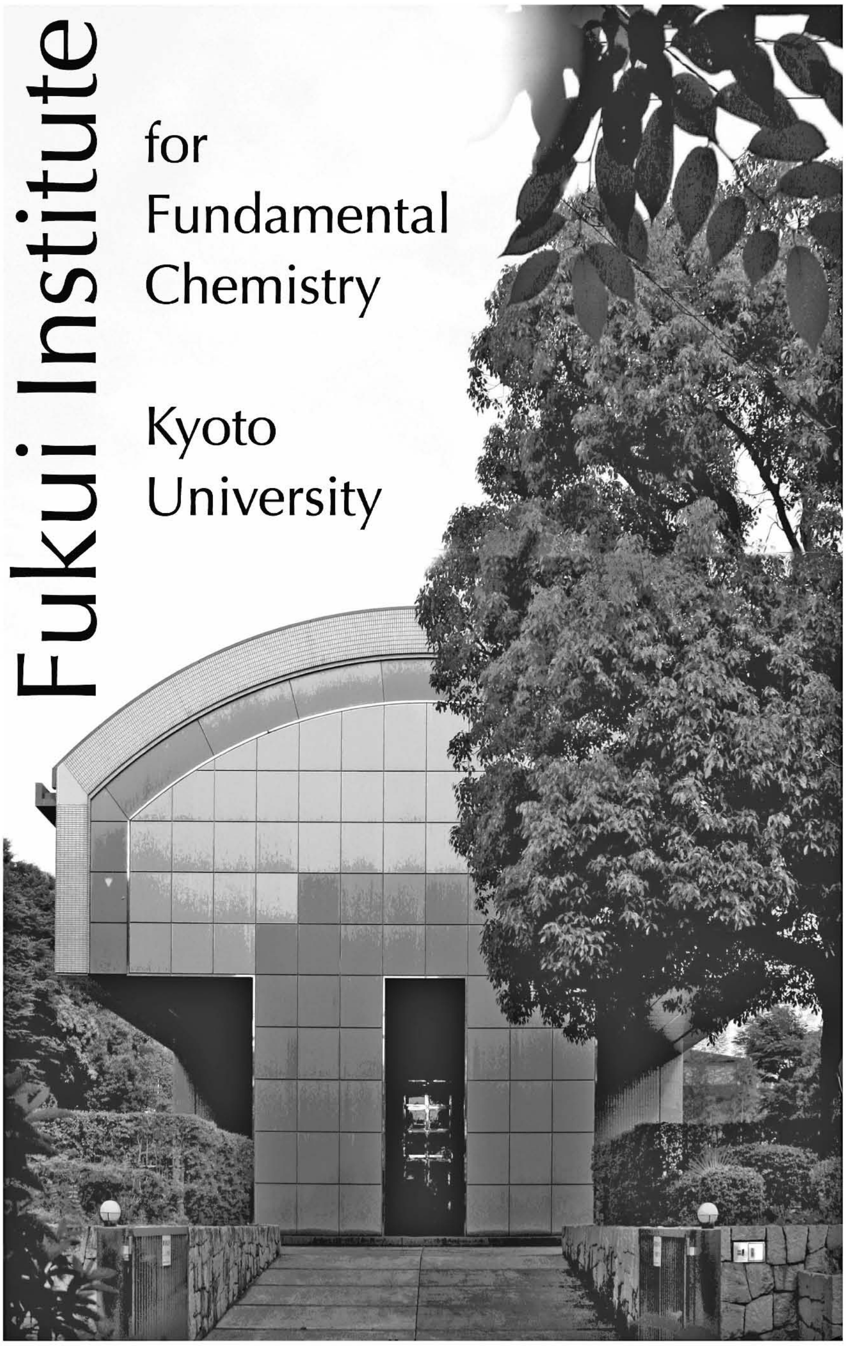
京都大学
福井謙一記念研究センター

Annual Report
2014

Fukui Institute for Fundamental Chemistry Kyoto University

年 報
2014



京都大学
福井謙一記念研究センター

はじめに

2014年度（平成26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、科学技術振興機構からの受託研究「多元素協働触媒作用メカニズムの解明と予測の理論・計算化学研究」を推進しておられます。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おられます。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おります。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。

ここで、当センターの歴史を簡単にご紹介いたします。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

て活躍しておられます。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、現在に至っております。京都大学の部局となった後、森島 績、中辻 博、榊 茂好、田中 功、田中 一義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いたしました。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いたしました。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おります。

また、現在本センターのFIFC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あります。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に存じます。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おります。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27年10月

京都大学福井謙一記念研究センター長

赤木　和夫

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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/AnnualReport2014.pdf）

Ⅰ　専任教員・スーパーバイザー

１．教員組織

平成２６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	伊藤 紳三郎	工学研究科高分子化学専攻
	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	物質－細胞統合システム拠点 （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・宇宙物理学専攻
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）
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【研究分野】	物理化学、量子化学
【現在の研究課題】	元素ブロックを有する分子、高分子の理論化学
【研究内容キーワード】	分子・高分子の電子物性、量子機能材料、量子統計力学
【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、2012 年 4 月京都大学福井謙一記念研究センター長併任、2015 年 4 月京都大学名誉教授ならびに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
【所属学会】	日本化学会・日本物理学会・高分子学会
【主な著書、学術論文】 （過去 5 年以内）	1. 炭素学（共編著，化学同人，2011） 2. 統計力学入門　化学者の視点から（単著，化学同人，2014） 3. Carbon Nanotubes and Graphene（共編著，Elsevier Science, 2014） （以上著書） 1. 今なぜグラフェンか？　ノーベル物理学賞の受賞理由、その本質を考える（単著）化学，66, No. 1, 31-35 (2011). 2. Woodward 教授の見果てぬ夢　－研究メモに遺された室温超伝導への想い（単著）化学，66, No. 10, 12-15 (2011). 3. HOMO-LUMO 概念の誕生（単著）化学，66, No. 11, 26-29 (2011). 4. 未来材料を創成する理論化学の進展（共著）未来材料，12, No. 2, 2-8 (2012). 5. グラフェンとそのフラグメントの電子状態と物性（単著）触媒，54, No. 6, 369-374 (2012). 6. 量子化学計算による有機 EL 電荷輸送材料の解析（共著）月刊ディスプレイ，19, No. 9, 49-52 (2013). 7. 福井先生の未完のテーマ －生命の起源への化学的試論（単著）化学，68, No. 11, 19-22 (2013). （以上和文総説） 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).

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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).
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6. Chemical Reactivity in Nucleophilic Cycloaddition to C_{70}: Vibronic Coupling Density and Vibronic Coupling Constants as Reactivity Indices (N. Haruta, T. Sato, and K. Tanaka) *J. Org. Chem.*, **77**, 9702-9706 (2012).
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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).
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27. A Light-Emitting Mechanism for Organic Light-Emitting Diodes: Molecular Design for Inverted Singlet-Triplet Structure and Symmetry-Controlled Thermally Activated Delayed Fluorescence (T. Sato, M. Uejima, K. Tanaka, H. Kaji, and C. Adachi) *J. Mater. Chem. C*, **3**, 870-878 (2015).
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30. Reactivity Index for Diels-Alder Cycloadditions to Large Polycyclic Aromatic Hydrocarbons Using Vibronic Coupling Density (N. Haruta, T. Sato, and K. Tanaka) *Tetrahedron Lett.*, **56**, 590-594 (2015).
31. Synthesis and Characterization of Heterofluorenes Containing Four-coordinated Group 13 Elements: Theoretical and Experimental Analyses and Comparison of Structures, Optical Properties and Electronic States (T. Matsumoto, K. Tanaka, K. Tanaka, and Y. Chujo) *Dalton Trans.*, **44**, 8697-8707 (2015).
32. Luminescent Coordination Glass: Remarkable Morphological Strategy for Assembled Eu (III) Complexes (Y. Hirai, T. Nakanishi, Y. Kitagawa, K. Fushimi, T. Seki, H. Ito, H. Fueno, K. Tanaka, T. Satoh, and Y. Hasegawa) *Inorg. Chem.*, **54**, 4364-4370 (2015).
33. Multiscale Simulation of Charge Transport in a Host Material, *N, N'*-Dicarbazole-3,5-benzene (mCP), for Organic Light-Emitting Diodes (F. Suzuki, K. Shizu, H. Kawaguchi, S. Furukawa, T. Sato, K. Tanaka, and H. Kaji) *J. Mater. Chem. C*, **3**, 5549-5555 (2015).

（以上学術論文）

【学術関係の受賞など】

2002-2007 年 科学技術振興機構 (JST) の戦略的創造研究推進事業 (CREST)「精密分子設計に基づくナノ電子デバイス構築」研究代表者

2004-2005 年 文部科学省知的クラスター創成事業「京都ナノテククラスター」のナノテク共同研究テーマ「mRNA の数理学的特異性抽出ソフトの開発と解析サービスの事業化展開」研究代表者

⑵ 副センター長

【氏名（ふりがな）】	赤木　和夫（あかぎ　かずお）
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【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
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【主な著書、学術論文】（過去5年以内）	1. S. Matsushita, K. Akagi, “Macroscopically Aligned Graphite Films Prepared from Iodine-Doped Stretchable Polyacetylene Films Using Morphology-Retaining Carbonization”, *J. Am. Chem. Soc.*, **137**, 9077 (2015). 2. J. Bu, K. Watanabe, H. Hayasaka, K. Akagi, “Photochemically Colour-Tuneable White Fluorescence Illuminants consisting of Conjugated Polymer Nanospheres”, *Nat. Commun.* **5**, 3799 (2014). 3. 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). 4. B. A. San Jose, J. Yan, K. Akagi, “Dynamic Switching of the Circularly Polarized Luminescence of Disubstituted Polyacetylene by Selective Transmission though a Thermotropic Chiral Nematic Liquid Crystal”, *Angew. Chem. Int. Ed.*, **53**, 10641, (2014). 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）

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【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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【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. 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. 4. T. Kawamoto, K. Fujita, H. Akamatsu, T. Nakamura, T. Kinoshita, M. Mizumaki, N. Kawamura, M. Suzuki, Y. Kususe, S. Murai, and K. Tanaka, “Eu M4,5- and L2,3-edge x-ray magnetic circular dichroism of ferromagnetic amorphous oxides in EuO-TiO$_2$ system”, *Physical Review B* **88** (2013) 024405-1-9. 5. 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. 6. 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 NaRETiO4 family”, *Physical Review Letters* **112** (2014) 187602-1-5. 7. M. Nishijima, T. Ootani, Y. Kamimura, T. Sueki, S. Esaki, S. Murai, K. Fujita, K. Tanaka, K. Ohira, Y. Koyama, and I. Tanaka, “Accelerated discovery of cathode materials with prolonged cycle life for lithium-ion battery”, *Nature Communications* **5** (2014) 4553-1-7. 8. T. Kawamoto, K. Fujita, I. Yamada, T. Matoba, S. J. Kim, P. Gao, X. Pan, S. D. Findlay, C. Tassel, H. Kageyama, A. J. Studer, J. Hester, T. Irifune, H. Akamatsu, and K. Tanaka, “Room-temperature polar ferromagnet ScFeO$_3$ transformed from a high-pressure orthorhombic perovskite phase”, *Journal of the American Chemical Society* **136** (2014) 15291-15299.
【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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【主な著書、学術論文】 （過去5年以内）	1. Synthesis, Structure and Reactivity of 1-Bromoalumole, Wasano, T.; Agou, T.; Sasamori, T.; Tokitoh, *Chem. Commun.* 2014, **50**, 8148-8150. 2. 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. 3. Synthesis and Properties of 4,5,6-Triphospha[3]radialene, Miyake, H.; Sasa-mori, T.; Tokitoh, N. *Angew. Chem. Int. Ed.* 2012, **51**, 3458-3461. 4. 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. 5. 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.
【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. Contactless measurements of charge migration within single molecules, Kiyonobu Nagaya, Hiroshi Iwayama, Akinori Sugishima, Yoshinori Ohmasa, Makoto Yao, *Appl. Phys. Lett.* **96** (2010) 233101. 2. Inhomogeneous charge redistribution in Xe clusters exposed to intense extreme ultraviolet free electron laser, H. Iwayama, A. Sugishima, K. Nagaya, M. Yao, H. Fukuzawa, K. Motomura, X.-J. Liu, A. Yamada,C. Wang, K. Ueda, N. Saito, M. Nagasono, K. Tono, M. Yabashi, T. Ishikawa, H. Ohashi, H. Kimura, and T. Togashi, *J. Phys. B: At. Mol. Opt. Phys. Fast track* **43** (2010) 161001. 3. Deep inner-shell multiphoton ionization by intense x-ray free-electron laser pulses,H. Fukuzawa, S.-K. Son, K. Motomura, S. Mondal, K. Nagaya, S. Wada, X.-J. Liu, R.Feifel, T. Tachibana, Y. Ito, M. Kimura, T. Sakai, K. Matsunami, H. Hayashita, J. Kajikawa, P. Johnsson, M. Siano, E. Kukk, B. Rudek, B. Erk, L. Foucar, E. Robert, C. Miron, K. Tono, Y. Inubushi, T. Hatsui, M. Yabashi, M. Yao, R. Santra, and K. Ueda, *Phys. Rev. Letts.* **110**, 173005 (2013). 4. Pulse delay effect in angular distribution of near-threshold EUV+IR two-photon ionization of Ne, S. Mondal, H. Fukuzawa, K. Motomura, T. Tachibana, K. Nagaya, T. Sakai, K. Matsunami, S. Yase, M. Yao, S. Wada, H. Hayashita, N. Saito, C. Callegari, K. C. Prince, C. Miron, M. Nagasono, T. Togashi, M. Yabashi, K. L. Ishikawa, A. K. Kazansky, N. M. Kabachnik, and K. Ueda. *Phys. Rev. A* **89**. 013415 (2014). 5. Inelastic x-ray scattering study of plasmon dispersions in solid and liquid Rb, K. Kimura, K. Matsuda, N. Hiraoka, T. Fukumaru, Y. Kajihara, M. Inui, M. Yao, *Phys. Rev. B*. **89**, 014206 (2014). 6. Nanoplasma Formation by High Intensity Hard X-rays, T. Tachibana, Z. Jurek, H. Fukuzawa, K. Motomura, K. Nagaya, S. Wada, P. Johnsson, M. Siano, S. Mondal, Y. Ito, M. Kimura, T. Sakai, K. Matsunami, H. Hayashita, J. Kajikawa, X.-J. Liu, E. Robert, C. Miron, R. Feifel, J. P. Marangos, K. Tono, Y.Inubushi, M. Yabashi, S.-K. Son,, B. Ziaja, M. Yao, R. Santra, and K. Ueda, *Science Report* **5**, 10977; doi: 10.1038/srep10977 (2015). 7. Inelastic X-ray Scattering Study on Plasmon Dispersion in Liquid Cs, Koji Kimura, Kazuhiro Matsuda, Nozomu Hiraoka, Yukio Kajihara, Tetsu Miyatake, Yotaro Ishiguro, Toru Hagiya, Masanori Inui, and Makoto Yao, *J. Phys. Soc.* Japan, (accepted).

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【主な著書、学術論文】 （過去5年以内）	1. Togo, A., Chaput, L. & Tanaka, I. Distributions of phonon lifetimes in Brillouin zones. *Physical Review B* **91**, 094306 (2015). 2. Seko, A. & Tanaka, I. Special quasirandom structure in heterovalent ionic systems. *Physical Review B* **91**, 024106 (2015). 3. Seko, A., Takahashi, A. & Tanaka, I. Sparse representation for a potential energy surface. *Physical Review B* **90**, 024101 (2014). 4. Seko, A., Shitara, K. & Tanaka, I. Efficient determination of alloy ground-state structures. *Physical Review B* **90**, 174104 (2014). 5. Seko, A., Maekawa, T., Tsuda, K. & Tanaka, I. Machine learning with systematic density-functional theory calculations: Application to melting temperatures of single- and binary-component solids. *Physical Review B* **89**, 054303 (2014). 6. Nishijima, M. et al. Accelerated discovery of cathode materials with prolonged cycle life for lithium-ion battery. *Nature Communications* **5**, 4553 (2014). 7. Ikeda, Y., Seko, A., Togo, A. & Tanaka, I. Phonon softening in paramagnetic bcc Fe and its relationship to the pressure-induced phase transition. *Physical Review B* **90**, 134106 (2014). 8. Akamatsu, H. et al. Inversion Symmetry Breaking by Oxygen Octahedral Rotations in the Ruddlesden-Popper NaRTiO4 Family. *Physical Review Letters* **112**, 187602, 187602 (2014). 9. Akamatsu, H. et al. Strong Spin-Lattice Coupling Through Oxygen Octahedral Rotation in Divalent Europium Perovskites. *Advanced Functional Materials* **23**, 1864-1872 (2013).
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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 hierarchical equations of motion in real and imaginary time: Correlated initial states and thermodynamic quantities, *J. Chem, Phys* **141**, 044114 [13 pages] (2014). [2014 JCP Editors’ Choice] 5. Y. Tanimura, Real-Time and Imaginary-Time Quantum Hierarchal Fokker-Planck Equations, *J. Chem, Phys* **142**, 144110 [20 pages] (2015).
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【主な著書、学術論文】 （過去 5 年以内）	1. A. J. Dunleavy, K. Wiesner, R. Yamamoto, and C. P. Royall, Mutual information reveals multiple structural relaxation mechanisms in a model glassformer, *Nature Communications* **6**, 6089 (2015). 2. S. Yasuda and R. Yamamoto, Synchronized molecular dynamics simulation via macroscopic heat and momentum transfer: an application to polymer lubrication, *Phys. Rev. X* **4**, 041011 (2014). 3. J. J. Molina and R. Yamamoto, Direct numerical simulations of rigid body dispersions. I. Mobility/Friction tensors of assemblies of spheres, *J. Chem. Phys.* **139**, 234105 (2013). 4. R. Tatsumi and R. Yamamoto, Velocity relaxation of a particle in a confined compressible fluid, *J. Chem. Phys.* **138**, 184905 (2013). 5. J. J. Molina, Y. Nakayama, and R. Yamamoto, Hydrodynamic interactions of self-propelled swimmers, *Soft Matter* **9**, 4923-4936 (2013). 6. H. Mizuno and R. Yamamoto, General constitutive model for supercooled liquids: Anomalous transverse wave propagation, *Phys. Rev. Lett.* **110**, 095901 (2013).
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【学歴】	2003年3月 京都大学工学部工業化学科卒業 2005年3月 京都大学大学院工学研究科分子工学専攻修士課程修了 2008年3月 京都大学大学院工学研究科分子工学専攻博士後期課程修了
【学位】	2008年3月 博士（工学）、京都大学
【略歴】	2008年4月 日本学術振興会特別研究員 PD（筑波大学物理学専攻）、2011年4月 モンペリエ第二大学シャルルクーロン研究所博士研究員、2012年12月 日本学術振興会海外特別研究員（モンペリエ第二大学シャルルクーロン研究所）、2014年2月 京都大学福井謙一記念研究センター准教授
【所属学会】	日本物理学会、日本化学会
【主な著書、学術論文】 （過去5年以内）	1. Atsushi Ikeda and Kunimasa Miyazaki “Glass transition of the monodisperse gaussian core model” *Phys. Rev. Lett.* (Editors’ Suggestion) **106**, 015701 (2011). 2. Atsushi Ikeda and Kunimasa Miyazaki ”Slow Dynamics of the High Density Gaussian Core Model” *J. Chem. Phys.* **135**, 054901 (2011). 3. Patrick Charbonneau, Atsushi Ikeda, Giorgio Parisi and Francesco Zamponi “Glass Transition and Random Close Packing above Three Dimensions” *Phys. Rev. Lett.* **107**, 185702 (2011). 4. 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). 5. Atsushi Ikeda, Ludovic Berthier and Giulio Biroli “Dynamic criticality at the jamming transition” *J. Chem. Phys.* **138**, 12A507 (2013). 6. 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). 7. Misaki Ozawa, Walter Kob, Atsushi Ikeda, Kunimasa Miyazaki “Equilibrium phase diagram of a randomly pinned glass-former” *Proc. Natl. Acad. Sci. USA* **112**, 6914 (2015).
【学術関係の受賞など】	2007年9月 分子科学会優秀講演賞、2008年-2011年 日本学術振興会特別研究員 PD、2012年-2014年 日本学術振興会海外特別研究員、2013年3月 日本物理学会若手奨励賞 (領域 12)、2015年4月 文部科学省「平成27年度科学技術分野の文部科学大臣表彰」若手科学者賞

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【現在の研究課題】	元素の特性とナノ構造を利用した分子設計の理論と計算
【研究内容キーワード】	高周期典型元素、遷移金属、ナノカーボン、機能性分子
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【所属学会】	日本化学会、分子科学会、ケイ素化学協会、アメリカ化学会
【主な著書、学術論文】（過去 5 年以内）	1. T. Akasaka, F. Wudl, and S. Nagase, Eds., Chemistry of Nanocarbons, John Wiley & Sons Ltd., Chichester (2010) 2. M. Yamada, T. Akasaka, and S. Nagase, Endohedral Metal Atoms in Pristine and Functionalized Fullerene Cages, *Acc. Chem. Res.*, **43**, 92-102 (2010). 3. X. Lu, L. Feng, T. Akasaka, and S. Nagase, Current Statues and Future Developments of Endohedral Metallofullerenes, *Chem. Soc. Rev.*, **41**, 7723-7760 (2012). 4. S. Nagase, Multiple Bonds between Lead Atoms and Short Bonds between Transition Metals, *Pure Appl. Chem.*, **85**, 649-659 (2013). 5. X. Lu, T. Akasaka, and S. Nagase, Carbide Cluster Metallofullerenes: Structure, Properties, and Possible Origin, *Acc. Chem. Res.*, **46**, 1627-1635 (2013). 6. M. Yamada, T. Akasaka, and S. Nagase, Carbene Additions to Fullerenes, *Chem. Rev.*, **113**, 7209-7264 (2013). 7. 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).
【学術関係の受賞】	2012 年 文部科学大臣表彰科学技術賞（研究部門）、2012 年 福井メダル (Asia-Pacific Association of Theoretical & Computational Chemists) 、2013 年 日本化学会賞

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【現在の研究課題】	複雑分子系の分子理論によるシミュレーション
【研究内容キーワード】	分子理論。複雑分子系、シミュレーション、ナノ構造、酵素反応
【最終学歴】	1962 年 3 月 京都大学大学院工学研究科博士課程単位修得退学
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【略歴】	1962 年 4 月京都大学工学部助手、1964 年 9 月 Columbia 大学客員助教授、1966 年 9 月 Harvard 大学博士研究員、1967 年 9 月 Rochester 大学助教授、1971 年 9 月同教授、1976 年 12 月分子科学研究所教授、1993 年 1 月 Emory 大学教授、2006 年 9 月 Emory 大学名誉教授、2006 年 9 月京都大学福井謙一記念研究センターリサーチリーダー、2012 年 4 月同シニアリサーチフェロー
【所属学会】	日本化学会、American Chemical Society、分子科学会
【主な著書、学術論文】（過去 5 年以内）	過去 5 年間に約 130 報 1. R. I. Kaiser, L. G. Muzangwa, T. Yang, D. S. N. Parker, A. M. Mebel, A. Jamal, and K. Morokuma, A Crossed Molecular Beam and Ab Initio Study on the Formation of 5- and 6-Methyl-1,4-Dihydronaphthalene ($C_{11}H_{12}$) via the Reaction of Meta-Tolyl (C_7H_7) with 1,3-Butadiene (C_4H_6). *Phys. Chem. Chem. Phys.* **17**, 7699-7706 (2015). 2. B. Liu, J. Liu, H.-B. Li, R. Bhola, E. A. Jackson, L. T. Scott, A. J. Page, S. Irle, K. Morokuma and C. Zhou, Nearly Exclusive Growth of Small Diameter Semiconducting Single-Wall Carbon Nanotubes from Organic Chemistry Synthetic End-Cap Molecules, *Nano Lett.* **15**, 586-595 (2015). 3. M. Hatanaka and K. Morokuma, Exploring the reaction coordinates for f-f emission and quenching of lanthanide complexes – thermo-sensitivity of terbium(III) luminescence. *J. Chem. Theo. Comp.* **10**, 4184-4188 (2014). 4. M. Isegawa, F. Liu, S. Maeda and K. Morokuma, Complete active space second order perturbation theory (CASPT2) study of $N(^2D) + H_2O$ reaction paths on D1 and D0 potential energy surfaces: direct and roaming pathways, *J. Chem. Phys.* **141**, 154303/1-9 (2014). 5. S. Maeda, Y. Harabuchi, T. Taketsugu, and K.Morokuma, Systematic Exploration of Minimum Energy Conical Intersection Structures near the Franck-Condon Region, *J. Phys. Chem. A* **118**, 12050-12058 (2014). 6. S. Maeda, Y. Harabuchi, Y. Ono, T. Taketsugu, and K. Morokuma, Intrinsic Reaction Coordinate: Calculation, Bifurcation, and Automated Search, *Int. J. Quant. Chem.* **115**, 258-269 (2015). 7. X. Li, L. W. Chung, K. Morokuma and G. Li, A Theoretical Study on the UVR8 Photoreceptor: Sensing Ultraviolet-B by Tryptophan and Dissociation of Homodimer, *J. Chem. Theo. Comp.* **10**, 3319-3330 (2014). 8. M. Isegawa, F. Liu, S. Maeda, and K. Morokuma, Ab initio reaction pathways for photodissociation and isomerization of nitromethane on four singlet potential energy surfaces with three roaming paths, *J. Chem. Phys.* **140**, 244310/1-11 (2014). 9. G. P. Petrova, H.-B. Li, K. Maruoka and K. Morokuma, Asymmetric phase-transfer catalysis with homo- and heterochiral quaternary ammonium salts: a theoretical study, *J. Phys. Chem. B*, **118**, 5154-5167 (2014). doi:10.1021/jp501520g
【学術関係の受賞など】	International Academy of Quantum Molecular Science Medal, 1978; 日本化学会賞, 1992; Schrödinger Medal, World Association of Theoretical Organic Chemists, 1993; 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

⑹ リサーチリーダー

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【研究分野】	理論化学・計算化学
【現在の研究課題】	遷移金属元素を含む複合電子系の構造、電子状態、反応過程の理論化学
【研究内容キーワード】	電子状態・遷移金属錯体・反応解析・触媒作用・金属微粒子
【学歴】	1974年3月　京都大学工学研究科燃料化学専攻博士課程単位取得退学
【学位】	1974年11月　工学博士（京都大学）
【略歴】	1975年4月 熊本大学工学部助手、1982年1月 同助教授、1990年4月 同教授を経て、2002年4月より京都大学工学研究科教授、2010年3月 定年、現在に至る。
【所属学会】	日本化学会、触媒学会、近畿化学協会、ケイ素化学協会
【主な著書、学術論文】（過去5年以内）	1. 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). 2. 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). 3. 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). 4. 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). 5. 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). 6. Efficient Catalyst for Acceptorless Alcohol Dehydrogenation: Interplay of Theoretical and Experimental Studies, G. Zeng, S. Sakaki, K. Fujita, H. Sano, R. Yamaguchi, *ACS Catal.* **4**, 1010-1020 (2014). 7. Catalytic Transfer Hydrogenation by Trivalent Phosphorus Compound: Phosphorus-Ligand Cooperation Pathway or P^{III}/P^{V} Redox Pathway? G. Zeng, S. Maeda, T. Taketsugu, and S. Sakaki, *Angew. Chem. Int. Ed.*, **128**, 4721-4725 (2014). 8. The Crucial Roles of $MgCl_2$ as a Non-innocent Additive in the Ni-Catalyzed Carboxylation of Benzyl Halide with CO_2, F. B. Sayyed, S. Sakaki, *Chem. Commun.*, **50**, 13026 - 13029 (2014). 9. σ-Bond Activation of Small Molecules and Reactions Catalyzed by Transition-Metal Complexes: Theoretical Understanding of Electronic Processes, W. Guan, F. B. Sayyed, G. Zeng, and S. Sakaki, *Inorg. Chem.*, **53**, 6444-6457 (2014). 10. Reasons Two Nonstrained C–C σ-Bonds Can Be Easily Cleaved in Decyanative [4 + 2] Cy-cloaddition Catalyzed by Nickel(0)/Lewis Acid Systems. Theoretical Insight, W. Guan, S. Sakaki, T. Kurahashi, S. Matsubara, *ACS Catalysis*, **5**, 1-10 (2015).
【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） Fukui Medal (2015; from APATCC)

Ⅱ　博士研究員

１．博士研究員組織

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職　名		氏　名
福井センターフェロー		嶺澤　範行
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		Wei-Wei Wang
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【研究内容キーワード】	時間依存密度汎関数法・円錐交差
【学歴】	2008 年 3 月　京都大学大学院理学研究科化学専攻博士課程修了
【学位】	2008 年 3 月　京都大学理学博士
【略歴】	2008 年 5 月　米国アイオワ州立大学（Mark S. Gordon 教授） 2011 年 10 月　京都大学福井謙一記念研究センター・センターフェロー
【所属学会】	アメリカ化学会
【主な著書、学術論文】（過去 5 年以内）	1. N. Minezawa, “Vertical excitation energies of linear cyanine dyes by spin-flip time-dependent density functional theory”, *Chem. Phys. Lett.* **622**, 115-119 (2015). 2. N. Minezawa, “State-specific solvation effect on the intramolecular charge transfer reaction in solution: A linear-response free energy TDDFT method”, *Chem. Phys. Lett.* **608**, 140-144 (2014). 3. N. Minezawa, “Optimizing minimum free-energy crossing points in solution: Linear-response free energy/spin-flip density functional theory approach”, *J. Chem. Phys.* **141**, article No. 164118 (2014). 4. 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). 5. 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).

