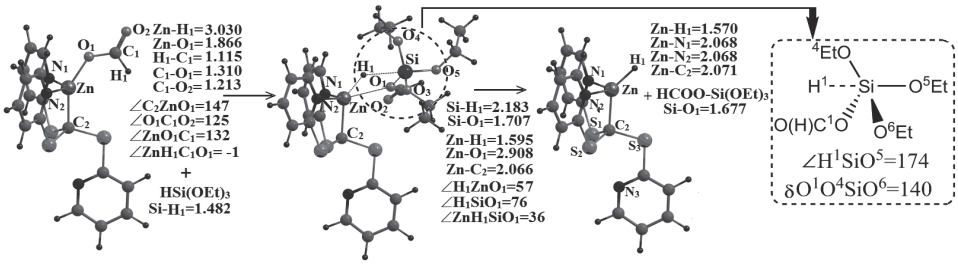
In this work, we theoretically investigated the reaction mechanism and proposed a complete catalytic cycle for CO_2 functionalization and also for the H_2 generation process. The CO_2 functionalization occurs via CO_2 insertion into the Zn-H bond of **1** (cf. Figure 1) followed by a metathesis of Zn-OCOH compound with hydrosilane to generate silyl formate (cf. Figure 2.)



1 + CO_2 **TS1** **P1**

0.00 **(G^a=12.5 kcal mol^{-1})** **(ΔG= -8.33 kcal mol^{-1})**

Figure 1: Detailed mechanism for the reaction of CO_2 with catalyst 1.



P1 + HSi(OEt)$_3$ **TS2** **1**

0.0 **(ΔG=14.07 kcal mol^{-1})** **(ΔG= +0.71 kcal mol^{-1})**

Figure 2: The reaction mechanism for the regeneration of catalyst **1** from **2** and HSi(OEt)$_3$

In CO_2 insertion, the second step (TS2) is rate determining step, wherein silicon moiety takes hypervalent structure. The formation of hypervalent silicon is seems to be important for the formation of silyl formate.

The reaction of **1** with methanol occurs through a metathesis between the Zn-H and the O-H bond of methanol to obtain molecular hydrogen and the Zn-OMe compound. The next step is the metathesis between the Zn-OMe bond and hydrosilane to regenerate **1** and silylether (cf. Figure 3). Here, on going from **TS4** to **TS5** via **Int 1**, the silicon center gradually changes its structure from tetrahedral to trigonal bipyramidal.

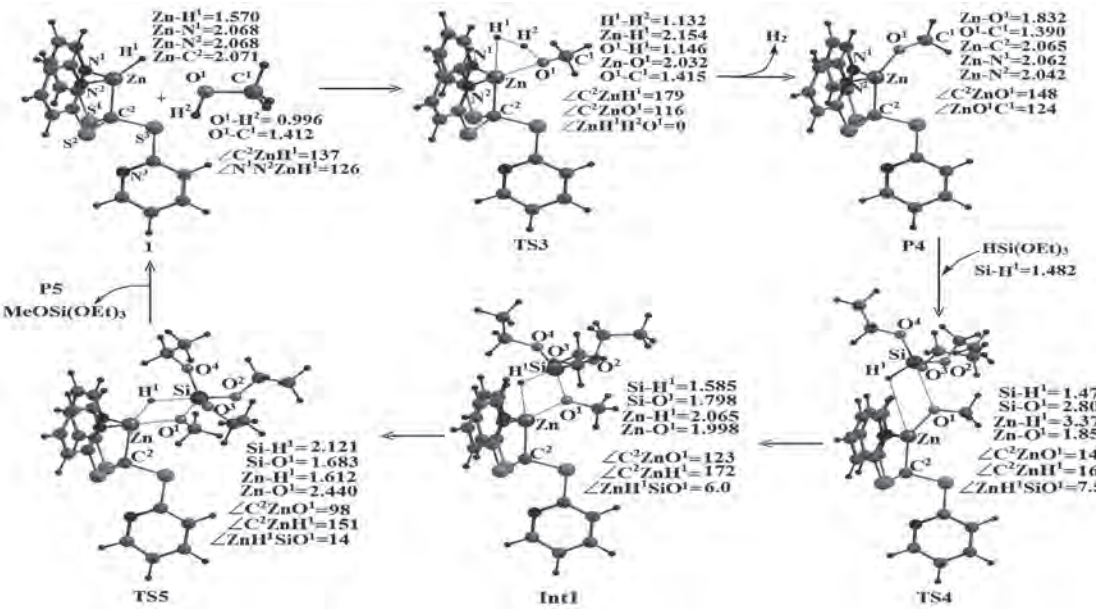
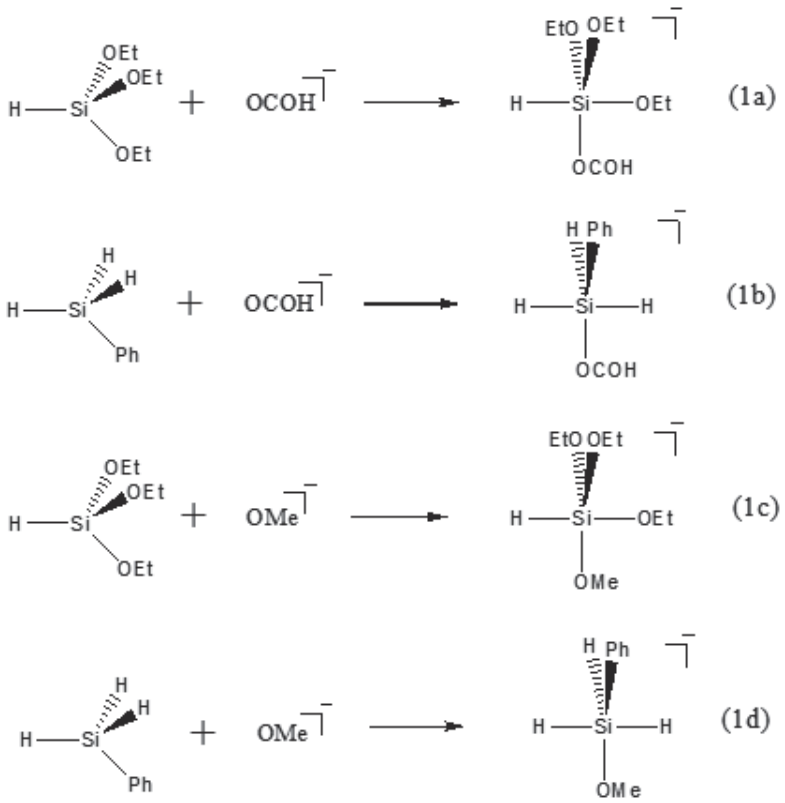


Figure 3: Catalytic cycle for H_2 generation using [K^3-Tptm]ZnH catalyst, **1.**

The small activation barrier and large exothermicity for the H_2 generation and CO_2 insertion reaction indeed suggest that **1** is effective catalyst and produces product **P4** and **P1**, respectively. The analysis of electronic structures suggests a strong charge transfer (CT) from the valence s- and p-orbital of Zn to the CO_2 moiety which stabilizes **TS1** for CO_2 insertion. Also, the rapid generation molecular hydrogen is facilitated by a strong CT from metal center to hydride hydrogen of **1** and also to the hydrogen of methanol through oxygen moiety.

For the regeneration of catalyst **1** and formation of silyl formate or silyl ether, the formation of respective hypervalent silicon structures are found to be important. For instance, the small activation barrier and exothermicity of these reactions is shown to nicely correlate with the stability of hypervalent structure.

Also we explored suitability of various hydrosilane molecules for the regeneration of **1**. The corresponding activation barrier for various hydrosilane in the regeneration reaction was correlated with the stabilization energy for the formation of hypervalent silicon species similar to that in the TS; See scheme 1 for the formation of hypervalent species. The results are nicely summarized in Table 1.



Scheme 1: The formation reaction of hypervalent Si species.

Table 1: The Gibbs activation barrier ($\Delta G^{o\ \ddagger}$) for the regeneration of **1** from **P1** and **P4** with hydrosilane, the stabilization energy ($\Delta E_{St.}$) of hypervalent silicon species (Scheme 1) and theoretically predicted $\Delta G^{o\ \ddagger}$ to complete the catalytic cycle. Values are presented in kcal mol^{-1}.

	P1 with Hydrosilane			$\Delta G^{o\ddagger}$ for full catalytic cycle
	$\Delta G^{o\ddagger}$		$\Delta E_{St.}$ [a)]	
$HSi(OEt)_3$	4.2		-17.3	23.1
$H_2Si(OEt)_2$	11.9		-14.3	25.9
$H_3Si(OEt)$	14.8		-10.2	27.4
$HSiF_3$	~0 [b)]		-32.5	22.4
H_2SiF_2	6.9		-24.1	25.0
H_3SiF	10.5		-16.5	25.5
$PhSiH_3$	16.6		-2.4	30.5
	P4 and Hydrosilane			
Silane	$\Delta G^{o\ddagger}$	ΔG^{o}	$\Delta E_{St.}$	
$HSi(OEt)_3$	0.4	-6.5	-51.5	
$PhSiH_3$	3.0	0.1	-39.4	

a) The stabilization energy in either eq. (1a) to eq. (1d).
b) This value is -0.8 kcal/mol; This negative value arises from the computational procedure .

As seen in Table 1, the reaction energy increases in the order $HSiF_3$ < H_2SiF_2 < $HSi(OEt)_3$ < H_3SiF $H_2Si(OEt)_2$ < $H_3Si(OEt)$. The $\Delta G^{0\ddagger}$ is 25.9 kcal/mol for $H_2Si(OEt)_2$ and 25.5 kcal/mol for H_3SiF, which are not different very much from the $\Delta G^{0\ddagger}$ (23.1 kcal/mol) of $HSi(OEt)_3$. Based on these results, we wish to present theoretical prediction that hydrosilane bearing three electronegative groups is the best and the hydrosilane bearing two OEt groups or one to three F groups can be applied to the hydrosilylation of CO_2; in other words, not only $HSi(OEt)_3$ but also $H_2Si(OEt)_2$, $HSiF_3$, H_2SiF_2, and H_3SiF are useful in the hydrosilylation of CO_2.

2. Original Papers

(1) Deshmukh Milind M.; Ohba Masaaki, Kitagawa Susumu, and Sakaki Shigeyoshi, "Absorption of CO_2 and CS_2 into the Hofmann-Type Porous Coordination Polymer: Electrostatic versus Dispersion Interactions."
J. Am. Chem. Soc. 135, 4840 (2013).

(2) Deshmukh Milind M. and Sakaki Shigeyoshi
"Generation of Dihydrogen Molecule and Hydrosilylation of Carbon Dioxide Catalyzed by Zinc Hydride Complex: Theoretical Understanding and Prediction"
Inorganic Chemistry, (Revision submitted: 2014)

3. Presentations at academic conferences

(1) Deshmukh Milind M. and Sakaki Shigeyoshi,
"Absorption of CO_2 and CS_2 into the Hofmann-type Porous Coordination Polymer: ONIOM(MP2.5:DFT) Study of Absorption Position and Energy"
Challenges in Organic Materials & supramolecular Chemistry (ISACS 10), Kyoto University, Japan, June 18-21, 2013.

(2) Deshmukh Milind M. and Sakaki Shigeyoshi,
"Reaction between CO_2 and Zinc Hydride: Interesting Theoretical Insights"
The 7th Annual Meeting of Japan Society for Molecular Science, Kyoto University, Kyoto Terrsa, Japan, September 24-27, 2013.

4. Others

Guixiang ZENG（會　桂香）

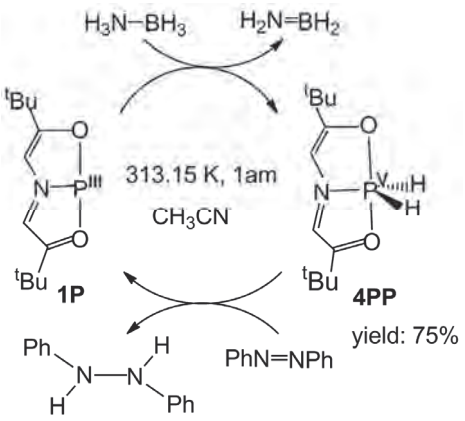
SPR Fellow, SAKAKI Group

1. Summary of the research of the year

Catalytic Transfer Hydrogenation by Trivalent Phosphorus Compound: Phosphorus-Ligand Cooperation Pathway or P^{III}/P^{V} Redox Pathway? [1]

Main-group element compounds experience a renaissance in the past two decades for their excellent reactivities similar to those of transition metal complexes. Although the elementary steps such as oxidative addition, reductive elimination, insertions, and metathesis were reported, full catalytic cycles by main-group element compounds are limited. It is well-known that the metal-ligand cooperation and the redox process are ubiquitous in the chemistry of transition metal complexes, but they have not been reported for the main group element compounds.

Recently, Radosevich and his coworkers reported a catalytic reaction by a trivalent phosphorus compound **1P**, where the P^{III}/P^{V} redox processes are involved; see Scheme 1. In this reaction, **1P** reacts with NH_3BH_3 to afford a pentavalent dihydridophosphorane **4PP**, which subsequently transfers hydrogen atoms to azobenzene to regenerate **1P**. However, the mechanistic details of these reactions are still unclear. Such knowledge is necessary for further development of the chemistry of main group element compounds.



Scheme 1. Catalytic cycle of transfer hydrogenation by **1P**.

Here, we theoretically investigated this reaction shown in Scheme 1. The discussion was presented based on the Gibbs energy changes relative to the sum of reactants (**1P** + ammonia-borane + azobenzene) unless otherwise noted. For convenience, the tri-ligated moiety coordinating with the phosphorus centre in **1P** is named as an ONO ligand hereafter.

For the NH_3BH_3 dehydrogenation step, the phosphorus-ligand cooperation and the concerted oxidative addition pathways were examined. As shown in Figure 2, the Gibbs energy barrier ($\Delta G^{0\neq}$) of the concerted oxidative addition pathway is 42.7 kcal/mol, which is too large for the reaction to occur at 313.15 K; see the Figure 1 for geometry changes. On the other hand, the P–O cooperation pathway occurs more favourably with a much smaller $\Delta G^{0\neq}$ value of 27.1 kcal/mol. Other phosphorus-ligand cooperation pathways such as P-C1, P-C2, and P-N1 cooperations were found to be unfavourable in energy. This dehydrogenation step occurs with an endothermicity of 13.5 kcal/mol, where the intermediate **4OP** is formed.

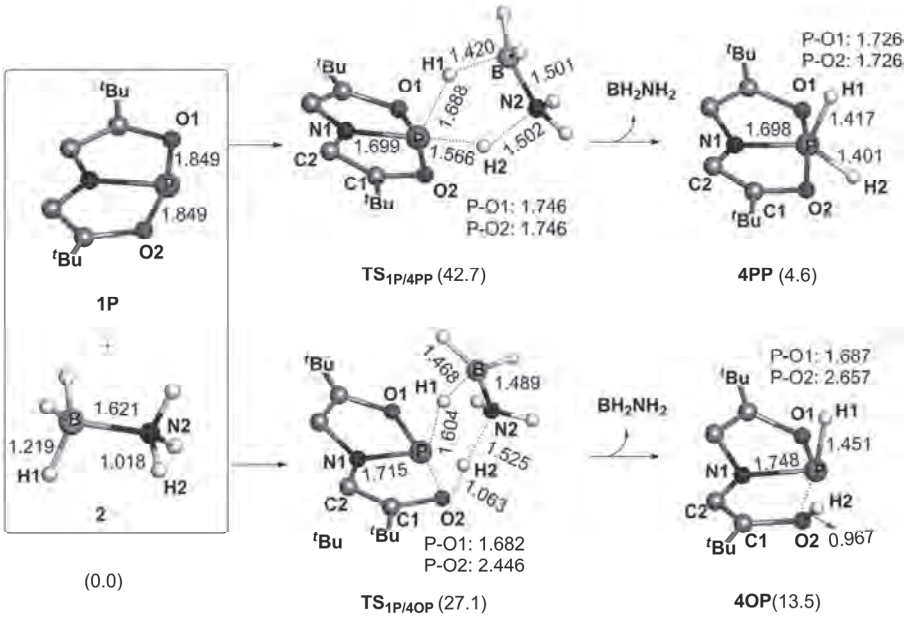


Figure 1. Geometry changes along the P–O cooperation and concerted oxidative addition pathways for the NH_3BH_3 dehydrogenation reaction.

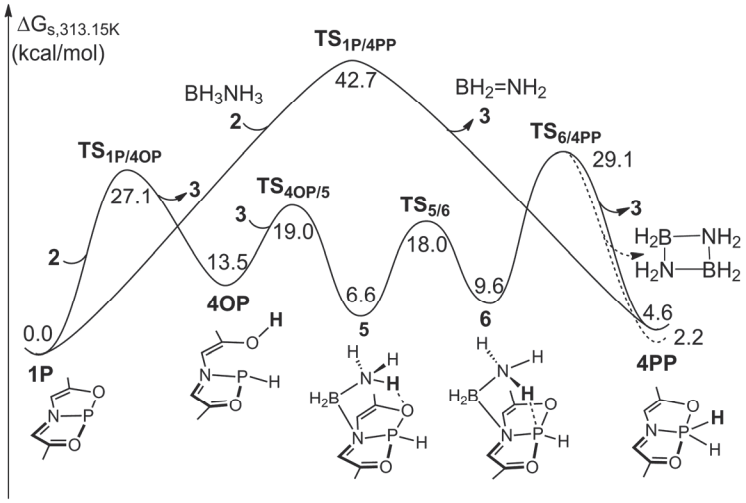


Figure 2. The Gibbs energy changes (in kcal/mol) for the dehydrogenation of NH_3BH_3 by **1P**.

In the absence of the hydrogenation substrate azobenzene, **4OP** transforms to a more stable compound **4PP**. In the NH_2=BH_2 assisted pathway, first, the N2 atom of NH_2=BH_2 lifts the H2 atom from the O2 atom to form a NH_3 moiety. Simultaneously, the boron atom forms a B-N1 bond with the ONO ligand. Then, the BH_2-NH_3 moiety rotates around the B–N1 bond to bring the H2 atom toward the phosphorus atom via the transition state $\mathbf{TS_{5/6}}$ to afford the intermediate **6**. At last, the hydrogen atom migrates from the NH_3 moiety to the phosphorus atom to form **4PP** via the transition state $\mathbf{TS_{6/4PP}}$. The last step is the rate-determining step, which occurs with the $\Delta G^{0\neq}$ value of 29.1 kcal/mol; see Figure 2. In the presence of azobenzene, **4OP** easily undergoes the transfer hydrogenation reaction through the transition state $\mathbf{TS_{4OP/1P}}$ with the $\Delta G^{0\neq}$ value of 28.1 kcal/mol; see Figure 3. On the other hand, in order to elucidate the active species of the hydrogenation reaction, the **4PP**-catalyzed hydrogenation reaction was also examined. This reaction involves the

hydrogenation transfer and the reductive elimination steps; see the upper half of Figure 3. The reductive elimination step (from **9** to **TS$_{9/1P}$**) occurs with the $\Delta G^{0\neq}$ value of 43.2 kcal/mol, indicating that **4PP** is not active species for the hydrogenation step.

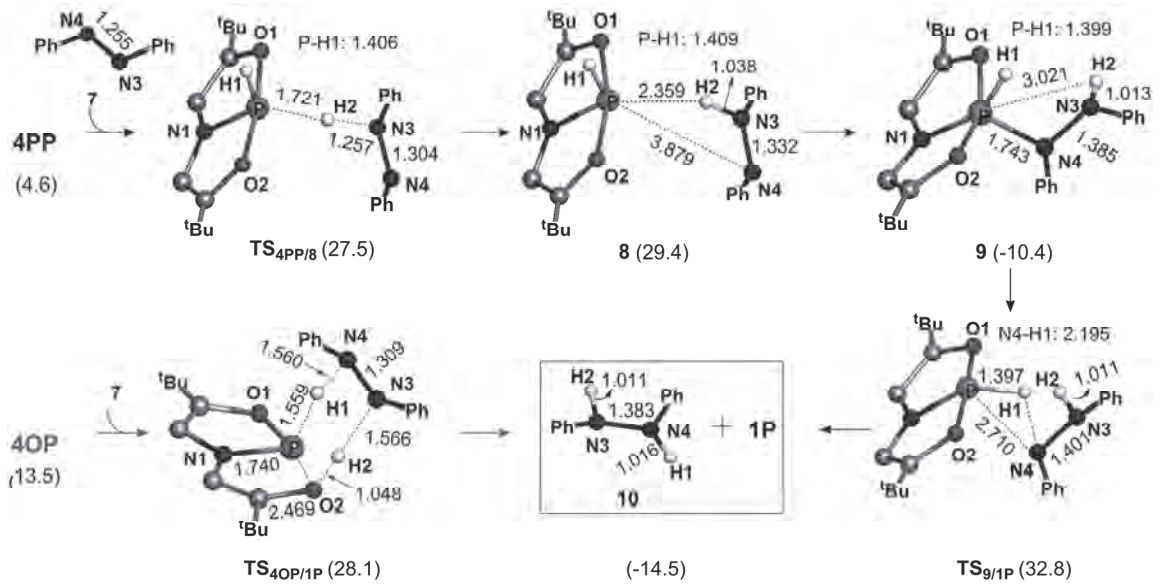
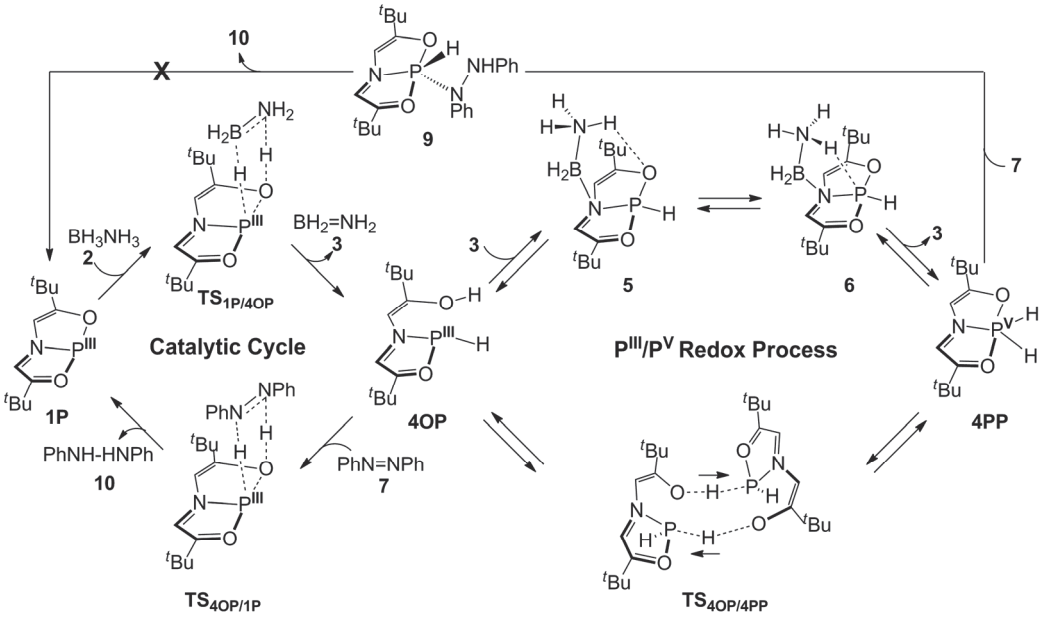


Figure 3. Geometry changes along the transfer hydrogenations starting from **4PP** and **4OP**, respectively. Distances are in Å. In parentheses are Gibbs free energy changes, in kcal/mol.