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【学歴】	March 2004, Master of Sci., Graduate School of Science, Kyoto University March 2007, Doctor of Sci., Graduate School of Science, Kyoto University
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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, “Rate in template-directed polymer synthesis”, *Phys. Rev. E,* **89**, 062716 (8 pages total) (2014). 2. Takuya Saito, Takahiro Sakaue, “Cis-trans dynamical asymmetry in driven polymer translocation”, *Phys. Rev. E*, **88**, 042606 (5 pages total) (2013). 3. Takuya Saito, Takahiro Sakaue, “Process time distribution of driven polymer transport”, *Phys. Rev. E*, **85**, 061803 (7 pages total) (2012). 4. 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). 5. 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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【研究分野】	Computational Soft Matter
【現在の研究課題】	Dynamics of Active Particles
【研究内容キーワード】	Active particles, swimmers,
【学歴】	July 2008, Master of Sci., Dept. Physics, ENS Lyon Sept. 2011, Doctor of Sci., Physical and Analytical Chemistry, Paris 6
【学位】	Doctor of Science from University of Paris 6
【略歴】	Oct. 2011, Postdoctoral Fellow, Kyoto University Apr. 2014, FIFC Fellow, Kyoto University
【主な著書、学術論文】（過去 5 年以内）	1. Thangh-Nghi Nguyen, Magali Duvail, Arnaud Villard, John J. Molina, Philippe Guilbaud, and Jean-François Dufrêche, “Multi-scale modeling of uranyl chloride solutions”, *J. Chem. Phys.* **142**, 024501 (2015) 2. John J. Molina and R. Yamamoto, “Diffusion of colloidal particles in swimming suspensions”, *Mol. Phys.* **112**, 1389 (2014) 3. Adnan Hamid, John J. Molina, and Ryoichi Yamamoto, “Direct numerical simulations of sedimenting spherical particles at finite Reynolds number”, *RSC Adv.* **4**, 53681 (2014) 4. Bertrand Siboulet, John J. Molina, Benoît Coasne, Pierre Turq and Jean-François Dufrêche, “Water self-diffusion at the surface of silica glasses: effect of hydrophilic to hydrophobic transition”, *Mol. Phys.* **111**, 3410 (2013) 5. John J. Molina and Ryoichi Yamamoto, “Direct Numerical simulations of rigid body dispersions. I. Mobility/friction tensors of assemblies of spheres”, *J. Chem. Phys.* **139**, 234105 (2013)

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【現在の研究課題】	Dispersion Force Effects on the Dissociation of “Jack-in-the-Box” Diphosphanes and Diarsanes.
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【学位】	Doctor of Philosophy, Royal Institute of Technology, Sweden
【略歴】	2007-2012, Postdoctoral Fellow, Institute for Molecular Science, Japan 2012-2015, Research Fellow, Institute for Chemical Research, Kyoto University
【主な著書、学術論文】（過去 5 年以内）	1. Jing-Dong Guo, Shigeru Nagase, and Philip P. Power, Dispersion Force Effects on the Dissociation of “Jack-in-the-Box” Diphosphanes and Diarsanes, *Organometallics* 2015, **34**, 2028. 2. Takahiro Sasamori, Tomohiro Sugahara, Tomohiro Agou, Jing-Dong Guo, Shigeru Nagase, Rainer Streubel, and Norihiro Tokitoh, Synthesis and Characterization of a 1,2-Digermabenzene, *Organometallics* 2015, **34**, 2106. 3. Takuya Kuwabara, Jing-Dong Guo, Shigeru Nagase, Takahiro Sasamori, Norihiro Tokitoh, and Masaichi Saito, Synthesis, Structures, and Electronic Properties of Triple- and Double-Decker Ruthenocenes Incorporated by a Group 14 Metallole Dianion Ligand, *J. Am. Chem. Soc.* 2014, **136**, 13059

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【現在の研究課題】	Theoretical study of functionalized nanomaterials
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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
【学位】	Ph.D. in Materials Physics and Chemistry, Xi'an Jiaotong University, China
【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】	・ 柔らかな不斉触媒を用いる C-C 結合生成反応の立体選択性発現機構の解明及び触媒設計 ・ Y^{3+} 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 ・ $4f^N$ エネルギーシフト法を用いるランタノイド発光プローブの発光・消光・励起エネルギー移動の機構解明 ・ 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、理論化学研究会
【主な著書、学術論文】 （過去 5 年以内）	1. M. Hatanaka, K. Morokuma, “How Can Fluctional Chiral Lanthanide(III) Complexes Achieve a High Stereoselectivity in Aqueous Mukaiyama-Aldol Reaction?” *ACS Catal*. **5**, pp 3731-3739 (2015). 2. M. Hatanaka, K. Morokuma, “Exploring the reaction coordinates for f-f emission and quenching of lanthanide complexes – thermosensitivity of terbium(III) luminescence”, *J. Chem. Theory Comput*. **10**, pp 4184-4188 (2014). 3. 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). 4. 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 5. 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).
【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】	Mechanistic studies of organic and organometallic reactions.
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【学歴】	2009, Master degree, Ecole Polytechnique and Ecole Normale Supérieure de Cachan, Palaiseau and Cachan, France 2013, Ph.D., Ecole Normale Supérieure de Lyon, Lyon, France
【学位】	Doctor of Philosophy, Ecole Normale Supérieure de Lyon, Lyon, France
【略歴】	2014, Chemistry Laboratory, ENS de Lyon, Lyon, France 2010, Organic Chemistry Laboratory, ENSTA, Paris, France 2008, Chemistry Laboratory, ENS de Cachan, Cachan, France 2007, Physical-Chemistry Laboratory, Paris XI University, Orsay, France
【主な著書、学術論文】（過去 5 年以内）	1. R. Ramozzi, K. Morokuma, Revisiting the Passerini reaction mechanism: existence of the nitrilium, organocatalysis of its formation and solvent effect, *J. Org. Chem.*, 2015, doi:10.1021/acs.joc.5b00594. 2. L. Wa Chung, W. M. C. Sameera, R. Ramozzi, A. J. Page, M. Hatanaka, G. P. Petrova, T. V. Harris, X. Li, Z. Ke, F. Liu, H.B. Li, L. Ding, and K. Morokuma, The ONIOM Method and its Applications, *Chem. Rev.*, 2015, doi:10.1021/cr5004419, 120 pages. 3. R. Ramozzi, N. Chéron, L. El Kaïm, L. Grimaud, and P. Fleurat-Lessard Predicting new Ugi-Smiles couplings: a combined experimental and theoretical study, *Chem. Eur. J.*, 2014, **20** (29), 9094-9099. 4. R. Ramozzi, N. Chéron, B. Braïda, P. C. Hiberty, P. Fleurat-Lessard, A Valence Bond view of isocyanides' electronic structure, *New. J. Chem.*, 2012, **36** (5), 1137-1140. 5. N. Chéron, R. Ramozzi, L. El Kaïm, L. Grimaud, P. Fleurat-Lessard Challenging 50 years of established views on Ugi reaction : a theoretical approach, *J. Org. Chem.*, 2012, **77** (3), 1361-1366.
【学術関係の受賞など】	FIFC fellowship, 2015 JSPS Fellowship, 2014 Ecole Normale Supériere de Cachan, PhD Fellowship, 2010-2013 Ecole Normale Supérieure de Cachan fellowship, 2007-2010

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【現在の研究課題】	蛍光分子の円錐交差探索
【研究内容キーワード】	励起状態、項間交差
【学歴】	2014 年 3 月　九州大学理学府　化学専攻修了
【学位】	2014 年 3 月　博士（理学）　九州大学
【略歴】	2014 年 4 月　福井謙一記念研究センター
【所属学会】	分子科学会、理論化学研究会
【主な著書、学術論文】 （過去 5 年以内）	1. T. Tsuneda, J.-W. Song,S. Suzuki, and K. Hirao ”On Koopmans'theorem in density functional theory” *J. Chem. Phys.* **133**, 174101 (2010). 2. S. Suzuki, T. Tsuneda, and K. Hirao “A theoretical investigation on photocatalytic oxidation on the TiO2 surface” 3. S. Suzuki, R. Ebisuzaki, Y. Watanabe, and H. Nakano “Relativistic Multireference Perturbation Theory and its Semi-Approximate Second-Order Form” *J. Comput. Chem. Jpn.* Vol.**13**, No.1, pp32 (2014)
【学術関係の受賞など】	2012 年 9 月　Best Poster Awardsat the Annual Meeting of the Japan Society for Molecular Science

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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】	2014, Visiting Assistant Professor, SUNY Oswego 2012, Postdoctoral Fellow, Fukui Institute
【主な著書、学術論文】（過去5年以内）	1. Chung, L. W.; Sameera, W. M. C.; Ramozzi, R.; Page, A. J.; Hatanaka, M.; Petrova, G. P.; Harris, T. V.; Li, X.; Ke, Z.; Liu, F.; Li, H. B.; Ding, L.; Morokuma, K. The ONIOM Method and its Applications. *Chem. Rev.* [Online early access]. DOI: 10.1021/cr5004419. Published Online: Apr 8, 2015. 2. 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. 3. 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. 4. 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. 5. Harris, T. V.; Szilagyi, R. K. Comparative Assessment of the Composition and Charge State of Nitrogenase FeMo-Cofactor. *Inorg. Chem.,* 2011, **50** (11), 4811.
【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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【研究分野】	理論化学、計算化学
【現在の研究課題】	(1) Modeling of blue copper protein for computation of EPR hyper fine coupling tensors, (2) Construction of basis set for 3d-transition metal for highly accurate ab initio method, (3) Redox potentials of organic molecules and 3d-transition metal complexes
【研究内容キーワード】	ハイブリッド分子理論、化学反応機構、スペクトロスコピー、機能分子
【学歴】	2009年9月　京都大学大学院理学研究科化学専攻博士課程修了
【学位】	2009年9月　京都大学理学博士
【略歴】	2010年1月　米国ミネソタ大学博士研究員 , 2013年3月　京都大学福井謙一記念研究センター研究員 2014年6月　独マックスプランク研究所化学エネルギー変換博士研究員
【主な著書、学術論文】 （過去5年以内）	1. Photochemical Ring Opening and Closing of Three Isomers of Diarylethene: Spin-Flip Time Dependent Density Functional Study, M. Isegawa and K. Morokuma, *J. Phys. Chem. A.* **119**, 4191 (2015) 2. Complete active space second order perturbation theory (CASPT2) study of N(^{2}D) + H_2O reaction paths on D_1 and D_0 potential energy surfaces: Direct and roaming pathway, M. Isegawa, F. Liu, S. Maeda, K. Morokuma, *J. Chem. Phys.* **141**, 154303 (2014) 3. Ab initio reaction pathways for photodissociation and isomerization of nitromethane on four singlet potential energy surfaces with three roaming paths, M. Isegawa, F. Liu, S. Maeda, K. Morokuma, *J. Chem. Phys.* **140**, 244310 (2014) 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). 5. Electrostatically Embedded Molecular Tailoring Approach and Validation for Peptides, M. Isegawa, B. Wang, D. G. Truhlar, *J.Chem. Theory Comput.* **9**, 1381 (2013) 6. Valence excitation energies of alkenes, carbonyl compounds, and azabenzenes by time-dependent density functional theory: linear response of the ground state compared to collinear and noncollinear spin-flip TDDFT with the Tamm-Dancoff , approximation. M. Isegawa. D. G. Truhlar, *J. Chem. Phys.* **138**, 134111 (2013).

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【現在の研究課題】	Hybrid methods, transition metal catalysis, florescent probs.
【研究内容キーワード】	QM/MM and QM/QM methods, reaction mechanisms.
【学歴】	July 2005, BSc (Hons), University of Sri Jayewardenepura, Sri Lanka.
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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. 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. 2. 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. 3. 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. 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. L. W. Chung, W. M. C. Sameera, R. Ramozzi, A. J. Page, M. Hatanaka, G. P. Petrova, T. V. Harris, X. Li, Z. Ke, F. Liu, H-B. Li, L. Ding and K. Morokuma, , “The ONIOM Method and its Applications”, *Chem. Rev.* 2015, **115**, 5678-5796.
【学術関係の受賞など】	JSPS postdoctoral fellowship, Japan. (2014) 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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【研究分野】	Computational Chemistry, Physical Organic Chemistry
【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
【学歴】	July, 2010, B.Sc (Hons), The University of Science & Technology of China January, 2014, Ph.D, University of Sheffield, The United Kingdom
【学位】	Ph.D, University of Sheffield (The United Kingdom)
【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, Piotr Raubo, “A Mechanistic Study of the Lewis Base Directed Cycloaddition of 2-Pyrones and Alkynylboranes”, *J. Am. Chem. Soc.* 2014, **136**, 8642-8653. 3. Julong Jiang, Jin-Quan Yu, Keiji Morokuma, “Mechanism and Stereoselectivity of Directed C(sp^3)-H Activation and Arylation Catalyzed by Pd(II) with Pyridine Ligand and TFA. A Computational Study”, *ACS Catal.* 2015*,* **5**, 3648-3661. 4. Julong Jiang, Romain Ramozzi, Keiji Morokuma, “Rh(III)-Catalyzed C(sp^3)-H Bond Activation *via* an External Base Metalation Deprotonation Mechanism: A Theoretical Study”, *Chem. Eur. J.* Accepted. 5. Julong Jiang, Romain Ramozzi, Shin Moteki, Asuka Usui, Keiji Maruoka, Keiji Morokuma, “The Mechanism of Metal-Free C-H Activation of Branched Aldehydes and Acylation of Alkenes Using Hypervalent Iodine Compound: A Theoretical Study”, *J. Org. Chem.* Submitted.
【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。
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【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
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【主な著書、学術論文】 （過去 5 年以内）	1. H. Zheng, X. Zhao, T. Ren, W. W. Wang, C_{74} Endohedral metallofullerenes violating the isolated pentagon rule: A density functional theory study, *Nanoscale*, **4**, 4530-4536 (2012) 2. H. Zheng, X. Zhao, W. W. Wang, T. Yang, S. Nagase, $Sc_2@C_{70}$ rather than $Sc_2C_2@C_{68}$: Density functional theory characterization of metallofullerene Sc_2C_{70}, *J. Chem. Phys.*, **137**, 014308 (2012) 3. H. Zheng, J. Li, X. Zhao, Regioselective Chlorine-Addition Reaction toward $C_{54}C_{18}$ and Role of Chlorine Atoms in Stone-Wales Rearrangement, *Dalton Trans*, **41**, 14281-14287 (2012) 4. H. Zheng, X. Zhao, W. W. Wang, J. S. Dang, 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) 5. H. Zheng, J. Zheng, L. He, X. Zhao, Unique Configuration of A Nitrogen-doped Graphene Nanoribbon: Potential Applications to Semiconductor and Hydrogen Fuel Cell, *J. Phys. Chem. C*, **118**, 24723-24729 (2014) 6. H. Zheng, X. Zhao, L. He, W. W. Wang, S. Nagase, Quantum Chemical Determination of Novel C_{82} Monometallofullerenes Involving a Heterogeneous Group, *Inorg. Chem.*, **53**, 12911-12917 (2014)

４．共同研究員プロフィール

【氏名（ふりがな）】	Maneeporn Puripat
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【研究分野】	Computational Chemistry
【現在の研究課題】	Computational and Theoretical Chemistry, Simulation of Physics Phenomena, Acoustics Physics
【研究内容キーワード】	Conversion of cellulose to Green energy, Biginelli reaction and Acoustic Analysis of Speech
【学歴】	May 2011, B.Sc. in Physics, Faculty of Science, Chulalongkorn University, Thailand March 2013, LL.B, Faculty of Law, Sukhothai Thammathirat Open University, Thailand May 2016 (Expected), Ph.D. in Nanoscience and Techology, Graduate School, Chulalongkorn University, Thailand
【学位】	Ph.D. student in Nanoscience and Technology program, Chulalongkorn University
【学術関係の受賞など】	Development and Promotion of Science and Technology talents project (DPST) 2004-present

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12回京都大学福井謙一記念研究センターシンポジウム　— 諸熊奎治先生傘寿記念 —

日　　時　2015年（平成27年）1月23日（金）

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　北川　進（京都大学 物質—細胞統合システム拠点 教授）
「多孔性金属錯体の化学と応用」
10:15－11:15

田中　肇（東京大学 生産技術研究所 教授）
「水の局所構造化と熱力学異常・結晶化におけるその役割 」
11:30－12:30

諸熊　奎治（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）
「Chemical Theory of Complex Molecular Systems: Discovery and Insights from Computational Studies of Chemical Reactions」
14:00－15:00

— 休 憩 —

ポスターセッション　15:30－17:20

お祝いの会・懇親会（１Ｆ多目的ルーム）　17:30－19:00

２．センターセミナー

第12回福井センターセミナー

日　　時　2014年（平成26年）4月8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 〜 15:00	Yuichi MASUBUCHI (Kyoto Univ.) “Modeling and Simulations of Polymer Dynamics”
15:15 〜 16:15	Atsushi Ikeda (FIFC) “Statistical Mechanics of the Glass Transition: Insights from Mean-Field Situations”
16:30 〜 17:30	Gernot FRENKING (Philipps-Univ. Marburg) “Main Group Complexes with Unusual Donor-Acceptor Bonds”

３．国際交流

当センター教員が海外の研究機関を訪問し、研究所の運営に関して意見交換を行った。
（資料編　を参照）

４．社会へのアウトリーチ活動

高等学校などへの出張講義

（1）畑中　美穂　特定研究員

兵庫県立北摂三田高等学校	2014年（平成26年）10月2日
〃	2015年（平成27年）1月15日

（2）榊　茂好　リサーチリーダー

京都府立南陽高等学校	2014年（平成26年）11月6日

(3) 諸熊　奎治　シニアリサーチフェロー
　　畑中　美穂　他　特定研究員
　　京都大学アカデミックデイ　2014年（平成26年）9月28日

メディアなどへの出演

(1) 池田　昌司　准教授
　　エフエム京都 Kyoto University Academic Talk 2014年（平成26年）12月24日

5．その他（報告）

諸熊　奎治　シニアリサーチフェローについては、2014年10月21～22日に日経産業新聞「日本のイノベーター」欄でその研究活動などの紹介がされている。
(資料編 を参照)

Ⅳ　研究業績

１．専任教員

Atsushi Ikeda

Associate Professor

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

Thinning or thickening? Multiple rheological regimes in dense suspensions of soft particles

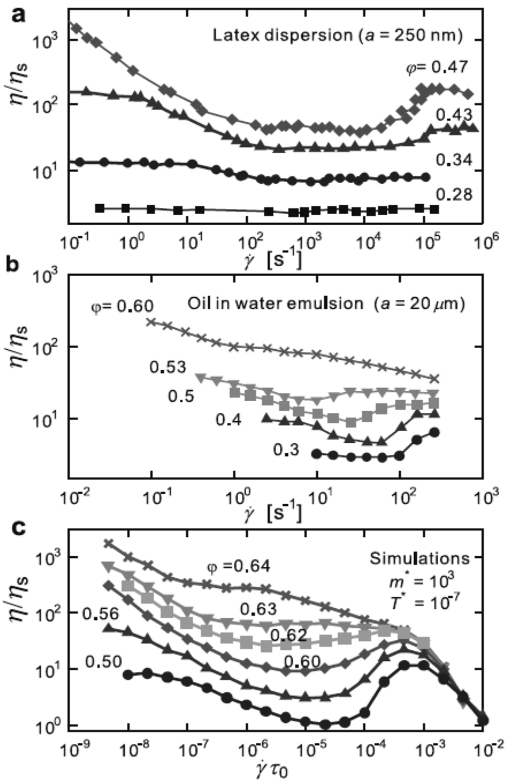

Fig. 1 Flow curves obtained in two experiments (a. Latex dispersion and b. Oil-in-water emulsion), and our simulation (c).

Understanding the shear rheology of dense colloidal and granular suspensions remains a central challenge at the crossroad between nonequilibrium statistical mechanics and soft matter physics, with a clear technological relevance. Simple liquids display simple rheological properties characterized by linear Newtonian behavior. However, in dense particle suspensions such as emulsions, colloidal assemblies, or granular materials, the viscosity is usually not a single number, but a nonlinear function of the applied flow rate. To characterize these materials, an entire flow curve is thus needed. When the viscosity varies with the applied shear rate, the system can either flow more easily as the shear rate increases (shear-thinning), or offer increasing resistance to flow (shear-thickening).

In order to understand the origin of this nonlinearity, we numerically study the rheology of a simple model of soft repulsive particles at large densities, and show that nonlinear flow curves reminiscent of experiments on real suspensions can be obtained (Fig 1). By using dimensional analysis and basic elements of kinetic theory, we rationalize these multiple rheological regimes and disentangle the relative impact of thermal fluctuations, glass and jamming transitions, inertia and particle softness on the flow curves. We characterize more specifically the shear-thickening regime and show that both particle softness and the emergence of a yield stress at the jamming transition compete with the inertial effects responsible for the observed thickening behaviour. This allows us to construct a dynamic state diagram, which can be used to analyze experiments.

Diverging viscosity and soft granular rheology in non-Brownian suspensions

The jamming transition is widely studied in dense disordered systems such as granular materials, emulsions, and suspensions of large colloids. Below the jamming packing density, the system flows with a finite viscosity when an external force if applied. On approaching the jamming transition from below, the viscosity increases dramatically and the system eventually develops a solid like behavior with a finite yield stress.

We use large scale computer simulations and finite size scaling analysis to study the shear rheology of dense three-dimensional suspensions of frictionless non-Brownian particles in the vicinity of the jamming transition. We perform simulations of soft repulsive particles at constant shear rate, constant pressure, and finite system size, and study carefully the asymptotic limits of large system sizes and infinitely hard particle repulsion. Extending earlier analysis by about two orders of magnitude, we first study the asymptotic behavior of the shear viscosity in the hard particle limit. We confirm its asymptotic power law divergence at the jamming transition, but show that a precise determination of the critical density and critical exponent is difficult due to the `multiscaling' behavior of the viscosity (Fig. 2). Additionally, finite-size scaling analysis suggests that this divergence is accompanied by a growing correlation length scale, which also diverges algebraically. We then study the effect of soft repulsion, and propose a natural extension of the standard granular rheology to account for softness effects, which we validate from simulations. Close to the jamming transition, this `soft granular rheology' offers a detailed description of the non-linear rheology of soft particles, which differs from earlier empirical scaling forms.

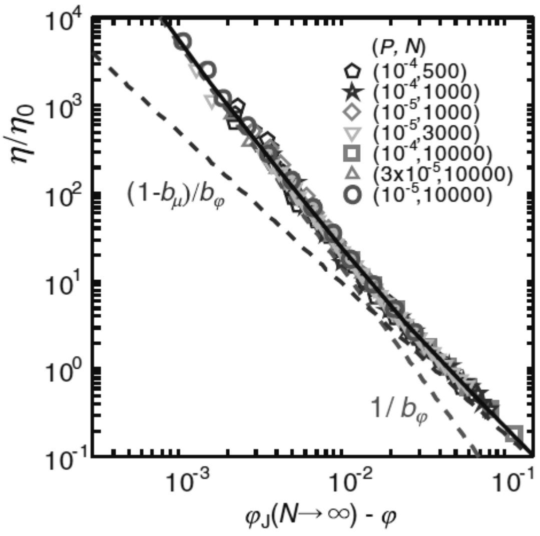

Fig. 2 Divergence of the shear viscosity near the jamming transition is controlled by two exponents.

Replica theory analysis of the glass transitions of Network-formers

When the crystallization is avoided, the dynamics of liquids slows drastically with decreasing temperature, ending up with the formation of amorphous solids. This glass transition is a highly common phenomenon. Many complicated systems present the glass transition and the associated slow dynamics, everyday examples include window glass, various plastics, optical fibers, etc, which are formed through the glass transitions of molecular liquids, colloidal suspensions, polymeric liquids, and so on. In experimental studies, the wide varieties of the systems have been studied, and their glass transitions are revealed to have rich phenomenologies. On the other hand in theoretical studies, in order to keep the analysis tractable, the simplified models, such as hard spheres and Lennard-Jones particles, have been focused. An extreme example is the hard spheres in infinite dimensions. Though never exist in reality, this system is the simplest glass former and is playing a great role for the construction of the mean-field theory of the glass transition and the understanding of the universal feature of the glass transition. We are attempting to bridge these theoretical and experimental efforts, by applying or extending the microscopic mean-field theory of the glass transition to more complicated systems. In particular we focus on the replica theory, which is the theory to calculate the structures and thermodynamics of supercooled liquids and glasses through a replication of systems and liquid state theory calculations of the replicated systems.

In this work, we especially focus on the problem of fragility. Experiments have showed that the increase of the viscosity is strongly dependent on the nature of liquids. The liquids which show a steeper increase of the viscosity are called ``fragile", and the others ``strong". Experimentally liquids tend to become ``strong" when the molecules tend to form a network structure in their liquid states, however the theoretical level of understanding on this tendency is still lacking. This is the fragility problem. We apply the replica theory (small cage expansion with the hyper-netted chain theory) to the standard binary mixture of Lennard-Jones particles (KALJ), which is a typical fragile glass former, and the simple network-forming fluid model (NTW) that was introduced by Coslovich and Pastore. The theory is found to predict that the temperature dependence of the configurational entropy of NTW is much milder than that of usual Lennard-Jones particles (Fig. 3). This result with Adam-Gibbs argument on the relaxation time explain well the difference between strong and fragile liquids.