In brief, the transfer hydrogenation reaction by **1P** occurs through the P-O cooperation, where the NH_3BH_3 dehydrogenation reaction leads to the intermediate **4OP**, which transfers hydrogen atoms to azobenzene to complete the catalytic cycle; see Scheme 2. In the absence of azobenzene, **4OP** transforms to **4PP** with the assistance of NH_2=BH_2 or through the intermolecular hydrogen shuttles.



Scheme 2. The most plausible mechanism for the transfer hydrogenation by **1P**.

As last, we examined the substituent effect and found that the electron withdrawing substituent enhanced the activity of **1P**; see the Figure 4 for energy changes.[2]

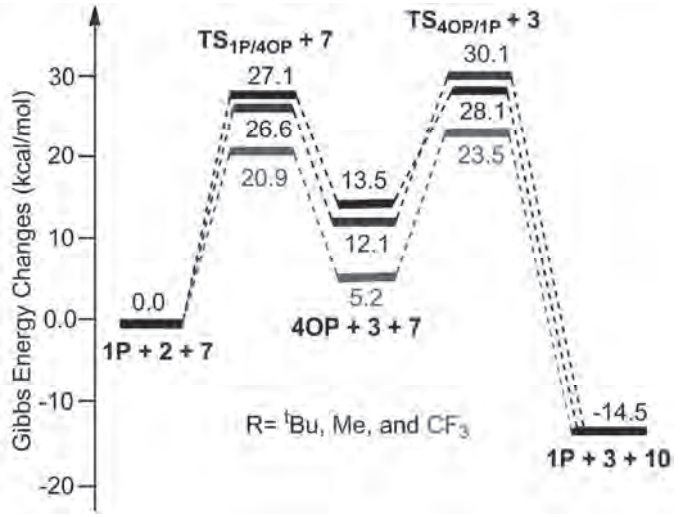


Figure 4. Reaction profile for the transfer hydrogenation reaction by **1P** with the substituents of *t*Bu, Me, and CF_3.

In order to explain the reason why the electron withdrawing ligand is favourable for the reaction, we made NBO analysis along the reaction pathway; see Figure 5.

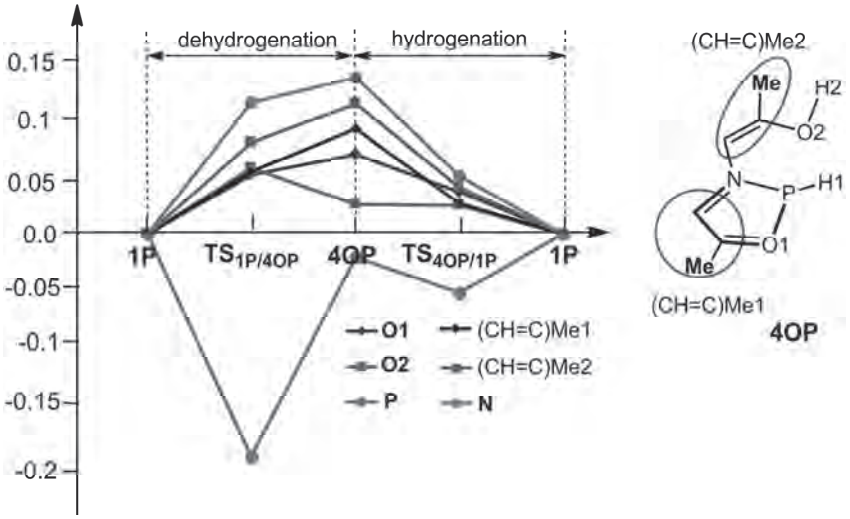


Figure 5. NBO analysis along the transfer hydrogenation reaction by 1P.

In the NH_3BH_3 dehydrogenation step, the electron population of the ONO ligand increases, indicating that the ligand accepts electrons during the reaction and thus the electron withdrawing substituent would enhance the activity of the catalyst in this reaction step. This is consistent with the energy changes that the Gibbs energy barrier ($\Delta G^{0\neq}$) of the NH_3BH_3 dehydrogenation step decreases in the order *t*Bu(27.1 kcal/mol) > Me (26.6 kcal/mol) > CF_3 (20.9 kcal/mol), where *t*Bu, Me and CF_3 are substituents on the ONO ligand. This reaction step is endothermic but the endothermicity decreases in the order *t*Bu(13.5 kcal/mol) > Me (12.1 kcal/mol) > CF_3 (5.2 kcal/mol), indicating that the active species **4OP** is also stabilized by the electron

withdrawing ligand.

In the azobenzene hydrogenation step, the electron population of the ONO ligand considerably decreases, indicating that the ONO ligand donates electrons in the reaction. As a result, the electron donating ligand would be favorable for this reaction step. This is consistent with the calculation results that the energy difference between $\mathbf{TS_{4OP/1P}}$ and (**4OP** + **7**) increases in the order *t*Bu (14.6 kcal/mol) < Me (18.0 kcal/mol) < CF_3 (18.3 kcal/mol). However, when the initial reactants (**1P** + **3** + **7**) is taken as the reference, the $\Delta G^{0\neq}$ value for the azobenzene hydrogenation step changes in the order Me (30.1 kcal/mol) > *t*Bu (28.1 kcal/mol) > CF_3 (23.5 kcal/mol), indicating that R=CF_3 enhances the activity of **1P**. One reason for this phenomenon is that the stabilization (8.3 kcal/mol, comparing with R=*t*Bu case) of **4OP** by R=CF_3 is larger than its destabilization (3.7 kcal/mol, comparing with R=*t*Bu case) of $\mathbf{TS_{4OP/1P}}$. This is because the increase of the electron population on the ONO ligand is larger when it goes from **1P** to **4OP** than its decrease when it goes from **4OP** to $\mathbf{TS_{4OP/1P}}$. As a result, the electron withdrawing substituent plays more important role in stabilizing **4OP** than its destabilization role in $\mathbf{TS_{4OP/1P}}$.

Original papers

[1] Guixiang ZENG, Satoshi MAEDA, Tetsuya, TAKETSUGU, and Shigeyoshi SAKSKI
"Catalytic Transfer Hydrogenation by a Trivalent Phosphorus Compound: Phosphorus-Ligand Cooperation Pathway or P^{III}/P^{V} Redox Pathway?" *Angew. Chem. Int. Ed.* 53, 4633 –4637(**2014**).

[2] Guixiang ZENG and Shigeyoshi SAKSKI
"Transfer Hydrogenation by a Trivalent Phosphorus Compound: Electronic Process and Prediction" *In preparation.*

2. Presentation at academic conferences

Guixinag Zeng, Shigeyoshi Sakaki "C–C bond Formation between Alkenes and Alcohols Catalyzed by a Cationic Ru(II) Hydride Complex: A Theoretical Study" The 60th Symposium of Organometallic Chemistry, Tokyo, September 7, 2013.

3. Others

Guixinag Zeng, Shigeyoshi Sakaki "Mechanistic Study of the Silylation Reaction of Allylic Alcohol Mediated by $[Pd(MeCN)_4](BF_4)_2$" The 10th symposium of Fukui Institute for Fundamental Chemistry, Kyoto, January. 23, 2014.

Nozomi TAKAGI

SPR Fellow

1. Summary of the research of the year

Theoretical Study of Reactivity of Ge(II)-hydride Compound: Comparison with Rh(I)-hydride Complex and Prediction of Full Catalytic Cycle by Ge(II)-hydride

The reaction of a Ge(II) hydride compound HC{CMeArN}$_2$GeH (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) **1** with 2,2,2-trifluoroacetophenone (CF_3PhCO) is theoretically investigated with DFT and SCS-MP2 methods. This reaction easily occurs with moderate activation barrier and considerably large exothermicity, to afford a Ge(II) alkoxide **2** through a four-membered metathesis-like transition state (Figure 1). In the transition state, the charge-transfer (CT) from the Ge-H σ-bonding molecular orbital (MO) to the C=O π*-antibonding MO of CF_3PhCO plays an important role. Acetone ($(CH_3)_2CO$) and benzophenone (Ph_2CO) are not reactive for **1**, because their π*-antibonding MOs exist at higher energy than that of CF_3PhCO. Though **2** is easily formed, the catalytic hydrogenation of CF_3PhCO by **1** is difficult because the reaction of **2** with a dihydrogen molecule needs a large activation energy (Figure 2). On the other hand, our calculations clearly show that the catalytic hydrogenation of ketone by *cis*-RhH(PPh$_3$)$_2$ **4** easily occurs, as expected. The comparison of catalytic cycle between **1** and **4** suggests that the strong Ge-O bond of **2** is the reason of the very large activation energy for the hydrogenation by **1**. To overcome this defect, we investigated various reagents and found that the catalytic cycle can be completed with the use of SiF_3H. The

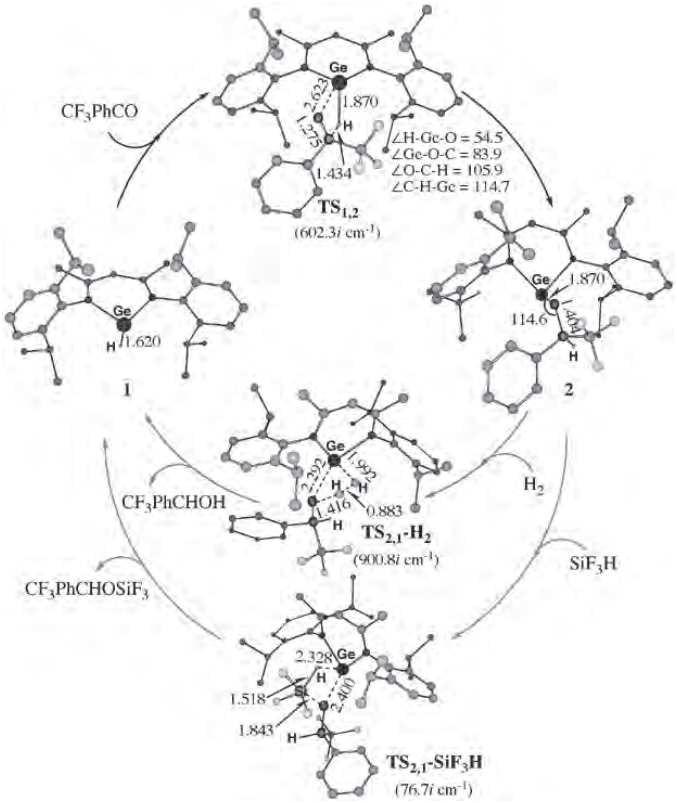


Figure 1. Geometry changes in hydrogenation and hydrosilylation of CF_3PhCO by the Ge(II) hydride **1** calculated at the B3PW91 level.

product is silylether $CF_3PhCHOSiF_3$, which is equivalent to alcohol because it easily undergoes hydrolysis to afford $CF_3PhCHOH$. The similar catalytic cycles are also theoretically predicted for hydrosilylations of CO_2 and imine. This is the first theoretical prediction of the full catalytic cycle with a heavier main-group element compound.

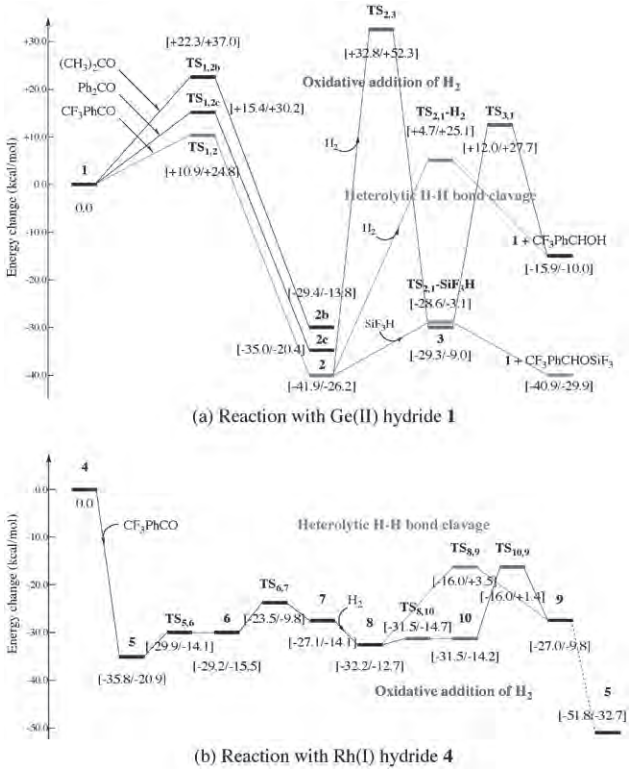
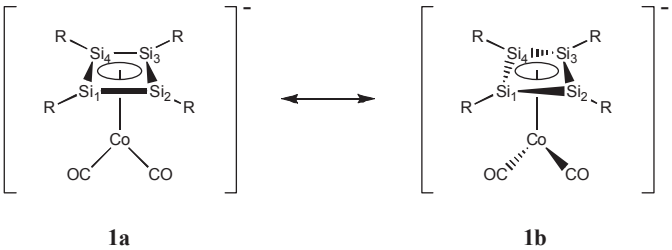


Figure 2. Potential (ΔE) and Gibbs (ΔG^0) energy changes (in kcal/mol) in (a) the hydrogenation and hydrosilylation of CF_3PhCO by the Ge(II) hydride **1** and (b) the hydrogenation of CF_3PhCO by the Rh(I) hydride **4** at the SCS-MP2//B3PW91 level, where ΔE and ΔG^0 are shown before and after the slash, respectively.

Planar D_{4h}-like vs. Non-planar C_{2v}-like Structure of η^4-Tetrasilacyclobutadiene Complex of Co(I). Theoretical Understanding

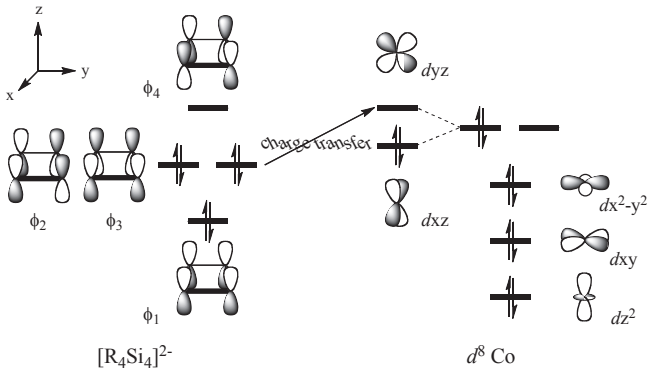
Heavier homologues of cyclobutadiene have been successfully synthesized and isolated as transition metal complexes. The experimentally reported tetrasilacyclobutadiene cobalt complex $[(SiMe\mathit{t}Bu_2)_4Si_4Co(CO)_2]^-$ **1** has a planar Si4-ring structure. This is considered as a complex between d^8 Co(I) and dianionic 6π-electron Si4 (Scheme 1a). However, theoretical calculations never present a planar Si4-ring structure as an energy minimum but a distorted non-planar structure (Scheme 1b). In the Fe(II) and Ru(II) analogues, on the other hand, the planar Si4-ring structure can be well reproduced by theoretical calculations. It is of considerable interest to elucidate the reason why the D_{4h}-like planar structure is experimentally observed but the non-planar C_{2v}-like one is calculated, because this difference deeply relates to aromaticity and electronic structure. Here, we investigated the geometry and electronic structure of **1**.



Scheme 1. Planar D_{4h}-like and non-planar C_{2v}-like structures of **1**.

As shown in Scheme 2, the $Co(CO)_2$

moiety has the d_{xz} orbital as the HOMO and the d_{yz} as the LUMO. Hence, the φ_2 of $[Si_4R_4]^{2-}$ overlaps with the d_{yz} to form a bonding CT interaction but the φ_3 overlaps with the d_{xz} to give rise to exchange repulsion. Hence, the D_{4h}-like structure is not stable. In contrast, both φ_2 and φ_3 overlaps with d_{xz} and d_{yz} in the Fe(II) and Ru(II) complexes, because these complexes have d^6 electron configuration. Though the non-planar C_{2v} structure is the most stable in **1**, the D_{4h}-like planar structure is found as a transition state connecting two non-planar C_{2v}-like structures. The Gibbs activation barrier is very small (about 2 kcal/mol). This result provides a clear explanation that the D_{4h}-like structure is experimentally observed as an average of two non-planar C_{2v}-like ones. A comparison was also made with the recently reported neutral tetrasilacyclobutadiene (Si_4EMind_4) because it takes a planar rhombic Si4-ring structure.



Scheme 2. Orbital interaction diagram of $[Si_4R_4]^{2-}$ and d^8 Co moieties.

2. Original papers

(1) "Theoretical Study of Reactivity of Ge(II)-hydride Compound: Comparison with Rh(I)-hydride Complex and Prediction of Full Catalytic Cycle by Ge(II)-hydride"
N. Takagi, and S. Sakaki, *J. Am. Chem. Soc.*, **135**, 8955-8965 (2013).

3. Presentation at academic conferences

(1) "ゲルマニウム（II）ヒドリド化合物による二酸化炭素およびイミン転換触媒サイクルの理論予測"
N. Takagi, and S. Sakaki, 第16回理論化学討論会, Fukuoka, May, 15 – 17, 2013.

(2) "A Theoretical Prediction of Catalytic Hydrosilylation of Ketone, Carbon Dioxide, and Imine by Ge(II) Hydride Compound"
N. Takagi, and S. Sakaki, 第60回有機金属化学討論会, Tokyo, September, 12 – 14, 2013.

(3) "A theoretical study of geometry and electronic structure of η^4-tetrasilacyclobutadiene complexes of Co(I) and Ru(II)"
N. Takagi, and S. Sakaki, Annual Meeting of Japan Society for Molecular Science, Kyoto, September, 24 – 27, 2013.

(4) "遷移金属錯体と高周期典型元素化合物の反応性と触媒活性の相違"
N. Takagi, and S. Sakaki, 化学反応経路探索のニューフロンティア, Kyoto, September, 27 – 28, 2013.

(5) "A Theoretical Study of Geometry and Electronic Structure of η^4-tetrasilacyclobutadiene Complex of Co(I) and Relevant Metal Complexes"
N. Takagi, and S. Sakaki, The 11th Fukui Institute for Fundamental Chemistry Symposium, Kyoto, January 23, 2014.

Masayuki NAKAGAKI

FIFC Fellow

1. Summary of the research of the year

Electronic Structure and Spin Multiplicity of Inverse Sandwich Type Dinuclear 3d Transition Metal Complexes of Ethylene: Comparison with that of Dinitrogen complexes

β-diketiminate ligands make low-valent and low-coordinate transition metal complexes and form the inversed sandwich type complexes (ISTCs). The spin states of ISTCs depend on not only the kind of metal atoms but also that of sandwiched molecule. The ISTCs of Cr(DDP); (DDPH = 2-(4-{(2,6-diisopropyl-phenyl)imino}pent-2-ene) were experimentally synthesized with several molecule. The magnetic moments of ethylene and dinitrogen complexes are 4.2 and 3.9, respectively, which correspond to the spin state between the triplet and quartet spin states, whereas the benzene and toluene complexes take septet state. Though the $(\mu\text{-}N_2)[Fe(DDP)]_2$ was also synthesized and it takes septet spin state which is completely different from that of the Cr complex, the other transition metals of ethylene complex have not been reported. In this study, we investigated the spin state and of ethylene ISTCs for 3d transition metals from Sc to Ni. The final goal of our work finding the general rule

We replaced the DDP ligands with AIP (AIPH = 1-amino-3-imino-prop-1-ene; Figure 1) for brevity. 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 π* orbitals of C_2H_4. The second-order perturbation theory with a CASSCF reference function (CASPT2) calculations were carried out at CASSCF optimized structures.

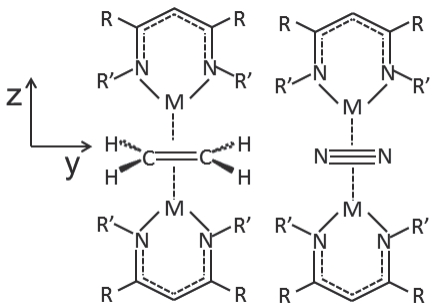


Figure 1. $(\mu\text{-}C_2H_4)[M(N^{\wedge}N)]_2$
(M= Sc-Ni; N^N = DDP or AIP)

Important structural parameters optimized for the singlet state by the CASSCF method are shown in Figure 2. The CASSCF optimized structures at the singlet to nonet spin states resemble each other. Both the Cr-Cr distance and the C-C bond length of ethylene are close to the experimental values. The geometry optimization also carried out under C_{2h} symmetry because two bond distances of Cr and each C atom of ethylene molecule were slightly different in the X-ray structure of real complex. Unfortunately, the distortion of ethylene molecule was overestimated and structural parameters are far from experiential values.

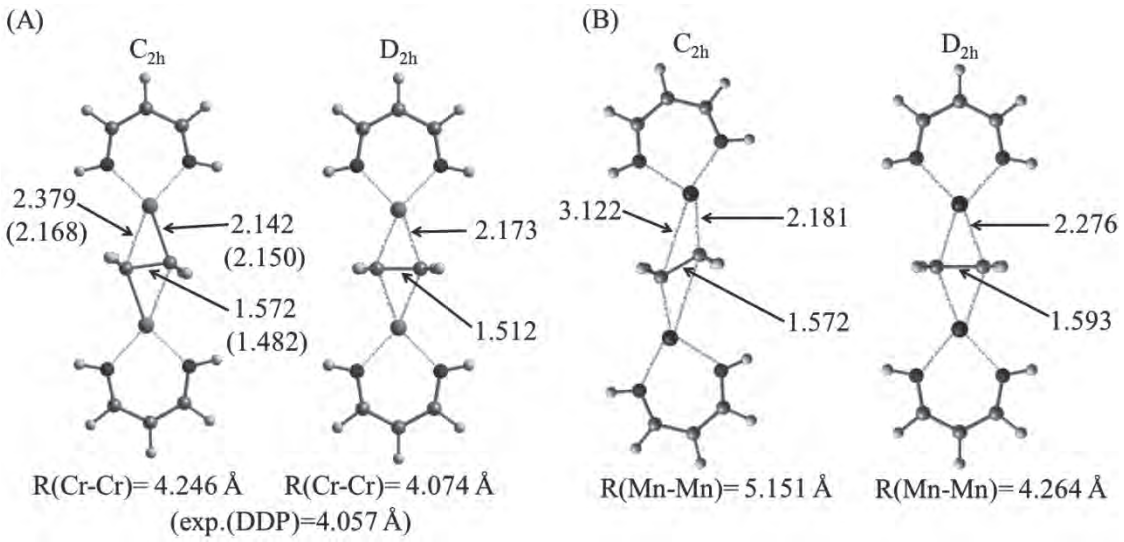


Figure 2. Optimized structure of (μ-C_2H_4)[M(AIP)]$_2$ (M=Cr, Mn) calculated by the CASSCF method. The spin states are singlet and parentheses are experimental values.