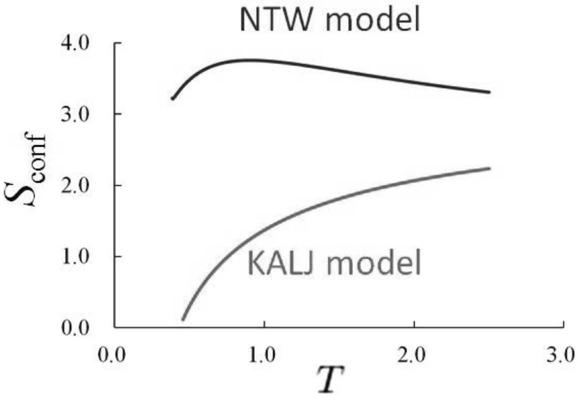

Fig. 3 Configurational entropy of NTW model and KALJ model calculated by the replica theory.

Correlation of Local Order with Particle Mobility in Supercooled Liquids is Highly System Dependent

Supercooled liquids display markedly heterogeneous dynamics, despite possessing structural properties that appear nearly unchanged from those of normal liquids from which they are prepared. Simulations of model supercooled liquids are useful for understanding the connections between structure and dynamics because particle locations may be followed precisely for all times. Recently, focus has turned to the study of specific structural motifs and their putative connection with the dynamics of supercooled liquids. The notion that the frustration of local order incommensurate with bulk crystalline periodicity may be related to glass formation is an old one. New evidence for the growth of domains associated with local packing motifs has been presented for several simple and realistic model systems, where particles tend to be found in certain "locally preferred structures" (LPS) with increased supercooling. As a general rule, more fragile systems display a more rapid increase in LPS concentration and domain extent.

In this study, we use extensive numerical simulation to investigate the connection between local structure and dynamical heterogeneity in supercooled liquids. Through the study of four different models we show that the correlation between a particle's mobility and the degree of local order in nearby regions is highly system dependent (Fig. 4). Our results suggest that the correlation between local structure and dynamics is weak or absent in systems that conform well to the mean-field picture of glassy dynamics and strong in those that deviate from this paradigm. Finally, we investigate the role of order-agnostic point-to-set correlations and reveal that they provide similar information content to local structure measures, at least in the system where local order is most pronounced.

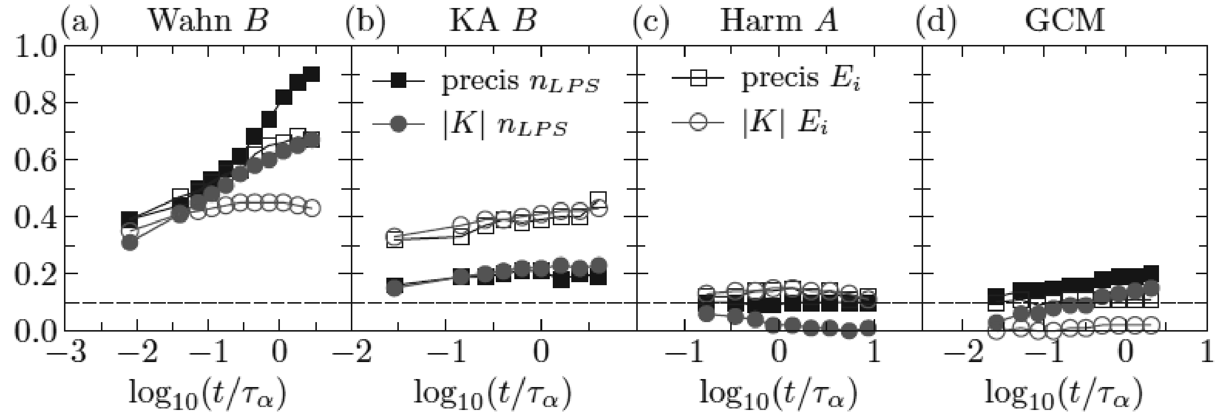

Fig. 4 Time dependence of the correlation between the dynamics and local structural motif.

2. Original papers

(1) Takeshi Kawasaki, Daniele Coslovich, Atsushi Ikeda and Ludovic Berthier
“Diverging viscosity and soft granular rheology in non-Brownian suspensions”
Phys. Rev. E 91, 012203 (2015). (This article was selected as “Editors' Suggestion”)

(2) Glen M. Hocky, Daniele Coslovich, Atsushi Ikeda and David R. Reichman
“Correlation of Local Order with Particle Mobility in Supercooled Liquids is Highly System Dependent”
Phys. Rev. Lett. 113, 157801 (2014). [arXiv:1402.6709]

(3) Takeshi Kawasaki, Atsushi Ikeda and Ludovic Berthier
“Thinning or thickening? Multiple rheological regimes in dense suspensions of soft particles”
EPL 107, 28009 (2014).

3. Presentation at academic conferences

(1) Atsushi Ikeda

“Disentangling glass and jamming physics: a rheological study”
Gordon Research Conference on Granular and Granular Fluid Flows, Massachusetts (USA), July 20-25, 2014. (Invited)

(2) 池田昌司
「ガラス転移とジャミング転移の統一的研究：力学物性とレオロジー」
第4回ソフトマター研究会、名古屋、2015年1月6日-8日(招待講演)

(3) Atsushi Ikeda
“A replica theory study of the glass and jamming transitions of hard ellipsoids”
日本物理学会第70回年次大会、東京、2015年3月21日-24日

(4) Harukuni Ikeda, Atsushi Ikeda
“Correlation length for the high dimensional hard sphere model near the glass and jamming transition point”
日本物理学会第70回年次大会、東京、2015年3月21日-24日

(5) Misaki Ozawa, Walter Kob, Atsushi Ikeda, Kunimasa Miyazaki
“Numerical Study of Ideal Glass Transition by Random Pinning”
日本物理学会第70回年次大会、東京、2015年3月21日-24日

(6) 枡井 基典, 佐藤 啓文, 池田 昌司
「ガラス転移における構造とフラジリティの関係：レプリカ理論によるアプローチ」
日本物理学会第70回年次大会、東京、2015年3月21日-24日

(7) 池田 晴國, 池田 昌司
「高次元剛体球のガラス・ジャミング転移における相関長」
第四回ソフトマター研究会、名古屋、2015年1月6日-8日

(8) 枡井 基典, 佐藤 啓文, 池田 昌司
「ガラス転移における構造とフラジリティの関係：レプリカ理論によるアプローチ」
第四回ソフトマター研究会、名古屋、2015年1月6日-8日

(9) 池田 昌司, Ludovic Berthier
「ランダム最密充填近傍での静的構造と振動」
日本物理学会2014年秋季大会、春日井、2014年9月7日-10日

4. Others

(1) Atsushi Ikeda
“Statistical mechanics of the glass transition: Insights from mean-field situations”
The 12th Fukui Center Seminar, Kyoto, 2014/4/8.

(2) 池田昌司
「高密度分散系のレオロジー：ガラス転移とジャミング転移とその間」
関西レオロジー研究会第66回例会, 京都, 2014年6月16日

(3) 池田昌司
「粒子のランダム最密充填における臨界性」
8th Mini-Symposium on Liquids, 岡山, 2014年7月5日

(4) 池田昌司
「高密度分散系のレオロジー：ガラス転移とジャミング転移」
計算粉体力学研究会, 京都, 2014年12月2日

２．シニアリサーチフェロー

Shigeru Nagase

Senior Research Fellow of FIFC

1. Summary of the Research of the Year

(a) Widely Believed Metallofullerene $Sc_2@C_{66}$ Revised

Fullerenes consists of pentagonal and hexagonal carbon rings, and have closed cage structures. The isolated pentagon rule (IPR) has been established in fullerenes chemistry, which states that there is no adjacent pentagon for stable fullerenes. The first example of IPR-violation was reported for endohedral metallofullerene $Sc_2@C_{66}$. The ^{13}C NMR spectrum showed that $Sc_2@C_{66}$ has C_{2v} symmetry. It was determined from MEM (maximum entropy method)/Rietveld analysis that two Sc atoms were encaged as a dimmer inside the C_{2v} isomer (coded #4348 in the spiral algorithm) of C_{66}.

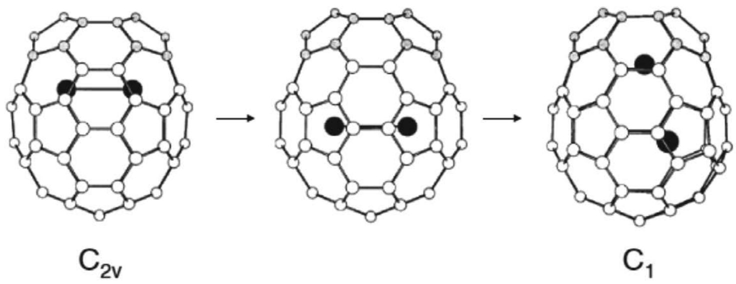

Fig. 1. Transformation of the C_{2v} structure of $Sc_2@C_{66}$ (#4348) to the C_1 structure without barriers.

However, we pointed out that the C_{2v} structure of $Sc_2@C_{66}$ (#4348) shown in Fig. 1 does not correspond to an energy minimum; it has two imaginary frequencies that destroy C_{2v} symmetry. This is explained by the fact that the two Sc atoms located in a narrow space on the upper side of the C_{66} cage undergo large electrostatic repulsion between the positively charged Sc atoms. Therefore, the two Sc atoms move down toward the central area of the C_{66} cage with a larger space, and then the Sc-Sc unit rotates in the way that each Sc atom points to the top and bottom of the C_{66} cage, so that the electrostatic repulsion between the positively charged Sc atoms is most reduced because of the increase in the Sc-Sc distance. The resultant C_1 structure becomes 62 kcal mol^{-1} more stable than the C_{2v} structure determined from MEM/Rietveld analysis. However, the C_1 structure does not fit the observed ^{13}C NMR spectrum.

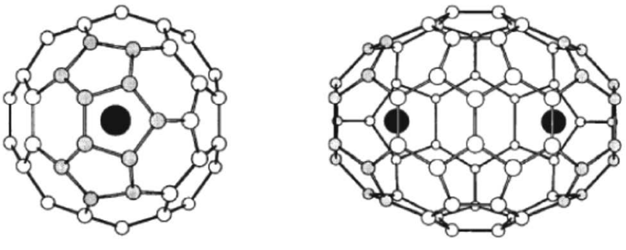

Fig. 2. Two views of the C_{2v} structure of $Sc_2@C_{66}$ (#4059).

Among the 4,478 isomers of C_{66}, 8 isomers have C_{2v} symmetry. Detailed calculations revealed that encapsulation of two Sc atoms inside the C_{2v} isomer coded #4059 are the most favorable. The C_{2v} structure of $Sc_2@C_{66}$ (#4059) with a larger separation of two Sc atoms, which is shown in Fig. 2, is 95 kcal mol^{-1} more stable than that of

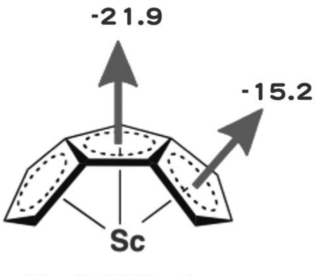

Fig. 3. NICS values

$Sc_2@C_{66}$ (#4348) determined by MEM/Rietveld analysis. It is noteworthy that the discrepancy between theoretical calculations and MEM/Rietveld analysis has been dissolved by 2D NMR spectroscopic and single-crystal X-ray structure analyses showing that the theoretically predicted $Sc_2@C_{66}$ (#4059) is correct, while the widely believed $Sc_2@C_{66}$ (#4348) is wrong. It is interesting that the carbon cage of $Sc_2@C_{66}$ (#4059) has two pairs of three adjacent pentagons, this fusion of three pentagons being the first example in the chemistry of endohedral metallofullerenes. As well known, fused pentagons are antiaromatic. However, they become aromatic by accepting electrons from the Sc atom coordinated to the fused pentagons, as indicated by the negative NICS (nuclear-independent chemical shift) values shown in Fig. 3.

(b) Structural Prediction of Endohedral Metallofullerenes

The smallest sulfide clusterfullerene $Sc_2S@C_{68}$ has been detected by mass spectrometry. However, it has been determined yet what is the endoheral structure of $Sc_2S@C_{68}$. Therefore, density functional theory (DFT) calculations were performed for a large number of possible isomers of C_{68}. It is found that the Sc_2S cluster is encapsulated inside the IPR-violating C_{2v}-C_{68} (#6078) isomer of C_{68} that has two pairs of fused pentagons, each Sc atom being coordinated to the fussed pentagons with an obtuse Sc–S–Sc angle of 151°. The ^{13}C NMR, UV-vis-NIR, and IR spectra of $Sc_2S@C_{2v}$-C_{68} (#6078) are calculated, which are useful for future experimental characterization. DFT calculations were also performed for $Sc_2S@C_{76}$, because its structure has not been experimentally determined. It is found that the Sc_2S cluster is encapsulated inside the IPR-satisfying T_d-C_{76} (#19151) isomer of C_{76}. In addition, it is suggested that the Sc_2S cluster can be encapsulated also inside the IPR-violating isomers of C_{76} at high temperatures. The ^{13}C NMR, UV-vis-NIR, and IR spectra are calculated to confirm the structures of $Sc_2S@C_{76}$ in future experimental characterization.

For the Gd_2C_{94} species, it is an interesting subject which is abundantly produced, dimetallofullerene $Gd_2@C_{94}$ or carbide clusterfullerene $Gd_2C_2@C_{92}$. DFT energy calculations show that $Gd_2@C_2$-C_{94} (#153480) is the most stable. However, relative concentrations (mole fractions) calculated via free energies as a function of temperatures reveal that $Gd_2C_2@D_3$-C_{92} (#126408) is the most abundant, and $Gd_2C_2@C_1$-C_{92} (#126390) and $Gd_2C_2@C_2$-C_{92}(#126387) are the second and third most abundant, respectively, for the temperatures at which endohedral metallofullerenes are generally produced, as shown in Fig. 4. This suggests that dimetallofullerenes

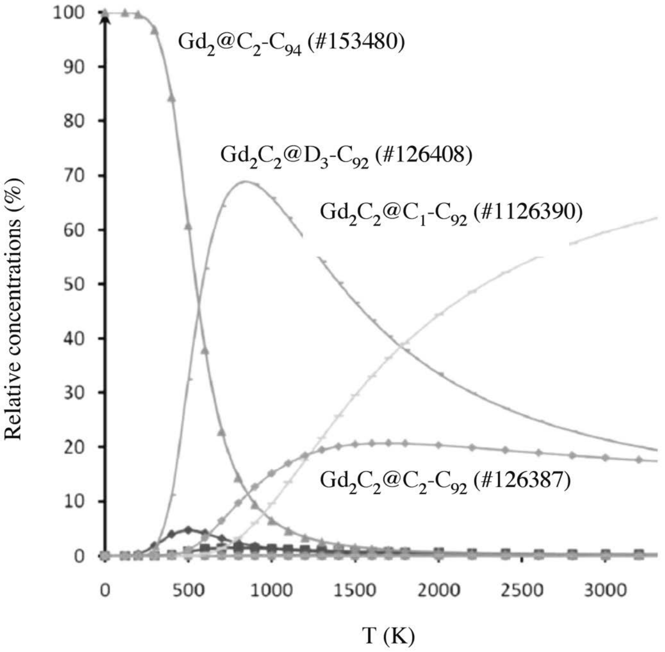

Fig. 4. Relative concentrations of the $Gd_2@C_{94}$ isomers

(encapsulation of two pure metals) are much less abundantly produced than carbide cluster fullerenes. In this context, it is interesting that $Gd_2C_2@D_3$-C_{92} (#126408) has been characterized experimentally as the example of the largest carbide clusterfullerene.

(c) Reactions of Endohedral Metallofullerenes

The DFT calculations were performed for the Diels–Alder reactions of the IPR-violating C_{68} and the corresponding $Sc_3N@C_{68}$ to investigate the effects of endohedrtal doping on the reactivities. For the empty C_{68}, the addition of dienes to the [5,6] bond is kinetically favorable, while the addition to the [5,5] bond is thermodynamically favorable. Upon encapsulation of the Sc_3N cluster, the addition to the [5,5] bond becomes favorable both kinetically and thermodynamically, though the reactivities are considerably reduced because of electron transfer from Sc_3N to C_{68}. It is found that the bonds around the adjacent pentagons are most reactive. This suggests that adjacent pentagons play an important role in the reactivities.

Synthesizing unprecedented diamagnetic adducts of an endohedral metallofullerene was achieved by using 1,3-dipolar cycloaddition reaction of paramagnetic La@C_s-C_{82} with a simultaneous hydrogen addition. The selective formation of two main products, La@C_s-C_{82}HCMe$_2$NMeCHPh (**2a** and **2b**), was first detected by HPLC analysis and MALDI-TOF mass spectrometry, as shown in Fig. 5. **2a** and **2b-O,** which was readily formed by the oxidation of **2b**, were isolated by multistep HPLC separation and were fully characterized by spectroscopic methods, including 1D-NMR, 2D-NMR, and UV−vis-NIR measurements and electrochemistry. The hydrogen atom was found to be connected to the fullerene cage directly in the case of **2a**, and the redox behavior indicated that the C−H bond can still be readily oxidized. The reaction mechanism as well as the structures of **2a** and **2b** were well disclosed by the close interplay between experimental observations and DFT calculations. The feasible order of the reaction process would involve a 1,3-dipolar cycloaddition followed by the hydrogen addition through a radical pathway. It was concluded that the characteristic electronic properties and structure of La@C_s-C_{82} result in a site-selective reaction, which afford a unique chemical derivative of an endohedral metallofullerene in high yields. Derivative **2a** constitutes the first endohedral metallofullerene where the direct linking of a hydrogen atom has been structurally proven.

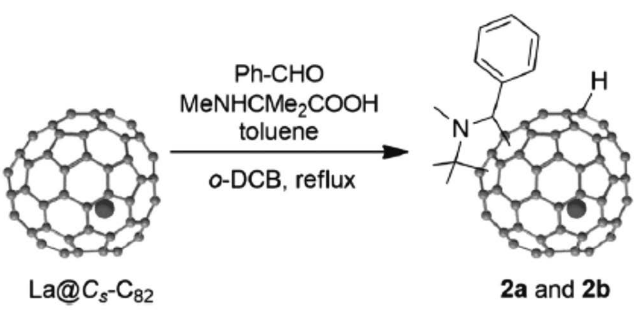

Fig. 5. Synthesis of the La@C_s-C_{82} derivative.

(d) Interesting Bonds Provided by Heavier Main Group Elements

Recent insightful reports have proposed that carbodiphosphoranes should be classified as a new class of carbone rather than a heteroallene. Carbones consist of two ligands (L) coordinated to its central zero-valent carbon atom, which maintains its four valence electrons as two orthogonal lone pairs, and therefore, is also described carbon complex of the general type L→C←L. Electronic effects on the central carbon atom of carbone, generated by the replacement of the S^{IV} ligand of carbodisulfane (CDS) with other chalcogen ligands (Ph_2E, E = S or Se), were investigated. As Fig. 6 shows, the carbones $Ph_2E \rightarrow C \leftarrow SPh_2(NMe)$ (E = S (**a**) or Se (**b**)) were synthesized from the corresponding salts, and their electronic properties as well as structures were characterized by DFT calculations. The carbone **b** is the first carbone containing selenium as the coordinated atom. DFT calculations revealed the electronic structures of carbones **a** and **b**, which have two lone pairs of electrons at the carbon center. The trend in HOMO energy levels, also estimated by cyclic voltammetry measurements as well as DET calculations, for the carbones and CDS follows the order of **b** > **a** > CDS. Analysis of a doubly protonated dication and trication complex revealed that the central carbon atom of **b** behaves as a four-electron donor.

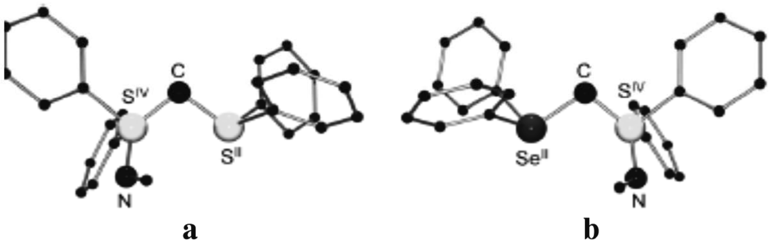

Fig. 6. Structures of carbones **a** and **b**

The linkage of hypercoordinated atoms is of considerable interest in the chemistry of group 14 elements. As Fig. 7 shows, the first dianionic compounds bearing a bond between two pentacoordinated Ge atoms have been synthesized in a stable form. X-ray crystallographic analysis as well as DFT calculations indicated that the two pentacoordinated Ge atoms are linked by a clear single σ bond. The dianionic compounds are reversibly converted to the anionic and neutral Ge−Ge bonded compounds while maintaining the coordination number of the germanium atoms. The interconversion features changes in electronic properties and structures around the germanium atoms. These new structures composed of such Ge-Ge bonds will be useful for the construction of functional materials that respond to acid-base reactions.

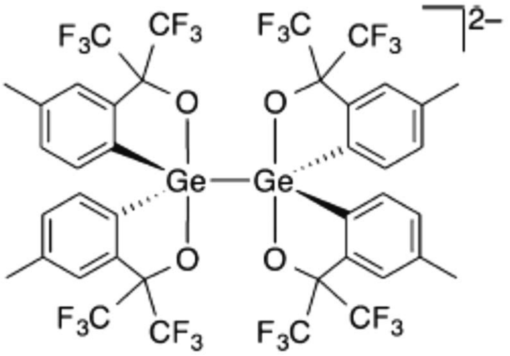

Fig. 7. Linkage of petacoordinated Ge atoms

(e) Other Research Subjects

(1) "Enhancement of Stannylene Character in Stannole Dianion Equivalents Evidenced by NMR and Mössbauer Spectroscopy and Theoretical Studies of Newly Synthesized Silyl-Substituted Dilithiostannoles", (2) "Photochemical Behavior of Single-Walled Carbon Nanotubes in the Presence of Propylamine", (3) "Regioselective Benzyl Radical Addition to an Open-Shell Cluster Metallofullerene. Crystallographic Studies of Cocrystallized $Sc_3C_2@I_h\text{-}C_{80}$ and Its Singly Bonded Derivative", (4) "Regioselective Synthesis and Molecular Structure of the First Derivative of

Praseodymium-Containing Metallofullerenes", (5) "Isolation and Characterization of [5,6]-Pyrrolidino-$Sc_3N@I_h$-C_{80} Diastereomers", (6) "Synthesis, Structures, and Electronic Properties of Triple- and Double-Decker Ruthenocenes Incorporated by a Group 14 Metallole Dianion Ligand", (7) "Magnetic Alignments of Endohedral Metallofullerene Nanorods under Magnetic Fields", (8) "Partial Charge Transfer in the Shortest Possible Metallofullerene Peapod, $La@C_{82}\subset$[11]Cycloparaphenylene", (9) "Quantum Chemical Determination of Novel C_{82} Monometallofullerenes Involving a Heterogeneous Group", (10) "Hiding and Recovering Electrons in a Dimetallic Endohedral Fullerene: Air-Stable Products from Radical Additions", (11) "Regioselective Cage Opening of $La_2@D_2(10611)$-C_{72} with 5,6-Diphenyl-3-(2-pyridyl)-1,2,4-triazine", and (12) "Water-Dimer Stability and Its Fullerene Encapsulations".

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(5) Y. Maeda, Y. Hasuike, K. Ohkubo, A. Tashiro, S. Kaneko, M. Kikuta, M. Yamada, T. Hasegawa, T. Akasaka, J. Zhou, J. Lu, S. Nagase, and S. Fukuzumi, "Photochemical Behavior of Single-Walled Carbon Nanotubes in the Presence of Propylamine", *ChemPhysChem,* **15**, 1821-1826 (2014).

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3. Review articles

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4. Books

(1) 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」、赤阪 健、大須賀篤弘、福住俊一、神取秀樹 監修「高次π空間の創発と機能開発」、シーエムシー出版、pp. 5-9 (2013).

(2) 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, Characterization, and Device Applications* (Eds. T. Torres and G. Bottari), John Wiley & Sons, Chapter 12, pp. 241-258 (2013).

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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. In 2013 and 2014 many veteran postdocs left FIFC to take up faculty positions in their respective countries. Dr. Miho Hatanaka, Fukui Fellow for the last four years, became Assistant Professor at Kinki University in Osaka as of April 1, 2015. Several new postdocs joined our group in 2014, and we had a total of 8 postdoctoral fellows (2 Fukui Fellows, 2 JSPS Postdoctoral Fellows and regular postdocs supported mainly by Kakenhi (grants from the Minister of Education, Culture, Sports, Science and Technology)). One Visiting Foreign Researcher (PhD student from Thailand) spent a year in the group working on her thesis. In addition, three Visiting Foreign Researchers (on Associate Professor on Sabbatical from US, and one Lecturer from Vietnam and two graduate students from US and Spain stayed in the group. Since detailed description on individual projects at FIFC can be found in the reports of postdoctoral fellows, here only the areas of studies and titles of individual projects are summarized.

I. Method Development

A. The ONIOM Method and Its Application

The ONIOM method, developed by Morokuma and collaborators since 1995, is a very powerful and robust hybrid method, in which a molecule is divided into two or more parts and different levels of theoretical methods are applied to different parts of the molecule, enabling calculation of large molecular systems with reasonable accuracy and cost. More than 100 scientific papers that refer to the ONIOM method have been published every year. Although some reviews of the method itself were published in the past, there were no comprehensive reviews of both recent developments and variations of the method and its applications have not been published. This was in part because applications cover very wide areas of chemistry, from organic, inorganic, catalysis to materials, solution, nano and bio. Some former and present members of the Morokuma group at FIFC decided to undertake such a review. It took over a year and resulted in a Chem. Rev. article with 13 authors and 119 printed pages, entitled “The ONOIM Method and its Applications”. Chem. Rev. 115, 5678–5796 (2015).

B. Development of the GRRM Strategy

In the last several years, in collaboration with Profs. Koichi Ohno and Satoshi Maeda, we have developed the Global Reaction Route Mapping (GRRM) strategy, combining the two methods of automatic potential energy search, the ADDF (adiabatic downward distortion following) method and the AFIR (artificial force-induced reaction (AFIR) method. These methods allow determination of important 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 or prejudice. The strategy can be applied to complex molecular systems by also combining with micro-iteration techniques. The GRRM strategy has been actively applied to homogenous catalysis systems such as transition metal catalysts and metal-free organocatalysts. The GRRM strategy has also been particularly powerful in finding reaction pathways of photo-activated molecules, in which multiple pathways involving various electronically excited states and crossings can efficiently be located. The GRRM14 program has been released to public in October 2014 and is available through http://grrm.chem.tohoku.ac.jp/GRRM/index_e.html.

a. Anharmonic Downward Distortion Following for Automated Exploration of Quantum Chemical Potential Energy Surfaces. (See Original Paper #9).
b. Intrinsic Reaction Coordinate: Calculation, Bifurcation, and Automated Search. (See Original Paper #8).
c. Systematic Exploration of Minimum Energy Conical Intersection Structures near the Franck-Condon Region. (See Original Paper #7).
d. From Roaming Atoms to Hopping Surfaces: Mapping out Global Reaction Routes in Photochemistry. (See J. Am. Chem. Soc. 137, 3433–3445 (2015).)

II. Theoretical Studies of Reactions of Complex Molecular 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 catalysis, 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 to find reaction pathways. GRRM turned out to be a very powerful tool for finding many important transition states and intermediates of complex multistep multipathway reactions. In some stereochemistry-determining steps of asymmetric catalytic reactions, sometimes more than 100 different pathways exist and the GRRM strategy allowed to properly sample all these. GRRM studies have shown that some organic multicomponent reactions, such as Passerini, Biginelli and Ugi reactions, are in fact organocatalytic reactions in which some component acts as catalyst in more than one step of multistep reactions.