The relative energies of various spin states of (μ-η^2:η^2-C_2H_4)[Cr(AIP)]$_2$ are listed in Table 1. We chose the D_{2h} structure for latter discussion because of the similarity of experimental structure. Though the C_{2h} structure is more stable than D_{2h} structure, the trends of spin states are similar in both structures.

The ground state takes a singlet state but the energy difference between the singlet and the nonet spin states is very small. This means that the experimentally observed magnetic moment corresponds to the thermal average of these spin multiplicities. According to the Boltzmann distribution law, the average of effective magnetic moments is estimated to be μ_{eff} = 3.4 and 1.6 μ_B with CASSCF and CASPT2 calculated relative energies, respectively, at 293 K. The calculated value is different from the experimental one (4.2 μ_B), compared to N_2 complex, which indicate that the stability of low spin state was overestimated.

In the (μ-C_2H_4)[Mn(AIP)]$_2$, on the other hand, the considering of D_{2h} symmetry is not appropriate assumption because the energy difference between C_{2h} and D_{2h} structures is very large, as shown in Table 1. The distances between Mn and ethylene C atoms are 2.18 and 3.12 Å, respectively; therefore the coordination of ethylene to Mn can be regarded as η^1-coodination.

The Mn complex also takes a singlet state and the energy difference between the singlet and the undectet spin states is small. However, different from the Cr complex, these spin states are almost degenerate at the CASSCF level; see Table 1. It indicates that, in the Mn complex, the stability of low spin state results from dynamical electron correlation and cannot be explained by the CASSCF wavefunction. The relative energies of various spin states of (μ-C_2H_4)[M(AIP)]$_2$ (M=Sc to Ni) are listed in Table 2. All analogues of 3d transition metals take the singlet state.

Table 1 Relative energies (kcal/mol) of various spin multiplicities in (μ-C_2H_4)[M(AIP)]$_2$ (M= Cr, Mn) with D_{2h} and C_{2h} structures.

spin multi.	(a) CASSCF				(b) CASPT2			
	Cr		Mn		Cr		Mn	
	C_{2h}	D_{2h}	C_{2h}	D_{2h}	C_{2h}	D_{2h}	C_{2h}	D_{2h}
11			0.00	31.5			1.8	36.4
9	1.1	6.0	0.02	31.0	4.3	12.5	1.4	35.4
7	0.8	5.4	0.04	30.6	3.0	10.5	1.0	33.9
5	0.4	4.8	0.05	30.3	1.6	8.8	0.6	32.7
3	0.1	4.4	0.06	30.1	0.6	7.5	0.3	31.7
1	0.0	4.2	0.06	30.0	0.0	6.8	0.0	31.2

Table 2 Relative energies (kcal/mol) of various spin multiplicities of (μ-C_2H_4)[M(AIP)]$_2$ calculated by CASPT2 method.

spin multi.	Sc	Ti	V	Cr	Mn	Fe	Co	Ni
11					1.8			
9				5.7	1.4	1.2		
7			2.3	3.8	1.0	0.9	0.8	
5		1.1	1.3	2.0	0.6	0.6	0.6	0.1
3	0.2	0.5	0.5	0.7	0.3	0.3	0.3	0.1
1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

The CASSCF(10,11) optimized orbitals for the ^1A_g state of (μ-C_2H_4)[Cr(AIP)]$_2$ are shown in Figure 3(a). The ψ_1 MO is a bonding MO and almost doubly occupied. The occupation numbers of ψ_2 to ψ_9 MOs are close to 1.0. These orbitals and its occupations are understood by the MO interaction diagram of (μ-C_2H_4)[Cr(AIP)]$_2$, as shown in Figure 4. In the isolated M(AIP), the d_{yz} orbital is considerably destabilized in energy by the anti-bonding overlap with the two lone pair orbitals of the AIP ligand. Other four d orbitals are nearly degenerate at lower energy because they are nearly non-bonding. Anti-bonding and bonding pairs of d orbitals in [M(AIP)]$_2$ moiety are named φ_i^a and φ_i^b (i=1 to 5), respectively. These bonding and anti-bonding MOs are nearly degenerate because of the long M-M distance. The φ_5^a, an anti-bonding pair of d_{yz} orbitals of two Cr centers, overlaps well with the π^* MO of C_2H_4 to form a bonding ψ_1 MO and an anti-bonding ψ_{11} MO in (μ-η^2:η^2-C_2H_4)[Cr(AIP)]$_2$; see Figure4. The ψ_1 MO is very stable in energy because of the well π-type overlap between the d_{yz} of [Cr(AIP)]$_2$ and the in-plane π^* MO of C_2H_4. The ψ_2 to ψ_9 MOs are essentially non-bonding and singly occupied. Four electrons of them have α-spin and the other four electrons have β-spin in the singlet state. This is not unreasonable because these eight electrons can afford singlet, triplet, quintet, septet, and nonet spin states through various combinations. In such case, the energy

differences between these states are small, as shown in Table 1. Though the both ψ_8 and ψ_9 are non-bonding MO which consist of same d orbitals, the occupation numbers of them are 1.03 and 0.97, respectively. This indicated that the orbital energy ψ_8 is slightly lower than that of ψ_9 by the forming of ISTC. Thus, two Cr atoms takes low-spin coupling to provide larger occupation numbers in more stable MOs than in their counterparts. In fact, the occupation numbers of these orbitals correspond to 1.0 in nonet state. The similar deviation of occupation number from 1.0 is observed in some bonding and anti-bonding pair of d orbitals in the Sc to V complexes. On the other hand, this deviation did not occur in Mn to Ni complexes, which is consistent with the fact that the singlet state is not ground state at CASSCF level.

The CASSCF(12,11) optimized orbitals for the ^1A_g state of (μ-C_2H_4)[Mn(AIP)]$_2$ are shown in Figure 3(b). In the Mn complex, the d_{yz} orbitals are singly occupied like other d orbitals. The doubly occupied MO ψ_1 is localized on C_2H_4 moiety, which indicated that the orbital energy of C_2H_4 π^* orbital is lower than d orbitals in Mn(AIP). Thus, when the all these orbitals are singly occupied, the next electron occupy to the π^* orbital. Because of the complete electron transfer from Mn(AIP) to C_2H_4, trans vent occurs for sp3 hybridization. After that, each lone pair orbital of $[C_2H_4]^{2-}$ coordinate to one Mn atom. This is the reason why the ethylene molecule takes η^1-coordination in Mn complex.

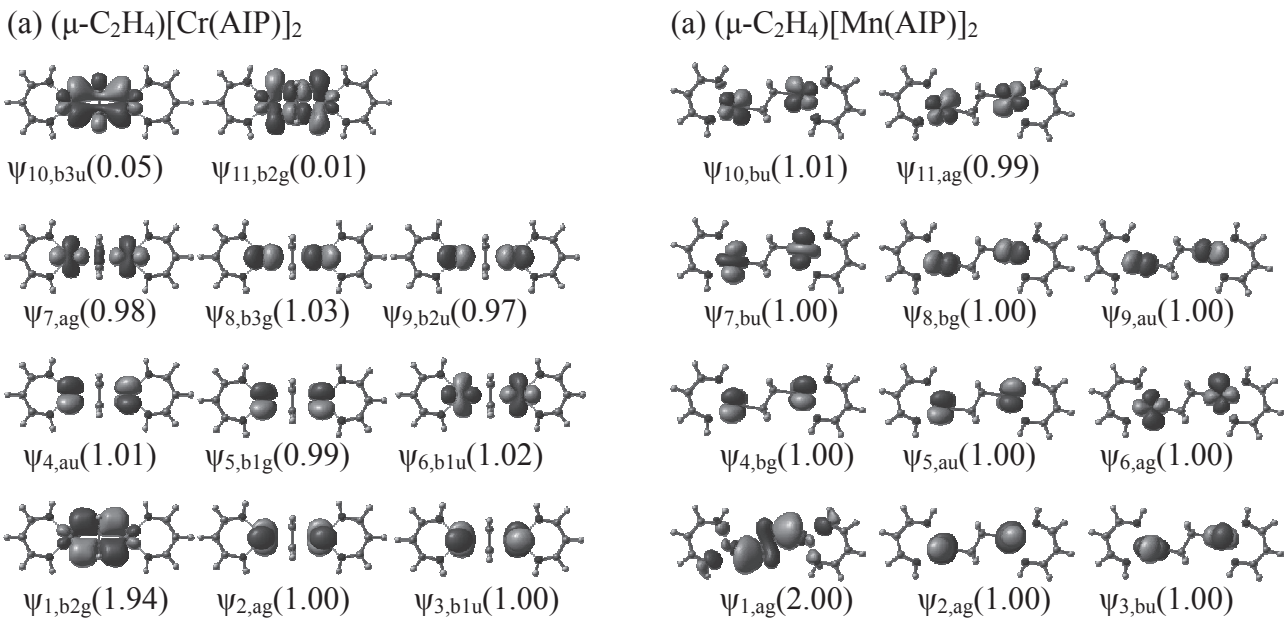


Figure 3. CASSCF optimized orbitals of (a) (μ-C_2H_4)[Cr(AIP)]$_2$ and (b) (μ-C_2H_4)[Mn(AIP)]$_2$. The subscript represents irreducible representation under D_{2h} and C_{2h} symmetries, respectively. Numbers in parentheses are occupation numbers of natural orbitals in the singlet state.

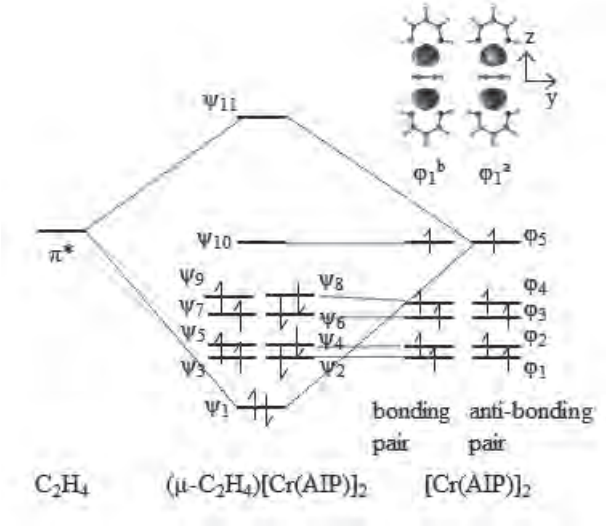


Figure 4. Schematical orbital pictures of (μ-C_2H_4)[Cr(AIP)]$_2$.

Summary

We theoretically investigated the inverse sandwich type complex, (μ-C_2H_4)[M(AIP)]$_2$ (AIPH = 1-amino-3-imino-prop-1-ene) for 3d transition metals from Sc to Ni. We found the similarity of the electronic structure between the (μ-C_2H_4)[M(AIP)]$_2$ and the (μ-N_2)[M(AIP)]$_2$ in the Sc to Cr complexes. In these complexes, the very stable bonding orbital is formed by the d_{yz} orbital of two metal atoms and the π* orbital of C_2H_4 or N_2 molecule, which is completely doubly occupied. Other singly occupying d electrons take singlet because the orbital energies of bonding and anti-bonding pair MOs slightly split by the interaction with the sandwiched molecule.

On the other hand, in the Mn to Ni complexes, the bonding nature and the spin multiplicity are completely different in (μ-C_2H_4)[M(AIP)]$_2$ and the (μ-N_2)[M(AIP)]$_2$. In the ethylene ISTCs, the each carbon atom of ethylene coordinates to individual metal atom, that is, η^1-coodination. Because two electron occupy to the π* orbital of C_2H_4, the trans vent occurs for sp3 hybridization. After that, each lone pair orbital of $[C_2H_4]^{2-}$ coordinate to individual one metal atom. Though the ground state of these complexes is a singlet state, the energy differences to high spin state are very small.

2. Original papers

(1) Masayuki Nakagaki and Shigeyoshi Sakaki

"CASPT2 Study of Inverse Sandwich-Type Dinuclear Cr(I) and Fe(I) Complexes of the Dinitrogen Molecule: Significant Differences in Spin Multiplicity and Coordination Structure between These Two Complexes"

J. Phys. Chem. A, 2014, 118 (7), pp 1247–1257

(2) Shinji Aono, Masayuki Nakagaki, Takuya Kurahashi, Hiroshi Fujii, and Shigeyoshi Sakaki

"Theoretical Study of One-Electron Oxidized Mn(III)– and Ni(II)–Salen Complexes: Localized vs Delocalized Ground and Excited States in Solution"

J. Chem. Theory Comput., 2014, 10 (3), pp 1062–1073

3. Presentation at academic conferences

(1) 中垣 雅之，青野信治，榊 茂好
「金属サレン錯体の電子構造：局在・非局在性に関する支配因子」
第 16 回理論化学討論会 2013 福岡 福岡 2013/5/15-26 2P22 ポスター

(2) 中垣 雅之、黒川 悠索、榊 茂好
「異種金属原子による窒素分子を挟んだ逆サンドイッチ型錯体の特異なスピン状態」
第 7 回分子科学討論会 2013 京都　京都　2013/9/24-27 2E18 口頭

(3) Masayuki Nakagaki, Shigeyoshi Sakaki
"Unique Spin State of Inverted Sandwich Type Complexes with Hetero Dinuclear Transition Metals Bridged by Dinitrogen Molecule"
5th JCS International Symposium on Theoretical Chemistry, Nara 2013/12/2-6 PIa-13 poster

4. Others

(1) Masayuki Nakagaki, Shigeyoshi Sakaki
"Unique Spin State of Inverted Sandwich Type Complexes with Hetero Dinuclear Transition Metals Bridged by Dinitrogen Molecule"
The 2nd International Symposium on Dynamical Ordering of Bipmolecular Systems for Creation of Integrated Functions 2014/1/11-12 P58 poster

(2) Masayuki Nakagaki, Shigeyoshi Sakaki
"Unique Spin State of Inverted Sandwich Type Complexes with Hetero Dinuclear Transition Metals Bridged by Dinitrogen Molecule"
第11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 2014/1/23

Wei GUAN

SPR Fellow, Fukui kenichi Memorial Research

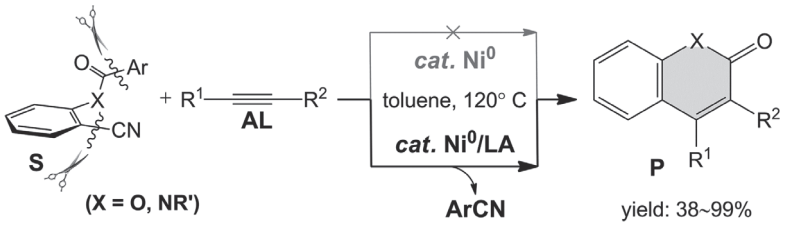
1. Summary of the research of the year

Selective Dual C–C σ-Bond Activation in Decyanative [4 + 2] Cycloaddition by Ni^0 Complex: The Role of Lewis Acid

Selective activation of inert C−C *σ*-bond attracts much attention because of its powerful and wide applications to organic syntheses. It still faces tremendous challenges. An efficient cooperation of transition metals (TMs) with Lewis acids (LAs) is expected to be a powerful tool in the C−C *σ*-bond activation. However, the mechanistic details and the origins of cooperative and synergistic functions of this TM/LA catalytic system are not clear at all. Also, the role of LA in TM-catalyzed C−C *σ*-bond activation has not yet been theoretically investigated.

Here, we theoretically investigated the Ni^0/LA_n (n = 0, 1, 2)-catalyzed decyanative [4 + 2] cycloaddition of *o*-arylcarboxybenzonitrile with alkyne via selective dual C−C σ-bond cleavages, using DFT method with the M06 functional (**Scheme 1**).

Scheme 1



(1) The most favorable catalytic cycle **A** consists of five key elementary steps: oxidative addition of C−CN *σ*-bond to the nickel(0) center (the first C−C *σ*-bond cleavage), alkyne insertion into the nickel−aryl bond, C−C coupling (ring-closing), β-aryl elimination (the second C−C *σ*-bond cleavage), and reductive elimination of coumarin (**P**), as presented in **Scheme 2**.

(2) In the oxidative addition to the Ni center, we need to investigate which of four *σ*-bonds (**a**, **b**, **c**, and **d**) of **S** undergoes the activation; see the inset in Figure 1. The C–CN *σ*-bond activation occurs via **TS1a-LA$_2$** with the smallest $\Delta G^{\circ\ddagger}$ value (12.9 kcal/mol), whereas the oxidative additions of the **b** and **c** bonds (via **TS1b-LA$_2$** and **TS1c-LA$_2$**) require much larger $\Delta G^{\circ\ddagger}$ values (30.9 and 23.4 kcal/mol,

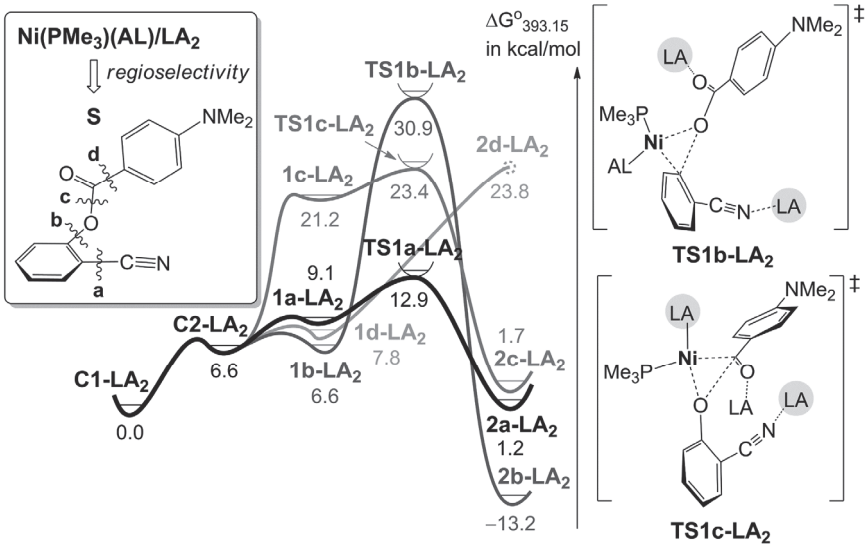
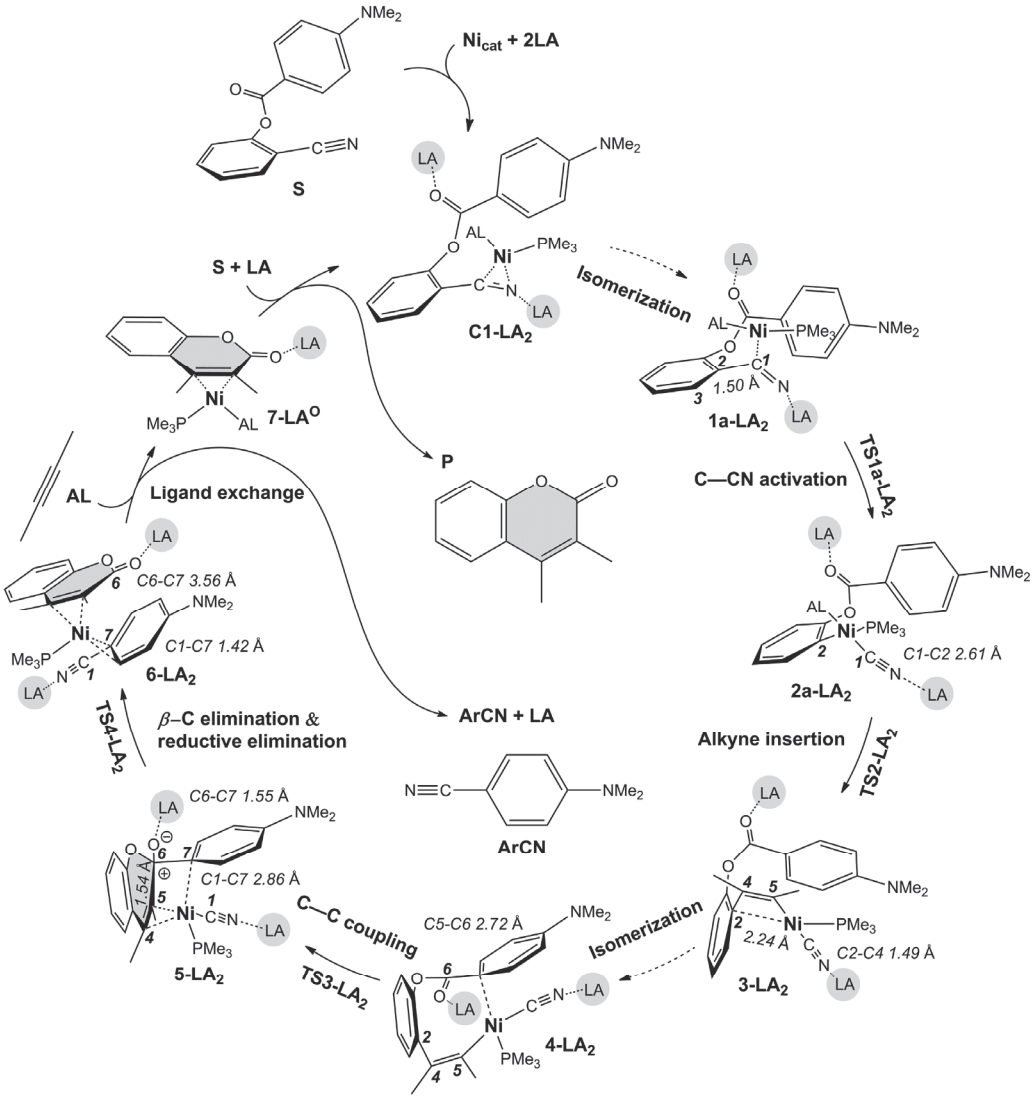


Figure 1. Energy profiles ($\Delta G^{\circ}_{393.15}$) of oxidative activation. **2d-LA$_2$** is a presumed Ni(II) intermediate with a fixed bond **d** distance of 2.39 Å.

respectively). In addition, the product of the oxidative addition of the **d** bond could not be located. It should be concluded that the first step is the oxidative addition of the **a** bond (the C–CN σ-bond).

Scheme 2



(3) After the oxidative addition, such two possible reaction courses as alkyne insertion into the Ni−C bond and activation of the second C−C (aryl−carbonyl) σ-bond must be investigated. In the alkyne insertion starting from **2a-LA$_2$**, two reaction routes were examined: in one, **AL** is inserted into the nickel−aryl (Ni−C2) bond and in the other into the nickel−cyanide (Ni−C1) bond. As shown in Figure 2, the former reaction (**2a-LA$_2$** → **TS2-LA$_2$** → **3-LA$_2$**) occurs more easily with a much smaller $\Delta G^{\circ\ddagger}$ value (14.4 kcal/mol relative to **C1-LA$_2$**) than the latter one (**8-LA$_2$** → **TS5-LA$_2$** → **9-LA$_2$**) with a $\Delta G^{\circ\ddagger}$ value (27.8 kcal/mol). On the other hand, the second C−C σ-bond activation is difficult; as shown in Figure 2, it occurs through **TS6-LA$_2$** to afford a six-coordinate Ni(IV) intermediate **10-LA$_2$** with a very large $\Delta G^{\circ\ddagger}$ value (56.8 kcal/mol relative to **C1-LA$_2$**) and a very positive ΔG° value (50.7 kcal/mol). Then, Ph−CN reductive elimination occurs through **TS7-LA$_2$** to form a four-coordinate Ni(II) intermediate **11-LA** with a very large $\Delta G^{\circ\ddagger}$ value (62.9 kcal/mol relative to **C1-LA$_2$**). Hence, it is concluded that the second step is not C−C σ-bond cleavage but alkyne insertion.

(4) **3-LA$_2$** isomerizes to an eight-member ring intermediate **4-LA$_2$** with a small ΔG°‡ value of 2.7 kcal/mol (Scheme 2 and Figure 3A). Starting from **4-LA$_2$**, the C−C coupling reaction occurs between the vinyl C5 and the carboxyl C6 atoms via **TS3-LA$_2$** to generate an intermediate **5-LA$_2$**. In **5-LA$_2$**, a new six-member ring (gray color) is formed and its C4−C5 double bond coordinates with the Ni center (Scheme 2). The ΔG°‡ and ΔG° values relative to **3-LA$_2$** are 14.0 and 0.7 kcal/mol, respectively, indicating that this process easily occurs.

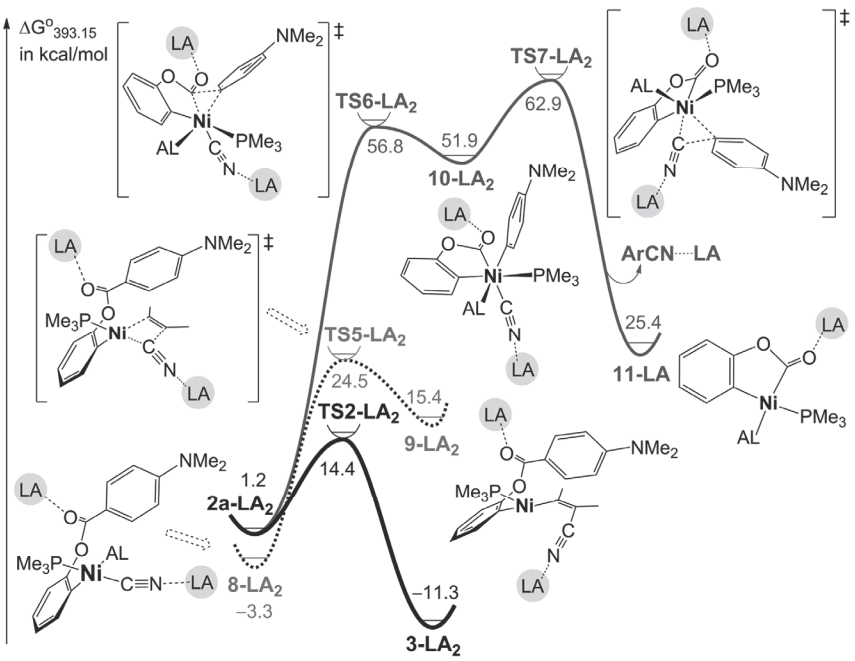


Figure 2. Energy profiles (ΔG°$_{393.15}$) of alkyne insertion and aryl-carbonyl bond activation.

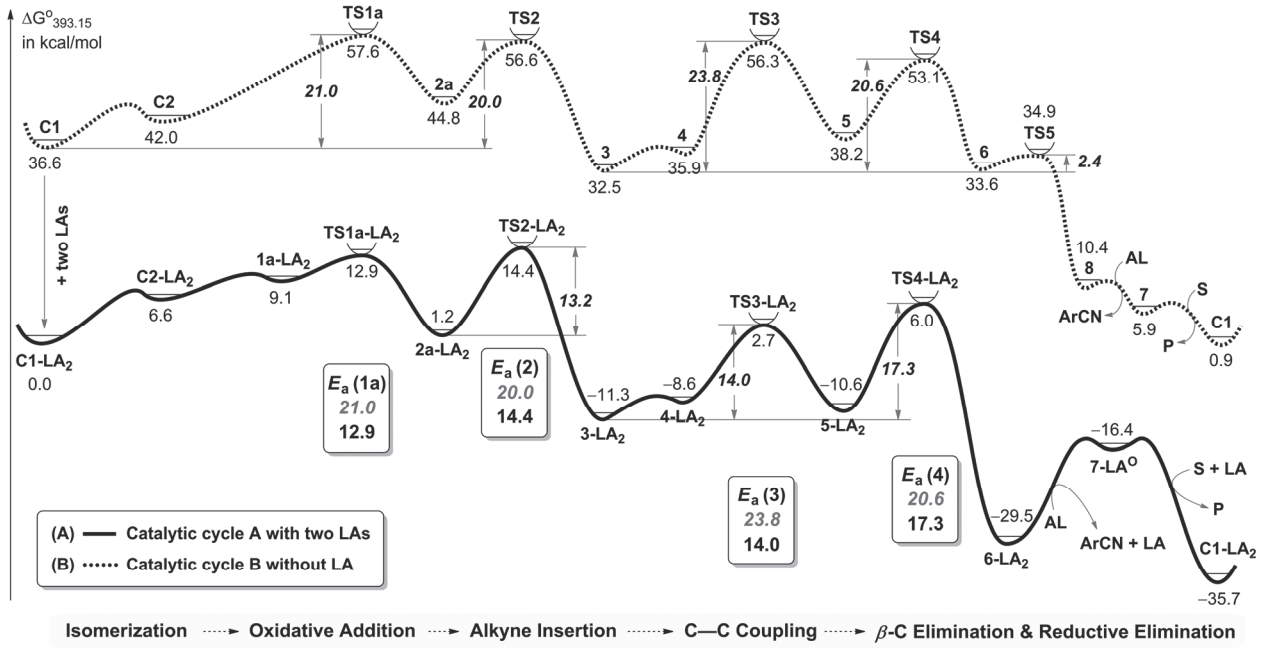


Figure 3. Energy profiles (ΔG°$_{393.15}$) of the catalytic cycles **A** and **B**.

(4) The final step of the catalytic cycle **A** is the C6−C7 bond cleavage via β-aryl elimination followed by the C1−C7 bond formation via reductive elimination (Scheme 2). These two processes occur through **TS4-LA$_2$** in one step to afford an intermediate **6-LA$_2$** in which the reductive elimination has been already completed. In **6-LA$_2$**, the C6−C7 bond is completely cleaved and the C1−C7 bond (1.42 Å) is formed

(Scheme 2). The $\Delta G^{\circ\ddagger}$ and ΔG° values relative to **5-LA$_2$** are 16.6 and −18.9 kcal/mol, respectively. Finally, a desired product coumarin **P** is released with a byproduct ArCN through ligand exchange to regenerate **C1-LA$_2$**. The rate-determining step is the β-aryl elimination followed by the reductive elimination. The $\Delta G^{\circ\ddagger}$ value for the whole catalytic cycle corresponds to the energy difference between **TS4-LA$_2$** and **3-LA$_2$**, which is 17.3 kcal/mol. The total ΔG° value is −35.7 kcal/mol. These values indicate that this catalytic reaction easily occurs with a moderate activation energy.

(5) We investigated the reaction without **LA**. Figure 3B describes the Gibbs energy profiles without **LA** (catalytic cycle **B**). Apparently, the presence of **LA** significantly stabilizes the stationary points on the potential energy surface, indicating that two **LA**s strongly coordinate with the substrate **S** through the cyano N and carbonyl O atoms. Also, it should be noted that in the catalytic cycle **B** the $\Delta G^{\circ\ddagger}$ value is 21.0, 20.0, 23.8, 20.6, and 2.4 kcal/mol for the oxidative addition, alkyne insertion, C−C coupling, β-aryl elimination, and reductive elimination, respectively. In the catalytic cycle **A**, on the other hand, those $\Delta G^{\circ\ddagger}$ values are considerably lower, 12.9, 14.4, 14.0, and 17.3 kcal/mol, respectively. These results lead to a clear conclusion that the presence of two **LA**s dramatically accelerates this catalytic reaction.

2. Original papers

(1) Wei Guan, Shigeyoshi Sakaki, Takuya Kurahashi, Seijiro Matsubara
"Theoretical Mechanistic Study of Novel Ni(0)-Catalyzed [6 − 2 + 2] Cycloaddition Reactions of Isatoic Anhydrides with Alkynes: Origin of Facile Decarboxylation"
Organometallics 32, 7564–7574(2013).

(2) Wei Guan, Fareed Bhasha Sayyed, Guixiang Zeng, Shigeyoshi Sakaki
"σ-Bond Activation of Small Molecules and Reactions Catalyzed by Transition-Metal Complexes: Theoretical Understanding of Electronic Processes"
Inorg. Chem. ic5003429(2014).

(3) Shinichi Yamabe, Gui-Xiang Zeng, Wei Guan, Shigeyoshi Sakaki
"SN1-SN2 and SN2-SN3 Mechanistic Changes Revealed by Transition States of the Hydrolyses of Benzyl Chlorides and Benzenesulfonyl Chlorides"
J. Comput. Chem. 35, 1140–1148(2014).

(4) Shinichi Yamabe, Gui-Xiang Zeng, Wei Guan, Shigeyoshi Sakaki
"Substrate dependent reaction channels of the Wolff–Kishner reduction reaction: A theoretical study"
Beilstein J. Org. Chem. 10, 259–270(2014).

(5) Zhong-Ling Lang, Guo-Chun Yang, Na-Na Ma, Shi-Zheng Wen, Li-Kai Yan, Wei Guan, Zhong-Min Su
"DFT characterization on the mechanism of water splitting catalyzed by single-Ru-substituted polyoxometalates"
Dalton Trans. 42, 10617–10625(2013).

3. Presentation at academic conferences

(1) Wei Guan, Shigeyoshi Sakaki
"Oxidative Addition of Anhydride to Nickel(0) Species: Reactivity and Regioselectivity"
The 7th Annual Meeting of Japan Society for Molecular Science (1P098) Kyoto, Sep. 19, 2013.

4. Others

(1) Wei Guan, Shigeyoshi Sakaki
"Origin of Dramatically Cooperative Catalysis on Selective Dual C–C Bond Activation in Ni^0/Lewis Acid-Catalyzed [4 + 2] Cycloaddition: Theoretical Insights" The 11th symposium of Fukui Institute for Fundamental Chemistry, Kyoto, Jan. 23, 2014.

Yue CHEN

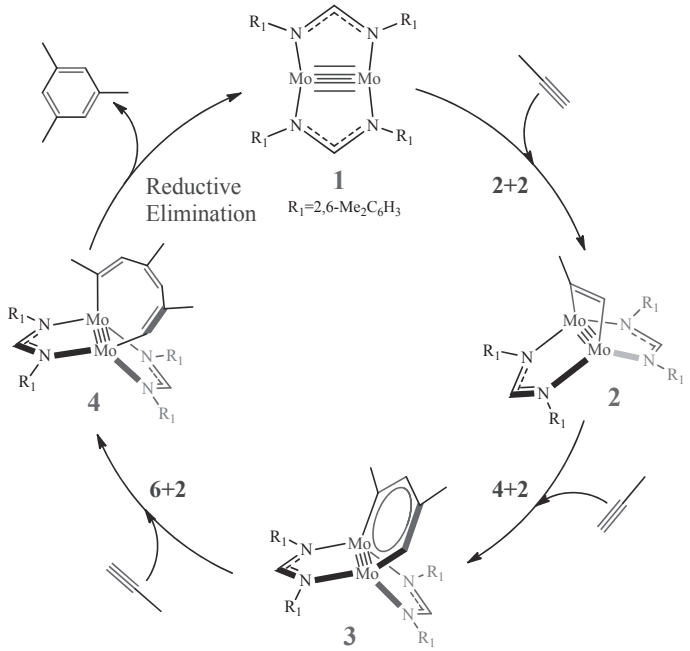
SPR Fellow

1. Summary of the research of the year

The important role of the Mo–Mo quintuple bond in catalytic synthesis of benzene from alkynes. A theoretical study

Because the metal-metal multiple bond has d_δ and/or d_π bonding orbitals at a high energy and their anti-bonding counterparts at a lower energy, the metal-metal multiple bond is expected to exhibit high reactivity. However, the reaction of the metal-metal multiple bond has not been reported until recent several pioneering works: Kempe, Theopold, and Tsai groups reported interesting reactions of the dichromium complexes with $AlMe_3$, N_2O, RN_3, NO, P_4, As_4, AsP_3, group 16 and 17 elements, and alkynes. Tsai and coworkers recently reported an interesting catalytic synthesis of benzene derivative by a dinuclear molybdenum complex $Mo_2(N^\wedge N)_2$ ($N^\wedge N$ = N,N'-$(DipN)_2CH$, Dip = 2,6-iPr$_2$C$_6$H$_3$) bearing a Mo-Mo quintuple bond, as shown in Scheme 1.

In this work, we theoretically investigated this interesting benzene formation reaction from alkyne catalyzed by **1**. Our purposes here are to (1) explore why the [2+2] cycloaddition reaction between the Mo-Mo quintuple bond and alkyne easily occurs despite of the symmetry-forbidden character, (2) elucidate how **3** reacts with one more alkyne to complete a full catalytic cycle, and (3) uncover why the Cr analogue of **1** cannot perform this catalytic reaction. Our final goal is to theoretically clarify the origin of the high reactivity of the Mo-Mo quintuple bond.



Scheme 1. Proposed catalytic cycle of benzene synthesis from three alkyne molecules by a Mo-Mo quintuple bond.

[2+2] cycloaddition between 1 and alkyne: We evaluated the potential energy surface of this pathway with the large model **1** bearing bulky substitutes (R_1 = 2,6-Me_2-C_6H_3). As shown in Figure 1, the coordination of propyne with one Mo atom occurs through a transition state **TS1** to afford a Mo-propyne complex **INT1**. Though **TS1** could be optimized with BS-I, it disappears in the DFT/BS-II calculation; E_a = -6.3 kcal/mol and $\Delta G^{0\ddagger}$ = -1.8 kcal/mol at the DFT/BS-II level. The exothermicity is considerably larger (ΔE = -30.2 kcal/mol). It is concluded that the acetylene coordination with the Mo center easily occurs with a negligible small activation barrier. The η^2-coordinate **INT1** converts to a four-member ring complex **2** through a transition state **TS2**. The $\Delta G^{0\ddagger}$

value is small (3.7 kcal/mol) and the ΔG^0 value is large (-8.6 kcal/mol) relative to **INT1**. These values are consistent with the experimental observation that the reaction occurs at very low temperature (-35 ℃).

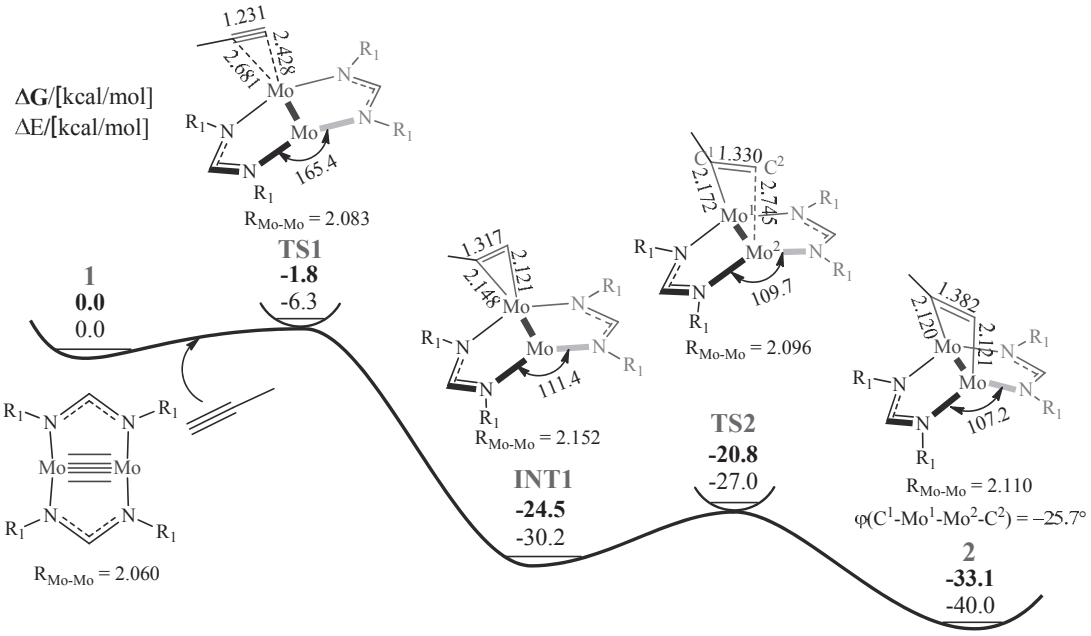


Figure 1. Energy change in the [2+2] cycloaddition via an asymmetric pathway

Formations of six-member dimolybdenacyclic compound 3. Because of the presence of bulky substituents of the N^N ligand, the incoming propyne interacts not with the $\pi_{d_{xz}}$ MO but with the $\pi_{d_{yz}}$ MO to afford an intermediate **INT2** through a transition state **TS3a**, as shown in Figure 2. The $\Delta G^{0\ddagger}$ is 4.7 kcal/mol relative to **2**, which is moderately higher than that of the first propyne coordination. This is because the $\pi_{d_{yz}}$ is more stable than the $\delta_{d_{xz}}$ and the steric repulsion with the bulky substituents on the N^N ligand becomes larger in **TS3a** than in **TS2**; note that **TS3a** is more congested than **TS2**. **INT2** turns into a less stable intermediate **INT3** via a transition state **TS3b**, where one N atom of the N^N ligand dissociates from the Mo^2 center to provide a vacant site and the second propyne moves to this vacant site. Starting from **INT3**, the C^3 of the second propyne approaches the C^2 of the first propyne to afford a dimolybdenacyclic compound **3** through a transition state **TS3c**. This elementary step is understood to be the coupling reaction between the C^1-C^2 double bond of **2** and the C^3-C^4 triple bond of the incoming propyne. The $\Delta G^{0\ddagger}$ of this C^2-C^3 bond formation is 13.5 kcal/mol and the ΔG^0 is very negative (ΔG^0 = -66.0 kcal/mol) relative to **INT3**.

[6+2] cycloaddition reaction to produce benzene. The next step is the reaction between the third propyne and **3**. Though the Mo-Mo $\pi_{d_{xy}}$ and $\pi_{d_{yz}}$ MOs of **3** can interact with the π^* MO of the incoming propyne through CT interaction, the bulky substituents on the N^N ligand and the congested six-member ring suppress the approach of propyne in both of the yz and xy planes. Because of this congested geometry, one N atom of the N^N ligand must dissociate from the Mo center to form an intermediate **INT4a** through a transition state **TS4a,** as shown in Figure 3. The $\Delta G^{0\ddagger}$ of this step is somewhat large (22.4 kcal/mol), which is consistent with the higher reaction temperature in the experiment compared to those of the previous steps. The subsequent C-C bond formation between the incoming propyne and **INT4a** leads to the generation of **INT4b** with a very

small $\Delta G^{0\ddagger}$ value of 4.6 kcal/mol. In **INT4b**, an eight-member ring has not been formed yet but a fused ring structure consisting of four-member and six-member rings is found interestingly. Then, the Mo-C bond breaking occurs to induce the ring extension, which leads to the formation of an eight-member ring complex **4** concomitantly with re-coordination of the N atom of the N^N ligand with the Mo center. These two steps both occur facilely; see $\Delta G^{0\ddagger}$ = -4.2 kcal/mol for **TS4c** and 4.6 kcal/mol for **TS4d**, as shown in Figure 3.

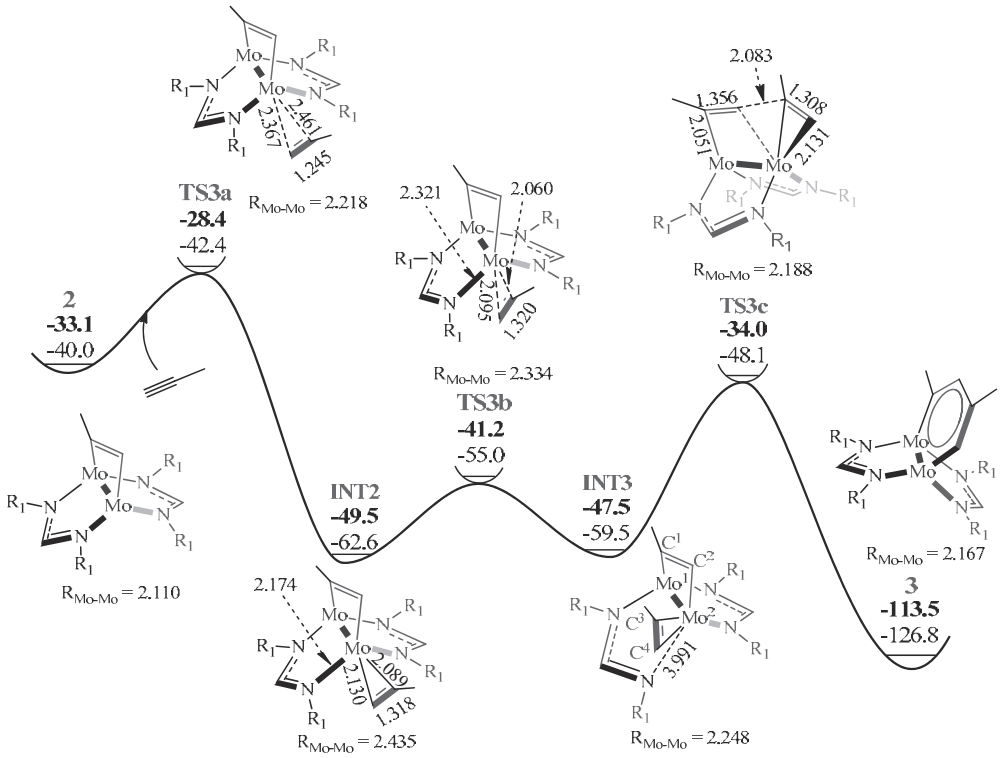


Figure 2. Energy change in the [4+2] cycloaddition between **2** and propyne.