A. The Mechanism of Metal-Free C-H Activation of Branched Aldehydes and Acylation of Alkenes Using Hypervalent Iodine Compound: A Theoretical Study (See research activities of J. Jiang)
B. The Biginelli reaction is a urea-catalyzed organocatalytic multicomponent reaction (see research activities of M. Puripat)
C. R. Ramozzi, K. Morokuma, Revisiting the Passerini reaction mechanism: existence of the nitrilium, organocatalysis of its formation and solvent effect. (See research activities of R. Ramozzi)
D. Hydroboration Mechanism Revisited: Alkene Addition Partner Depends on Ligand and Substrate. (See research activities of T. Harris)
E. Theoretical investigation on the Pd-catalyzed C(sp^3)-H activation in the synthesis of unnatural amino acids. (See research activities of J. Jiang)
F. Rh(III)-Catalyzed C(sp3)-H Bond Activation via an External Base Metalation Deprotonation Mechanism: A Theoretical Study. (See research activities of J. Jiang)
G. Mukaiyama aldol reactions catalyzed by a chiral Fe(II) complex (See research activities of W. M. C. Sameera)
H. Pd-catalysed borylation of 2-arylaziridines See research activities of W. M. C. Sameera)
I. G. P. Petrova, H.-B. Li, K. Maruoka and K. Morokuma, Asymmetric phase-transfer catalysis with homo- and heterochiral quaternary ammonium salts: a theoretical study (See Original Paper #13)
J. The origin of enantioselectivity for intramolecular Friedel-Crafts reaction catalyzed by the supramolecular Cu / DNA catalyst complex (See Original Paper #14)
K. A Theoretical Study on the UVR8 Photoreceptor: Sensing Ultraviolet-B by Tryptophan and Dissociation of Homodimer. (See Original Paper #10).

III. 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 nanotubes (SWCNTs) and graphenes, for which the growth mechanism is still poorly understood. The chirality control in the CNT growth is one of the most important pending issues. The nucleation and growth of graphenes on transition metal surfaces have been studied using a variety of model systems. The research activity in this area is slowed down, as we feel that we have accomplished what we can hope for using the present methodology and techniques.

A. Graphene Nucleation from Amorphous Nickel Carbides: QM/MD Studies on the Role of Subsurface Carbon Density. (See Original Paper #16)

B. Graphene Nucleation on a Surface-Molten Copper Catalyst: Quantum Chemical Molecular Dynamics Simulations. (See Original Paper #12)

C. Nearly Exclusive Growth of Small Diameter Semiconducting Single-Wall Carbon Nanotubes from Organic Chemistry Synthetic End-Cap Molecules. (See Original Paper #3)

D. Insights into Carbon Nanotube and Graphene Formation Mechanisms from Molecular Simulations. (See Review Article #2)

IV. Theoretical Studies of Photofunctional Molecular Systems

The functionality of photofunctional molecules, such as fluorescence probes, photoswitches and photosensitizers, is often controlled by the energy and geometry of minimum energy conical intersections (MECIs) between the ground S_0 and the first excited S_1 electronic states. If an MECI can be reached easily from the Franck-Condon (FC) state of the first excited state, the excited molecule makes nonadiabatic transition from S_1 to S_0 through this MECI and its emission is quenched. It is therefore very important to determine the S_1/S_0 MECI theoretically. The GRRM method (see section I) allows one to search and determine MECIs automatically and is a very essential tool for clarification of the origin of quenching of such molecules. We have recently used the GRRM method in conjunction to inexpensive DFT methods for the quenching mechanism of large organic and inorganic molecules.

A. Exploring the reaction coordinates for f-f emission and quenching of lanthanide complexes – thermo-sensitivity of terbium(III) luminescence. (See research activities of M. Hatanaka)

B. Reason of the low quantum yield (QY) of Eu(III) helical ligand complexes and computational molecular design for higher QY. (See research activities of M. Hatanaka)

C. Photochemical Ring Opening and Closing of Three Isomers of Diarylethene: Spin-Flip Time Dependent Density Functional Study (See research activities of M. Isegawa)

D. Exploration of quenching pathway of multiluminescent acenes using the GRRM strategy with the SF-TDDFT method. (See research activities of S. Suzuki)

V. Theoretical Studies of Chemical Reactions of Small Radical Species

We have collaborated with a molecular beam experimental group to study the reaction of phenyl and tolyl radicals with butadiene and vinyl acetylene to form naphthalene derivatives, the reaction that is considered to be important in terrestrial as well as combustion environments.

A. An Experimental and Theoretical Study on the Formation of 2-Methylnaphthalene ($C_{11}H_{10}/C_{11}H_3D_7$) in the Reactions of the Para-Tolyl (C_7H_7) and Para-Tolyl-d7 (C_7D_7) with Vinylacetylene (C_4H_4). (See Original Paper #15)

B. Formation of 6-Methyl-1,4-Dihydronaphthalene in the Reaction of the Para-Tolyl Radical with 1,3-Butadiene under Single Collision Conditions, J. Phys. Chem. A 118, 12111-12119 (2014). (See Original Paper #4)

C. A Crossed Molecular Beam and Ab Initio Study on the Formation of 5- and 6-Methyl-1,4-Dihydronaphthalene ($C_{11}H_{12}$) via the Reaction of Meta-Tolyl (C_7H_7) with 1,3-Butadiene (C_4H_6). (See Original Paper #1).

D. Complete active space second order perturbation theory (CASPT2) study of N(^{2}D) + H_2O reaction paths on D_1 and D_0 potential energy surfaces: direct and roaming pathways. (See Original Paper #6)

E. Initial gas phase reactions between $Al(CH_3)_3/AlH_3$ and ammonia: a theoretical study. (See Original Paper #2)

2. Original Papers

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4. D. S. N. Parker, B. B. Dangi, R . I. Kaiser, A. Jamal, M. Ryazantsev and K. Morokuma, Formation of 6-Methyl-1,4-Dihydronaphthalene in the Reaction of the Para-Tolyl Radical with 1,3-Butadiene under Single Collision Conditions, J. Phys. Chem. A 118, 12111-12119 (2014).
5. M. Hatanaka and K. Morokuma, Exploring the reaction coordinates for f-f emission and quenching of lanthanide complexes – thermo-sensitivity of terbium(III) luminescence. J. Chem. Theo. Comp. 10, 4184-4188 (2014).
6. M. Isegawa, F. Liu, S. Maeda and K. Morokuma, Complete active space second order perturbation theory (CASPT2) study of N(^{2}D) + H_2O reaction paths on D_1 and D_0 potential energy surfaces: direct and roaming pathways, J. Chem. Phys. 141, 154303/1-9 (2014).
7. S. Maeda, Y. Harabuchi, T. Taketsugu, and K.Morokuma, Systematic Exploration of Minimum Energy Conical Intersection Structures near the Franck-Condon Region, J. Phys. Chem. A 118, 12050-12058 (2014).
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13. G. P. Petrova, H.-B. Li, K. Maruoka and K. Morokuma, Asymmetric phase-transfer catalysis with homo- and heterochiral quaternary ammonium salts: a theoretical study, J. Phys. Chem. B, 118, 5154–5167 (2014).

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16. M. Jiao, H. Qian, A. Page, K. Li, Y. Wang, Z. Wu, S. Irle, and K. Morokuma, Graphene Nucleation from Amorphous Nickel Carbides: QM/MD Studies on the Role of Subsurface Carbon Density, J. Phys. Chem. C 118, 11078–11084 (2014).

3. Review Articles.

1. L. W. Chung, W. M. C. Sameera, R. Ramozzi, A. J. Page, M. Hatanaka, G. P. Petrova, T. V. Harris, X. Li, Z. Ke, F. Liu, H.-B. Li, L. Ding, and K. Morokuma, The ONOIM Method and its Applications. Chem. Rev. 115, 5678–5796 (2015).
2. A. J. Page, F. Ding, S. Irle and K. Morokuma, Insights into Carbon Nanotube and Graphene Formation Mechanisms from Molecular Simulations: A Review. Rep. Prog. Phys. 78, 036501/1-38 (2015).

4. Invited Presentation at Academic Conferences and Universities

1. Keiji Morokuma, Exploring potential energy surfaces with GRRM automatic search strategy, Theory and Computation Provide Insights and Discovery on Chemical Reactions of Complex Molecular Systems. the 2014 AATACC Seminar, University of New Castle, Canberra, Australia, April 28, 2014
2. Theory and Computation Provide Insights and Discovery on Chemical Reactions of Complex Molecular Systems, the 2014 AATACC Seminar, University of Sydney, Sydney, Australia, April 29, 2014
3. Theory and Computation Provide Insights and Discovery on Chemical Reactions of Complex Molecular Systems, the 2014 AATACC Seminar, Australian National University, Canberra, Australia, May 1, 2014
4. Exciting World of Theoretical Studies of Chemical Reactions − From Gas Phase Reactions to Catalysts, and Enzymatic Reactions, Swiss Chemical Society Lecture, University of Basel, Basel, Switzerland, May 19, 2014
5. Chemical Theory of Complex Molecular Systems: Discovery and Insights from Computational Studies of Chemical Reactions, Swiss Chemical Society Lecture, University of Fribourg, Fribourg, Switzerland, May 20, 2014
6. Theoretical Studies of Complex Molecular Systems. Methods and Applications, Swiss Chemical Society Lecture, University of Basel, Basel, Switzerland, May 21, 2014
7. Complex Chemical Reaction Pathways Explored by Automatic Search Strategy, Swiss Chemical Society Lecture, ETH, Zurich, Switzerland, May 22, 2014
8. Exciting World of Theoretical Studies of Chemical Reactions − From Gas Phase Reactions to Catalysts, and Enzymatic Reactions, Swiss Chemical Society Lecture, EPFL, Lausanne, Switzerland, May 23, 2014
9. Multiscale Computational Approaches And Applications in Biochemistry And Biomaterials, Annual Conference of Canadian Chemical Society, Vancouver, Canada, June 4, 2014
10. 複雑分子系のシミュレーション〜生体分子の反応への応用とその周辺，情報計算化学生物学会（CBI 学会）講演会、東京、2014年7 月29 日
11. Quantum chemical molecular dynamics (QM/MD) simulations of nucleation, growth and healing processes of fullerenes, carbon nanotubes and graphenes, the 17th International Symposium on Small Particles and Inorganic Clusters (ISSPIC XVII), Fukuoka, September 7, 2014

12. Theory and Computation Provide Insights and Discovery on Chemical Reactions of Complex Molecular Systems, International Conference "Molecular Complexity in Modern Chemistry" (MCMC-2014), Moscow, Russia, September 16, 2014
13. Theory and Computation Provide Insights and Discovery on Chemical Reactions of Complex Molecular Systems, Japan-Russia Joint-Symposium on Chemical Theory for Complex Systems, St. Petersburg State University, Russia, September 19, 2014
14. Chemical Theory of Complex Molecular Systems: Discovery and Insights from Computational Studies of Chemical Reactions CRC-SU Joint International Symposium on Chemical Theory of Complex Systems: “Interplay between Theory and Experiments; New Trends in Catalysis”, Stockholm University, Stockholm, Sweden, October 31, 2014
15. Theory and Computation Provide Insights and Discovery on Chemical Reactions of Complex Molecular Systems, Advanced Molecular Transformations by Organocatalysts, 2nd International Conference and 7th Symposium on Organocatalysis, Tokyo, November 21, 2014
16. GRRM法を用いた複雑分子系の反応機構、GRRM誕生十周年・GRRM14発表記念講演会「GRRMで拓く化学のニューフロンティア」、東京、2014年11月30日
17. Fascinating World of Theoretical Studies of Chemical Reaction--From Gas Phase Reactions to Catalysts, and Enzymatic Reactions, Hiroshima University, December 3, 2014
18. Chemical Reactions of Complex Molecular Systems -- Discovery and Insights from Computational Studies, 12th Fukui Institute Symposium, Fukui Institute for Fundamental Chemistry, Kyoto University, January 23, 2015
19. Exciting World of Theoretical Studies of Chemical Reactions − From Gas Phase Reactions to Catalysts, and Enzymatic Reactions, Argonne National Laboratory, USA, March 17, 2015
20. Gas-Phase Photochemical and Homogenous Catalytic Reactions Explored Using the Automated Reaction Route Mapping (GRRM) Method, American Chemical Society Spring Meeting, Denver, USA, March 23, 2015

5. Other Activities.

1. The Morokuma group (Satoshi Suzuki, Miho Hatanaka, Julong Jiang, W.M.C. Sameera, Romain Ramozzi and Keiji Morokuma) participated in the 2014 Kyoto University Academic Day, at the Kyoto University Centennial Clock Tower on September 28, 2014, in the Section “Conversation with Researchers” by presenting a poster “Exploring the World of Chemistry by Computer.”

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 2014

The d electron complex systems which consist of transition metal element(s), organic moiety, main group element(s), and hypervalent species are attractive research targets in wide areas of modern chemistry. Actually, the d electron complex systems play important roles as metal enzymes, molecular catalysts, photo-sensitizer, molecular switch, luminescence material and so on. Also, they exhibit a variety of geometry, molecular property, bonding nature, reactivity and catalysis 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 is indispensable in further development of chemistry.

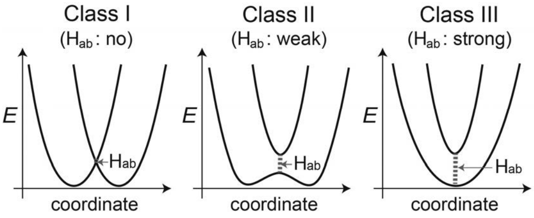
Also, those d-electron complex systems are interesting and challenging research targets from the point of view of theoretical/computational chemistry, because their electronic structures are not simple but complicated in many cases. In particular, transition metal complexes bearing large correlation effects are challenging research targets even nowadays. Our group is theoretically investigating those d-electron complex systems bearing complicated electronic structure.

This year, we theoretically investigated (i) electronic structure and absorption spectra of mixed-valence Mn(III)- and Ni(II)-salen radical complexes, (ii) CASPT2 study of inverse dinitrogen complexes of dinuclear metal complexes of the first row transition metal element, (iii) catalysis of Mo-Mo quintuple bond in benzene synthesis from acetylelene, (iv) generation of dihydrogen molecule and hydrosilylation of carbon dioxide catalyzed by zinc hydride complex, and (v) efficient catalyst for acceptorless alcohol dehydrogenation: interplay of theoretical and experimental studies, (vi) catalytic transfer hydrogenation by at trivalent phosphorus compound, (vii) the crucial roles of $MgCl_2$ as a non-innocent additive in the Ni-catalyzed carboxylation of benzyl halide with CO_2 and (viii) the crucial role of a Ni(I) intermediate in Ni-catalyzed carboxylation of aryl chloride with CO_2.

. We wish to report summaries of them.

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

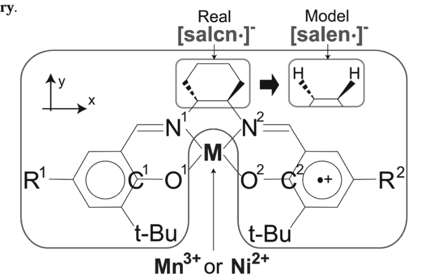
The mixed-valence complexes are classified into three categories by Robin and Day, as shown in Scheme 1. The classification is of considerable importance in both of fundamental chemistry and applied chemistry, because it deeply relates to the electronic structure and also switching function. Though one can expect that the classification significantly depends on solvation, such dependency has not been theoretically investigated well.



Scheme 1. Classification of Mixed-Valence complexes by Robin and Day

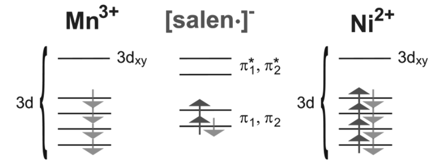
One-electron oxidized Mn(III)− and Ni(II)−salen complexes exhibit unique mixed-valence electronic structures and charge transfer (CT) absorption spectra. We theoretically investigated them to elucidate the reason why the Mn(III)−salen complex takes a localized electronic structure (class II mixed valence compound by Robin−Day classification) and the Ni(II)-analogue has a delocalized one (class III) in solution, where solvation effect was taken into consideration either by the three-dimensional reference interaction site model self-consistent field (3D-RISM-SCF) method or by the mean-field (MF) QM/MMMD simulation. The geometries of these complexes were optimized by the 3D-RISM-SCF-U-DFT/M06. The vertical excitation energy and the oscillator strength of the first excited state were evaluated by the general multiconfiguration reference quasidegenerate perturbation theory (GMC-QDPT), including the solvation effect based on either 3D-RISM-SCF- or MF-QM/MMMD-optimized solvent distribution. The computational results well agree with the experimentally observed absorption spectra and the experimentally proposed electronic structures. The one-electron oxidized Mn(III)−salen complex with a symmetrical salen ligand belongs to the class II, as experimentally reported, in which the excitation from the phenolate anion to the phenoxyl radical moiety occurs. In contrast, the one-electron oxidized Ni(II)−salen complex belongs to the class III, in which the excitation occurs from the doubly occupied delocalized π1 orbital of the salen radical to the singly occupied delocalized π2 orbital; the π1 is a bonding combination of the HOMOs of two phenolate moieties and the π2 is an antibonding combination. Solvation effect is indispensable for correctly describing the mixed-valence character, the geometrical distortion, and the intervalence CT absorption spectra of these complexes. The number of d electrons and the d orbital energy level play crucial roles to provide the localization/delocalization character of these complexes.

(a) Geometry.



Real: (R^1,R^2) = (t-Bu,t-Bu), (OMe,OMe), or (Cl,OMe)
Model: (R^1,R^2) = (Me,Me), (OMe,OMe), or (Cl,OMe)

(b) Electron configuration.



Scheme 2. Ni(II) and Mn(III)-salen radical complexes and their electronic structure.

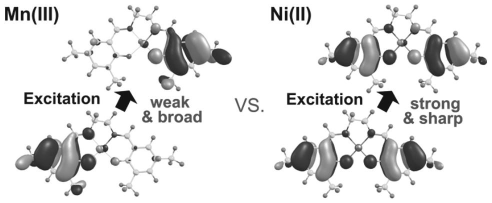
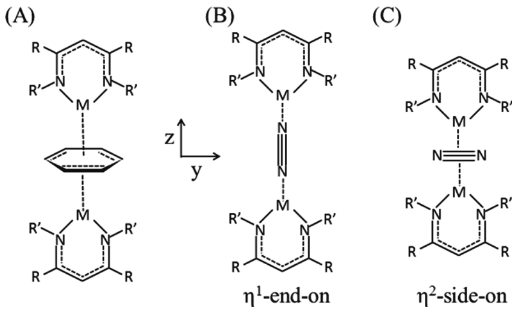


Figure 1. One-electron excitation in Mn(III) and Ni(II) Complexes

(ii) 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:

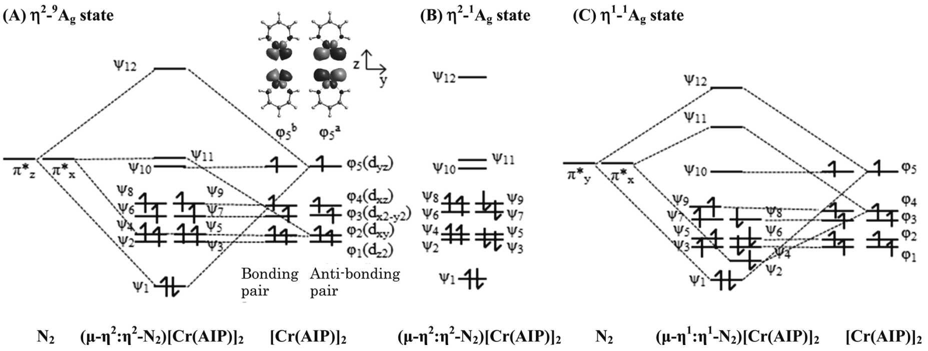
Dinuclear transition metal complexes exhibit complicated electronic structure and interesting molecular properties. Inverse sandwich-type dinuclear complexes (ISTCs), (μ-C_6H_6 or N_2)[M(AIP)]$_2$ (AIPH = (Z)-1-amino-3-imino-prop-1-ene; M = Cr and Fe; Scheme 2), exhibit variety of spin multiplicity. This year, the dinitrogen ISTCs of the first row transition metal elements were investigated with the CASPT2 method. In the ISTC of Cr, the ground state takes a singlet spin multiplicity. However, the singlet to nonet spin states are close in energy to each other. The thermal average of effective magnetic moments (μ_{eff}) of these spin multiplicities is close to the experimental value. The η^2-side-on coordination structure of N_2 is calculated to be more stable than the η1-end-on coordination one. This is because the d-orbital of Cr forms a strong dπ−π* bonding interaction with the π* orbital of N_2 in molecular plane. The MO diagram and occupation number of



Scheme 2. Benzene and dinitrogen inverse sandwich dinuclear metal complexes

MO (Scheme 3) provide us with consistent understanding of these features.

In the ISTC of Fe, on the other hand, the ground state takes a septet spin multiplicity, which agrees well with the experimentally reported μ_{eff} value. The η^1-end-on structure of N_2 is more stable than the η^2-side-on structure. In the η^1-end-on structure, two doubly occupied d-orbitals of Fe can form two dπ–π* bonding interactions. The negative spin density is found on the bridging N_2 ligand in the Fe complex but is not in the Cr complex. All these interesting differences between ISTCs of Cr and Fe are discussed on the basis of the electronic structure and bonding nature.

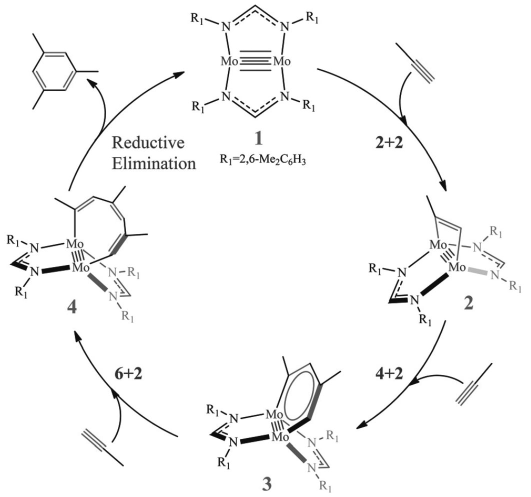


Scheme 3. Schematic orbital pictures of (μ-N_2)[Cr(AIP)]$_2$.

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

Though the metal-metal multiple bond was found very old days by Cotton and his coworkers. Since then, its interesting bonding nature has attracted many researchers in theoretical and experimental fields. However, its theoretical study was not easy because of its complicated electronic structure due to multi-reference nature. Also, the reaction of metal-metal multiple bond has not been reported until recent several pioneering works.

The Mo–Mo quintuple bond was recently applied to catalytic synthesis of benzene from alkynes, which is the first example of the catalytic reaction of the metal–metal multiple bond. This new reaction was studied using DFT and CASSCF/CASPT2 methods. The entire catalytic cycle consists of four steps: [2 + 2], [4 + 2], and [6 + 2] cycloadditions, and reductive elimination of benzene. The symmetry-forbidden [2 + 2] cycloaddition and asymmetric [2 + 2] cycloaddition are two possible pathways for the reaction between an alkyne and the Mo–Mo quintuple bond. Though the barrier of the former pathway is moderate because of the presence of the multi-reference character of the Mo–Mo quintuple bond, the asymmetric pathway is much more favorable because of its symmetry-allowed feature.



Scheme 4. Catalytic Cycle theoretically elucidated.

The C–C bond formation in the next [4 + 2] cycloaddition occurs through charge transfer (CT) from the π orbital of the incoming alkyne to the π* orbital of another alkyne coordinating with the Mo center to afford a novel dimolybdenacyclic species **3**. In **3**, the δd_{xz} and δd_{xz}* orbitals of the Mo–Mo moiety and four π orbitals of the [C_4H_4] moiety construct the π and π* orbitals in the six-membered ring. The next [6 + 2] cycloaddition between 3 and one more alkyne affords an eight-membered ring compound **4** which has a Mo–Mo quadruple bond. This is the rate-determining step of the entire catalytic cycle, the $\Delta G^{0\ddagger}$ value of which is 22.4 kcal mol−1. The subsequent reductive elimination of benzene easily occurs to yield a μ^2–η^2:η^2-benzene dinuclear Mo complex with a Mo–Mo quintuple bond. On the other hand, further [8 + 2] cycloaddition between **4** and one more alkyne is much more unfavorable than the reductive elimination of benzene. The similar [4 + 2] process between alkyne and a Cr–Cr quadruple bond is calculated to be difficult, which is consistent with the experimental result that only the Mo–Mo quintuple bond was successfully applied to this reaction. It is likely that the crowded coordination environment and the much more stable π d_{yz} orbital in the Cr–Cr quadruple bond are responsible for the difficulty in the reaction.

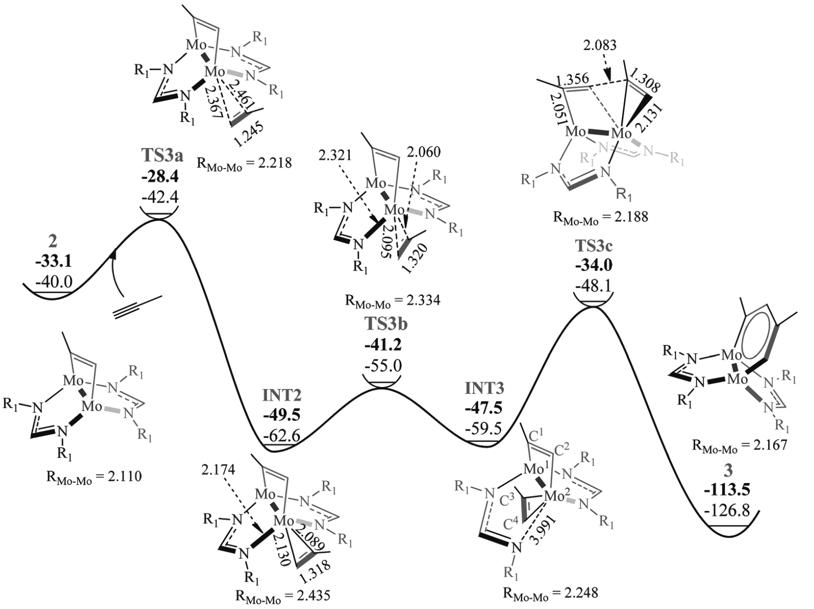
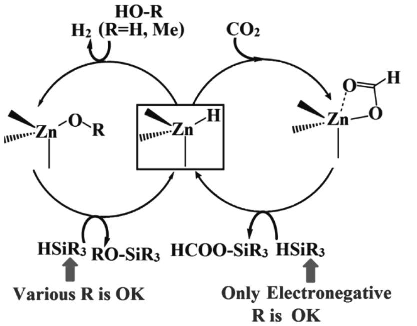


Figure 2. Energy changes in the first 4+2 coupling process leading to the formation of unusual six-member intermediate **3** .

(iv) Generation of Dihydrogen Molecule and Hydrosilylation of CarbonDioxide Catalyzed by Zinc Hydride Complex: Theoretical Understanding and Prediction

The H_2 production from water and alcohol becomes important nowadays. Also, the CO2 fixation is another important reaction for sustainable society. Though many catalytic systems have been proposed successfully for these reactions, the valuable metals are used in those catalysts. That is also one of the problem. We need to use cheap and abundant metal for catalysts because of the limit of such metals in the earth.

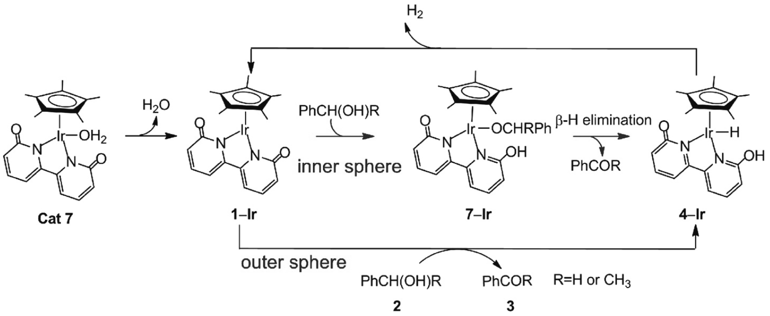


Scheme 5. Catalytic cycle of H_2 production from water or alcohol and CO_2 fixation by Zn-H complex **1**

In this work, the generation of H_2 from methanol/water and hydrosilylation of CO_2 catalyzed by [tris(2-pyridylthio)methyl]zinc hydride [κ^3-Tptm]ZnH **1** were investigated with DFT and MP2 methods. The hydrosilylation of CO_2 occurs via the CO_2 insertion into the Zn−H bond of **1** followed by the metathesis of a Zn−(η1-OCOH) bond with hydrosilane to yield silyl formate and regenerate **1**. The CO_2 insertion easily occurs, but the metathesis is difficult because of the formation of a very stable Zn−(η^2-O_2CH) species before the metathesis. The ΔG°‡ value of the metathesis with triethoxysilane is much smaller than that with phenylsilane because electronegative methoxy groups stabilize the transition state bearing hypervalent Si center, which is consistent with the experimental result that triethoxysilane is used in the hydrosilylation of CO_2. It is theoretically predicted here that hydrosilane with two electronegative OEt groups or one to three F groups can be applied to this reaction. In the generation of H_2 from methanol/water by **1**, the first step is the metathesis of 1 with the O−H bond of methanol/water to produce [κ3-Tptm]Zn(OMe)/[k^3-Tptm]Zn(OH) and dihydrogen molecule. The next step is the metathesis of the Zn−OMe/Zn−OH bond with hydrosilane to yield silyl ether and regenerate **1**. The first metathesis is rate-determining but the second one occurs with very small activation energy, indicating that various hydrosilanes can be applied to this reaction.

(v) Efficient Catalyst for Acceptorless Alcohol Dehydrogenation: Interplay of Theoretical and Experimental Studies

As mentioned above, the H_2 production from alcohol is one of important catalytic reactions now. Recently, Fujita and Yamaguchi reported excellent catalyst with Ir complex to perform this reaction under mild conditions without any acceptor. Such reaction is of considerable interest and theoretical knowledge is necessary to understand well the catalytic mechanism and the prediction.



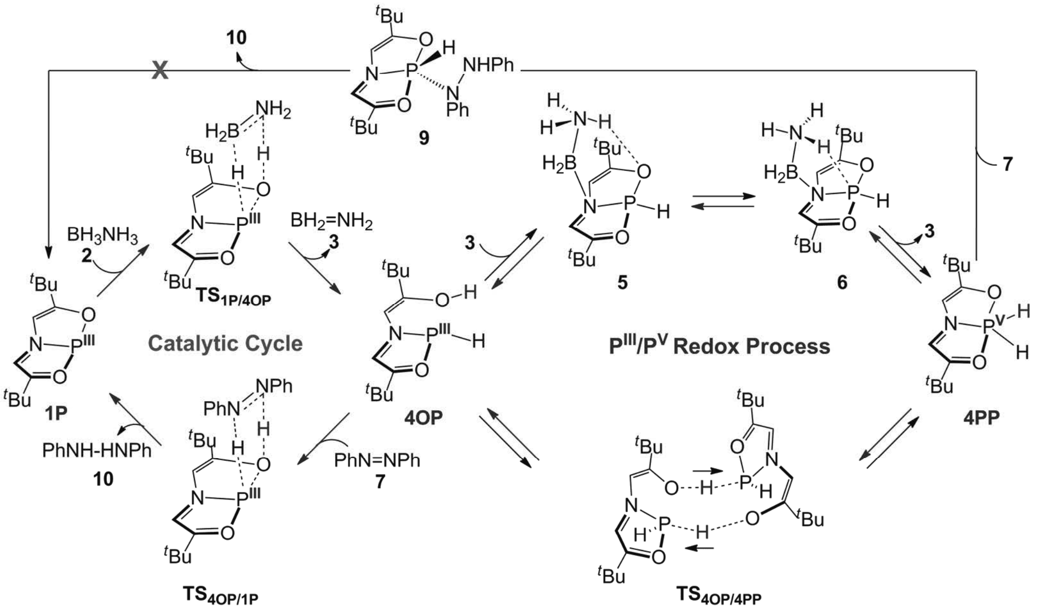
Scheme 6. Reaction scheme of acceptorless alcohol dehydrogenation reaction and excellent Ir catalyst

In this work, the promoterless AAD (acceptorless alcohol dehydrogenation) reaction mediated by an iridium catalyst Cp*Ir(bpyO) **1−Ir** (Cp* = pentamethylcyclopentadienyl, bpyO = α,α′-bipyridonate) has been theoretically investigated with the density functional theory. The reaction occurs through three steps, including alcohol dehydrogenation, formation of dihydrogen complex, and H_2 elimination from the iridium center. In the first two steps, the metal center and the bpyO ligand work cooperatively via the aromatization/dearomatization process of the bpyO ligand. The second step is ratedetermining, where the $\Delta G0\neq$ and $\Delta G0$ values are 23.9 and 13.9 kcal/mol, respectively. Our calculations demonstrate that the aromatization of the bpyO ligand as well as the charge transfer (CT) from the Cp* ligand to the iridium center plays important roles in stabilizing the transition state of the rate-determining step. We have theoretically and experimentally examined the 4d rhodium analogue Cp*Rh(bpyO) **1−Rh** and found that it exhibits similar activity to that of **1−Ir**. On the basis of those results, a new catalyst (HMB)Ru(bpyO) **1−Ru** (HMB = hexamethylbenzene) is designed both theoretically and experimentally, where a cheaper and more abundant 4d ruthenium element is employed with the HMB and bpyO ligands. Theoretical calculations certainly show that **1−Ru** is active for the promoterless AAD reaction via the same reaction mechanism as that of the reaction by **1−Ir.** The experiments also demonstrate that **1−Ru** is as efficient as **1−Ir** for the AAD reaction.

(vi) Catalytic Transfer Hydrogenation by a Trivalent Phosphorus Compound: Phosphorus-Ligand Cooperation Pathway or P(III)/P(V) Redox Pathway?

Main-group-element catalysts are a desirable alternative to transition-metal catalysts because of natural abundance and cost. However, the examples are very limited. Catalytic cycles involving a redox process and E-ligand cooperation (E=main-group element), which are often found in catalytic cycles of transition-metal catalysts, have not been reported.

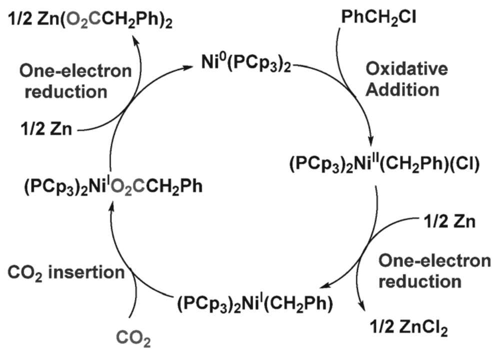
Herein theoretical investigations of a catalytic hydrogenation of azobenzene with ammonia–borane using a trivalent phosphorus compound, which was experimentally proposed to occur through PIII/PV redox processes via an unusual pentavalent dihydridophosphorane, were performed. The geometry was optimized by the DFT and the energy change was evaluated by the ONIOM(CCSD(T):MP2) method. These calculations disclosed that this catalytic reaction occurs through a P-O cooperation mechanism, which resembles the metal-ligand cooperation mechanism of transition-metal catalysts. As summarized in Scheme 7: 1) the catalytic cycle occurs through a new concerted P-O cooperation mechanism, 2) the active species of the transfer hydrogenation is **4OP**, which is produced from **1P** through the dehydrogenation of ammonia–borane, 3) this PO cooperative reaction resembles the metal-ligand cooperation reaction by the transition-metal complex with a pincer ligand, 4) the P^{III}/P^{V} redox reaction certainly occurs in the mutual conversions between **4OP** and **4PP**, but it is not involved in the catalytic cycle, and 5) the substitution of the electron-withdrawing CF_3 group for ^{t}Bu improves the catalytic activity of the trivalent phosphorus compound



Scheme 7. Transfer hydrogenation of azobenzene with ammonia-borane by **1P** via a P(III) compound **4OP** which further isomerizes to **4PP** with a stepwise reaction

(vii) The crucial roles of $MgCl_2$ as a non-innocent additive in the Ni-catalyzed carboxylation of benzyl halide with CO_2

The transformation of CO_2 into useful chemicals has been one of the important topics in the last decade.1 In this regard, various attempts have been made using transition-metal complexes as catalysts for the CO_2 transformation. Among those efforts, direct carboxylation of organic halide with CO_2 is in particular attractive because of the importance of carboxylic acid in various applications.3 However, the reports of such direct carboxylation have been elusive except for several pioneering studies of the Martin group4 and the Tsuji group.5 Interestingly, Martin and co-workers succeeded in the transformation of the C(sp^3)–Cl bond of benzyl halide to phenylacetic acid with CO_2 using a Ni catalyst, very recently. This Ni-catalytic system contains the Zn powder and $MgCl_2$. If the Zn powder is absent, no catalytic conversion occurs. If $MgCl_2$ is not added, the yield is very low. The experimentally proposed reaction mechanism suggests that a Ni(I) intermediate might be crucial in the catalytic cycle, as shown in Scheme 8. However, mysterious is the role of $MgCl_2$; it is not clear at all what roles $MgCl_2$ plays in this catalytic carboxylation to provide good yield of the product.



Scheme 8. Experimentally proposed and theoretically evidenced reaction mechanism

Herein, we theoretically investigated this Ni-catalyzed carboxylation of benzyl chloride to phenylacetic acid in the presence of $MgCl_2$. The Gibbs free energy profile for the total catalytic cycle clearly indicates that $MgCl_2$ promotes the carboxylation of benzyl chloride with CO_2. Based on the computational results, we disclosed here that $MgCl_2$ stabilizes the Ni(I)-CO_2 adduct and accelerates the CO_2 insertion as a non-innocent additive and one-electron reduction as one reagent. To the best of our knowledge, this is the first report that shows the unprecedented roles of $MgCl_2$. The knowledge of the interplay between the metal catalysis and non-innocent additive is crucial for new development in catalytic reactions by transition metal complexes.

Original Papers

(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) Masayuki Nakagaki and Shigeyoshi Sakaki,
"CASPT2 Study of Inverse Sandwich-Type Dinuclear Cr(I) and Fe(I) Complexes of the Dini-trogen Molecule: Significant Differences in Spin Multiplicity and Coordination Structure between These Two Complexes”
J. Phys. Chem. A, 118, 1247−1257 (2014).

(3) Shinji Aono, Masayuki Nakagaki, Takuya Kurahashi, Hiroshi Fujii, and Shigeyoshi Sakaki, J. Chem. Theory Comput. 2014, 10, 1062−1073
“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).

(4) Hiroshi Sato, Wataru Kosaka, Ryotaro Matsuda, Akihiro Hori, Yuh Hijikata,Rodion V. Belosludov, Shigeyoshi Sakaki, Masaki Takata, Susumu Kitagawa,
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(5) 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, 1010−1020 (2014).

(6) Guixiang Zeng, Satoshi Maeda, Tetsuya Taketsugu, and Shigeyoshi Sakaki,
“Catalytic Transfer Hydrogenation by Trivalent Phosphorus Compound: Phosphorus-Ligand Cooperation Pathway or PIII/PV Redox Pathway?”
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(7) Yue Chen and Shigeyoshi Sakaki,
“The important role of the Mo–Mo quintuple bond in catalytic synthesis of benzene from alkynes. A theoretical study”
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(8) Farreed Basha Sayyed and Shigeyoshi Sakaki,
“The Crucial Roles of $MgCl_2$ as a Non-innocent Additive in the Ni-Catalyzed Carboxylation of Benzyl Halide with CO_2”
Chem. Commun., 50, 13026 – 13029 (2014).

(9) Masayuki Wakioka, Yuki Nakamura, Yoshihiro Hihara, Fumiyuki Ozawa, and Shigeyoshi Sakaki,
“Effects of PAr_3 Ligands on Direct Arylation of Heteroarenes with Isolated $[Pd(2,6\text{-}Me_2C_6H_3)(\mu\text{-}O_2CMe)(PAr_3)]_4$ Complexes”
Organometallics, 33, 6247–6252 (2014).

(10) Keisuke Kishida, Yumiko Watanabe, Horike Satoshi, Yoshihiro Watanabe, Yoshikuni Oku-mura, Yuh Hijikata, Shigeyoshi Sakaki, and Susumu Kitagawa,
“DRIFT and Theoretical Studies of Ethylene/Ethane Separation on Flexible Microporosity of $[Cu_2(2,3\text{-pyrazinedicarboxylate})_2(\text{pyrazine})]_n$”
Eur. J. Inorg. Chem., 2747–2752 (2014).

(11) Tetsuaki Fujihara, Yuichiro Horimoto, Taiga Mizoe, Fareed Bhasha Sayyed, Yosuke Tani, Jun Terao, Shigeyoshi Sakaki, and Yasushi Tsuji
"Nickel-Catalyzed Double Carboxylation of Alkynes Employing Carbon Dioxide"
Org. Lett., 16, 4960−4963 (2014).

(12) Milind Madhusudan Deshmukh and Shigeyoshi Sakaki,
"Generation of Dihydrogen Molecule and Hydrosilylation of Carbon Dioxide Catalyzed by Zinc Hydride Complex: Theoretical Understanding and Prediction"
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3. Presentation at academic conferences

(1) Shigeyoshi Sakaki,
"Reaction Behavior of Main-Group Element Compound in Comparison with Transition-Metal Complex. Theoretical Understanding and Prediction
The International Symposium on Reactive Intermediates and Unusual Molecules (ISRIUM) 2014, April, 1-6, 2014, Hiroshima (Invited)

(2) Shigeyoshi Sakaki
"Catalytic Reactions by Transition Metal Complexes with Unusual Valence: Theoretical Study
XXVI International Conference on Organometallic Chemistry, July 13 – 18, 2014, Sapporo, Japan. (Invited)

(3) Shigeyoshi Sakaki
"Spin-Multiplicity Issues of Transition Metal Complexes: Theoretical Understanding",
41th International Conference on Coordination Chemistry (41 ICCC), July 21 – 25, 2014, Singapole (Invited)

(4) Shigeyoshi Sakaki
"σ-Bond Activation Reaction by Transition Metal and Main-Group Element Compounds and Catalytic Reaction Including It, International Conference". Molecular Complexity in Modern Chemistry (MCMC2014)", Sept, 13 – 19, Moscow, Russia (Invited)

(5) Shigeyoshi Sakaki
"Flexibility in Spin-Multiplicity of Transition Metal Complex"
CRC-SU (Catalysis Research Center-Stockholm Univeristy) Joint Symposium for Chemical Theory for Complex Systems, Oct. 30-31, 2014, Stockholm University, Stockholm, Sweden, (Plenary)

(6) Shigeyoshi Sakaki
"Flexible Electronic Structures of Inverse Sandwich-type Dinuclear Metal Complex and Metal Salen Complex"
QSCP XIX (XIXth International Workshop on Quantum Systems in Chemistry, Physics and Biology), Nov. 11-17, 2014, Tamsui, Taiwan, (Invited)

(7) Shigeyoshi Sakaki
"Theoretical Study of Complex System Consisting of Transition Metal Element From Mononuclear Metal Complex to Multinuclear Metal Complex and Metal Complex System in Surrounding Atmosphere"
Lead-Lecture, Eurasia-13 Conference on Chemical Sciences, Dec. 15 – 18. 2014, Bangalore, India (Invited./Lead Lecture)

(8) Shigeyoshi Sakaki
"Molecular Property and Reactivity of Transition Metal Complex: Theoretical Understanding and Prediction", The 4th Modeling of Chemical and Biological (Re)Activity, Feb. 23-25, 2015. Heiderberg, Germany (Invited)

4. Others

(1) σ-Bond Activation of Small Molecules and Reactions Catalyzed by Transition-Metal Complexes: Theoretical Understanding of Electronic Processes
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3-3 多核金属錯体の理論化学　中谷直輝、榊　茂好　pp250-268
5-5-2　理論化学･計算化学分野から見た錯体化学の理論的研究の将来展望と今後への期待
榊　茂好　pp500-518.

(4) 日本化学会編　化学便覧　応用編　10. 榊　茂好、山下晃一；計算機シミュレーションと情報科学

４．博士研究員

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、(1)時間依存密度汎関数法 (TDDFT) のプログラム開発と(2)溶液内における光化学反応の解析を行った。後者は、昨年度から引き続きの研究課題である。

【Non-collinear SF-TDDFT 法のプログラム開発】

スピン反転励起をもとに電子励起状態を記述する SF-TDDFT 法は、ポテンシャル面の交差を同定することができることを過去の研究において報告した[1-2]。したがって、光化学における反応機構を解明する上で非常に有用な方法である。SF-TDDFT 法は３重項を参照系として、スピン反転励起を考える:

$$\mathbf{AX} = \omega \mathbf{X} \tag{1}$$

もっとも単純な collinear (C) 型の場合[3]、

$$A_{i\bar{a},j\bar{b}} = \left(\varepsilon_{\bar{a}} - \varepsilon_i\right)\delta_{ij}\delta_{\bar{a}\bar{b}} - c_x\left(ij \mid \bar{a}\bar{b}\right) \tag{2}$$

で表される。ここで、$i, j, \cdots$ はアルファスピンをもつ占有軌道、 $\bar{a}, \bar{b}, \cdots$ はベータスピンをもつ非占有軌道、$\{\bullet\}$ は軌道エネルギー、そして係数 c_x は Hartree-Fock (HF) 交換項の割合を示す。上式から明らかなように、適用可能な汎関数は HF 項をもったものに限られ、計算では c_x □ 0.5 のものが用いられる。

今年度の研究では、適用可能な汎関数の幅を増やすため、いわゆる non-collinear (NC) 型の SF-TDDFT 法[4,5]を実装した。NC-SF-TDDFT 法は、

$$A_{i\bar{a},j\bar{b}} = \left(\varepsilon_{\bar{a}} - \varepsilon_i\right)\delta_{ij}\delta_{\bar{a}\bar{b}} - c_x\left(ij \mid \bar{a}\bar{b}\right) + f_{ij\bar{a}\bar{b}}^{\mathrm{NC}} \tag{3}$$

で付加項が現れる。

$$f_{ij\bar{a}\bar{b}}^{\mathrm{NC}} = \int d\mathbf{r} \frac{\frac{\partial E^{\mathrm{xc}}}{\partial n_\alpha}(\mathbf{r}) - \frac{\partial E^{\mathrm{xc}}}{\partial n_\beta}(\mathbf{r})}{n_\alpha(\mathbf{r}) - n_\beta(\mathbf{r})} \psi_i(\mathbf{r})\psi_j(\mathbf{r})\bar{\psi}_a(\mathbf{r})\bar{\psi}_b(\mathbf{r}) \tag{4}$$

この付加項が存在することで、HF 交換項がない汎関数でも SF-TDDFT 法で計算を行うことができる。

本研究ではテスト計算として、シアニン色素のモデル分子の系列を選んだ (図 1)。

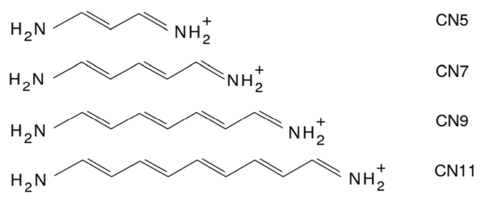

図 1: シアニン分子

計算結果の一部を表 1 に示した (詳しい結果および解析については文献[7]を参照)。従来の C-SF-TDDFT 法で $c_x \approx 0.5$ の汎関数 (BHHLYP) を用いることで、精度よく記述できた。今回導入した NC-SF-TDDFT 法で $c_x = 0$ の汎関数 (SVWN, BLYP) を試したが、~1 eV の過小評価をしてしまうことがわかった。したがって、この分子系では HF 交換項が重要であることが示唆される。実際、NC-SF-TDDFT 法でも c_x が大きな汎関数では精度がよいことを確認した。

今後、NC-SF-TDDFT 法をポテンシャル面の交差に応用し、汎関数の依存性について研究する予定である。

表 1: シアニンの励起エネルギー (単位: eV)

	CN5	CN7	CN9	CN11	MSE^{a}
C-BHHLYP	5.18	4.00	3.32	2.87	+0.20
NC-BHHLYP	5.15	3.87	3.19	2.76	+0.10
NC-SVWN	3.95	2.80	2.17	1.77	−0.97
NC-BLYP	3.85	2.73	2.12	1.74	−1.03
DMC^{ba}	5.03	3.83	3.34	2.88	

^{a}Mean signed error w.r.t. DMC.

^{b}Diffusion Monte Carlo.

【水和チミン分子における自由エネルギー面交差の解析】

生体内に存在する DNA は有害な紫外線により損傷を受ける可能性がある。遺伝情報が適切に保存されないことは、生物にとって致命的である。しかし、DNA 塩基では非常に速い緩和過程が存在し、有害な副次的反応を抑制する。本研究では、チミン分子 (図 2) の水溶液における非断熱緩和過程を、自由エネルギーの交差の観点から解析する。

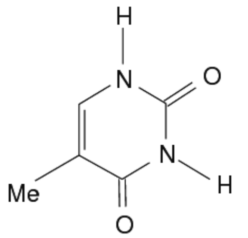

図 2: チミン分子

自由エネルギーの交差点を求める方法は、昨年度の研究で確立した。すなわち、非平衡自由エネルギー $F(\mathbf{R},\mathbf{V})$ を定義し、2 つのエネルギー面の交差を考える。ここで、$\mathbf{V}$ は溶媒和座標を表しており、核座標 $\mathbf{R}$ と同時に最適化を行う。

本研究では３つの自由エネルギー交差点が同定された。分子構造を図 3 に示す。いずれの構造においても６員環の炭素原子に結合した (a)メチル基、(b)水素原子、あるいは (c)酸素原子の面外振動の寄与がある。特に(c)の構造では、水素結合の生成によって酸素原子の面外角が強調されている。酸素原子と水との相互作用による安定化は、表 2 からも明らかである。水和により(c)の構造が特に大きく安定化している。これは、最近報告された水和チミンの非断熱分子動力学シミュレーションで現れた分子構造を再現している[9]。

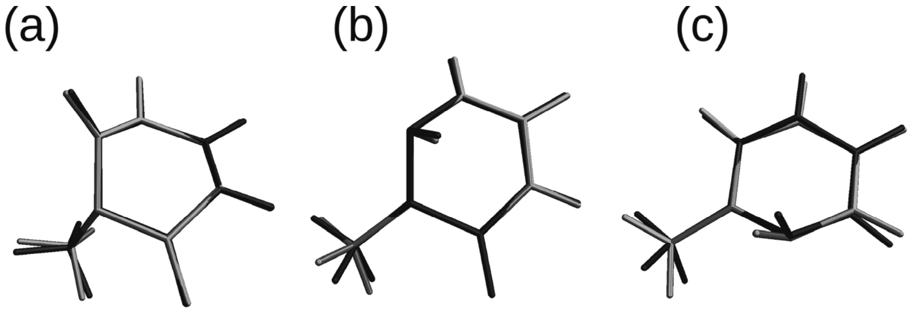

図 3: チミン分子の円錐交差における分子構造 (灰色: 気相、黒: 水溶液)
(a) MEX(C5), (b) MEX(C6), and (c) MEX(C4).

表 2: チミン分子の相対エネルギー^a (単位: eV)

	Franck-Condon	MEX (C5)	MEX (C6)	MEX (C4)
Gas	5.92	4.54	5.52	5.60
Water	5.79	4.48	5.53	4.94

^{a} エネルギーの原点は基底状態の再安定構造

【文献】

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7. N. Minezawa, “Vertical excitation energies of linear cyanine dyes by spin-flip time-dependent density functional theory”, Chem. Phys. Lett. **622**, 115 (2015).
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2. 論文

1. N. Minezawa, “Vertical excitation energies of linear cyanine dyes by spin-flip time-dependent density functional theory”, Chem. Phys. Lett. **622**, 115-119 (2015).
2. N. Minezawa, “State-specific solvation effect on the intramolecular charge transfer reaction in solution: A linear-response free energy TDDFT method”, Chem. Phys. Lett. **608**, 140-144 (2014).
3. N. Minezawa, “Optimizing minimum free-energy crossing points in solution: Linear-response free energy/spin-flip density functional theory approach”, J. Chem. Phys. **141**, article No. 164118 (2014).

3. 学会発表

(1) 嶺澤 範行
「GFP 発色団分子の水溶液における円錐交差の理解: SF-TDDFT/LRFE 法」
第１７回理論化学討論会 名古屋大学 2014/05/23 2P20

(2) 嶺澤 範行
「溶液における分子内電荷移動: 状態固有の溶媒和効果」
第８回分子科学討論会 広島大学 2014/09/21 1P108

4. その他

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第１２回京都大学福井謙一記念研究センターシンポジウム
京都大学　2015/01/23　P20

Takuya Saito

FIFC Fellow

1. Summary of the research of the year

Driven anomalous diffusion in polymer stretching

Small particles or soft matters in solutions exhibit diffusive motion due to thermal agitation. One of the way to approach the diffusion characteristics is to examine the time evolution of the position variance $<(x(t)-x(0))^2>-<(x(t)-x(0))>^2 \sim t^{\alpha}$. While the diffusion of the simple particle is normal with the exponents being $\alpha \sim 1$, viscoelastic conditions such as soft matter or cells make the dynamics anomalous. For example, if a monomer of polymer is tracked, the diffusion is usually characterized by the smaller exponent $\alpha<1$, i.e., subdiffusion because of the chain connectivity.

There are various underlying mechanisms generating the anomalous diffusion. In our study, we narrowed down a target to a tagged monomer dynamics of a driven single polymer. The polymer initially relaxes, but the chain end starts to be pulled with constant force at time t=0. We then track the stochastic motion of the tagged monomer, where the other connected monomers create the colored noise against it. So far, the fluctuation has been discussed on the basis of the generalized Langevin equation (GLE) with the power-law memory kernel and the previous studies reported that some polymer model retains the fluctuation-dissipation like normal diffusion in a simple colloid. Indeed, we can confirm it under weak driving force (or the Rouse model). This relates the variance to the average drift;

$$f<(x(t)-x(0))^2>/<x(t)>=2k_BT. \quad (1)$$

Here question arise: does it hold beyond the near equilibrium? Our study addressed the issue and pointed out that it does not necessarily hold under strong driving force and what deviates eq. (1).

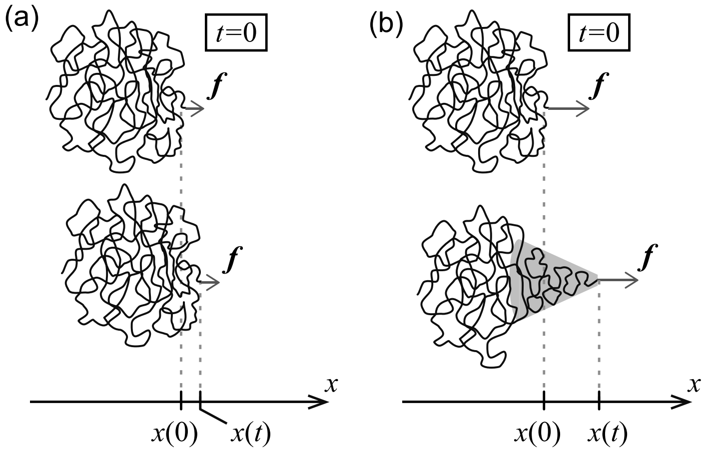

Fig. 1. Schematic representation of polymer stretching.