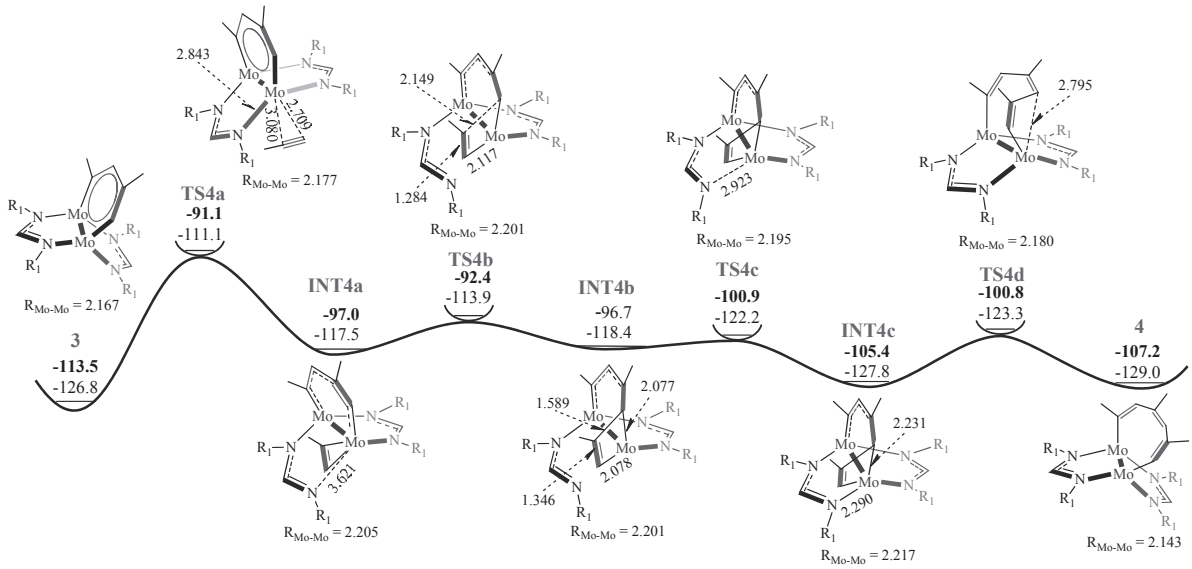


Figure 3. The energy change in the [6+2] cycloaddition between **3** and propyne.

Starting from **4**, two reaction pathways are possible; in one, benzene is produced via reductive elimination (blue line in Figure 4) and in another, one more propyne is inserted into the Mo-C bond to produce a ten-member ring which is ring extension (black line in Figure 4). In the reductive

elimination, the $\Delta G^{0\ddagger}$ value is 6.9 kcal/mol and the ΔG^{0} is -55.3 kcal/mol relative to **4**, indicating that the reductive elimination easily occurs with a moderate activation barrier and a significantly large exothermicity. In the ring extension pathway, the $\Delta G^{0\ddagger}$ value of alkyne insertion is 13.5 kcal/mol and the $\Delta G^{0\ddagger}$ value of reductive elimination of 1,3,5,7-tetramethyl-cyclooctatetraene is 13.6 kcal/mol, indicating that this reaction can occur thermally but it is more difficult than the reductive elimination of benzene.

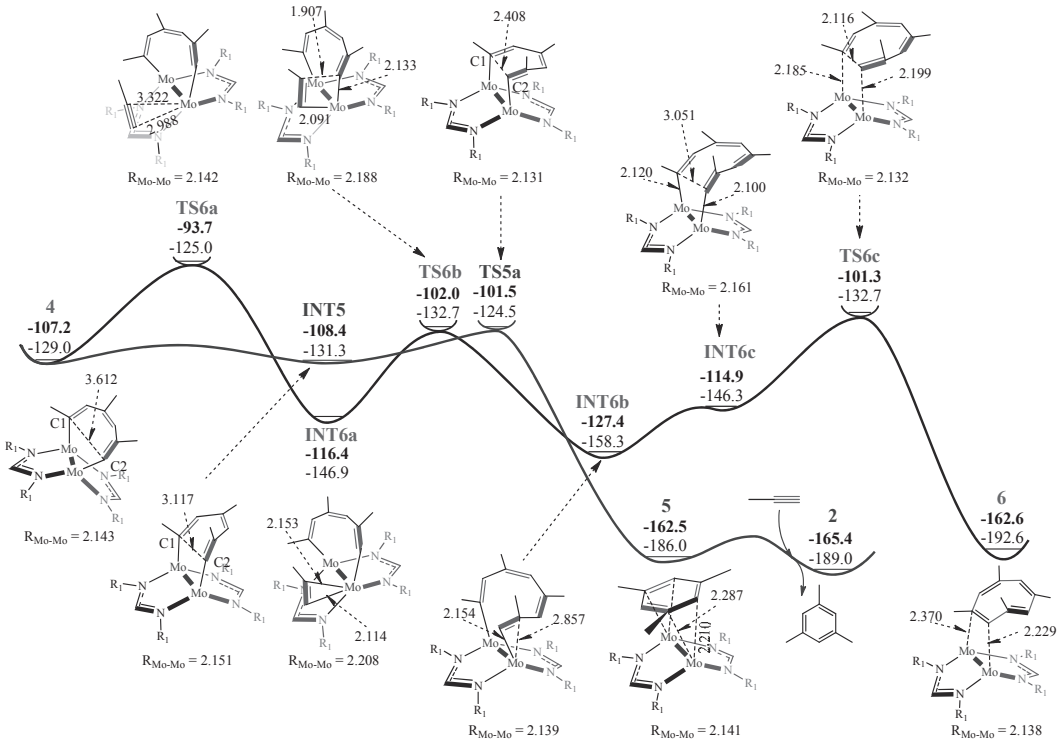


Figure 4. The energy change in the reductive elimination of benzene and [8+2] cycloaddition between **4** and propyne.

The [4+2] cycloaddition for the Cr-Cr analogue of 2. The reaction between propyne and the Cr-Cr analogue of **2** (**2**^{Cr}) was studied with the DFT method, where the superscript "Cr" means the Cr analogue. In **2**^{Cr}, the dihedral angle $\varphi(C^1\text{-}Cr^1\text{-}Cr^2\text{-}C^2)$ is -31.4º, which agrees well with the experimental value (-33.6º). The formation of **2**^{Cr} from **1**^{Cr} and propyne is significantly exothermic by -43.9 kcal/mol. The [4+2] cycloaddition between **2**^{Cr} and one

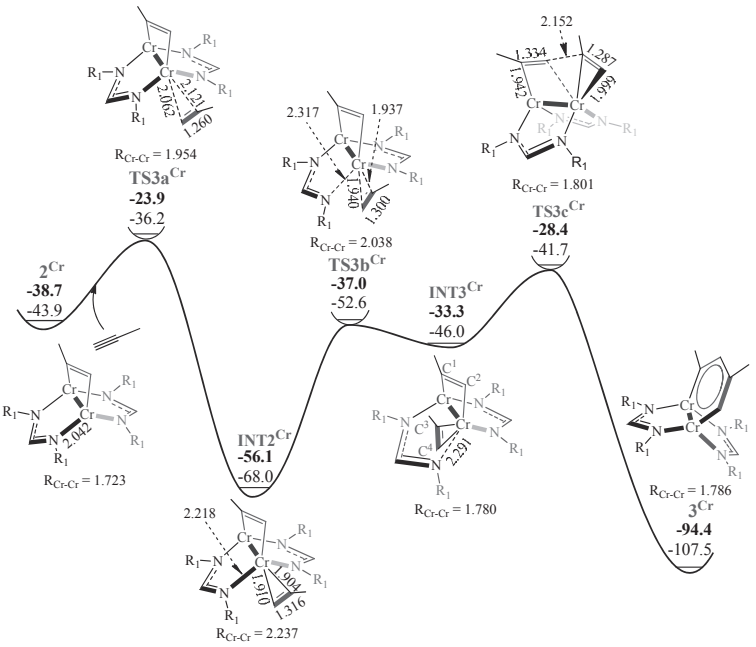


Figure 5. The energy change in the [4+2] cycloaddition between **2**^{Cr} and propyne.

more propyne occurs similarly to the Mo system, as follows: Propyne coordinates with $\mathbf{2^{Cr}}$ to afford a stable intermediate $\mathbf{INT2^{Cr}}$ via a transition state $\mathbf{TS3a^{Cr}}$. The $\Delta G^{0\ddagger}$ value is 14.8 kcal/mol, which is much larger than that (4.7 kcal/mol) of the Mo reaction system; see Figure 5. The $\Delta G^{0\ddagger}$ value of the C-C bond formation is 27.7 kcal/mol, which is also much larger than that (15.5 kcal/mol) of the Mo system. In $\mathbf{TS3a^{Cr}}$, the distance between the Cr^2 and the C^3-C^4 bond is about 2.09Å, which is shorter than that of 2.43Å in **TS3a**. The larger coordination barrier of $\mathbf{TS3a^{Cr}}$ is likely due to (1) the smaller radius of the Cr 3*d* orbital than the Mo 4*d* orbital, which leads to a more congested geometry around the Cr center, and (2) the much more stable $\pi_{d_{yz}}$ (-6.86 eV) in $\mathbf{2^{Cr}}$ than that (-6.25 eV) in **2**, which is unfavorable for the alkyne coordination with the Cr center.

Based on these results it should be concluded that $\mathbf{1^{Cr}}$ cannot be applied to catalytic synthesis of benzene from three molecules of alkyne.

In this work, the reaction mechanism of catalytic synthesis of benzene from alkynes by the Mo-Mo quintuple bonded complex **1** was investigated by DFT method. The [2+2] cycloaddition occurs with a negligibly small activation barrier in which alkyne interacts with one Mo center in a symmetry-allowed manner. The next [6+2] reaction between **3** and one more alkyne occurs with the moderate $\Delta G^{0\ddagger}$ value of 22.4 kcal/mol to afford an eight-member ring compound **4**. This is the rate-determining step of the whole catalytic cycle. The subsequent reductive elimination of benzene easily occurs and a μ_2-η^2:η^2-C_6H_6 coordinated Mo-Mo complex is formed. The [8+2] cycloaddition between **4** and one more alkyne is much more difficult than the reductive elimination of benzene. In should be emphasized that the $d_\delta - p_\pi$ π MO plays crucial roles in this catalytic cycle.

In the case of the Cr-Cr quintuple bond, the [4+2] cycloaddition needs a much more larger $\Delta G^{0\ddagger}$ value because of the much more stable $\pi_{d_{yz}}$ orbital and the more congested transition state arising from the small radius of Cr atom.

2. Original papers

(1) Yue Chen and Shigeyoshi Sakaki
"Theoretical Study of Mononuclear Nickel(I), Nickel(0), Copper(I), and Cobalt(I) Dioxygen Complexes: New Insight into Differences and Similarities in Geometry and Bonding Nature."
Inorg. Chem., 52, 13146-13159 (2013).

(2) Yue Chen and Shigeyoshi Sakaki
"The important role of the Mo-Mo quintuple bond in catalytic synthesis of benzene from alkynes. A theoretical study."
Dalton Trans., 2014, Advance Article. **DOI:** 10.1039/C4DT00595C

3. Presentation at academic conferences

(1) Yue Chen and Shigeyoshi Sakaki

"Catalytic Synthesis of Benzene from Acetylene with Dinuclear Molybdenum Complex: A Theoretical Study"
第 60 回有機金属化学討論会 (P1A-09),Tokyo, Sept. 12, 2013

(2) Yue Chen and Shigeyoshi Sakaki
"Theoretical Study of Mononuclear Nickel(I), Nickel(0), Copper(I), and Cobalt(I) Dioxygen Complexes:New Insight into Differences and Similarities in Geometry and Bonding Nature"
第 7 回分子科学討論会, Kyoto, Sept. 24, 2013

(3) Yue Chen and Shigeyoshi Sakaki
"Electronic Structure of N_2-bridged lanthanide single-molecule magnet"
5th JCS International Symposium on Theoretical Chemistry, Kyoto, Dec. 2, 2013

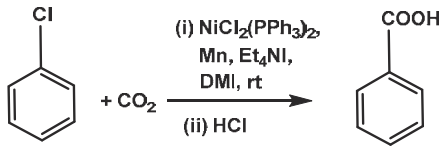
Sayyed Fareed BHASHA

SPR Fellow

1. Summary of the research of the year

The Crucial role of Ni(I) species in Ni-catalyzed Carboxylation of Aryl Halides with CO_2

The increasing concentration of carbon dioxide (CO_2) in the atmosphere poses a severe threat to environmental safety due to greenhouse effect. Over the past few years efforts have been increased to reduce the CO_2 emission from the industries or to store CO_2 and most of these attempts are inauspicious. Although reducing the CO_2 concentration directly from the atmosphere is a difficult task but indirectly it can be reduced by utilizing CO_2 to prepare useful chemicals. CO_2 is thermodynamically stable and kinetically inert, the transformation of CO_2 to useful materials need powerful catalysts. Transition metal complexes have been used as promising catalysts for CO_2 activation. In particular, synthesis of carboxylic acids and its derivatives from CO_2 is of much recent interest because they are important chemicals in the industry and they can also serve as starting materials for other organic transformations. However, the direct carboxylation of aryl halides with CO_2 has remained elusive. Correa and Martin proposed a Pd-catalyzed direct carboxylation reaction of aryl bromides with CO_2. However, this reaction occurs only when reactive aryl bromides are employed but cannot when aryl chlorides are employed. Very recently, Tsuji and his co-workers succeeded to overcome this limitation by developing a nickel catalytic system. As shown in Scheme 1, aryl chloride is directly transformed to corresponding carboxylic acids with CO_2 in the presence of Ni(0) complex and Mn.

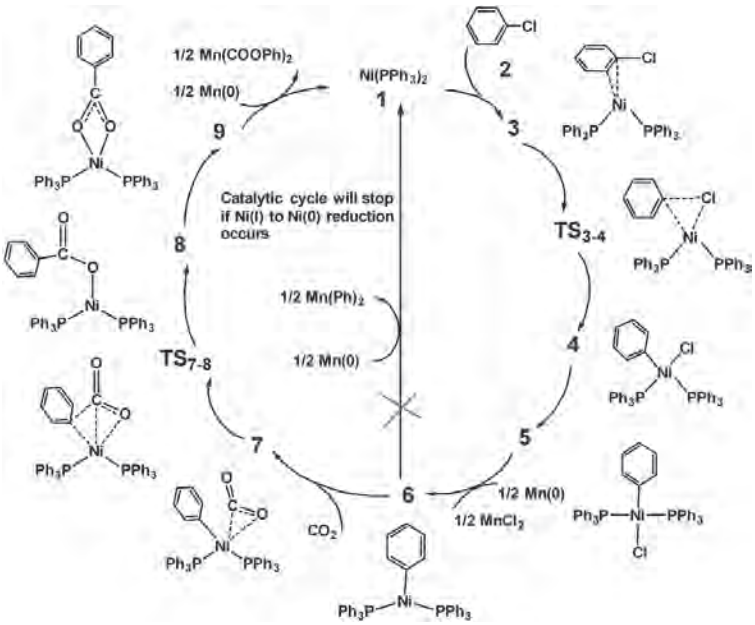


Scheme 1. Ni(0) catalyzed direct carboxylation of phenyl chloride with CO_2.

As shown in Scheme 1, aryl chlorides can be easily converted to the carboxylic acids using Ni-catalyst. This is the first example showing the metal mediated C-C coupling of carbon dioxide and aryl halides at ambient temperature. This reaction is selective only to the aryl chlorides and bromides but not the flourides. Why aryl chlorides and bromides are susceptible to carboxylation? What is the mechanism of the catalytic reaction? what Ni(I) species participates in the reaction? why Ni(I) species is necessary? what elementary step is accelerated by the Ni(I) species? The originality of the proposal comes out by unveiling the origin of these facts, and I expect that probably some guidelines would be feasible for the designing of new and efficient catalysts.

Shown in Scheme 2 is the most plausible mechanism for the Ni-catalyzed direct carboxylation of PhCl with CO_2. The reaction starts with oxidative addition of PhCl to $Ni(PPh_3)_2$.

Coordination of PhCl leads to the formation of a η^2-coordinated precursor complex $Ni(PPh_3)_2(PhCl)$ **3** in which the C=C bond of PhCl coordinated with the Ni-center. From **3**, the C-Cl bond cleavage occurs through a 3-membered transition state $\mathbf{TS_{3\text{-}4}}$ to afford a *cis*-nickel chlorophenyl complex **4** as shown in Scheme 2. Complex **4**



Scheme 2. Catalytic cycle of Ni(0) catalyzed carboxylation of aryl chlorides with CO_2.

isomerizes to the more stable squareplanar *trans*-form **5**. Because **5** is a Ni(II) complex, it can undergo one electron reduction by Mn to afford **6**. CO_2 approaches **6** to form a η^2-coordinated $Ni(Ph)(PPh_3)_2(CO_2)$ adduct **7**. From **7**, CO_2 insertion into the Ni(I)-Ph bond gives a η^1-coordinated $Ni^I(PPh_3)_2(\eta^1\text{-OCOPh})$ **8** through a transition state $\mathbf{TS_{7\text{-}8}}$. The most important result is the existence of Ni(I) intermediate which is essential for the conversion of CO_2 to COOH group. We hope that this interesting result will open up new Ni-catalysts in the transition metal catalyzed conversion of CO_2.

2. List of original papers

(1) Sayyed Fareed Bhasha, Yasushi Tsuji, and Shigeyoshi Sakaki,
"The crucial role of a Ni(i) intermediate in Ni-catalyzed carboxylation of aryl chloride with CO_2: A theoretical study"
Chem. Commun. **49**(91), 10715-10717 (2013).

3. List of review articles

(1) Guan, Wei, Sayyed Fareed Bhasha, Guixiang Zeng, Shigeyoshi Sakaki.
"σ-Bond Activation of Small Molecules and Reactions Catalyzed by Transition-Metal Complexes: Theoretical Understanding of Electronic Processes"

Inorg. Chem. DOI: 10.1021/ic5003429 (2014).

4. List of presentations at meetings

(1) CO_2 Insertion into Ni(I)-Alkyl and Ni(II)-Alkyl Bonds.Interesting Differences. Sayyed, F. B and Sakaki, S. The 7th Annual Meeting of Japan Society for Molecular Science, Kyoto, September 24-27, 2013.

(2) Crucial role of a Ni(I) intermediate in Ni-catalyzed carboxylation of aryl chloride with CO_2.
F.B. Sayyed, Y. Tsuji and S. Sakaki*, FIFC symposium, k The 6th symposium of Fukui Institute for Chemistry, Kyoto, January 23, 2014.

山田　健太

特推研究フェロー

1. 今年度の研究の要約

今年度は、プロトン還元触媒作用を示す Ni(II)錯体の構造や電子状態に関する研究を行った。

【はじめに】

水素ガスは、燃焼で二酸化炭素を生成しない、かつ高いエネルギー密度をもつ優れた燃料であり、低炭素社会に向けた次世代エネルギーの１つとして大きな期待が寄せられている。しかしながら、入手可能な天然資源として決して大量にあるわけではない。そこで、近年、遷移金属錯体の存在下で、電気化学的な酸化・還元反応を用いた水の分解による水素ガスの生成が注目されている[1]。この分解では副次生成物は酸素ガスであり、有害な物質を排出しないことが特長である。

水１分子の分解（式１）は吸熱反応であり、必要であるエネルギーは 2.46 eV と知られている。

$$H_2O \rightarrow H_2 + (1/2)O_2 \qquad (1)$$

逆に言えば、これは水素ガスの酸化（燃焼）によって 2.46 eV ものエネルギーが得られることを示している。分解を進行させるために必要なエネルギーとして化石燃料によるものを使うのは、明らかに本末転倒である。そこで、「人口光合成」、つまり、太陽光などの光エネルギーを用いて水の分解を実施し、そのエネルギーを化学エネルギーに変換し蓄えることが考えられてきた。

可能な限り少ないエネルギーによって水素ガスを生成するために、これまで多くの実験研究によって、プロトン還元活性をもった遷移金属触媒が報告されてきた。特に、コスト面から Pt などの貴金属ではなく、Co や Ni、Mo などを用いた触媒の提案が盛んになっている。本研究では、これまで提案されてきた遷移金属触媒のなかで、長時間にわたって高い水素発生活性を示す Ni(II)錯体[2]を取り上げ、その１電子還元体、２電子還元体、プロトン付加体のスピン状態や電子構造を明らかにするとともに、Ni(II)−H と配位子に付加したプロトン(N–H)とのカップリングにより、水素ガスを生成する素反応の電子的過程の解明を目指した。

【計算方法】

DFT(B3PW91 汎関数)法を使用し、CPCM 法で溶媒効果を考慮して構造最適化を行なった。このとき、GD3BJ 経験的分散力モデルを用いた。Ni には、内殻電子を Stuttgart グループの ECP(SSD)で置き換え、原子価電子には(311111/22111/411/11)基底を用いた。生成する水素ガスに関与する H には 6-311++G(d,p)基底を、そして残りの原子には 6-311G(d)基底を使用し、N と S には diffuse 関数を加えた。また、CPCM 法で使用する誘電率は、288 K で EtOH:H2O=1:1 の混合溶媒を用いている実験条件を再現するために、複数の温度での実験値を使った内挿によって決定した。

【結果と考察】

注目するNi(II)錯体には、図１に示すようにmeridional型(**1**)とfacial型(**1'**)の異性体が考えられる。ただし、X線結晶構造解析で観測できるのはmer型だけである。電子状態については、**1**、**1'**ともに一重項状態より18–23 kcal/mol程度、三重項状態が安定になった。

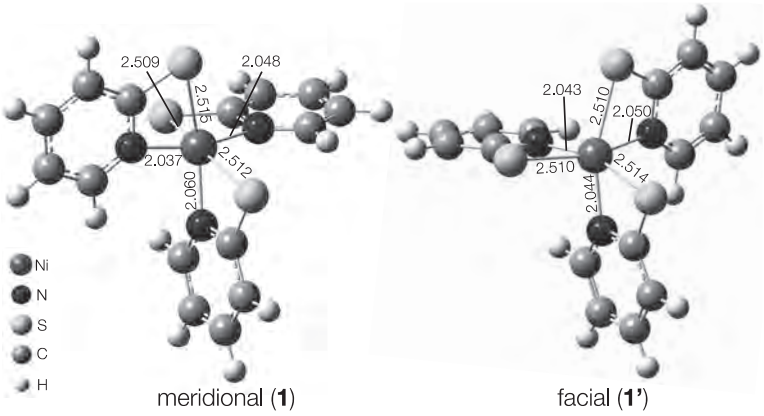
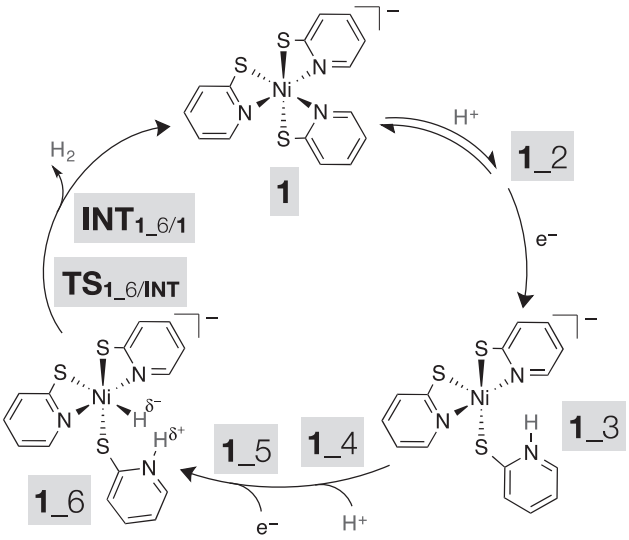