Hereafter, we will describe our investigation on the anomalous dynamics of polymer stretching under strong driving force by combining different approaches.

(i) We first discussed it at the scaling level in (a) weak and (b) strong force regimes (see Fig. 1). In both, the tension propagation mechanism is a key word to interpret the dynamics. The tension gets transmitted along the polymeric chain from the forced monomer. On the other hand, the dominant factors are different. The fluctuations dominate in the weak force regime compared with the drift, while the drift has a major contribution in the strong force regime. From eq. (1), we can estimate the drift or fluctuation in weak or strong force, respectively, but we have to stress out that it does not necessarily hold in strong force as will be mentioned below. Except ideal chains, the memory kernel or spring constant depends on the force magnitude due to the self-avoiding (SA) effects, which eventually deviates normalized ratio eq.(1).

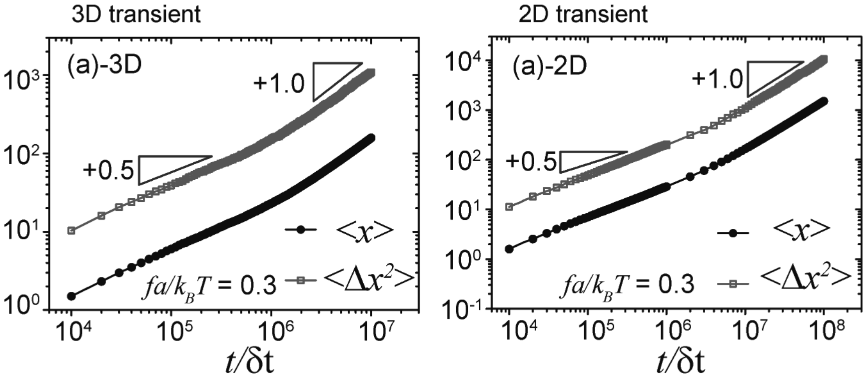

Fig. 2 MD simulation results in 3D (left) and 2D (right). Time evolutions of average drift and variance in the displacement are plotted. All axes are double logarithmic scale.

(ii) To numerically verify it, we carried out molecular dynamics simulation of the self-avoiding chain (free-drraining). We calculated the average drift and the variance in the displacement (Fig.2). There are two regimes in the time evolutions; first, anomalous dynamics is observed, and later the center of mass mode shows up.

We then plotted the normalized ratio, i.e., left hand side of eq (1) (see Fig. 3). The 3D results are in a good agreement with the prediction by eq. (1), but the deviations are clearly seen in 2D.

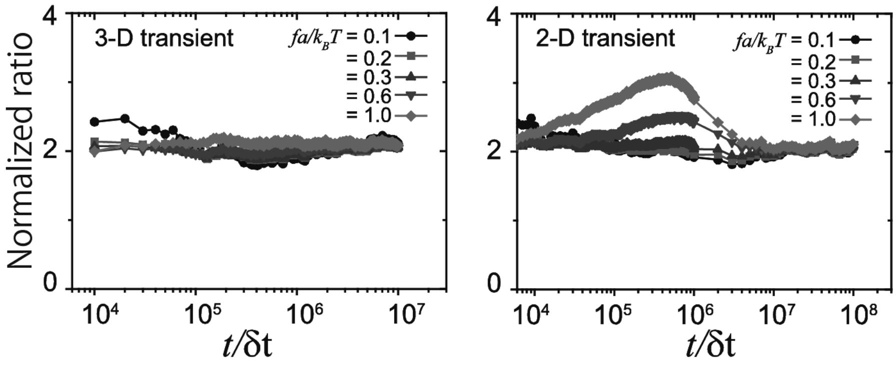

Fig. 3. Normalized Ratio.

(iii) To construct the microscopic model to analyze the results of (ii), we first reviewed the Rouse chain known as the simple polymer model idealized by not considering the self-avoidance (SA) and hydrodynamic interactions (HIs). The Rouse model was reported to be described by the GLE. We there discussed the connection between real and mode spaces for the response and correlation.

Next we again reviewed the near equilibrium fluctuation with the SA and/or HIs, which are generally non-linear effects. The dynamics is described in the mode space by using friction and spring constants pre-averaged over the equilibrium distribution. From this, we investigated the non-linear force dependence, and the relation of the response with the velocity autocorrelation was discussed.

(iv) Mono-block picture was found to be available to describe the fluctuation in the transient process as well as around the steady stretching state used in the previous work. Indeed, the average dynamics is equivalent to that obtained by the scaling theory (two state approximation). Developing this approach, we investigated the normalized rate and then we found eq. (1) is not satisfied in the self-avoiding chain, since the restoring force is essentially changed from the initial equilibrium to stretching. The theoretical predictions qualitatively meet with MD results (Fig. 3).

Rate in template-directed polymer synthesis

Genomic DNAs are synthesized by DNA polymerase through driven process. Synthesizing time and accuracy are expected to be important in this process. However, how to simultaneously weigh those has been an issue. In this study, we proposed the template-directed polymer synthesis rate to weigh the time and accuracy through the same unit. The rates in several models were discussed.

2. Original papers

(1) Takuya Saito,
“Rate in template-directed polymer synthesis”
Phys. Rev. E 89, 062716(2014).

3. Presentation at academic conferences

(1) 齋藤拓也, 坂上貴洋
“伸張した高分子鎖の揺らぎと応答”
日本物理学会 2014 秋季大会, 中部大学 春日井キャンパス, Sep 8, 2014

(2) 齋藤拓也、坂上貴洋
“引き伸ばされていく過渡的過程の高分子の揺らぎと移動距離”
日本物理学会第 70 回年次大会, 早稲田大学 早稲田キャンパス, Mar 22, 2015

4. Others

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“引き伸ばされていく過渡的過程の高分子の揺らぎ”
The 12th symposium of Fukui Institute for Fundamental Chemistry, Kyoto, Jan. 23, 2015.

John Jairo Molina

FIFC Fellow

1. Summary of the research of the year

Dynamics of passive and active particles

Colloidal dispersions make up most of the materials we use in our everyday life, such as foams, emulsions, or gels. Specific examples include blood, pigmented ink, milk, and gelatin. Understanding the properties of such dispersions is crucial to control many industrial and engineering processes. Additionally, recent experiments have shown the possibility of creating active colloidal particles, which are able to extract local energy from their environment to perform work. Unfortunately, accurately simulating such systems requires that one be able to solve for the fluid and particle motions over large scales with a very fine resolution (for example, to accurately resolve turbulent motion).

Here, we have contributed to the development of a direct numerical simulation method that can be used to study dense dispersions of complex particles (both passive and active) with fully resolved hydrodynamics, called the Smooth Profile Method (SPM). We have studied the collective behavior of swimming particles under confinement, as well as the dynamics of sedimenting colloidal particles at high Reynolds number, and the frequency dependent polarizability of charged particles in oscillating electric fields. In addition, we have also worked to extend the SPM to handle rheological measurements of complex particle dispersions (i.e. non-spherical particles).

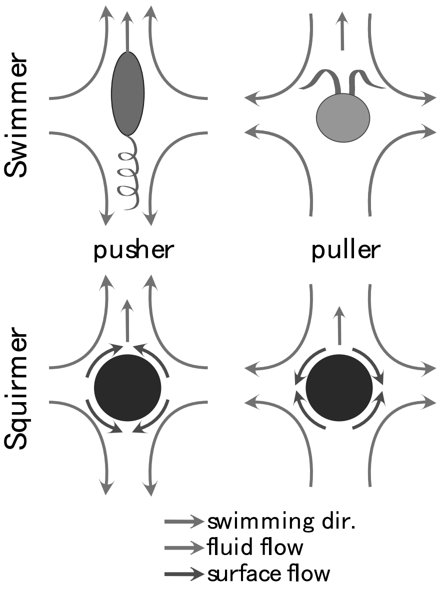


Figure 1. Schematic representation of the squirmer model.

In our study of active or swimming particles, we have adopted the simple “squirmer” model, in which the swimmers are modeled as spherical particles with modified stick boundary conditions at their surface. By changing the velocity profile of the fluid at the particle/fluid interface, one can easily represent the two basic types of swimming motion: “pusher” and “pullers” (see Figure 1). As a first approximation, the fluid velocity at the surface is given by

$$\boldsymbol{u} = \frac{3}{2}U_0\left(\sin\theta + \frac{\alpha}{2}\sin 2\theta\right)\hat{\boldsymbol{\theta}}$$

where U_0 is the swimming velocity of an isolated particle, θ is the polar angle, and $\hat{\theta}$ the tangential unit vector. If $\alpha > 0 (\alpha < 0)$ we the flow profile generated by the particle is that of a puller (pusher). For the special case when $\alpha = 0$ we have a neutral or potential squirmer. The value of α is crucial when determining the hydrodynamic interactions between pairs of particles, as they will be pushed/pulled in different directions, depending on their relative position an orientation. In addition, the strength of the hydrodynamic interactions also depends strongly on α: if α is zero, the flow field disturbance is more localized, decaying as $1/r^3$ (where r is the distance between the swimmers), otherwise it will decay as $1/r^2$. Such differences have important consequences when one considers the collective behavior of swimming dispersions. In particular, we have considered pseudo-2D geometries that mimic experiments on active Janus particles, in which particles are placed between two flat parallel walls, and constrained to move in two dimensions. We have found that only neutral particles ($\alpha = 0$) are able to exhibit a flocking state (all particles moving in the same direction). Furthermore, we have seen that this collective behavior can be attributed to the short-range hydrodynamic interactions, since introducing an additional short-range repulsive force F between the particles makes the flocking state unstable. Figure 2 shows the order parameter e as a function of time (e is one for an ordered system, zero for completely disordered system), obtained from simulations for different values of α. The instability of the flocking state for $\alpha \neq 0$ is also due to the hydrodynamic interactions, as the long-range disturbances generated by the swimming motion give rise to fluctuations in the fluid, which themselves cause a diffusive type of motion for the particles (even in the absence of any thermal fluctuations). These fluctuation are enough to hinder any global flocking, particularly for $|\alpha| > 1$, where strong vortices are generated at the front/back of the pushers/pullers. To measure the strength of these fluctuations, we have computed an effective hydrodynamic diffusion coefficient $\tilde{D}_T$ for the particles (which considers only the fluctuating motion around the inherent swimming), as well as the enstrophy in the fluid (which is directly related to the energy dissipation). As seen in Figure 3, both quantities present the same overall behavior: A minimum for $\alpha = 0$, and a rapid increase as $|\alpha|$ increases. In addition, we see a clear asymmetry between pushers and

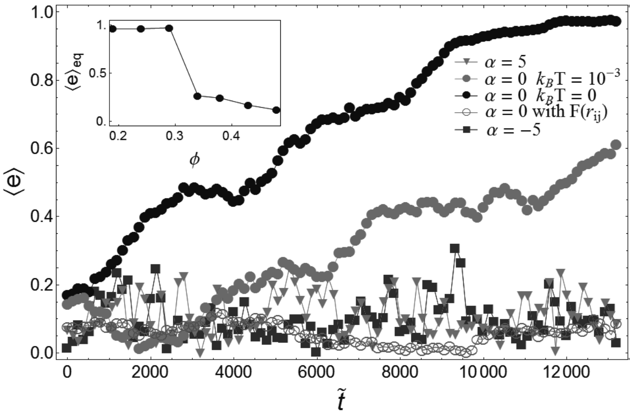


Figure 3. Time evolution of the order parameter for different types of swimmers.

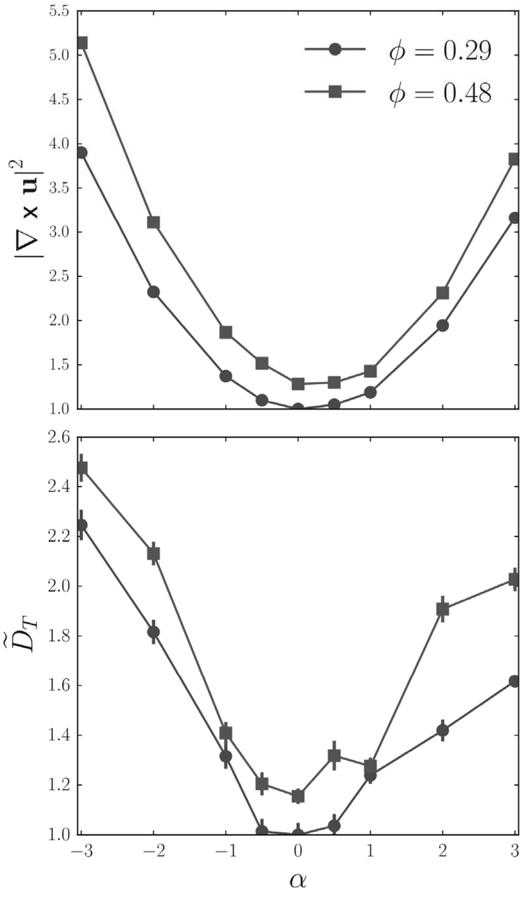


Figure 2. (top) Enstrophy and (bottom) effective diffusion coefficient as a function of swimming mode for two concentrations. All quantities are scaled with respect to the corresponding value at $\alpha = 0$.

pullers, with the latter showing stronger diffusion/energy dissipation. Understanding this asymmetry between pushers and pullers, and how it affects the physical properties of the dispersion is still a work in progress. Finally, in order to overcome the effect of these fluctuations on the stability of the flocking state, we are now considering additional alignment mechanisms which can make such flocking stable, even for $\alpha \neq 0$; for example, by considering patchy or dipolar interactions between the particles. In this way, we will also be able to make a more direct comparison with experiments on Janus particles.

2. Original papers

(1) Tanh-Nghi Nguyen, Magali Duvail, Arnaud Villard, John J. Molina, Philippe Guilbaud, and Jean-François Dufrêche
"Multi-scale modeling of uranyl chloride solutions"
J. Chem. Phys. 142(2), 024501 (2014).

(2) Adnan Hamid, John J. Molina, and Ryoichi Yamamoto
"Direct numerical simulations of sedimenting spherical particles at non-zero Reynolds number"
RSC Advances, 4(96), 53681 – 53693 (2014)

(3) Adnan Hamid, John J. Molina, and Ryoichi Yamamoto
"Simulation studies of microstructure of colloids in sedimentation"
Mol. Sim., Proceedings of the 3d International Conference on Molecular Simulation,
DOI:10.1080/00268976.2015.1059510 (2015)

(4) Chunyu Shih, John J. Molina, and Ryoichi Yamamoto
"Dynamic polarization of a charged colloid in an oscillating electric field"
Mol. Phys., DOI:10.1080/00268976.2015.1059510 (2015)

3. Presentation at academic conferences

(1) John J. Molina, Jean-Baptiste Delfau, Masaki Sano, and Ryoichi Yamamoto
"Emergence of Collective Dynamics in Active Particle Suspensions" [poster]
Physics of Structural and Dynamical Hierarchy in Soft Matter, Tokyo, March 16-18, 2015

4. Others

1) John J. Molina
"Dynamics of Swimming Particles: A DNS approach"
YITP Seminar (Hayakawa Lab), Kyoto, June 25, 2014

2) John J. Molina
"Computational Modeling of Active Matter: Collective Dynamics in Swimming

Suspensions"
ISSP Seminar (Noguchi Lab), Tokyo, November 21, 2014

3) John J. Molina, Jean-Baptiste Delfau, Masaki Sano, and Ryoichi Yamamoto
"Emergence of Collective Dynamics in Active Particle Suspensions" [poster]
Kyoto Winter School for Statistical Mechanics, Kyoto
February 4-17, 2015
4) John J. Molina, Norihiro Oyama, Ryoichi Yamamoto
"Computational Modeling of Active Matter"
Curie Institute Seminar (J.-F. Joanny Lab), Paris, February 26, 2015

Jing-Dong Guo

Research Fellow

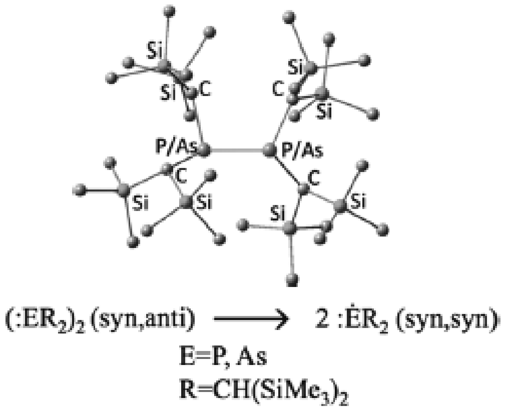
1. Summary of the research of the year

Dispersion Force Effects on the Dissociation of “Jack-in-the-Box” Diphosphanes and Diarsanes

The earlier EPR experiments showed that the reduction of the sterically crowded dialkyl or diamido phosphorus or arsenic halides $ClER_2$ (E = P or As; R = $-CH(SiMe_3)_2$ or $-N(SiMe_3)_2$) yielded solutions containing the persistent radicals $:\dot{E}\{CH(SiMe_3)_2\}_2$ or $:\dot{E}\{N(SiMe_3)_2\}_2$. The V-shaped monomeric structures of the alkyl substituted radicals $:\dot{E}\{CH(SiMe_3)_2\}_2$ (E = P or As) were further confirmed by gas electron diffraction (GED). However, in the solid, crystalline state they were shown to be dimerized with relatively long P−P (2.3103(7) Å) and As−As (2.5384(16) Å) bonds. The attractive dispersion forces between the hydrocarbon-substituted sterically bulky dialkyl or diamido groups may play important role for the dimerization under ambient conditions..

With hybrid density functional theory (DFT) at the B3PW91 and B3PW91-D3 levels, we explored the attractive dispersion forces on the present P and As compounds. Here we only present the calculated results for alkyl substituted compounds shown in Scheme 1.

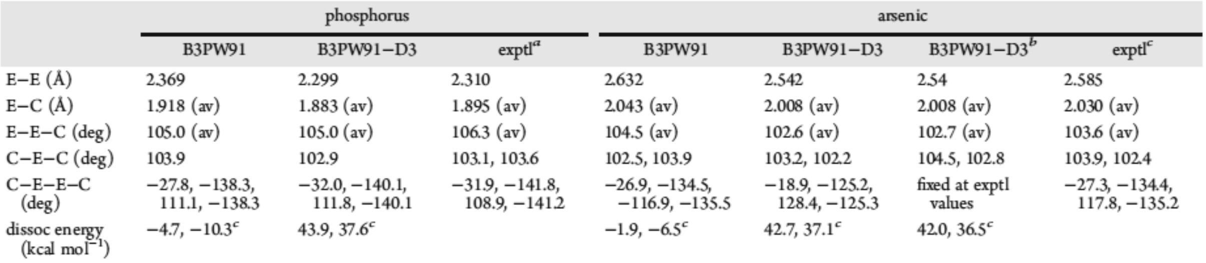
Scheme 1. The Dissociation of the $[:E\{CH(SiMe_3)_2\}_2]_2$ (E = P or As) Dimers with syn,anti Arrangement of $-CH(SiMe_3)_2$ Substituents to Two $:\dot{E}\{CH(SiMe_3)_2\}_2$ in the syn,syn Conformation.



§1. Comparison in geometry between theoretical and experimental results.

It can be seen in Table 1 that there is close agreement between the calculated and experimental distances in the case of the tetraalkyls. But the calculated CAsAsC torsion angles show deviations in the range 8.4−11.5° from the experimentally measured values when the D3 dispersion term is included. To estimate the effect of the angular deviations in the calculated diarsane angles on the dispersion energy, an additional calculation was carried out in which the real system model was fully optimized but with the dihedral angles fixed at the experimentally measured positions. The very small dissociation energy difference, 37.1 vs 36.5 kcal mol^{-1}, indicates little effect on the dispersion energy upon changing the torsion angle.

Table 1. Calculated Structural Parameters and Dissociation Energies of $[E\{CH(SiMe_3)_2\}_2]_2$ (E = P, As) at the B3PW91 and B3PW91−D3 Levels of Optimization



	phosphorus			arsenic			
	B3PW91	B3PW91−D3	exptl[a]	B3PW91	B3PW91−D3	B3PW91−D3[b]	exptl[c]
E−E (Å)	2.369	2.299	2.310	2.632	2.542	2.54	2.585
E−C (Å)	1.918 (av)	1.883 (av)	1.895 (av)	2.043 (av)	2.008 (av)	2.008 (av)	2.030 (av)
E−E−C (deg)	105.0 (av)	105.0 (av)	106.3 (av)	104.5 (av)	102.6 (av)	102.7 (av)	103.6 (av)
C−E−C (deg)	103.9	102.9	103.1, 103.6	102.5, 103.9	103.2, 102.2	104.5, 102.8	103.9, 102.4
C−E−E−C (deg)	−27.8, −138.3, 111.1, −138.3	−32.0, −140.1, 111.8, −140.1	−31.9, −141.8, 108.9, −141.2	−26.9, −134.5, −116.9, −135.5	−18.9, −125.2, 128.4, −125.3	fixed at exptl values	−27.3, −134.4, 117.8, −135.2
dissoc energy (kcal mol^{-1})	−4.7, −10.3[c]	43.9, 37.6[c]		−1.9, −6.5[c]	42.7, 37.1[c]	42.0, 36.5[c]	

[a]Experimental. [b]With fixed CAsAsC torsion angles. [c]With BSSE correction.

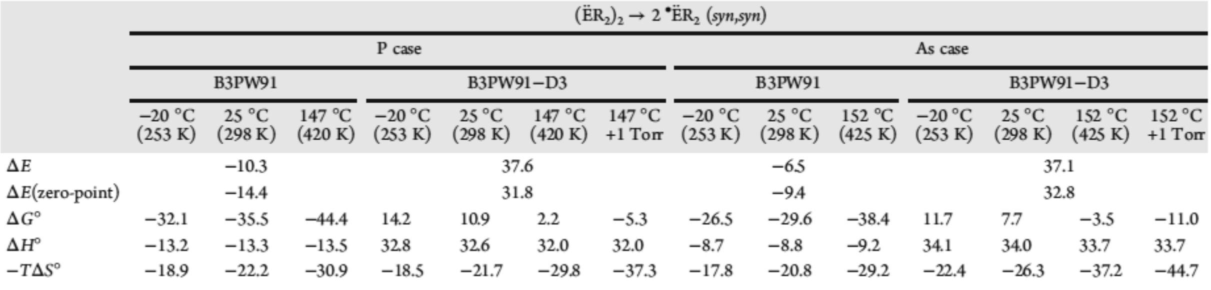
§2. The attractive dispersion forces play important role in the P and As alkyl dimers.

As shown in Table 1, the calculated dissociation energies without the inclusion of dispersion force effects are negative: −10.3 (P) and −6.5 (As) kcal mol^{-1}. In contrast, the incorporation of dispersion force effects changes in these numbers to +37.6 (P) and +37.1 (As) kcal mol^{-1}. In other words, without the dispersion forces the monomeric radical form is preferred over the dimeric structure, presumably because of steric repulsion between the substituents and the accumulated strain energies. However, the attractive dispersion force between the ligands overcomes these dissociation tendencies to favor the diphosphane and diarsane structures.

§3. Dimeric structure is favored under ambient conditions, while dissociation is favored at high temperature.

The data in Table 2 show that the inclusion of the dispersion correction (−D3) has a very large effect on the ΔH and ΔG energies, and a smaller but significant effect on the ΔS values. Without the dispersion optimization, dissociation is strongly favored at all temperatures, whereas with the dispersion correction the dimeric structure is favored at −20 and 25 °C, while dissociation is favored at high temperatures near 150 °C. For phosphorus, the ΔG(−D3) value is slightly positive, having a value of 2.2 kcal mol^{-1} at 147 °C (the temperature of the GED studies) and at 1 atm pressure. Upon lowering of the pressure to 1 Torr, this becomes −5.3 kcal mol^{-1}, showing that dissociation to radicals is favored, consistent with the observed structure in the gas phase. At lower temperatures (i.e., −20 and 25 °C) the associated structure is favored (ΔG = 14.2 and 10.9 kcal mol^{-1}), consistent with the dimeric structure observed in the crystalline phase. For the arsenic derivative, the dissociated structure is energetically favored at 152 °C (GED studies temperature) at both 760 and 1 Torr pressure, consistent with the experimental data, whereas at 25 and −20 °C, the dimeric structure is favored, consistent with the crystal structure observed for $:As\{CH(SiMe_3)_2\}_2]_2$.

Table 2. Thermodynamic Data (kcal/mol) for the Dissociation of $[\ddot{E}\{CH(SiMe_3)_2\}_2]_2$ into Two $:\dot{E}\{CH(SiMe_3)_2\}_2$ Radicals.



	$(\ddot{E}R_2)_2 \rightarrow 2\,{}^{\bullet}\ddot{E}R_2$ (*syn,syn*)													
	P case							As case						
	B3PW91			B3PW91−D3				B3PW91			B3PW91−D3			
	−20 °C (253 K)	25 °C (298 K)	147 °C (420 K)	−20 °C (253 K)	25 °C (298 K)	147 °C (420 K)	147 °C +1 Torr	−20 °C (253 K)	25 °C (298 K)	152 °C (425 K)	−20 °C (253 K)	25 °C (298 K)	152 °C (425 K)	152 °C +1 Torr
Δ*E*		−10.3			37.6				−6.5			37.1		
Δ*E*(zero-point)		−14.4			31.8				−9.4			32.8		
Δ*G*°	−32.1	−35.5	−44.4	14.2	10.9	2.2	−5.3	−26.5	−29.6	−38.4	11.7	7.7	−3.5	−11.0
Δ*H*°	−13.2	−13.3	−13.5	32.8	32.6	32.0	32.0	−8.7	−8.8	−9.2	34.1	34.0	33.7	33.7
−*T*Δ*S*°	−18.9	−22.2	−30.9	−18.5	−21.7	−29.8	−37.3	−17.8	−20.8	−29.2	−22.4	−26.3	−37.2	−44.7

[a] All energies with BSSE correction.

In conclusion, the DFT calculations using different methods on the dipnictane tetraalkyl species with inclusion of attractive dispersion forces show that the dimeric structures are favored over the radical monomers under ambient conditions. The attractive forces exceed those that stabilize the radicals through relaxation and conformational changes. The results underline the general necessity of incorporating the dispersion force effects in calculations on sterically crowded molecules. Calculations for the monomer−dimer equilibrium in the tetraalkyl species indicate that they are governed mainly by dispersion force attraction and entropic factors.

2. Original papers:

Jing-Dong Guo, Shigeru Nagase, and Philip P. Power,
"Dispersion Force Effects on the Dissociation of “Jack-in-the-Box” Diphosphanes and Diarsanes"
Organometallics 34, 2028-2033 (2015).

Wei-Wei Wang

SPR Fellow

1. Summary of the research of the year

Multistep Reconstructions of Half-saturated Zigzag Carbon Nanotubes

Since the first discovery in 1991, carbon nanotubes (CNTs) have drawn much attention as promising functionalized materials in nanoelectronics and spintronics. Similar to the 1D graphene nanoribbon (GNR), the edge states, and in particular of two primary edge structures (armchair and zigzag edges) of CNTs are considered to play a prominent role on the electronic, magnetic and mechanical properties. In the field of CNT chemistry, hitherto studies on the armchair edge, *i.e.* the bottom-up cycloaddition growth mechanisms of CNTs, have been well-developed in both theory and experiments. However, investigations on the case of zigzag edge of CNTs are still limited. In the present work, a novel multistep reconstruction mechanism of the open-ended zigzag CNTs were introduced by using DFT calculations. We aim to uncover the kinetic process of edge deformation and to elucidate the impact of deformed edge on the stability and electronic properties of CNTs.

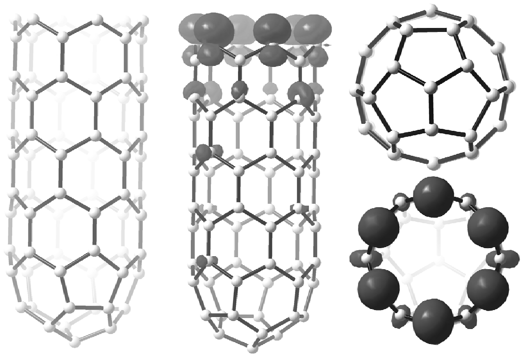


Figure 1. Structure and spin density distribution of half-capped (6,0)CNT

A finite C_{3v} symmetric (6,0)CNT was selected as the CNT model. As shown in Figure 1, one side of the tube is terminated by the carbonic cap and the other side is open-ended. It should be mentioned that (6,0)CNT can be capped by only one type of carbonic hemisphere in theory and the hydrogen-terminated model is not used to avoid the impact of hydrogen atoms. All computations were performed with the HSEH1PBE density functional in conjunction with the basis sets of 6-311G(d) by using the Gaussian 09 program.

First, we optimized the pristine (6,0) CNT under different electronic spin states and a heptet state was proved as the ground state. The calculated spin distribution (Figure 1) suggests that the high-spin state of this CNT structure results from the bared carbon atoms at the open edge, which contribute six unpaired σ electrons. The kinetic process of the first reconstruction step is depicted in Figure 2. By overcoming a concerted 10-membered cyclic transition state (TS1), the fused two hexagons at edge transform into a pentagon-heptagon (5-7) pair. This process is similar to the reconstruction of GNR at edge and an edge cut of the classical Stone-Wales transformation (SWT) of fullerenes. Energetically, this process is exothermic with the reaction energy ($E_r = E_{product} - E_{reactant}$) of -31.4 kcal/mol, indicating a self-stabilization character of the reconstruction from the zigzag edge to the deformed 5-7 edge. Kinetically, the reaction barrier $E^{\ddagger}$ is 41.4 kcal/mol which is significantly lower than that of the SWT on the sidewall network of CNTs. Furthermore, the total spin of CNT was found to reduce by one after the rearrangement and the electronic ground state was quintet for the deformed product P1. As elucidated in Figure 2, after the unsaturated zigzag fragment in the reactant transforms to the 5-7 edge, a triple C-C bond was formed in the heptagonal ring, which eliminate two pristine unpaired electrons and lead to the decrease of the total spin by one.

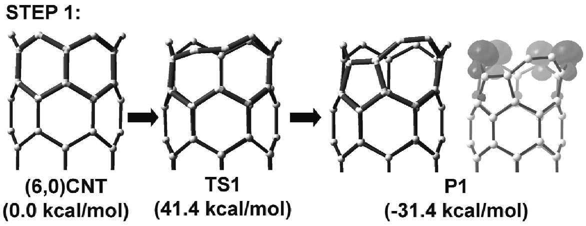
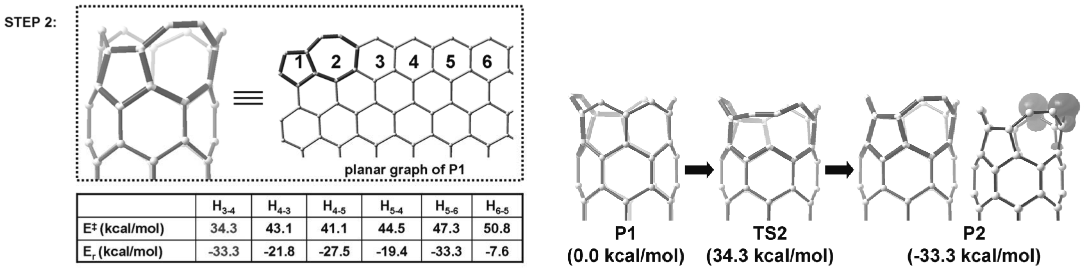


Figure 2. The first step reconstruction of half-capped (6,0)CNT

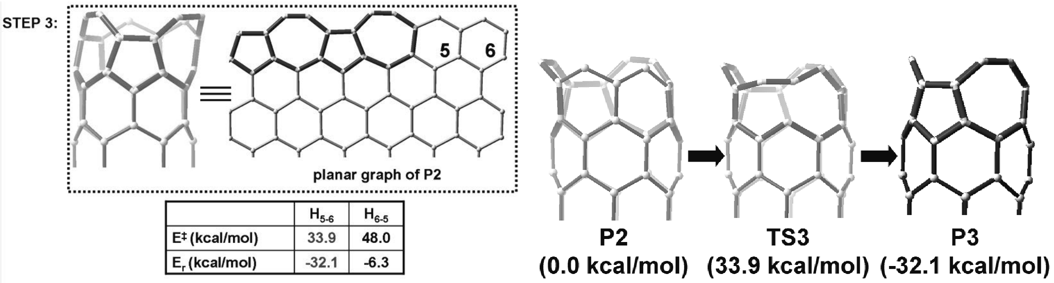
Subsequently, since the symmetry of CNT is broken after the first step, the regioselectivity of second step rearrangement on P1 was taken into account. As shown in Figure 3, all the six possible SWT reactions were calculated and the reconstruction takes place on the site that next to the heptagon was proved to exhibit the lowest $E^{\ddagger}$ (34.3 kcal/mol) as well as the most negative E_r (-33.3 kcal/mol), implying that the multistep reconstruction of zigzag edge is a sequential rather than a random process. Moreover, it should be mentioned that the second step is spontaneous because it is thermodynamically exothermic and the barrier is 7.1 kcal/mol lower that that of the first step kinetically. The spin density diagram of P2 is exhibited in Figure 3. In accord with the initial step, the total spin after reconstruction is reduced by one and the ground state of P2 is triplet.



	$H_{3\text{-}4}$	$H_{4\text{-}3}$	$H_{4\text{-}5}$	$H_{5\text{-}4}$	$H_{5\text{-}6}$	$H_{6\text{-}5}$
$E^{\ddagger}$ (kcal/mol)	34.3	43.1	41.1	44.5	47.3	50.8
E_r (kcal/mol)	-33.3	-21.8	-27.5	-19.4	-33.3	-7.6

Figure 3. The regioselective second step reconstruction of half-capped (6,0)CNT

In the final step, two hexagons are surviving at the open edge of P2 and therefore only two deformed structures are available after reaction: the alternating 5-7 edge or the edge with fused 5-5 and 7-7 fragments. Calculations demonstrate that formation of the former one with the $E^{\ddagger}$ of 33.9 kcal/mol and the E_r of -32.1 kcal/mol is more favored both thermodynamically and kinetically, whereas the latter one is unfavorable in energy because of the much higher molecule strain caused by the pentagon-pentagon and heptagon-heptagon fragments. From the viewpoint of molecular spintronics, interestingly, we found the ground state of final product P3 is closed-shell singlet with a large singlet-triplet splitting energy of 10.7 kcal/mol. The total spin of half-saturated (6,0)CNT dramatically transforms from a high-spin state (heptet) to an unpolarized singlet after three steps of reconstructions, indicating the structural deformation of zigzag edge not only enhances the stability but also significantly modifies the magnetic property of materials.



	$H_{5\text{-}6}$	$H_{6\text{-}5}$
$E^‡$ (kcal/mol)	33.9	48.0
E_r (kcal/mol)	-32.1	-6.3

Figure 4. The regioselective third step reconstruction of half-capped (6,0)CNT

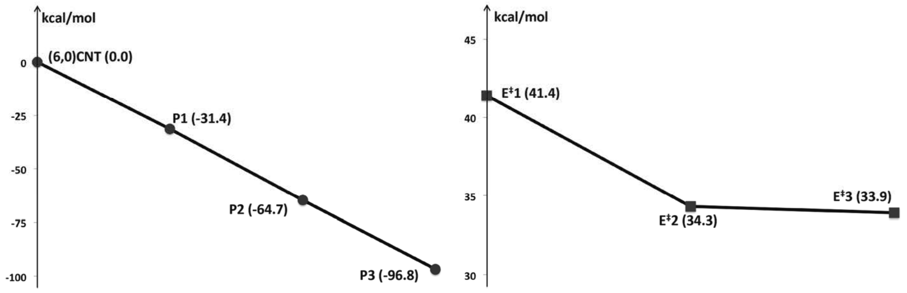


Figure 5. Relative energies of (6,0)CNT and reconstructed products (left) and Energy barriers of multistep reconstructions (right)

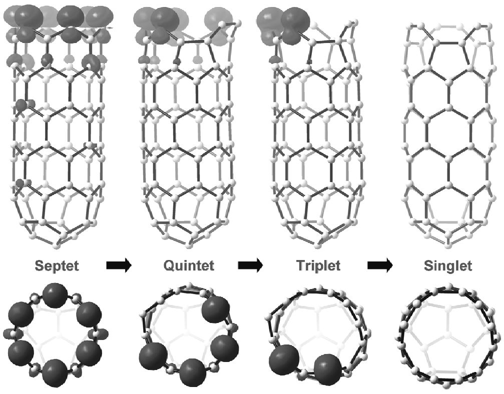


Figure 6. Spin density distributions of (6,0)CNT and reconstructed products

Overall, the multistep reconstructions of the open edge of zigzag (6,0) CNT have been explored by quantum chemistry calculations. Thermodynamically, the deformation from unsaturated zigzag edge to deformed 5-7 edge was demonstrated as a stabilization process and the stability enhanced linearly with the increase of 5-7 pairs. Kinetically, Because of the reactive dangling bonds at edge, the barriers of rearrangements (<50.0 kcal/mol) are much lower than those of reactions on the sidewall network of CNTs or fullerenes (100.0 ~ 200.0 kcal/mol). As drawn in Figure 5, the first step exhibits the largest energy barrier, suggesting that the initial transformation from two hexagons is the rate-determining step and the following steps can take place spontaneously like an unzipping process. Moreover, the regioselectivity of the multistep reactions were studied. We proposed that the reconstructions prefer occur in a sequence because successive transformation next to the already existing 5-7 pair is much more feasible in energy. Furthermore, our calculations indicate that the reconstruction is a special process in which the total spin decreased gradually in each step, revealing that the half-saturated zigzag CNT can be utilized to design novel intramolecular spin-transfer materials.

2. **Original papers**

1. T. Morosaki, T. Suzuki, W. W. Wang, S. Nagase, and T. Fujii, "Syntheses, Structures, and Reactivities of Two Chalcogen-Stabilized Carbones" *Angew. Chem. Int. Ed.* **2014**, 53, 9569.
2. Q. Zhou, H. Li, Y. Lian, M. Suzuki, L. Bao, W. Cai, W. W. Wang, S. Nagase, X. Lu and T. Akasaka, "Regioselective synthesis and molecular structure of the first derivative of praseodymium-containing metallofullerenes" *Chem. Commun.*, **2014**, 50, 9876.
3. Y. Maeda, M. Kimura, C. Ueda, M. Yamada, T. Kikuchi, M. Suzuki, W. W. Wang, N. Mizorogi, N. Karousis, N. Tagmatarchis, T. Hasegawa, M. M. Olmstead, A. L. Balch, S. Nagase and T. Akasaka "Isolation and characterization of [5,6]-pyrrolidino-$Sc_3N@I_h$-C_{80} diastereomers" *Chem. Commun.*, **2014**, 50, 12552.
4. H. Zheng, X. Zhao, L. He, W. W. Wang, and S. Nagase "Quantum Chemical Determination of Novel C82 Monometallofullerenes Involving a Heterogeneous Group" *Inorg. Chem.*, **2014**, 53, 12911.

Miho Hatanaka

FIFC Fellow

1. Summary of the research of the year

1.1. Theoretical study of the thermo-sensitive luminescence of Ln(III) compounds

Lanthanide (Ln) compounds have been widely used for luminescence materials, such as *in vivo* probes, lasers, optical fibers etc. Some of the advantages of Ln(III) compounds are that the shapes of the emission spectra are very sharp (like isolated cations), the emission wavelengths are independent of the surrounding environment, and only the emission intensities depend heavily on the surroundings. These characters can be explained by the inner-core 4f electrons. Ln(III) have distinct electronic configurations, such as $1s^2 2s^2 \ldots 4f^N 5s^2 5p^6$, in which open-shell 4f electrons are shielded by closed-shell 5s and 5p electrons from outside. Therefore, the properties caused by 4f electrons, such as the excitation energies of $4f^N$ excited states, and the shapes of potential energy surfaces (PESs) of $4f^N$ states, are not affected by the change of surrounding environment.

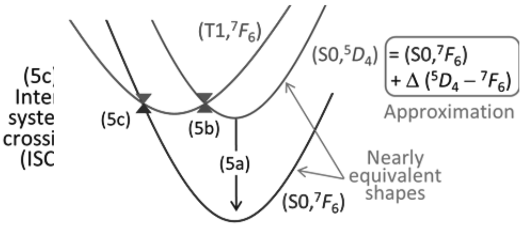


Figure 2. Energy shift approximation

Figure 1. Possible mechanism of Tb(III) luminescence and quenching

One of the interesting applications of Ln luminescence is thermo-sensitive luminescent probes that use Eu(III) and Tb(III). Eu(III) and Tb(III) show red and green emissions caused by the f-f transitions ($^5D_J \rightarrow {}^7F_{J'}$), respectively. With appropriate ligands, the intensity of the f-f emission decreases (or sometimes increases) as temperature increases, enabling these complexes to be used as temperature sensors. The mechanism of Ln(III) luminescence has been explained by five steps shown in Figure 1. The process starts from (1) ligand-centered excitation from the singlet ground state (S0) to a singlet excited states (Sn), followed by (2) intersystem crossing (ISC) from the excited state Sn to the lowest triplet state (T1), (3) excitation energy transfer (EET) from the ligand T1 to Ln-centered $4f^N$ excited state(s), (4) internal conversion (IC) from the $^5D_{J''}$ state to the lowest quintet state ^5D_J, and (5a) f-f emission from ^5D_J to $^5F_{J'}$. The quenching process also can be explained based on Figure 1. The lifetime of Ln-centered excited state (^5D_J) is rather long because the f-f transitions from ^5D_J to $^5F_{J'}$ are parity-forbidden as well as spin-forbidden transitions. Thus, the quenching process, such as (5b) the backward EET and (5c) the ISC on the ligand, can take place when the crossing pointes shown as (5b) and (5c) in Figure 1 are enough low. To control the quenching process, which directory affects the intensity of the f-f emission, we need to control the energy levels of the two crossing points.

How can we compute the energy levels and structures of these two crossing points as well as LM on the ligand-centered T1 and Ln-centered excited states? The *ab initio* calculations of such excited states in Ln compounds are highly demanding because relativistic effects, electron correlation need to be considered explicitly. Here, we change the view point. As mentioned above, the PESs of $4f^N$ excited states have almost the identical shapes to that of the $4f^N$ ground state, and the excitation energies are independent of the surrounding environment. Thus, the PESs of $4f^N$ excited states can be described by that of the $4f^N$ ground state corrected by an "energy shift" that is unique for each excited state. We call this approximation, the "energy shift method". (See Figure 2)

- Case study 1: Tb(III) complexes

As the first case study, we apply this approximation to tree Tb(III) complexes containing different ligands; hexafluoroacetylacetonato (hfa), acetylacetonate (acac), and nitrate ion (NO_3^-). According to the experimental studies by Hasegawa group, as the temperature increases, the green emission intensities of β-diketone ligand (hfa and acac) coordinated Tb(III) complexes decrease, whereas that of NO_3^- coordinated Tb(III) complex increase a little. To explain the reason for the different behaviors of the three complexes, the critical points on and between the PESs were determined for the three complexes, $Tb(X)_3(H_2O)_2$ (X = hfa, acac, and NO_3^-). The full geometry optimizations of LM and minimum seams of crossing (MSXs) were performed using the Global Reaction Route Mapping (GRRM) program with energies and energy derivatives of S0 and T1 states computed at the B3LYP-D3 level by the Gaussian09 program. As a result, the dependence of the thermo-sensitivity on the ligands can be understood by the different rate-determining steps for emission or quenching. For β-diketone coordinated Tb(III) complexes, the MSX for the ISC on the ligand (5c in Figure 1) is the highest point among the emission and quenching process. Thus, as the temperature increases, only the rate for the quenching increases, which results in the decrease of the emission intensity. For NO_3^- coordinated Tb(III) complex, the highest point is the MSX for the EET (3 and 5b in Figure 1). Therefore, as the temperature increases, the rate for the forward EET increases, which results in the slight increase of the emission intensity.

- Case study 2: Tb(III)/Eu(III) containing polymers

Next, we focus on another temperature sensor, called the Chameleon, whose emission color changes from green, yellow, to red as the temperature increases. The Chameleon sensor is a polymer in which $Tb(hfa)_3$ and $Eu(hfa)_3$ are connected by a phosphoryl linkage ligand (dpbp: 4,4'-bis(diphenylphosphoryl) biphenyl). According to the experimental study, (i) the intensity of red emission of the polymer including only Eu(III) was almost independent on the temperature. (ii) The green emission intensity of the Chameleon sensor was more sensitive to the temperature change than that including only Tb(III). These experimental results mean that the excitation energy on Tb(III) could transfer to Eu(III). In the conventional theoretical study based on the crystal field theory, only the direct EET between two Ln(III) has been considered. However, in this mechanism, the rate of the direct EET becomes quite slow with more than 10 Å distance between two Ln(III), which is shorter than the Tb-Eu distance in the Chameleon. Thus, we focused on the T1 state of the linkage ligand (dpbp) and considered that the EET from Tb(III) to Eu(III) takes place through the T1 state of the linkage ligand. To examine this idea, we searched the MEXs where the EET from Tb-centered excited state to the ligand T1 and from the ligand T1 to Eu-centered excited state by using the energy shift approximation with the DFT-D3 method. Figure 3 shows the energy levels of the critical points on and between PESs in the model molecule (Tb(hfa)$_3$-dpbp-Eu(hfa)$_3$). The critical points (LM and MSXs) relating to T1 on dpbp are lower than the MSXs on the hfa. Thus, we can say that the T1 state of the linkage ligand mediates the EET from Tb(III) to Eu(III). In other words, we can control the rate of the EET between two Ln(III) by changing the linkage ligand with the different T1 energy levels. To explore the temperature sensors whose thermo-sensitivity is different from the original Chameleon, we examined three compounds including different phosphoryl linkage ligand (dpb, dppcz, and dpbt). The MSXs between ligand T1 and Tb- (or Eu-) centered excited states as well as the LM on ligand T1 state is the highest for dpb, followed by dppcz, dpbp (in the original Chameleon), and dpbt. This result is consistent with the experimental thermo-luminescence measured by Hasegawa group. As shown above, the newly proposed energy shift method can be a reasonable approximation to explore the PESs and to explain the mechanism of emission, quenching, and EET qualitatively.

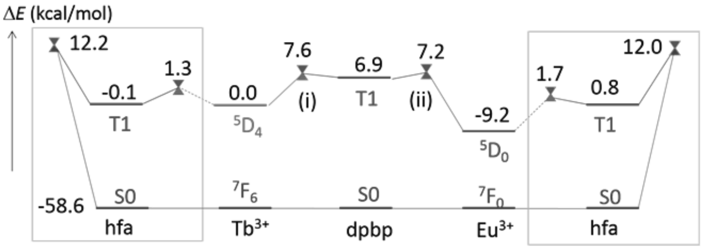


Figure 3. Energy levels of the LM and MSXs in the Chameleon (Energies in orange are calculated for Ln(tfa)$_3$(H$_2$O)$_2$)

1.2. Reason of the low quantum yield (QY) of Eu(III) helical ligand complexes and computational molecular design for higher QY

One of the recent topics for the luminescence materials is the computational molecular design which shows high quantum yield (QY). As mentioned above, the rate for the quenching process is determined by the energy levels of the crossing points. Thus, one way to design the luminescence material with higher QY is to make the energy levels of the ISC on the ligand (5c in Figure 1) less stable. In this study, we focus on Eu(III) complex with a hexadentate ligand (abbreviated to EuL shown in Figure 4). The QY depends on the state and temperature: in the

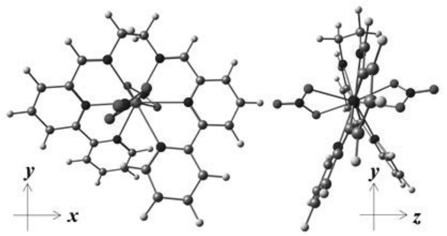


Figure 4. The top and side views of the geometry of EuL optimized on (S0, $^7F_0$)

solid state of EuL, the QYs of f-f emission are 64 % and 53 % at 77 K and room temperature, respectively, while that in the solution is only 12 % (at r.t.). To understand the different QYs in solid and solution, we searched the critical points on and between the PESs (shown in Figure 1). As the result in vacuum, three critical points; LMs on the ligand S0 and T1, and the MSX where the EET takes place (3 in Figure 1) had quite similar structures. Only the structure of the MSX where the ISC on the ligand takes place (5c in Figure 1) were quite different as shown in Figure 5. If we can find a ligand in which the structural motions from T1 to MSX for the ISC, such as twist the C_2 unit in diamine part and bent the C-H bond, are restrained, we could achieve a luminescence complex with a higher QY. Several hexadentate ligands including different substituents were examined. The substituents on the N atom shown in pink circle in Figure 5 affected the energy levels of T1 states changed. In contrast, the substituents on the C_2 unit in the diamine part affected the T1 level a little. Finally, we found that the hexadentate ligand with 1,2-dimethylcyclohexane on the diamine part had the low energy barrier for the forward EET and high barrier for the ISC process.

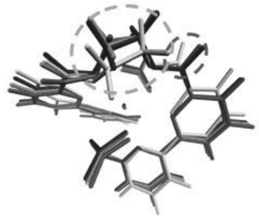


Figure 5. Structures of critical points. Blue, red, green, and yellow are LMs on S0, T1, MSXs for EET and ISC, respectively.

The reason of the higher QY in the solid state can also understood by the MSX for the ISC. In the solid state, the motion of the two biphenyl parts were limited by the $\pi-\pi$ interaction from the surrounding biphenyl groups. Those of C_2 unit and N-H bond were also limited by the ionic interactions from surrounding acetonitrile molecules. As discussed above, the QY can be understood and controlled by the energy level and structure of the MSX where the ISC on the ligand takes place. This study could be the first example in which a higher QY of Ln(III) compound is achieved by controlling the ISC process.

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(2) L.W. Chung, W.M.C. Sameera, R. Ramozzi, A.J. Page, M. Hatanaka, G.P. Petrova, T. Harris, X. Li, Z. Ke, F. Liu, H.-B. Li, L. Ding, K. Morokuma, “The ONIOM Method and its Applications” *Chem. Rev.* in press.

(3) M. Hatanaka, K. Morokuma, “How Can Fluctional Chiral Lanthanide(III) Complexes Achieve a High Stereoselectivity in Aqueous Mukaiyama-Aldol Reaction?” *ACS. Catal.* **5**, pp 3731-3739 (2015).

(4) M. Puripat, R. Ramozzi, M. Hatanaka, W. Parasuk, V. Parasuk, K. Morokuma, “The Biginelli reaction is a urea-catalyzed organocatalytic multicomponent reaction”, *J. Org. Chem*. in press.

3. Presentations at academic conferences

(1) ○M. Hatanaka, “Theoretical Study of Stereoselective C-C Bond Formations Catalyzed by Lanthanide Complexes”, 錯体化学会第 64 回討論会, Tokyo, Japan, September, 2014 (Invited Talk)

(2) ○畑中美穂, 諸熊奎治, “ランタノイドの発光を用いた感温センサーにおける励起エネルギー移動に関する理論的研究”,第 8 回分子科学討論会 2014, 広島, 2014 年 9 月. (Oral)

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4. Others (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—”, 人間科学類型特別授業, 兵庫県立北摂三田高等学校, 2015 年 1 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”,理系インスパイアー講演会, 兵庫県立北摂三田高等学校, 2014 年 10 月. (高校 2 年生(理系限定約 120 人)対象)

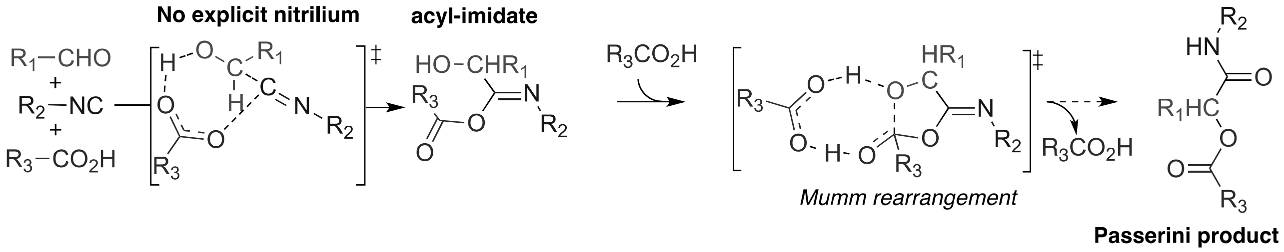
(3) 諸熊グループ(畑中美穂, Julong Jiang, Romain Ramozzi, WMC Sameera, 鈴木聡), “コンピュータで化学反応の世界を探る”, 京都大学アカデミックディ 2014, 2014 年 9 月（「研究者と立ち話」のコーナーでポスター発表)

Romain Ramozzi

Research Fellow (JSPS and FIFC), Fukui Kenichi Memorial Research Group 1

1. Summary of the research of the year

With atoms economy, easy practical set up, the multicomponent reactions have been particularly popular during the past twenty years.[1] Among them, the Passerini reaction is known to be the first isocyanide based multicomponent reaction. This reaction involves an aldehyde, an isocyanide and a carboxylic acid. Maeda et al. studied the mechanism in 2011 by using the AFIR method in conjunction with DFT calculations in gas phase.[2] They found that in *gas phase* the acyl-imidate formation step proceeds concertedly, as widely represented in organic textbooks and publications. Remarkably, the next step, an acyl transfer step called a Mumm rearrangement, was found to be catalyzed by a second acid molecule and makes the Passerini reaction an organocatalytic reaction (see Scheme 1).

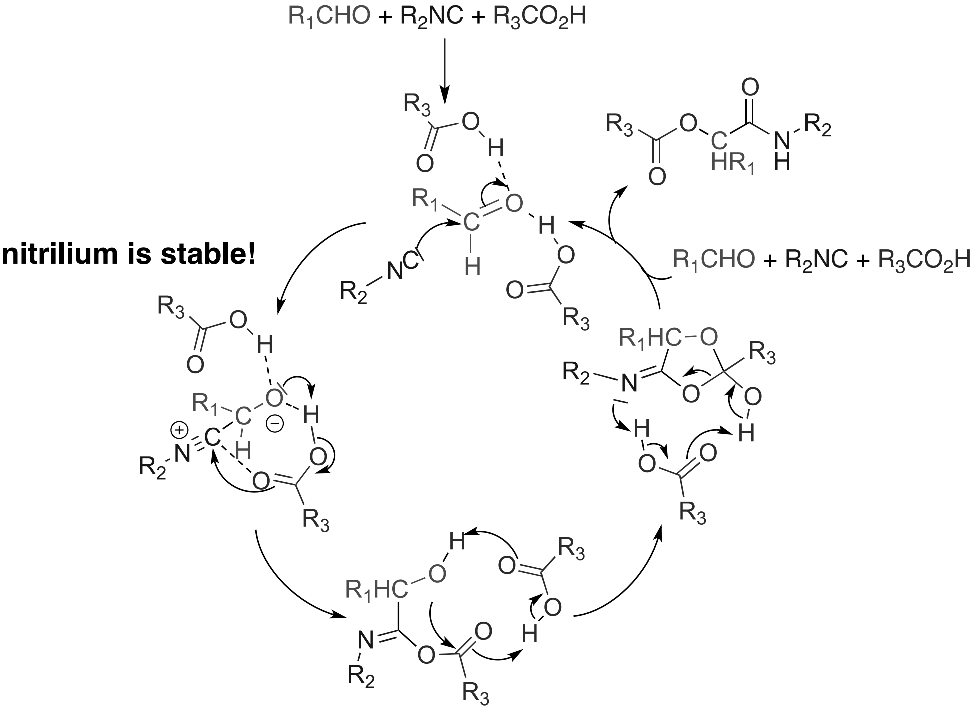


Scheme1: Proposed mechanism for the Passerini reaction by Maeda et al. in 2011.