図１：注目したNi(II)錯体における異性体の構造。図中の数字は結合長を表し、単位はÅである。

実験報告では、**1**, **1'**が仲介する水素発生サイクルは、スキーム１に示すように、プロトン付加→１電子還元→プロトン付加→１電子還元で進むと考えられている。



スキーム１

まず、プロトン非存在下ならびに存在下における cyclic voltammetry(CV)の結果と比較するために、**1**と**1'**のプロトン付加体(**1_2**)、および、その１電子還元体(**1_3**)を求め、これらの自由エネルギーから還元電位を計算した。１回目のプロトン付加では、プロトンはピリジン環のNに付加し、結果として４つの異性体を生じる。この４つの異性体に対して、式２による還元電位の結果を表１にまとめた。

$$E = -\Delta G \times 27.211 - E_{SRP} \qquad (2)$$

ここで、ΔG は自由エネルギー差であり、E_{SRP} は標準還元電位（ここでは飽和カロメル電極、SCE）である。表１より、実験を概ね再現していることが分かった。しかしながら、実験は単一水溶媒を使用していないため、用いる E_{SRP} に議論の余地がある。

表１：４つの異性体をもつプロトン付加体(**1_2**)の還元電位［in V vs SCE］

	E_{SRP}				Exptl.
	4.522[a]		4.681[b]		
1_2/**1_3**	−1.3	−1.4	−1.5	−1.6	−1.2
	−1.3	−1.5	−1.5	−1.6	

[a] 実験値から求めた、真空中 0 K での電子エネルギーを基準としたときの、水中における SCE 還元電位[3]

[b] 水中 298.15 K での IUPAC 推奨値

２回目のプロトン付加(**1_4**)は、Niに付加するよりも、ピリジン環のNに付加する方が安定である。そのため、２回目の１電子還元（**1_5**）の前後で、プロトンがNからNi(I)に移動する異性化反応が起こっていると考えられる。ただし、２回目の１電子還元が、２回目のプロトン付加に先んじて起こっている可能性があり、現在検討を行っている。

Ni(II)–Hとピリジル環のNに付加したプロトンのカップリングにより、水素ガスが発生する素反応(**1_6**→**TS$_{1_6/INT}$**→**INT$_{1_6/1}$**)に関し、異性体における構造および点電荷(Natural charges)の変化を図２に示す（４つの異性体のうち、１つのみ示した）。電荷の変化から、水素分子の生成はプロトンと

ヒドリドによるヘテロカップリング反応であることを確認した。この異性体における反応障壁は、自由エネルギーでわずか 0.58 kcal/mol であり、さらに **INT$_{1_6/1}$** からは障壁なく H_2 が解離するので、**1** と **1'**は効率よく水素を発生すると予想される。これは、実験報告にある、単位時間あたり発生する水素分子の数である初期ターンオーバー頻度(initial TOF)が高いことに対応している。また、実験では、ピリジル基の５位の H を Cl や CF_3 に置換した系も取り扱っている。そこで、このような電子求引基だけでなく、CH_3 といった電子供与基を用いた計算の実施により、スキーム１における各構造の特徴や反応障壁の変化について引き続き調査を行なっていく。

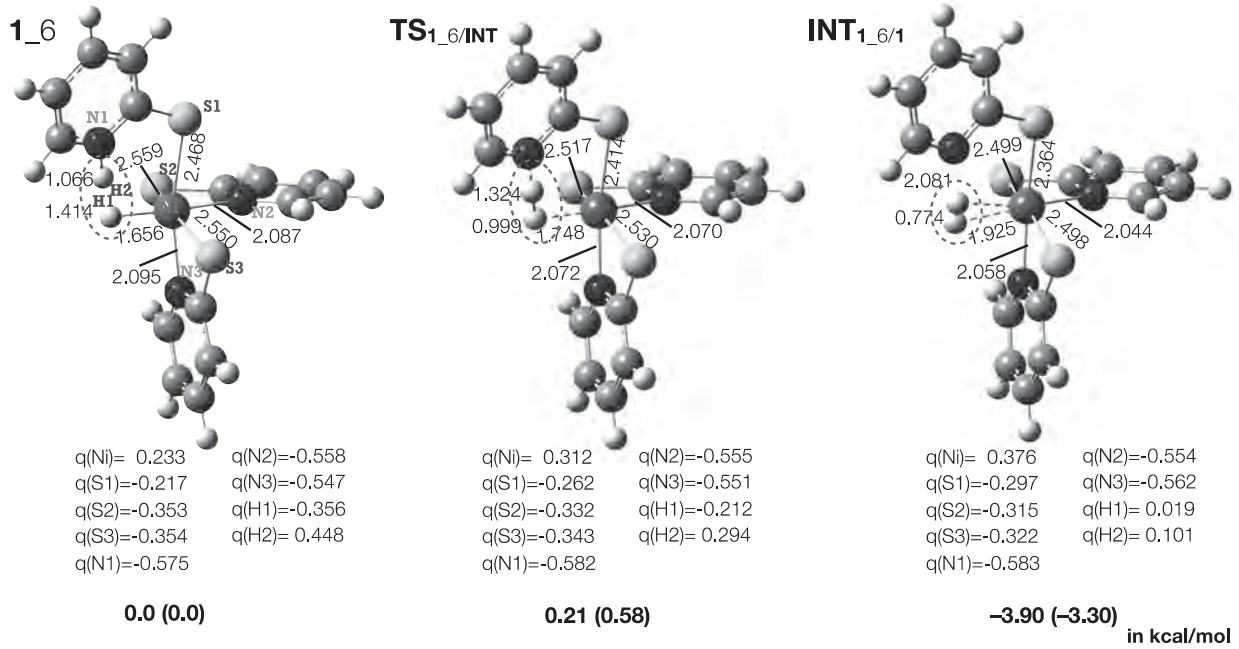


図２：Ni(II)–H とピリジル基に付加した H の反応に付随した構造および点電荷(Natural charges)の変化。図中の数字のうち、構造に付したものは結合長で単位は Å であり、構造下の数値が電荷であり単位は *e* である。また、点線で囲んだ部分が反応中心である。

【文献】

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V　資料

1．外国人共同研究者受入れ状況（平成 25 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
PETROVA Galina	外国人 共同研究者	平成24年5月13日～ 平成25年5月29日	University of Sofia （ブルガリア）・教授	諸熊奎治	DNAのキラリティに基づいた銅触媒の立体化学選択性の理論モデル
RYAZANTSEV Mikhail	外国人 共同研究者	平成25年3月1日～ 平成25年4月30日	Emory University （アメリカ）・研究員	諸熊奎治	ロドプシンの光動力学の理論的研究
DANG Jing-Shuang	外国人 共同研究者	平成25年4月16日～ 平成25年10月15日	西安交通大学（中国） ・博士課程学生	永瀬　茂	高周期典型元素と遷移金属元素化学種の理論化学
ZHAO Xiang 趙　翔	招へい 外国人学者	平成25年7月19日～ 平成25年9月1日	西安交通大学（中国） ・教授	永瀬　茂	金属内色フラーレン生成機構に関する理論解析
RAMOZZI Romain Raoul Marcel	外国人 共同研究者	平成26年2月2日～ 平成27年2月1日	リヨン高等師範大学 （フランス）・博士課程学生	諸熊奎治	有機多成分反応の反応機構と設計の理論化学的研究
PURIPAT Maneeporn	外国人 共同研究者	平成26年2月27日～ 平成27年2月26日	Chualongkorn University（タイ）・ PhD 学生	諸熊奎治	複雑分子系の理論化学・計算化学

２．海外渡航一覧（平成 25 年度）

職　　名	氏　　名	期間（自）	期間（至）	目 的 地
研究員（学術研究奨励）	諸熊　奎治	2013.5.7	2013.5.10	中　　国
研究員（学術研究奨励）	諸熊　奎治	2013.5.13	2013.6.7	アメリカ合衆国
特定研究員	畑中　美穂	2013.7.10	2013.7.13	韓　　国
研究員（学術研究奨励）	諸熊　奎治	2013.7.10	2013.7.13	韓　　国
研究員（学術研究奨励）	榊　　茂好	2013.7.10	2013.7.13	韓　　国
研究員（学術研究奨励）	永瀬　　茂	2013.7.10	2013.7.13	韓　　国
研究員（学術研究奨励）	諸熊　奎治	2013.8.25	2013.8.31	アメリカ合衆国
特定研究員	岡本　隆一	2013.9.14	2013.9.21	イタリア
研究員（学術研究奨励）	榊　　茂好	2013.10.13	2013.10.19	スウェーデン
研究員（学術研究奨励）	榊　　茂好	2013.10.23	2013.10.28	アメリカ合衆国
研究員（学術研究奨励）	諸熊　奎治	2013.11.11	2013.11.19	アメリカ合衆国
研究員（学術研究奨励）	諸熊　奎治	2014.1.6	2014.1.13	アメリカ合衆国

3．研究業績一覧（平成 25 年度）

№	Authors	Title	Journal	Volume (Number), first page to last page	year
池田　昌司					
1	Daniele Coslovich, and Atsushi Ikeda	Cluster and reentrant anomalies of nearly Gaussian core particles	*Soft Matter*	9, 6786-6795	2013
2	Atsushi Ikeda, Ludovic Berthier, and Peter Sollich	Disentangling glass and jamming physics in the rheology of soft materials	*Soft Matter*	9, 7669-7683	2013
3	Atsushi Ikeda and Ludovic Berthier	Yield stress in amorphous solids: A mode-coupling-theory analysis	*Physical Review E*	88, 052305 (1-14)	2013
4	池田昌司	ガラス転移とジャミング転移を分離する	日本物理学会誌	68 (7), 464-467	2013
永瀬　茂					
5	T. Kuwabara, M. Saito, J. –D. Guo, and S. Nagase	Unexpected Formation of Ru_2Sn_2 Bicyclic Four-Membered Ring Complexes with Butterfly and Inverse-Sandwich Structures	*Inorg. Chem.*	52, 3585-3587	2013
6	S. Sato, Y. Maeda, J. –D. Guo, M. Yamada, N. Mizorogi, S. Nagase, and T. Akasaka	Mechanistic Study of the Diels-Alder Reaction of Paramagnetic Endohedral Metallofullerene: Reaction of La@C_{82} with 1,2,3,4,5-Pentamethylcyclopentadiene	*J. Am. Chem. Soc.*	135, 5582-5587	2013
7	Y. Maeda, J. Higo, Y. Amagai, J. Matsui, K. Ohkubo, Y. Yoshigoe, M. Hashimoto, K. Eguchi, M. Yamada, T. Hasegawa, Y. Sato, J. Zhou, J. Lu, T. Miyashita, S. Fukuzumi, T. Murakami, K. Tohji, S. Nagase, and T. Akasaka	Helicity-Selective Photoreaction of Single-Walled Carbon Nanotubes with Organosulfur Compounds in the Presence of Oxygen	*J. Am. Chem. Soc.*	135, 6356-6362	2013
8	Y. Xie, M. Suzuki, W. Cai, N. Mizorogi, S. Nagase, T. Akasaka, and X. Lu	Highly Regioselective Addition of Admantylidene Carbene to Yb@C_{2v}(3)-C_{80} to Afford the First Derivative of Divalent Metallofullerenes	*Angew. Chem. Int. Ed.*	52, 5142-5145	2013
9	T. Akasaka, T. Tsuchiya, L. Feng, Y. Takano, and S. Nagase	New Vistas in Fullerene Chemistry: Organosulfer Compounds Expand the Performance of Carbon Nanomaterials	*Phosphorus, Sulfur Silicon Relat. Elem.*	188, 317-321	2013
10	P. Jin and S. Nagase	Density Functional Theory Study of Fullerene-Carbene Lewis Acid-Base Adducts: Critical Role of Dispersion Interactions	*RSC Adv.*	3, 10177-10180	2013
11	J. –S. Dang, W. –W. Wang, S. Nagase, and X. Zhao	Regiochemistry of Nonclassical C_{62} Fullerene: Role of Tetragonal Carbocyclic Ring in Cycloadditions and Thermal/ Photoinduced Interconversions of Fulleroid Derivatives	*J. Phys. Chem. C*	117, 12882-12889	2013
12	G. Luo, Q. Zheng, W. –N. Mei, J. Lu, and S. Nagase	Structural, Electronic, and Optical Properties of Bulk Graphdiyne	*J. Phys. Chem. C*	117, 13072-13079	2013
13	Y. Takano, C. Schubert, N. Mizorogi, L. Feng, A. Iwano, M. Katayama, M. A. Herranz, D. M. Guldi, N. Martion, S. Nagase, and T. Akasaka	Intramolecular versus Intermolecular Electronic Interactions between [5,6]-Open and [6,6]-Closed Adducts with exTTF	*Chem. Sci.*	4, 3166-3171	2013
14	X. Lu, T. Akasaka, and S. Nagase	Carbide Cluster Metallofullerenes: Structure, Properties, and Possible Origin	*Acc. Chem. Res.*	46, 1627-1635	2013

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15	J. N. Boynton, J. –D. Guo, J. C. Fettinger, C. E. Melton, S. Nagase, and P. P. Power	Linear and Nonlinear Two-Coordinate Vanadium Complexes: Synthesis, Characterization, and Magnetic Properties of V(II) Amides	*J. Am. Chem. Soc.*	135, 10720-10728	2013
16	M. Rudolf, L. Feng, Z. Slanina, T. Akasaka, S. Nagase, and D. M. Guldi	A Metallofullerene Electron Donor that Powers an Efficient Spin Flip in a Linear Electron Donor- Acceptor Conjugate	*J. Am. Chem. Soc.*	135, 11165-11174	2013
17	R. Fei, G. Luo, Y. Wang, Z. Gao, S. Nagase, D. Yu, and J. Lu	Enhanced Many-Body Effects in One-Dimensional Linear Atomic Chains	*Phys. Status. Solidi B*	250, 1636-1643	2013
18	W. Zhang, M. Suzuki, Y. Xie, L. Bao, W. Cai, Z. Slanina, S. Nagase, M. Xu, T. Akasaka, and X. Lu	Molecular Structure and Chemical Property of a Divalent Metallofullerene Yb@C_2(13)-C_{84}	*J. Am. Chem. Soc.*	135, 12730-12735	2013
19	T. Yang, X. Xhao, and S. Nagase	1,3-Dipolar Cycloadditions of Stone-Wales Defective Single-Walled Carbon Nanotubes: A Theoretical Study	*J. Comput. Chem.*	34, 2223-2232	2013
20	M. Yamada, T. Akasaka, and S. Nagase	Carbene Additions to Fullerenes	*Chem. Rev.*	113, 7209-7264	2013
21	T. Agou, T. Wasano, P. Jin, S. Nagase, and N. Tokitoh	Synthesis and Structures of an Alumole and its Dianion	*Angew. Chem. Int. Ed.*	52, 10031-10034	2013
22	C. Schubert, M. Rudolf, D. M. Guldi, Y. Takano, N. Mizorogi, M. A. Herranz, N. Martín, S. Nagase, and T. Akasaka	Rates and Energetics of Intramolecular Electron Transfer Processes in Conjugated Metallofullerenes	*Phil. Trans. R. Soc. A*	371, 20120490	2013
23	M. Tanaka, M. Katouda, and S. Nagase	Optimization of RI-MP2 Auxiliary Basis Functions for 6-31G** and 6-311G** Basis Sets for First-, Second-, and Third-Row Elements	*J. Comput. Chem.*	34, 2568-2575	2013
24	H. Zheng, X. Zhao, W. –W, Wang, J. –S. Dang, and S. Nagase	Quantum Chemical Insight into Metallofullerenes M_2C_{98}: M_2C_2@C_{96} or M_2@C_{98}, Which Will Survive?	*J. Phys. Chem. C*	117, 25195-25204	2013
25	C. -Y. Lin, J. –D. Guo, J. C. Fettinger, S. Nagase, F. Grandjean, G. J. Long, N. F. Chilton, and P. P. Power	Dispersion Force Stabilized Two-Coordinate Transition Metal-Amido Complexes of the -N($SiMe_3$)Dipp (Dipp = C_6H_3-2,6-Pr^i_2) Ligand: Structural, Spectroscopic, Magnetic, and Computational Studies	*Inorg. Chem.*	52, 13584-13593	2013
26	T. Yang, X. Zhao, and S. Nagase	Cycloaddition of Benzyne to Armchair Single-Walled Carbon Nanotubes: [2+2] or [4+2]?	*Org. Lett*	15, 5960-5963	2013
27	M. Suzuki, N. Mizorogi, T. Yang, F. Uhlik, Z. Slanina, X. Zhao, M. Yamada, Y. Maeda, T. Hasegawa, S. Nagase, X. Lu, and T. Akasaka	La_2@C_s(17490)-C_{76}: A New Non-IPR Dimetallic Metallofullerene Featuring Unexpectedly Weak Metal-Pentalene Interactions	*Chem. Eur. J.*	19, 17125-17130	2013
28	F. Uhlík, Z. Slanina, S. –L. Lee, T. Akasaka, and S. Nagase	Predicting Stabilities of Endohedral Metallofullerenes Yb@C_{84}	*Phys. Status Solidi B*	250, 2709-2712	2013
29	J. N. Boynton, J. –D. Guo, F. Grandjean, J. C. Fettinger, S. Nagase, G. J. Long, P. P. Power	Synthesis and Characterization of the Titanium Bisamide Ti{N(H)Ar^{iPr6}}$_2$ (Ar^{iPr6} = C_6H_3-2,6-(C_6H_2-2,4,6-$^iPr_3$)$_2$ and its TiCl{N(H)Ar^{iPr6}}$_2$ Precursor: Ti(II) ® Ti(IV) Cyclization	*Inorg. Chem.*	52, 14216-14223	2013

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30	J. –S. Dang, W. –W. Wang, X. Zhao, and S. Nagase	Regioselective Derivatization of C_{84} by Diels-Alder Reactions: Applications to Photovoltaic Solar Cells and Fullerene Polymerization	*Org. Lett.*	16, 170-173	2014
31	T. Kuwabara, J. D. Guo, S. Nagase, and M. Saito	Diversity of the Structures in a Distannene Complex and its Reduction to Generate a Six-Membered Ti_2Sn_4 Ring Complex	*Angew. Chem. Int. Ed.*	53, 434-438	2014
32	J. Ruan, Y. Xie, W. Cai, Z. Slanina, N. Mizorogi, S. Nagase, T. Akasaka, and X. Lu	Chemical Properties of Divalent Metallofullerenes Yb@D_{3h}(1)-C_{74} and Yb@C_2(13)-C_{84}	*Fullerenes, Nanotubes, Carbon Nanostruct.*	22, 138-146	2014
33	Z. Slanina, F. Uhlík, S. –L. Lee, M. Suzuki, X. Lu, N. Mizorogi, S. Nagase, and T. Akasaka	Calculated Temperature Development of the Relative Stabilities of Yb@C_{82} Isomers	*Fullerenes, Nanotubes, Carbon Nanostruct.*	22, 147-154	2014
34	Z. Slanina, F. Uhlík, S. –L. Lee, L. Adamowicz, H. Kurihara, H. Nikawa, X. Lu, M. Yamada, S. Nagase, and T. Akasaka	Computations on Metallofullerenes Derivatized during Extraction: La@C_{80}-$C_6H_3Cl_2$ and La@C_{82}-$C_6H_3Cl_2$	*Fullerenes, Nanotubes, Carbon Nanostruct.*	22, 173-181	2014
35	Z. Slanina, F. Uhlík, S. –L. Lee, L. Adamowicz, L. Feng, M. O. Ishituka, T. Tsuchiya, X. Zhao, and S. Nagase	Sm@C_{74}: Computed Relative Isomeric Populations	*Fullerenes, Nanotubes, Carbon Nanostruct.*	22, 235-242	2014
36	Z. Slanina, F. Uhlík, S. –L. Lee, B. C. Wang, L. Adamowicz, M. Suzuki, M. Haranaka, L. Feng, X. Lu, S. Nagase, and T. Akasaka	Towards Relative Populations of Non-Isometric Metallofullerenes: La@C76 (Td) vs. La2@C76 (Cs, 17490)	*Fullerenes, Nanotubes, Carbon Nanostruct.*	22, 299-306	2014
37	S. Nagase	Theory and Calculations of Molecules Containing Heavier Main Group Elements and Fullerenes Encaging Transition Metals: Interplay with Experiment	*Bull. Chem. Soc. Jpn. (Award Accounts)*	87, 167-195	2014
諸熊　奎治					
38	M. Hatanaka, S. Maeda and K. Morokuma	Sampling of Transition States for Predicting Diastereoselectivity Using Automated Search Method – Aqueous Lanthanide-Catalyzed Mukaiyama Aldol Reaction	*J. Chem. Theory Comput.*	9, 2882–2886	2013
39	A. J. Page, Y. Wang, H.-.B Li, K. Morokuma, and S. Irle	Nucleation of Graphene Precursors on Transition Metal Surfaces: Insights from Theoretical Simulations	*J. Phys. Chem. C.*	117, 14858-14864	2013
40	H. Xiao, S. Maeda and K. Morokuma	Theoretical Study on the Photodissociation of Methylamine Involving S1, T1, and S0 States	*J. Phys. Chem. A*	117, 5757–5764	2013
41	H.-B. Li, A. J. Page, S. Irle, and K. Morokuma	the Dual Role of Hydrogen for Defect Healing and Growth Inhibition In Polycyclic Aromatic Hydrocarbon Formation with QM/MD Simulations	*J. Phys. Chem. Lett.,*	4, 2323-2327	2013
42	F. Liu and K. Morokuma	Multiple Pathways for Primary Step of Spiropyran Photochromic Reaction: a CASPT2//CASSCF Study	*J. Am. Chem. Soc.*	135, 10693-10702	2013
43	S. Maeda, T. Taketsugu, and K. Morokum,	Exploring Pathways of Photoaddition Reactions by Artificial Force Induced Reaction Method: A Case Study on the Paternò-Büchi Reaction	*Zeit. Phys. Chem.*	227, 1421-1433	2013

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44	H. Xiao, S. Maeda and K. Morokuma	A CASPT2 Study of Photodissociation Pathways of Ketene	*J. Phys. Chem. A,*	117, 7001-7008	2013
45	T. V. Harris and K. Morokuma	QM/MM Structural and Spectroscopic Analysis of the Di-iron(II) and Di-iron(III) Ferroxidase Site in M Ferritin	*Inorg. Chem.*	52, 8551-8563	2013
46	Y. Harabuchi, S. Maeda, T. Taketsugu, N. Minezawa, and K. Morokuma,	Automated search for minimum energy conical intersection geometries between the lowest two singlet states S0/S1-MECIs by the spin-flip TDDFT method	*J. Chem. Theory Comput.*	9, 4116-4123	2013
47	W. Piao, S. Tsuda, Y. Tanaka, S. Maeda, F. Liu, S. Takahashi, Y. Kushida, T. Komatsu, T. Ueno, T. Terai, T. Nakazawa, M. Uchiyama, K. Morokuma, T. Nagano, and K. Hanaoka	Development of a New Class of Azo-based Fluorescence Probes to Detect Different Levels of Hypoxia	*Angew. Chem. Int. Ed.*	52, 13028-13032	2013
48	M. Hatanaka and K. Morokuma	Role of Water in Mukaiyama–Aldol Reaction Catalyzed by Lanthanide Lewis Acid: A Computational Study	*J. Am. Chem. Soc.*	135, 13972-13979	2013
49	F. Liu, Y, Kurashige, T. Yanai, and K. Morokumq	Multireference Ab Initio Density Matrix Renormalization Group (DMRG)-CASSCF and -CASPT2 Study on the Photochromic Ring-Opening of Spiropyran	*J. Chem. Theory. Comput.*	9, 4462-4469	2013
50	H.-B. Li, A. J. Page, S. Irle, and K. Morokuma	Temperature Dependence of Catalyst-Free Chirality-Controlled Single-Walled Carbon Nanotube Growth from Organic Templates	*J. Phys. Chem. Lett.*	4. 3176-3180	2013
51	S. Komagawa, C. Wang, K. Morokuma, S. Saito and M. Uchiyama	Mechanistic Origin of Chemo- and Regioselectivity of Nickel-Catalyzed [3+2+2] Cyclization Reaction	*J. Am. Chem. Soc.*	135, 14508-14511	2013
52	S. Maeda, T. Taketsugu, and K. Morokuma	Exploring Transition State Structures for Intramolecular Pathways by the Artificial Force Induced Reaction (AFIR) Method	*J. Comput. Chem.*	35, 166-173	2014
53	Y. Wang, A. J. Page, H.-B. Li, H.-J. Qian, M.-G, Jiao, Z.-J. Wu, K. Morokuma, and S. Irle	Step-Edge Self-Assembly During Graphene Nucleation on a Ni Surface: QM/MD Simulations	*Nanoscale*	6, 140-144	2014
54	L. Ding, N. Ishida, M. Murakami, and K. Morokuma	sp3–sp2 vs sp3–sp3 C-C Site-Selectivity in Rh-Catalyzed Ring Opening of Benzocyclobutenol: A DFT Study	*J. Am. Chem. Soc.*	136, 169-178	2014
55	Y. Wang, X. Gao, H.-J. Qian, Y. Ohta, X. Wu, G. Eres, K. Morokuma, and S. Irle	Quantum Chemical Simulations Reveal Acetylene-Based Growth Mechanisms in the Chemical Vapor Deposition Synthesis of Carbon Nanotubes	*Carbon*	72, 22-37	2014
56	T. V. Harris, Y. Kurashige, T. Yanai, and K. Morokuma	Ab Initio Density Matrix Renormalization Group Study of Magnetic Coupling in Dinuclear Iron and Chromium Complexes	*J. Chem. Phys.*	140, 054303/1-10	2014
57	L. Ding, L. W. Chung, and K. Morokuma	Excited-State Proton Transfer Controls Irreversibility of Photoisomerization in Mononuclear Ruthenium(II) Monoaquo Complexes: A DFT Study	*J. Chem. Theory Comput.*	10, 668-675	2014
58	M. Isegawa, S. Maeda, D. J. Tantillo and K. Morokuma	Predicting Pathways for Terpene Formation from First Principles – Routes to Known and New Sesquiterpenes	*Chem. Sci.*	5, 1555-1560	2014
59	M. Hatanaka, M. Saito, M. Fujita and K. Morokuma	σ-Aromaticity in Hexa-Group 16 Atom-Substituted Benzenes Dications. A Theoretical Study	*J. Org. Chem.*	79, 2640-2646	2014

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60	前田理, 畑中美穂, 植松遼平, 武次徹也, 諸熊奎治	人工力誘起反応法による化学反応経路の自動探索 : 有機合成化学への応用と展望	有機合成化学協会誌	72, 567-579	2014
61	諸熊奎治	この人に聞く“見えないものを理論と計算で探る”諸熊奎治博士	現代化学	507, 20-25	2013
62	諸熊奎治	複雑化学系のマルチスケールモデルの開発	現代化学	521, 38-42	2013
63	諸熊奎治	2013年度ノーベル化学賞に寄せて	科学	84, 29	2014
榊　茂好					
64	Toru Matsui, Yasutake Kitagawa, Mitsutaka Okumura, Yasuteru Shigeta, Shigeyoshi Sakaki	Consistent scheme for computing standard hydrogen electrode and redox potentials	*J. Comp. Chem.*	34 (1), 21-26	2013
65	Shinji Aono, Takashi Hosoya, and Shigeyoshi Sakaki	A 3D-RISM-SCF method with dual solvent boxes for a highly polarized system: ap-plication to 1,6-anhydrosugar formation reaction of phenyl a- and b-D-glucosides under basic conditions	*Phys. Chem. Chem. Phys.*	15, 6368-6381	2013
66	Milind Madhusudan Deshmukh, Masaaki Ohba,Susumu Kitagawa, and Shigeyoshi Sakaki	Absorption of CO2 and CS2 into the Hofmann-Type Porous Coordination Polymer: Electrostatic versus Dispersion Interactions	*J. Am. Chem. Soc..*	135, 4840-4849	2013
67	Guixiang Zeng, S. Sakaki	Unexpected Electronic Process of H2 Activation by a New Nickel Borane Complex: Comparison with the Usual Homolytic and Heterolytic Activations	*Inorg. Chem.*	52, 2844-2853	2013
68	Shinya Tsukamoto and Shigeyoshi Sakaki	A theoretical study of luminescent vapochromic compounds including an AuCu2(NHC)2 core	*Dalton Trans.*	42, 4809-4821	2013
69	Terutaka Yoshizawa, Shigeyoshi 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	*J. Comp. Chem.*	34, 1013-1023	2013
70	Wei Guan, Shinichi Yamabe and Shigeyoshi Sakaki	Interests in new heterodinuclear transition-metal/main-group-metal complexes: DFT study of electronic structure and mechanism of fluoride sensing function	*Dalton Trans.*	42 (24), 8717-8728.	2013
71	Nozomi Takagi and Shigeyoshi Sakaki	Theoretical Study of Reactivity of Ge(II)-hydride Compound: Comparison with Rh(I)- Hydride Complex and Prediction of Full Catalytic Cycle by Ge(II)-hydride	*J. Am. Chem. Soc..*	135, 8955-8965	2013
72	Fareed Bhasha Sayyed,a Yasushi Tsujib and Shigeyoshi Sakaki	Crucial Role of Ni(I) Intermediate in Ni-Catalyzed Direct Carboxylation of Aryl Chloride with CO2: A Theoretical Study	*Chem. Commun.*	49 (91), 10715-10717	2013
73	Masayuki Wakioka, Yuki Nakamura, Yoshihiro Hihara, Fumiyhuki Ozawa, and Shigeyoshi Sakaki	Factors Controlling the Reactivity of Heteroarenes in Direct Arylation with Arylpalladium Acetate Complexes	*Organometallics*	32, 4423 4430	2013
74	Wei Guan, Shigeyoshi Sakaki, Tetgsuya Kurahashi, and Seijiro Matsubara.	Theoretical Mechanistic Study of Novel Ni(0)-Catalyzed [6-2+2] Cycloaddition Reactions of Isatoic Anhydrides with Alkynes: Origin of Facile Decarboxylation	*Organometallics*	32, 7564-7574	2013

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75	Yue Chen and Shigeyoshi Sakaki	Theoretical Study of Mononuclear Nickel(I), Nickel(0), Copper(I), and Cobalt(I) Dioxygen Complexes: New Insight into Differences and Similarities in Geometry and Bonding Nature	*Inorg. Chem.*	52, 13146-13159	2013
76	Takashi Hosoya and Shigeyoshi Sakaki	Levoglucosan Formation from Crystalline Cellulose: Importance of a Hydrogen Bonding Network in the Reaction	*ChemSusChem*	6, 2356-2368	2013
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77	Shunsuke F. Shimobayashi1, Takafumi Iwaki, Toshiaki Mori, and Kenichi Yoshikawa	Probability of double-strand breaks in genome-sized DNA by g-ray decreases markedly as the DNA concentration increases	*J. Chem Phys.*	138, 174907 (4 pages)	2013
78	Masatoshi Ichikawa, Fumi Takabatake, Keitaro Miura, Takafumi Iwaki, Nobuyuki Magome, and Kenichi Yoshikawa	Controlling negative and positive photothermal migration of centimeter-sized droplets	*Physical Review E*	88, 012403 (8pages)	2013
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79	Noriyuki Minezawa	Excited-state free energy surfaces in solution: Time-dependent density functional theory/reference interaction site model self-consistent field method	*J. Chem. Phys.*	138(24), 244101 [8 pages]	2013
80	Yu Harabuchi, Satoshi Maeda, Tetsuya Taketsugu, Noriyuki Minezawa, and Keiji Morokuma	Automated search for minimum energy conical intersection geometries between the lowest two singlet states S0/S1-MECIs by the spin-flip TDDFT method	*J. Chem. Theory Comput.*	9(9), 4116-4123	2013
81	Nuwan De Silva, Noriyuki Minezawa, and Mark S. Gordon	Excited-state hydrogen atom transfer reaction in solvated 7-hydroxy-4-methylcoumarin	*J. Phys. Chem. B*	117 (49), 15386-15394	2013
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82	Ryuichi Okamoto, Youhei Fujitani and Shigeyuki Komura	Drag coefficient of a rigid spherical particle in a near-cirtical binary fluid mixture	*J. Phys. Soc. Jpn*	82, 084003	2013
83	Ryuichi Okamoto and Akira Onuki	Attractive interaction and bridging transition between between neutral colloidal particles due to preferential adsorption in a near-critical binary mixture	*Phys. Rev. E*	88, 22309	2013
齋藤　拓也					
84	Takuya Saito and Takahiro Sakaue	Cis-trans dynamical asymmetry in driven polymer translocation	*Phys. Rev. E*	88, 042606 (5)	2013
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85	Jie Chen, Jian Wang, Fu-Quan Bai, Li Hao, Qing-Jiang Pan, and Hong-Xing Zhang	Connection style and spectroscopic properties: Theoretical understanding of the interface between N749 and TiO2 in DSSCs	*Dyes and Pigments*	99 (1), 201-208	2013
86	Jie Chen, Jian Wang, Fu-Quan Bai, Qing-Jiang Pan, and Hong-Xing Zhang	Theoretical Studies on Structural and Spectroscopic Properties of Photoelectrochemical Cell Ruthenium Sensitizers, Derivatives of AR20	*Int. J. Quant. Chem.*	113 (7), 891-901	2013

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88	Vladimir Ya. Lee, Shinji Aoki, Taka Yokoyama, Satoru Horiguchi, Akira Sekiguchi, Heinz Gornitzka, Jing-Dong Guo, and Shigeru Nagase	Toward a Silicon Version of Metathesis: From Schrock-Type Titanium Silylidenes to Silatitanacyclobutenes	*J. Am. Chem. Soc.*	135, 2987-2990	2013
89	Satoru Sato, Yutaka Maeda, Jing-Dong Guo, Michio Yamada, Naomi Mizorogi, Shigeru Nagase, and Takeshi Akasaka	Mechanistic Study of the Diels-Alder Reaction of Paramagnetic Endohedral Metallofullerene: Reaction of La@C82 with 1,2,3,4,5-Pentamethylcyclopentadien e	*J. Am. Chem. Soc.*	135, 5582-5587	2013
90	Takuya Kuwabara, Masaichi Saito, Jing-Dong Guo, Shigeru Nagase	Unexpected Formation of Ru2Sn2 Bicyclic Four-Membered Ring Complexes with Butterfly and Inverse-Sandwich Structures	*Inorg. Chem.*	52, 3585-3587	2013
91	Chun-Yi Lin, Jing-Dong Guo, James C. Fettinger, Shigeru Nagase, Fernande Grandjean, Gary J. Long, Nicholas F. Chilton, and Philip P. Power	Dispersion Force Stabilized Two-Coordinate Transition Metal−Amido Complexes of the −N(SiMe3)Dipp (Dipp = C6H3-2,6-Pri Structural, Spectroscopic, Magnetic, and Computational Studie	*Inorg. Chem.*	52, 13584-13593	2013
92	Jessica N. Boynton, Jing-Dong Guo, James C. Fettinger, Christopher E. Melton, Shigeru Nagase, and Philip P. Power	Linear and Nonlinear Two-Coordinate Vanadium Complexes: Synthesis, Characterization, and Magnetic Properties of V(II) Amides	*J. Am. Chem. Soc.*	135, 10720-10728	2013
Wei-Wei Wang					
93	J. –S. Dang, W. –W. Wang, S. Nagase, and X. Zhao	Regiochemistry of Nonclassical C62 Fullerene: Role of Tetragonal Carbocyclic Ring in Cycloadditions and Thermal/ Photoinduced Interconversions of Fulleroid Derivatives	*J. Phys. Chem. C*	117, 12882-12889	2013
94	H. Zheng, X. Zhao, W. –W, Wang, J. –S. Dang, and S. Nagase	Quantum Chemical Insight into Metallofullerenes M_2C_{98}: $M_2C_2@C_{96}$ or $M_2@C_{98}$, Which Will Survive?	*J. Phys. Chem. C*	117, 25195-25204	2013
95	J. –S. Dang, W. –W. Wang, X. Zhao, and S. Nagase	Regioselective Derivatization of C_{84} by Diels-Alder Reactions: Applications to Photovoltaic Solar Cells and Fullerene Polymerization	*Org. Lett.*	16, 170-173	2014
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96	Miho Hatanaka, Masaichi Saito, Masahiro Fujita, and Keiji Morokuma	σ-Aromaticity in Hexa-Group 16 Atom Substituted Benzene Dications. A Theoretical Study	*J. Org. Chem.*	79 (6), 2640-2646	2014
97	Miho Hatanaka, and Keiji Morokuma	Role of Water in Mukaiyama–Aldol Reaction Catalyzed by Lanthanide Lewis Acid: A Computational Study	*J. Am. Chem. Soc.*	135 (37), 13972-13979	2013
98	Miho Hatanaka, Satoshi Maeda, and Keiji Morokuma	Sampling of Transition States for Predicting Diastereoselectivity Using Automated Search Method—Aqueous Lanthanide-Catalyzed Mukaiyama Aldol Reaction	*J Chem. Theory Comput.*	9 (7), 2882-2886	2013

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100	Fengyi Liu, Yuki Kurashige, Takeshi Yanai, and Keiji Morokuma	Multireference Ab Initio Density Matrix Renormalization Group (DMRG)-CASSCF and DMRG-CASPT2 Study on the Photochromic Ring Opening of Spiropyran	*J. Chem. Theory Comput.*	9, 4462-4469	2013
101	Piao, W., Tsuda, S., Tanaka, Y., Maeda, S., Liu, F., Takahashi, S., Kushida, Y., Komatsu, T., Ueno, T., Terai, T., Nakazawa, T., Uchiyama, M., Morokuma, K., Nagano, T. and Hanaoka, K.	Development of Azo-Based Fluorescent Probes to Detect Different Levels of Hypoxia	*Angew. Chem. Int. Ed.*	52, 13028-13032	2013
Lina Ding					
102	Lina Ding, Lung Wa, Chung, Keiji Morokuma	Excited-State Proton Transfer Controls Irreversibility of Photoisomerization in Mononuclear Ruthenium(II) Monoaquo Complexes: A DFT Study	*J. Chem. Theory Comput.*	10 (2), 668-675	2014
103	Lina Ding, Naoki Ishida, Masahiro Murakami, and Keiji Morokuma	sp^3–sp^2 vs sp^3–sp^3 C–C Activation in Rh-Catalyzed Ring Opening of Benzocyclobutenol: A DFT Study	*J. Am. Chem. Soc.*	136 (1),169-178	2014
104	Lina Ding, Lung Wa Chung, Keiji Morokuma	Reaction Mechanism of Photoinduced Decarboxylation of the Photoactivatable Green Fluorescent Protein: An ONIOM(QM:MM) Study	*J. Phys. Chem. B*	117 (4), 1075-1084	2013
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105	Hai-Bei Li, Alister J. Page,Christian Hettich,Bálint Aradi,Christof Köhler, Thomas Frauenheim,Stephan Irle, and Keiji Morokuma	Graphene Nucleation on a Surface-Molten Copper Catalyst: Quantum Chemical Molecular Dynamics Simulations	*Chem. Sci*	accepted	2014
Lung Wa Chung					
106	Lina, Ding, Lung Wa Chung, Keiji Morokuma	Reaction Mechanism of Photo-induced Decarboxylation of the Photoactivatable Green Fluorescent Protein: An ONIOM(QM:MM) Study	*J. Phys. Chem. B*	117 (4), 1075-1084	2013
107	Shengtao Ding, Lijuan Song, Lung Wa Chung, Xinhao Zhang, Jianwei Sun, Yundong, Wu	Ligand-Controlled Remarkable Regio- and Stereodivergence in Intermolecular Hydrosilylation of Internal Alkynes: Experimental and Theoretical Studies	*J. Am. Chem. Soc.*	135 (37), 13835-13842	2013
108	Lina, Ding, Lung Wa Chung, Keiji Morokuma	Excited-State Proton Transfer Controls Irreversibility of Photoisomerization in Mononuclear Ruthenium(II) Monoaquo Complexes: A DFT Study	*J. Comput. Theory Chem.*	10 (2), 668-675	2014
Galina P. Petrova					
109	Galina P. Petrova, Hai-Bei Li, Keiji Maruoka, and Keiji Morokuma	Asymmetric Phase-Transfer Catalysis with Homo- and Heterochiral Quaternary Ammonium Salts: A Theoretical Study	*J. Phys. Chem. B*	118 (19), pp 5154-5167	2014

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111	Travis V. Harris, Yuki Kurashige, Takeshi Yanai, and Keiji Morokuma	*Ab Initio* Density Matrix Renormalization Group Study of Magnetic Coupling in Dinuclear Iron and Chromium Complexes.	*J. Chem. Phys.*	140 (5), 054303 (10 pages)	2014
112	Travis V. Harris and Robert K. Szilagyi	Iron-Sulfur Bond Covalency from Electronic Structure Calculations for Classical Iron-Sulfur Clusters.	*J. Comput. Chem.*	35 (7), 540-552	2014
113	Travis V. Harris and Keiji Morokuma	QM/MM Structural and Spectroscopic Analysis of the Di-iron(II) and Di-iron(III) Ferroxidase Site in M Ferritin	*Inorg. Chem.*	52 (15), 8551-8563	2013
伊勢川　美穂					
114	Miho Isegawa, Satoshi Maeda, Dean J. Tantillo, Keiji Morokuma	Predicting pathways for terpene from first principles-routes to known and new sesquiterpenes	*Chemical Science*	5, 1555-1560	2014
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115	J. Llaveria, Á. Beltrán, W. M. C. Sameera, A. Locati, M. M. Díaz-Requejo, M. I. Matheu, S. Castillón, F. Maseras, P. J. Pérez	Regio- and Stereoselective Silver-catalyzed aziridination of dienes: scope, mechanistic studies and ring-opening reactions	*J. Am. Chem. Soc.*	136, 14, 5342-5350.	2014
116	E. M. Zueva, R. Herchel, S. Borshch, E. V. Govor, W. M. C. Sameera, R. McDonald, J. Singleton, Y. Sanakis, J. Krzystek, J. E. McGrady, and R. G. Raptis.	E. M. Zueva, R. Herchel, S. Borshch, E. V. Govor, W. M. C. Sameera, R. McDonald, J. Singleton, Y. Sanakis, J. Krzystek, J. E. McGrady, and R. G. Raptis.	*Dalton Trans.*	In Press.	2014
117	L. Maestre, W. M. C. Sameera, M. M. Díaz-Requejo, F. Maseras, P. J. Pérez.	A General Mechanism for the Copper- and Silver-Catalyzed olefin aziridination reactions: concomitant involvement of the singlet and triplet pathways	*J. Am. Chem. Soc.*	135, 1338-1348	2013
118	I. Rivilla, W. M. C. Sameera, E. Alvarez, M. M. Díaz-Requejo, F. Maseras, P. J. Pérez.	Catalytic cross-coupling of diazo compounds with coinage metal-based catalysts: an experimental and theoretical study	*Dalton Trans.*	42, 4132-4138.	2013
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119	Shinichi Yamabe, Takeshi Fukuda and Shoko Yamazaki	A new intermediate in the Prins reaction	*Beilstein J. Org. Chem.*	9, 476-485	2013
120	Shinichi Yamabe, Wei Guan and Shigeyoshi Sakaki	Three Competitive Transition States at the Glycosidic Bond of Sucrose in Its Acid-Catalyzed Hydrolysis	*J. Org. Chem.*	78 (6), pp 2527-2533	2013
121	Shinichi Yamabe, Guixiang Zeng, Wei Guan and Shigeyoshi Sakaki	An aniline dication-like transition state in the Bamberger rearrangement	*Beilstein J. Org. Chem.*	9, 1073-1082.	2013
122	Wei Guan, Shinichi Yamabe and Shigeyoshi Sakaki	Interest in new heterodinuclear transition-metal/main-group-metal	*Dalton Trans.*	42, 8717-8728	2013

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123	Shinichi Yamabe, Guixiang Zeng, Wei Guan, Shigeyoshi Sakaki	Substrate dependent reaction channels of the Wolff-Kishner reduction reaction: A theoretical study	*Beilstein J. Org. Chem.*	10, 259-270	2014
124	Naokazu Y., Shinichi Y.,*, Shigeyoshi S., Nobuko K.,	A DFT Study of the Triplet Excited States of Iridium(III) Complexes with Terpyridine Ligands	*Canadian Chemical Transactions*	vol.2, issue 2, 134-148	2014
125	Shinichi Yamabe, Guixiang Zeng, Wei Guan and Shigeyoshi Sakaki	SN1-SN2 and SN2-SN3 mechanistic changes revealed by transition states of the hydrolyses of benzyl chlorides and benzenesulfonyl	*Journal of Computational Chemistry*	vol.35, issue 15, pages 1140-1148	2014
126	Shinichi Yamabe, Guixiang Zeng, Wei Guan, Shigeyoshi Sakaki	Proton Transfers in the Strecker Reactions revealed by DFT calculations	*Beilstein Journal of Organic Chemistry*	in press	2014
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128	Hiroyuki Nakashima, Yuh Hijikata, and Hiroshi Nakatsuji	Solving the non-Born-Oppenheimer Schrödinger equation for the hydrogen molecular ion with the free complement method II. Highly accurate electronic, vibrational and rotational excited states	*Astrophys. J*	770, 144-1-9	2013
129	Yasuko Mito-oka, Satoshi Horike, Yusuke Nishitani, Tadao Masumori, Munehiro Inukai, Yuh Hijikata, and Susumu Kitagawa	Siloxane D4 capture by hydrophobic microporous materials	*J. Mater. Chem. A*	1, 7885-7888	2013
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131	Hiroshi Sato, Wataru Kosaka, Ryotaro Matsuda, Akihiro Hori, Yuh Hijiakta, Shigeyoshi Sakaki, Masaki Takata, and Susumu Kitagawa	Self-accelerating CO sorption in a soft nanoporous crystal	*Science*	343, 167-170	2014
132	Yuh Hijikata and Shigeyoshi Sakaki	Interaction of various gas molecules with paddle-wheel-type open metal sites of porous coordination polymers: theoretical investigation	*Inorg. Chem.*	53, 2417-2426	2014
青野　信治					
133	Shinji Aono, Masayuki Nakagaki, Takuya Kurahashi, Hiroshi Fujii, and Shigeyoshi Sakaki	Theoretical Study of One-Electron Oxidized Mn(III)− and Ni(II)−Salen Complexes: Localized vs Delocalized Ground and Excited States in Solution	*J. Chem. Theory Comput.*	10, 1062-1073	2014
Milind Madhusudan Deshmukh					
134	Deshmukh, Milind M.; Ohba, Massaki.; Kitagawa, Susumu.; Sakaki Shigeyoshi	Absorption of CO2 and CS2 into the Hofmann-type Porous Coordination Polymer:Electrostatic versus Dispersion Interactions	*J. Am. Chem. Soc.*	135, 4840-4849	2013

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Guixiang Zeng（會　桂香）					
136	Shinichi Yamabe, Guixiang Zeng, Wei Guan, and Shigeyoshi Sakaki	Substrate Dependent Reaction Channels of the Wolff-Kishner Reduction Reaction: A Theoretical Study	*Beilstein J. Org. Chem.*	10 (1), 259-270	2014
137	Guixiang Zeng, Shigeyoshi Sakaki, Ken-ichi Fujita, Hayato Sano, and Ryohei Yamaguchi	Efficient Catalyst for Acceptorless Alcohol Dehydrogenation: Interplay of Theoretical and Experimental Studies	*ACS Catal.*	4 (3), 1010-1020	2014
138	Guixiang Zeng, Satoshi Maeda, Tetsuya Taketsugu, and Shigeyoshi Sakaki	Catalytic Transfer Hydrogenation by a Trivalent Phosphorus Compound: Phosphorus-Ligand Cooperation Pathway or P^{III}/P^{V} Redox Pathway?	*Angew. Chem. Int. Ed.*	53 (18), 4633-4637	2014
139	Shinichi Yamabe, Guixiang Zeng, Wei Guan, and Shigeyoshi Sakaki	S_N1-S_N2 and S_N2-S_N3 Mechanistic Changes Revealed by Transition States of the Hydrolyses of Benzyl Chlorides and Benzenesulfonyl Chlorides	*J Comput. Chem.*	35 (15), 1140-1148	2014
140	Wei Guan, Ferred Bhasha Sayyed, Guixiang Zeng, and Shigeyoshi Sakaki	σ-Bond Activation of Small Molecules and Reactions Catalyzed by Transition-Metal Complexes: Theoretical Understanding of Electronic Processes	*Inorg. Chem.*	DOI 10.1021/ ic5003429	2014
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141	Shinichi Yamabe, Guixiang Zeng, Wei Guan, and Shigeyoshi Sakaki	Substrate Dependent Reaction Channels of the Wolff-Kishner Reduction Reaction: A Theoretical Study	*Beilstein J. Org. Chem.*	10 (1), 259-270	2014
中垣　雅之					
142	Masayuki Nakagaki and Shigeyoshi Sakaki	CASPT2 Study of Inverse Sandwich-Type Dinuclear Cr(I) and Fe(I) Complexes of the Dinitrogen Molecule: Significant Differences in Spin Multiplicity and Coordination Structure between These Two Complexes	*J. Phys. Chem. A*	118 (7), 1247-1257	2014
143	Shinji Aono, Masayuki Nakagaki, Takuya Kurahashi, Hiroshi Fujii, and Shigeyoshi Sakaki	Theoretical Study of One-Electron Oxidized Mn(III) and Ni(II) Salen Complexes: Localized vs Delocalized Ground and Excited States in Solution	*J. Chem. Theory Comput.*	10 (3), 1062-1073	2014
Wei Guan					
144	Wei Guan, Shigeyoshi Sakaki, Takuya Kurahashi, Seijiro Matsubara	Theoretical Mechanistic Study of Novel Ni(0)-Catalyzed [6 − 2 + 2] Cycloaddition Reactions of Isatoic Anhydrides with Alkynes: Origin of Facile Decarboxylation	*Organometallics*	32, 7564-7574	2013
145	Wei Guan, Fareed Bhasha Sayyed, Guixiang Zeng, Shigeyoshi Sakaki	σ-Bond Activation of Small Molecules and Reactions Catalyzed by Transition-Metal Complexes: Theoretical Understanding of Electronic Processes	*Inorg. Chem.*	ic5003429	2014
146	Shinichi Yamabe, Gui-Xiang Zeng, Wei Guan, Shigeyoshi Sakaki	SN1-SN2 and SN2-SN3 Mechanistic Changes Revealed by Transition States of the Hydrolyses of Benzyl Chlorides and Benzenesulfonyl Chlorides	*J. Comput. Chem.*	35, 1140-1148	2014

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147	Shinichi Yamabe, Gui-Xiang Zeng, Wei Guan, Shigeyoshi Sakaki	Substrate dependent reaction channels of the Wolff–Kishner reduction reaction: A theoretical study	*Beilstein J. Org. Chem.*	10, 259-270	2014
148	Zhong-Ling Lang, Guo-Chun Yang, Na-Na Ma, Shi-Zheng Wen, Li-Kai Yan, Wei Guan, Zhong-Min Su	DFT characterization on the mechanism of water splitting catalyzed by single-Ru-substituted polyoxometalates	*Dalton Trans.*	42, 10617-10625	2013
Yue Chen					
149	Yue Chen, Shigeyoshi Sakaki	Theoretical Study of Mononuclear Nickel(I), Nickel(0), Copper(I), and Cobalt(I) Dioxygen Complexes: New Insight into Differences and Similarities in Geometry and Bonding Nature	*Inorg. Chem.*	52 (22), 13146-13159	2013
150	Yue Chen, Shigeyoshi Sakaki	The important role of the Mo-Mo quintuple bond in catalytic synthesis of benzene from alkynes. A theoretical study	*Dalton Trans.*	DOI: 10.1039/ C4DT00595C	2014
Sayyed Fareed Bhasha					
151	Fareed Bhasha Sayyed and Shigeyoshi Sakaki	The crucial role of a Ni(I) intermediate in Ni-catalyzed carboxylation of aryl chloride with CO_2: a theoretical study	*Chem. Commun.*	49, 10715-10717	2013
152	Wei Guan, Fareed Bhasha Sayyed, Guixiang Zeng, and Shigeyoshi Sakaki	σ-Bond Activation of Small Molecules and Reactions Catalyzed by Transition-Metal Complexes: Theoretical Understanding of Electronic Processes	*Inorg. Chem.*	53, in press	2014
山田　健太					
153	Miyabi Hiyama, Hidefumi Akiyama, Kenta Yamada and Nobuaki Koga	Theoretical Study of Fluorescence Spectra Utilizing the pKa Values of Acids in Their Excited States	*Photochem. Photobio.*	90 (1), 35-44	2014
154	Takako Mashiko, Kenta Yamada, Tatsuo Kojima, Shuichi Hiraoka, Umpei Nagashima and Masanori Tachikawa	Molecular dynamics and principal component analysis for a self-assembled nanocube in aqueous solution	*Chem. Lett.*	43 (3), 366-368	2014
155	Kenta Yamada, Yukio Kawashima and Masanori Tachikawa	Muon-electron hyperfine coupling constants of muoniated ethyl radical: a path integral simulations study with semiempirical molecular orbital method	*Chin. J. Phys.*	52 (1-I), 126-137	2014
156	Miyabi Hiyama, Hidefumi Akiyama, Toshimitsu Mochizuki, Kenta Yamada and Nobuaki Koga	Analysis of Photoexcitation Energy Dependence in the Photo Luminescence of Firefly Luciferin	*Photochem. Photobio.*	90 (4), 820-828	2014

＊以下に表示の研究業績（論文）は、共著である

No5&90. No6&89. No11&93. No15&92. No24&94. No25&91. No30&95.

No38&98. No42&99. No45&113. No46&80. No47&101. No48&97.

No49&100. No54&103. No56&111. No57,102&108. No58&114. No59&96.

No66&134. No70&122. No72&151. No74&144. No75&149. No104&106.

No123,141&147. No125&146. No133&143. No140,145&152.

4．福井謙一記念研究センター　シンポジウム　ポスター・プログラム

第11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 2014年1月23日(木)10時～

会 場 京都大学福井謙一記念研究センター　３F大会議室
Fukui Institute for Fundamental Chemistry, Kyoto University

プログラム

●10:00-10:05
開会の辞　田中 一義(センター長)

●10:05-10:15
ご 挨 拶　北野 正雄(京大・工学研究科長)

●10:15-11:15
谷口 正輝(阪大・産研教授)
「1分子接合の物性」

●11:30-12:30
永瀬 茂(福井センター・シニアリサーチフェロー)
「高周期元素を骨格にもつ分子とフラーレン」

－昼休み－

●14:00-15:00
時任 宣博(京大・化研教授)
「高周期典型元素を含む新規なπ電子系の創出」

●15:15-17:15
ポスターセッション

●17:30-19:00
懇親会(１F多目的ルーム)

問い合わせ先
京都市左京区高野西開町34-4　Tel : 075-711-7708　Fax : 075-781-4757
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第 11 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　2014(平成 26)年 1 月 23 日(木)
場所　京都大学福井謙一記念研究センター

講演会

(3F 大会議室　10:00-15:00)

● 開会の辞　田中 一義（京都大学 福井謙一記念研究センター長）　・・・10:00-10:05

● ご挨拶　北野 正雄（京都大学 工学研究科長）　・・・10:05-10:15

● 谷口 正輝（大阪大学 産業科学研究所 教授）　司会: 榊 茂好（福井センター）
「1 分子接合の物性」　・・・10:15-11:15

－ 休憩 －

● 永瀬 茂（福井謙一記念研究センター シニアリサーチフェロー）　司会: 山邊 信一（福井センター）
「高周期元素を骨格に持つ分子とフラーレン」　・・・11:30-12:30

－ 昼休み －

● 時任 宣博（京都大学 化学研究所 教授）　司会: 永瀬 茂（福井センター）
「高周期典型元素を含む新規なπ電子系の創出」　・・・14:00-15:00

ポスターセッション

(3F 大会議室 15:15-17:15)

懇親会

(1F 多目的ルーム 17:30-19:00)

ポスターセッション　15:15-17:15（3F 大会議室）

※ 番号が奇数の方は前半(15:15-16:15)に、番号が偶数の方は後半(16:15-17:15)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 (15:15-16:15) if your poster number is odd, and at the second half (16:15-17:15) if the number is even.

1. First Principles DFT+U Study of Electronic Structures of Lantanide Oxides

(Central Research Laboratory, Hitachi Ltd[1], National Institite of Materials Science[2], Japan Atomic Energy Agency[3]) ○Tomoyuki Hamada[1], Takahisa Ohno[2], and Sadamichi Maekawa[3]

2. ナイロンオリゴマー分解酵素の酵素基質複合体の相互作用の理論解析

(阪大院基礎工[1]、東大生産技術研[2]、立教大理[3]) ○安東寛之[1]、馬場剛史[1]、重田育照[1]、渡邉千鶴[2]、沖山佳生[2]、望月祐志[3]、中野雅由[1]

3. 高周期典型元素を含む開殻一重項縮環共役系のジラジカル性と非線形光学現象に関する理論的研究

(阪大院基礎工[1]、阪大基礎工[2]) ○廣崎裕多[1]、福田幸太郎[1]、松井啓史[1]、高椋章太[2]、上田幸平[2]、岸亮平[1]、中野雅由[1]

4. ニトロキシド系ジラジカル分子の構造と光吸収特性に関する理論研究

(阪大院基礎工[1]、阪市大院理[2]、青山学院大理工[3]) ○中村亮太[1]、重田育照[1]・奥野克樹[1]、鈴木修一[2]、小寄正敏[2]、岡田惠次[2]、長谷川美貴[3]、中野雅由[1]

5. シクロペンタン-1,3-ジラジカル化合物の開殻性と非線形光学特性に対するドナー/アクセプター置換基効果の理論研究

(阪大院基礎工[1]、広島大院理[2]) ○齋藤 真和[1]、岸亮平[1]、福田幸太郎[1]、松井啓史[1]、高椋章太[1]、安倍学[2]、中野雅由[1]

6. Donor-π-Donor 性を有する開殻一重項分子系のジラジカル因子と第二超分極率に関する理論的研究

(阪大院基礎工) ○福田幸太郎、中野雅由

7. ポリアセンの電気伝導の外場応答と開殻性の相関についての理論

(阪大院基礎工) ○竹林拓、福田幸太郎、重田育照、中野雅由

8. 1,3-ジラジカル型化合物の構造一光学応答特性相関についての理論研究

(阪大院基礎工) ○村田裕介、岸亮平、齋藤真知、中野雅由

9. 開殻一重項分子系の開殻性と電子ダイナミクスの相関についての理論研究

(阪大院基礎工) ○森田啓介、　岸亮平、　中野雅由

10. 対称及び非対称ペリレンオリゴマー誘導体の一重項開殻性に関する理論的研究

(阪大院基礎工) ○上田幸平、福田幸太郎、松井啓史、廣崎裕多、高椋章太、中野雅由

11. 高周期典型元素を含む四員環化合物の開殻一重項性と第二超分極率の相関

(阪大院基礎工) ○松井啓史、福田幸太郎、廣崎裕多、高椋章太、中野雅由

12. アキシアル型配位子を有する開殻一重項二核遷移金属錯体のジラジカル因子と三次非線形光学物性についての理論的研究

(阪大院基礎工) ○山田大志、　高椋章太、中野雅由

13. 一次元異核遷移金属鎖の一重項開殻性と三次非線形光学物性の相関

(阪大院基礎工) ○高椋章太、山田大志、中野雅由

14. 開殻一重項キノイダルオリゴチオフェンの開殻性と三次非線形光学特性についての理論的研究

(阪大院基礎工) ○岸亮平、植中英樹、村田裕介、森田啓介、齋藤真和、中野雅由

15. CAM-B3LYP 汎関数の非経験的チューニング法：ジアリールエテン誘導体の励起エネルギー計算への応用

(阪大院基礎工) ○奥野克樹、重田育照、岸亮平、中野雅由

16. Ras-GAP の GTP 加水分解触媒作用に関する理論的研究

(京大院理[1]、琉球大理[2]、分子研[3]) ○公文啓瑛[1]、　東雅大[2]、斎藤真司[3]、林重彦[1]

17. 溶液内におけるピリジンの超高速緩和過程についての理論的研究

(京大院・理[1], 分子研[2]) ○中野勝博[1], 森俊文[2], 林重彦[1], 加藤重樹[1]

18. Ａサイト秩序型ルドルスデン-ポッパー相の構造解析と物性

(京大院工[1]、京都大学学際融合教育研究推進センター[2]、ペンシルバニア州立大[3]、ドレクセル大[4]) ○久家俊洋[1]、藤田晃司 [1]、田中功[1]、田中勝久[1]、東後篤史 [2]、赤松寛文 [3]、Arnab S. Gupta [3]、Shiming Lei [3]、Fei Xue [3]、Greg Stone[3]、Long-Qing Chen [3]、Venkatraman Gopalan [3], and James M. Rondinelli [4]

19. 導電性金属酸化物の赤外域におけるプラズモニック特性の評価

(京大院工) ○鎌倉涼介、藤田晃司、村井俊介、田中勝久

20. 差電子密度と振電相互作用に対する多体効果：ホール輸送分子への応用

(京大院工[1]、京大触媒電池[2]、京大化研[3]) ○三村貴信[1]、佐藤徹[1, 2]、田中一義[1]、梶弘典[3]

21. C_{62} 異性体からの C_2 脱離の活性化エネルギー

(京大院工[1]、京大触媒電池[2]) ○長島大[1]、佐藤徹[1, 2]、田中一義[1]

22. 金属内包フラーレンの環化付加反応における位置選択性：振電相互作用密度解析

(京大院工[1]、京大触媒電池[2]) ○春田直毅[1]、佐藤徹[1, 2]、田中一義[1]

23. Structure of [6]Cycloparaphenylene and Pseudo Jahn-Teller Effect

(Grad. School of Eng. Kyoto Univ.[1], ESICB, Kyoto Univ.[2], Grad. School of Human and Environ. Stud., Kyoto Univ.[3], Kyoto Univ. Institute for Liberal Arts and Sciences[4]) ○Yuichiro Kameoka [1], Tohru Sato [1, 2], Takahiko Koyama[3], Kazuyoshi Tanaka[1], and Tatsuhisa Kato[3, 4]

24. 有機ラジカルを用いた有機分子ワイヤ中の電子トンネリングに対する計算化学的アプローチ

(京大院工[1]、 北大触セ[2]) ○西澤尚平[1]、 長谷川淳也[2]、 松田建児[3]

25. リチウムイオン二次電池の電解質溶液中における分解反応とイオン拡散

(京大院工[1], 京大触媒電池[2]) ○笠原健人[1], 佐藤啓文[1,2]

26. 荷電壁の濡れ：静力学と動力学

(京大福井セ[1], 京大理[2]) ○岡本隆一[1]、小貫明[2]

27. Crumpled Globule における標識されたモノマーの異常拡散現象

(京大福井セ[1]、九州大学理[2]) ○齋藤拓也[1]、坂上貴洋[2]

28. DFT and DFT/MM Methods for Mechanistic and Selectivity Studies of Transition Metal Homogeneous Catalysis

(京大福井セ[1], ICIQ[2], Departament de Química, Universitat Autónoma de Barcelona[3]) ○W. M. C. Sameera[1, 2] and Feliu Maseras[2, 3]

29. 円錐交差における溶媒効果の理論的研究

(京大福井セ) 嶺澤範行

30. Origin of Dramatically Cooperative Catalysis on Selective Dual C-C Bond Activation in NiO/Lewis Acid-Catalyzed [4 + 2] Cycloaddition: Theoretical Insights

(京大福井セ) Wei Guan

31. フッ化物アニオンを含む多孔性配位高分子の CO_2 吸着に関する理論的研究

(京大福井セ) ○土方優、榊茂好

32. 三角両錘型 Co, Fe 錯体の構造と電子状態

(京大福井セ) ○塚本晋也、榊茂好

33. 異種金属原子による窒素分子を挟んだ逆サンドイッチ型錯体の特異なスピン状態

(京大福井セ) ○中垣雅之，榊茂好

34. 平面四配位型金属サレン錯体の 局在・非局在性吸収スペクトルと溶媒効果

(京大福井セ) ○青野信治、 中垣雅之、榊茂好

35. 塩化ベンジルと塩化ベンゼンスルフォニルの加水分解の遷移状態構造

(京大福井セ) ○山邊信一、Guixiang Zeng, Wei Guan, 榊茂好

36. ニッケル錯体の水素発生に関する理論的研究

(京大福井セ) ○山田健太、榊茂好

37. テトラシラシクロブタジエン-コバルト(I)錯体および類似の遷移金属錯体の分子構造と電子構造に関する理論的考察

(京大福井セ) ○高木望、榊茂好

38. Theoretical Study on the Electronic Structure of N_2-bridged Lanthanide Complex

(京大福井セ) ○ Yue Chen and Shigeyoshi Sakaki

39. The crucial role of a Ni(I) intermediate in Ni-catalyzed carboxylation of aryl chloride with CO_2

(京大福井セ) ○ S. F. Bhasha, Y. Tsuji, and S. Sakaki

40. Theoretical Study of the Silylation and Borylation of Allylic Alcohol by $[Pd(MeCN)_4](BF4)_2$: Mechanism and Stereoselectivity

(京大福井セ) ○ Guixiang Zeng and Shigeyoshi Sakaki

41. Thermal Reduction and Nitrogen Doping of Graphene Oxide

(京大福井セ) ○ Wei-Wei Wang and Shigeru Nagase

42. Analysis of the SnC_4-ring-bending feature in three stannole-Ru complexes

(京大福井セ) ○Jing-Dong Guo and Shigeru Nagase

43. Predicting Pathways for Terpene Formation from First Principles-Routes to Known and New Sequiterpenes

(京大福井セ[1]、北大理[2]、University of Carfornia[3]) ○伊勢川美穂[1]、前田理[2]、D. J. Tantillo[3]、 諸熊奎治[1]

44. Theoretical Study of Highly Stereoselective Mukaiyama-Aldol Reaction in Aqueous Media

(京大福井セ) ○Miho Hatanaka and Keiji Morokuma

45. Ab Initio Density Matrix Renormalization Group Study of Magnetic Coupling in Dinuclear Iron and Chromium Complexes

(京大福井セ[1], 分子研[2]) ○Travis V. Harris[1], Yuki Kurashige[2], Takeshi Yanai[2], and Keiji Morokuma[1]

5．福井謙一記念研究センター　セミナー　ポスター・プログラム

第11回
福井センターセミナー
(The 11th Fukui Center Seminar)

2013年7月24日(水) 14:00-17:30

〒606-8103　京都市左京区高野西開町34-4
京都大学福井謙一記念研究センター(TEL075-711-7708)
1F 多目的室　(Room: 1F 106)　http://www.fukui.kyoto-u.ac.jp/

14:00～14:05　Opening by Professor Kazuyoshi Tanaka
(Director, Fukui Institute for Fundamental Chemistry)

14:05～15:05　Professor Shin-ichi Yamabe
(Fukui Institute for Fundamental Chemistry)
Proton transfers in some organic reaction pathways

15:05 ～16:05 Professor Mitsutaka Okumura
(Osaka University)
Theoretical study for the characteristics and catalytic reactions of Au clusters

16:05 ～16:20 Break

16:20～17:30　Professor Odile Eisenstein
(Université Montpellier 2, France)
Computational studies and chemical complexity: A half full/half empty glass story illustrated by the computational studies of the olefin metathesis catalysis with the Schrock alkylidene complexes

多数の方のご来場を歓迎いたします

６．その他（報告）

その他(報告)：諸 熊 奎 治 シニアリサーチフェロー

諸熊奎治シニアリサーチフェローは、スウェーデン王立科学アカデミーが発表した２０１３年のノーベル化学賞の授賞研究の業績説明の中で、重要な貢献をした７人に含まれていることが判った。

今回受賞したマーティン・カープラス氏など３人の米国の科学者は、排ガスの浄化から光合成までさまざまな化学反応がどのように起きているのか、その過程を理解するためのコンピューター・シミュレーションの基礎を築き、複雑な化学反応を伴う新薬の開発などに貢献した。

これらのことが、平成２５年１０月１０日付けの京都・読売・朝日・毎日・産経の各新聞に取り上げられている。

１０月１７日付け以降の朝日新聞では、諸熊奎治シニアリサーチフェローが、複雑な分子のふるまいをコンピューターで効率よく計算出来る「オニオム(ＯＮＩＯＭ)法」という手法を１９９５年に開発し、それが、計算化学ソフトに組み込まれ、世界中で活用されていることを「キセキを語る」のシリーズで紹介している。

また、１２月２２日にＢＳフジテレビで放映された「ガリレオＸ(ｴｯｸｽ)」の番組で、諸熊シニアリサーチフェロー他の科学者による計算化学の分野の今後の発展によって生命現象の解明が促進され、コンピューターが描く化学現象が医療の分野などで新しい未来を拓くことが大きく期待されていると紹介されている。

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