In the present study, we decided to investigate the solvent effect of this reaction. Indeed, this reaction is known to react better in an aprotic apolar solvents, like the dichloromethane, contrary to the very close reaction the Ugi coupling, which is known to react better in a protic polar solvent like methanol.[3]

Interestingly, the new calculations performed at the mPW2PLYP/6-311++G(d,p) level predicted the stability of a nitrilium species during the acyl-transfert formation step. This method and result were confirmed with various functionals (M06 familly, B2PLYP-D3, …), basis sets (from 6-31G(d) to aug-cc-pVTZ) and the ab-initio level CCSD(T)//MP4(SDQ)/aug-cc-pVTZ was taken as a reference to confirm the choice of this method.

Moreover, the initial step, which is the addition of the isocyanide on the aldehyde was found to be activated, not by one (as previously observed), but by two carboxylic acid molecules despite the entropic contribution of the second carboxylic acid molecule. Therefore, a revised mechanism was proposed as shown in scheme 2 involving the organocatalyst from the beginning of the reaction, as well as the existence of the nitilium intermediate.



Scheme2: Revised mechanism for the Passerini reaction in 2015.

To understand the solvent effect, the PCM approach was found to be not good enough to reproduce the experimental results and various microsolvated model systems were then investigated. Surprisingly, the absence of hydrogen bonds was found to increase the reactivity of the aldehyde and isocyanide during the rate determining step (the nitrilium formation step) and thus explains the experimental observations. Moreover, the analysis of these results permits to understand the true solvent effect in the rate-determining step of the Passerini and Ugi couplings. While for the Ugi coupling the polarity of the solvent is crucial, it is the absence of proticity in the Passerini reaction that leads to better yields.

Bibliography:

[1] J. Zhu and H. Bienaymé, Multicomponent Reactions ; Wiley-VCH, **2005**

[2] S. Maeda, S. Komagawa, M. Uchiyama and K. Morokuma, *Angew. Chem. Int. Ed.* **2011**, 50, 644.

[3] a) L. El Kaïm, L. Grimaud, *Tetrahedron,* **2009**, 65, 2153-2171; b) N. Chéron, R. Ramozzi, L. El Kaïm, L. Grimaud and P. Fleurat-Lessard, *J. Org. Chem.*, **2012**, 77, 1361.

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- R. Ramozzi, N.Chéron, L. El Kaïm, L. Grimaud, and P. Fleurat-Lessard, Chem. Eur. J., 2014, 20 (29), 9094-9099.
- L. Wa Chung, W. M. C. Sameera, R. Ramozzi, A. J. Page, M. Hatanaka, G. P. Petrova, T. V. Harris, X. Li, Z. Ke, F. Liu, H.B. Li, L. Ding, and K. Morokuma, Chem. Rev., 2015, doi:10.1021/cr5004419, 120 pages.
- R. Ramozzi, K. Morokuma, J. Org. Chem., 2015, doi:10.1021/acs.joc.5b00594
- J. Jiang, R. Ramozzi, K. Morokuma, Rh(III)-Catalyzed C(sp3)-H Bond Activation via an External Base Metalation Deprotonation Mechanism, Chem. Eur. J., *accepted*

3. Presentations at academic conferences

Oral communication: The Isocyanide Multicomponent Reactions: a never-ending source of innovation, 14th RCTF, Paris (France), July 2014.

Poster communication: The solvent effect in the Passerini reaction, 12th FIFC symposium, Kyoto (Japan), 2015

4. Others

Poster presentation in "Conversation with Researchers" in the Academic Day of Kyoto University

Title: Explore the world of chemistry reactions by computers

Authors: Morokuma Group (Miho Hatanaka, Julong Jian, Romain Ramozzi, W.M.C. Sameera, and Satoshi Suzuki), Fukui Institute for Fundamental Chemistry, Kyoto University

Date and Place: September 28 (Sunday), 2014. Clock Tower Centennial Hall, Kyoto University

Satoshi Suzuki

Research Fellow

1. Summary of the research of the year

Exploration of quenching pathway of multiluminescent acenes using the GRRM strategy with the SF-TDDFT method

Owing to their optical and electronic properties, π-conjugated systems have attracted much attention as a functional material. Recently a series of π systems that consists of a flexible cyclooctatetraene (COT) core and aceneimide wings with different conjugation lengths has been synthesized. A significant feature of this system is to show environment dependent emission from single component fluorophore. The system shows a blue emission from the V-shaped structure in a polymer matrix or in a frozen solution, a green emission from the planar geometry in solution, and a red emission in the crystalline state. The molecule with anthraceneimide wings is emissive both in solution and in the solid state, while the molecule with phenyleneimide has no emission either in solution or in the solid state. For the molecule with naphthaleneimide moiety, although no fluorescence is observed in the various common organic solvents at room temperature, the compound shows fluorescence in the solid state.

In many photochemical processes such as photochemcial reactions and fluorescence quenching, the conical intersections (CIs) plays an important role because nonadiabatic transitions from excited states to the ground state take place very efficiently in the vicinity of the CI.

In order to explain the difference in emission behavior of the present molecules, we adopted the GRRM (Global Reaction Route Mapping) strategy to explore and locate minimum energy conical intersections (MECI) between S_1 and S_0 for the three aceneimide **1-3** in figure 1**.** and to determine possible quenching pathways, starting from the Franck-Condon region. The difference in quenching pathway among the three systems would lead to the difference of emission behavior.

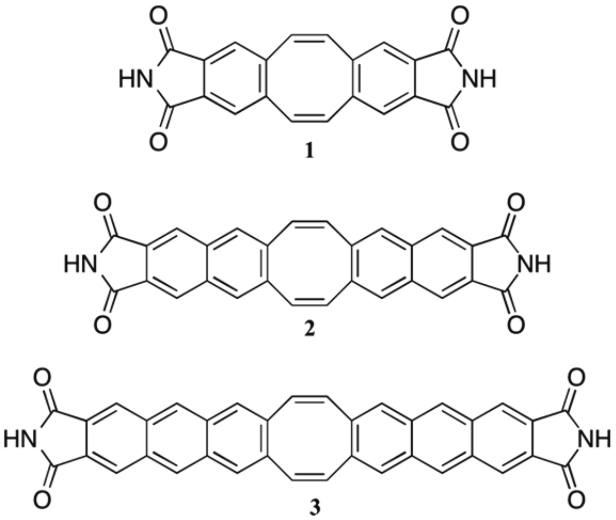


Figure 1. Chemical structure of aceneimide compound **1-3**

Figure 2 shows structure of important critical points and their energies for molecule **1**. A local minimum **LM** on S_1 surface is found near the C_{2v} **FC** point (the ground state minimum **GM**) with a planar symmetric D_{2h} structure. The optimized MECI **CI_F** also has a planar symmetric D_{2h} geometry. **CI_F** is higher in energy than **LM** only by 11.7kJ mol^{-1}. We also found a different type of MECI, CI_B. This CI_B shows large out-of-plane bending of two neighboring CH bond in COT. In molecule **1**, after vertical excitation, the molecule can reach to CI_F easily. This quenching pathway should be most preferable in solution. In addition, there is another pathway to reach CI. Moreover, transition between S_1 and S_0 is forbidden by symmetry at **LM**. This is why molecule **1** shows nonradiative decay rather than emission.

For molecule **3**, different from **1** and **2**, two C2v local minima for S_1 state were found(Figure 3). There are one local minimum that has shallow V shape (**LM_V**) and the other local minimum with flat C_2v geometry (**LM_F**). At **LM**$_F$, S_1 state belongs to $^1B_2$ and thus transition from S_1 to S_0 is allowed. MECI for **3** near local minimum has twisted structure, which has higher energy than FC by 50kJ mol^{-1}. For this molecule, barrier toward CI is high enough. Thus, in this molecule, fluorescence is more likely to take place at **LM**$_F$ than internal conversion around CI.

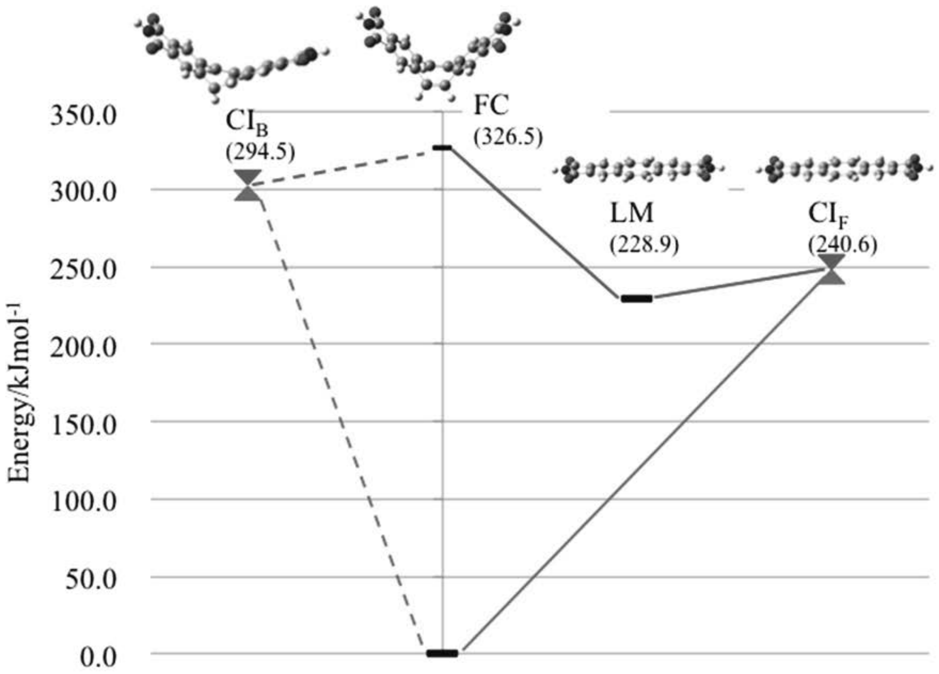


Fig.2 Energy profile of molecule **1**.

Solid lines mean connections between points are confirmed by IRC or geometry optimization.

Connection for dotted line is not confirmed.

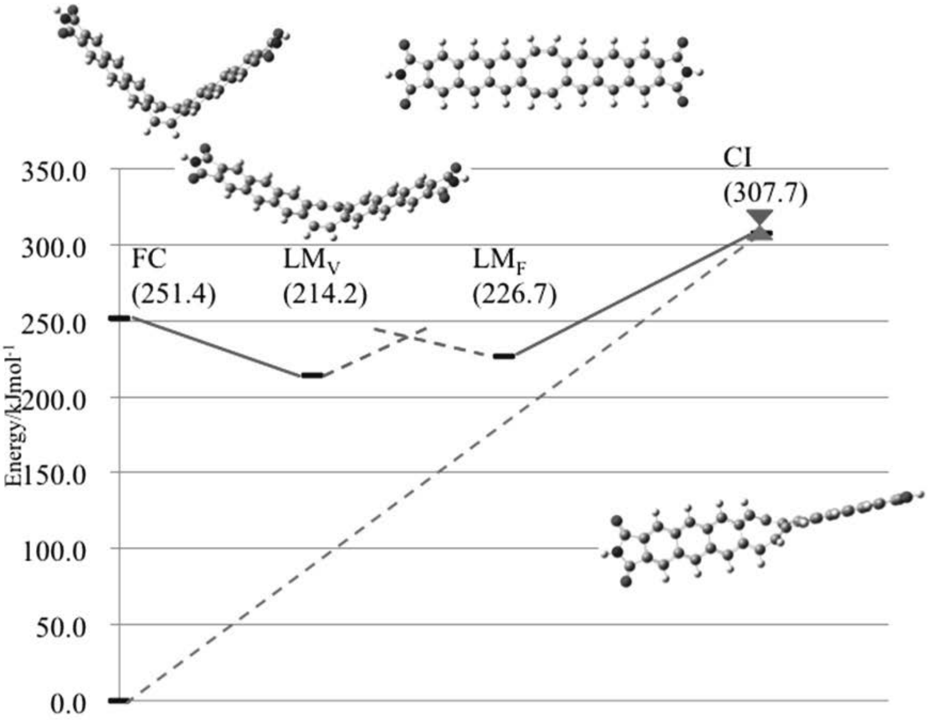


Fig 3 Energy profile of molecule **3**.

Solid lines mean connections between points are confirmed by IRC or geometry optimization.

Connection for dotted line is not confirmed.

2. Original papers

(1) Satoshi Suzuki, Satoshi Maeda, and Keiji Morokuma,"Exploration of quenching pathway of multiluminescent acenes using the GRRM strategy with the SF-TDDFT method"(in prepartion)

3. Presentation at academic conferences

(1) ◯鈴木聡,諸熊奎治, "環境依存発光を示すアセン類縁体の消光経路探索",第八回分子科学討論会 2014,広島,2014 年 9 月

4. Others

4.1 presentations at symposiums

(1) Poster presentation in "Conversation with Researchers" in the Academic Day of Kyoto University
Title: Explore the world of chemistry reactions by computers
Authors: Morokuma Group (Miho Hatanaka, Julonh Jianb, Romain Romazzi, WMC Sameera, and Satoshi Suzuki), Fukui Institute for Fundamental Chemistry, Kyoto University
Date and Place: September 28 (Sunday), 2014. Clock Tower Centennial Hall, Kyoto University

(2) ◯鈴木聡,諸熊奎治, "環境依存発光を示すアセン類縁体の消光経路探索", 新学術領域「高次複合光応答分子システムの開拓と学理の構築」,大阪,2015 年 1 月

Travis Harris

Research Fellow, Fukui Kenichi Memorial Research Group 1

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

Rh(I)-catalyzed hydroboration of alkenes has become a widely used reaction, producing boronate esters with good regio- and stereoselectivity. These organoboranes can then be functionalized via such processes as oxidation, amination, and C-C bond formation, while retaining chirality. Depending on the nature of the catalyst, the conditions, and the substrate, vinyl boronates can also be produced as the major or sole product. Thus, to reliably predict the products that will be obtained from new substrates, and to rationally design ligands that enable greater selectivity, it is important to understand the mechanism and the factors that control it in detail.

The hydroboration mechanism for Wilkinson's catalyst ($RhCl(PPh_3)_3$) has been studied in detail, whereas fewer studies have examined catalysts with chelating ligands, which are commonly employed for asymmetric hydroboration. In this work we calculate full hydroboration mechanisms of neutral Rh(I) catalysts with pinacolborane (HBPin) and a series of bidentate ligands: 1,2-bis(dimethylphosphino)ethane (dmpe), 1,2-bis(diisopropylphosphino)ethane (dippe), and 1,2-bis(ditertbutylphosphino)ethane (dtbpe). There are two distinct mechanisms, shown by the catalytic cycle in Figure 1.

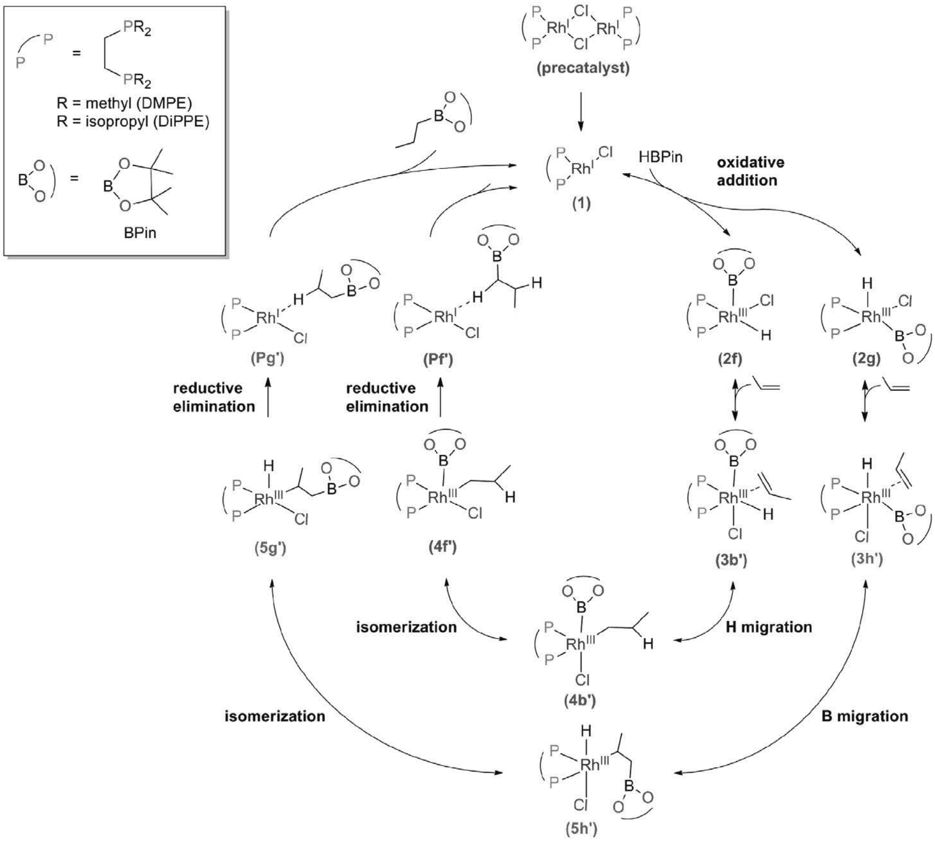


Figure 1. Catalytic cycle for Rh(I)-catalyzed hydroboration.

After oxidative addition of HBPin, addition of the alkene yields intermediates 3b’ and 3h’, which lead to migratory insertion into the Rh-H or Rh-B bond, respectively. The resulting pentacoordinate compounds isomerize to the reactive intermediates 4f’ and 5g’, before undergoing C-B or C-H reductive elimination, respectively.

This investigation was specifically prompted by an experimental finding that norbornene reacts faster than 1-octene, both yielding alkyl boranes. We thus employed norbornene and the computationally efficient propene as substrates in the DFT calculations, using B3LYP-D3 with the SDD effective core potential basis set for rhodium and 6-31G* for other atoms. The THF solvent was modeled by PCM. Free energy profiles for the H migration and B migration mechanisms were calculated for both substrates using the dippe ligand. For propene, the H migration step was rate limiting with a 20.2 kcal/mol barrier. The alternative, B migration pathway was more hindered, with a B migration barrier of 23.3 kcal/mol followed by a rate-limiting reductive elimination step (27.1 kcal/mol). By contrast, 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, propene (and likely 1-octene) and norbornene undergo hydroboration via distinct mechanisms; the addition partner is the hydride for propene, and BPin for norbornene.

The free energy profiles for the least hindered hydroboration pathways for propene and norbornene are compared in Figure 2.

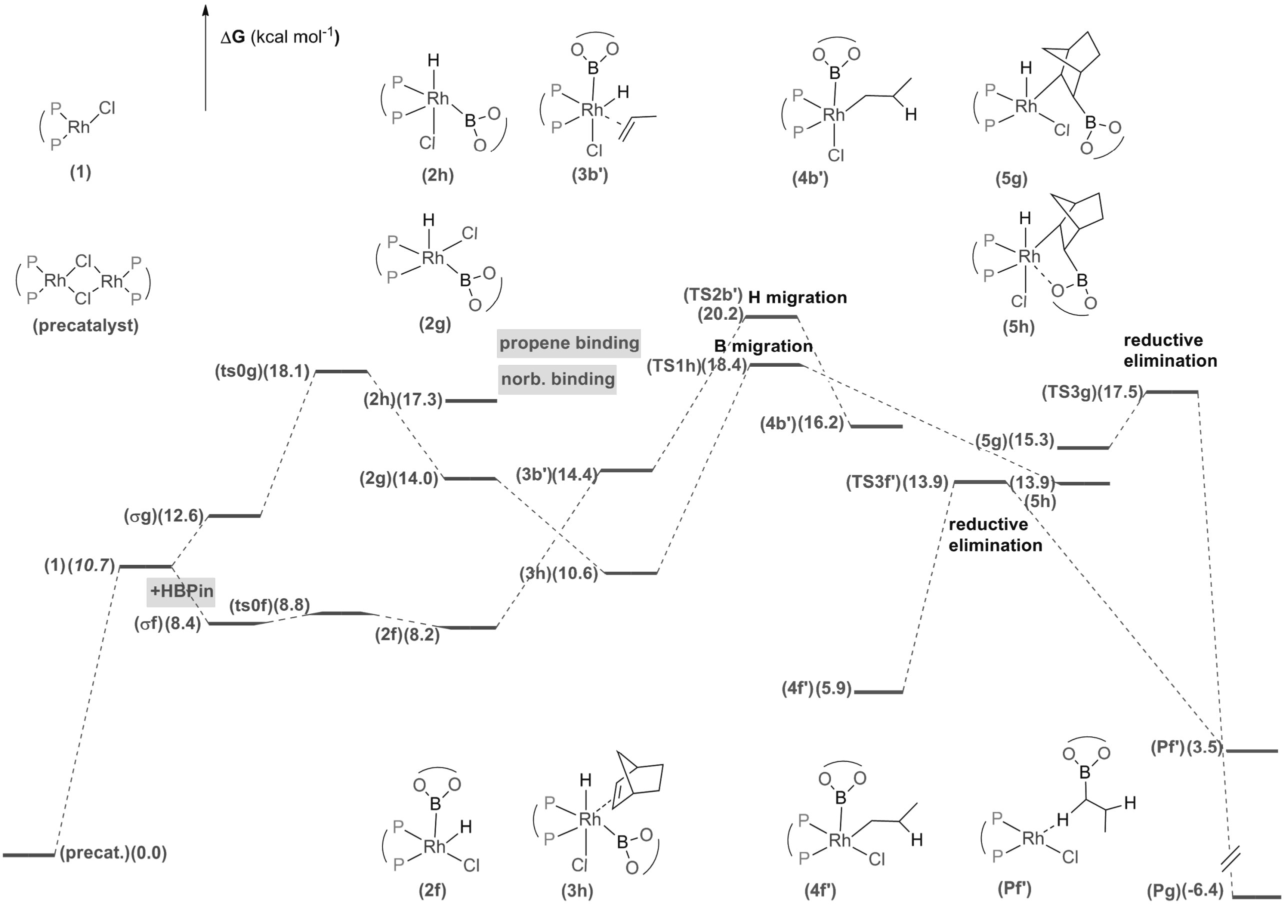


Figure 2. Free energy profiles of Rh-catalyzed hydroboration of propene and norbornene.

Norbornene has a lower rate-limiting barrier (18.4 kcal/mol) than propene (20.2 kcal/mol), which is consistent with the experimental results. The reason H migration is unfavorable for norbornene is that intermediate 3b, which leads to H migration, is unstable (20.1 kcal/mol) due to steric interaction between the methylene bridge of norbornene and the Cl ligand, causing norborene to bind with a weak, rotated orientation as shown in Figure 3a. The C-Rh bond distances are 2.37 Å and 2.43 Å in 3b, compared to 2.22 Å and 2.25 Å in 3h, which leads to B migration.

In addition to the substrate dependence, the mechanisms are significantly affected by varying the ligand. Calculations with dmpe showed that the addition partner is the hydride for both substrates, whereas with dtbpe the addition partner is BPin for both. Figure 3b shows that intermediate 3b, which leads to H migration, is sterically hindered with dippe compared to dmpe, as BPin is sandwiched between two ligand substituents. On the other hand, BPin only interacts with one ligand substituent in intermediate 3h, and is thus less affected by the bulky isopropyl group. The result is that bulky ligands disfavor H migration relative to B migration. In summary, this study shows how ligands and substrates both affect the mechanism of hydroboration and control the relative rates of two competing pathways.

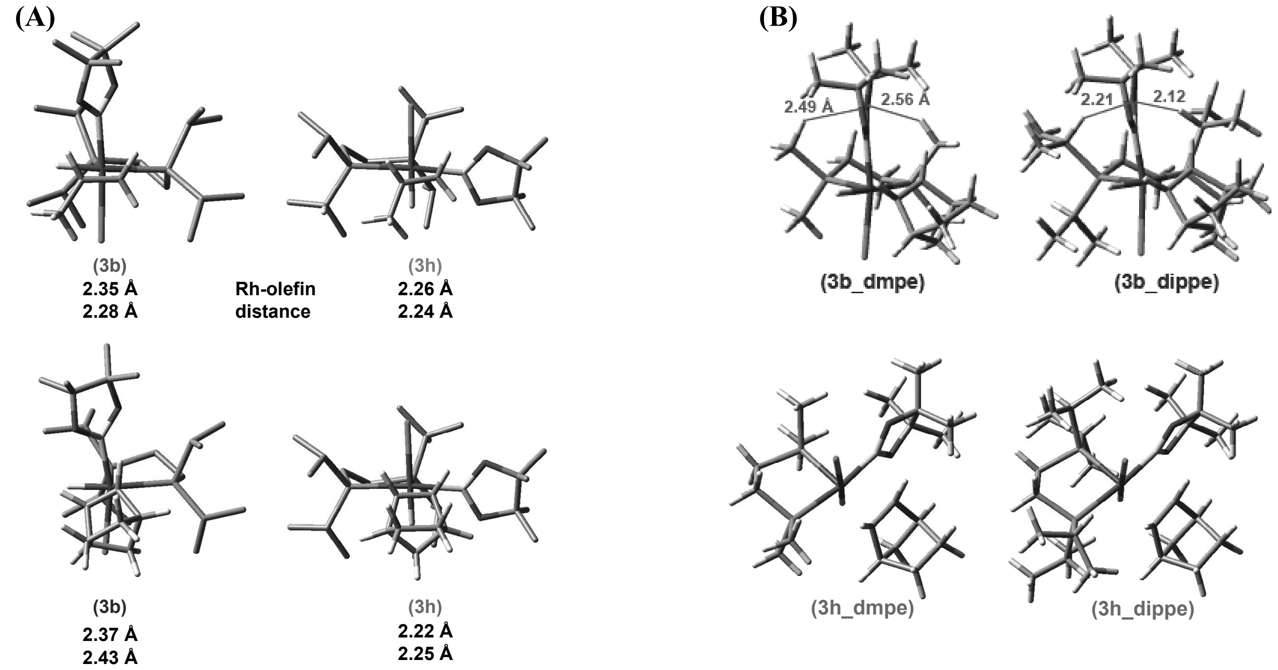


Figure 3. Structural comparison of intermediates 3b and 3h. The substrates propene and norbornene are compared in (A); the ligands dmpe and dippe are compared in (B).

2. Original papers

(1) Chung, L.W.; Sameera, W.M.C.; Ramozzi, R.; Page, A.J.; Hatanaka, M.; Petrova, G.P.; Harris, T.V.; Li, X.; Ke, Z.; Liu, F.; Li, H.B.; Ding, L.; Morokuma, K.
"The ONIOM Method and its Applications."
Chem. Rev. [Online early access]. DOI: 10.1021/cr5004419. Published Online: Apr 8, 2015.

Miho Isegawa

Research Fellow

Photochemical Ring Opening and Closing of Three Isomers of Diarylethene: Spin-Flip Time Dependent Density Functional Study

The reaction mechanism of photochemical ring opening and closing transformation was investigated for diarylethene (DAE), which works as molecular switch and photo device. Spin-flip time dependent density functional theory is employed to map the potential energy surfaces and to elucidate the photochemical mechanism of three isomers (normal, inverse, and mixed types) of 1,2-dithienylethene, a model DAE.

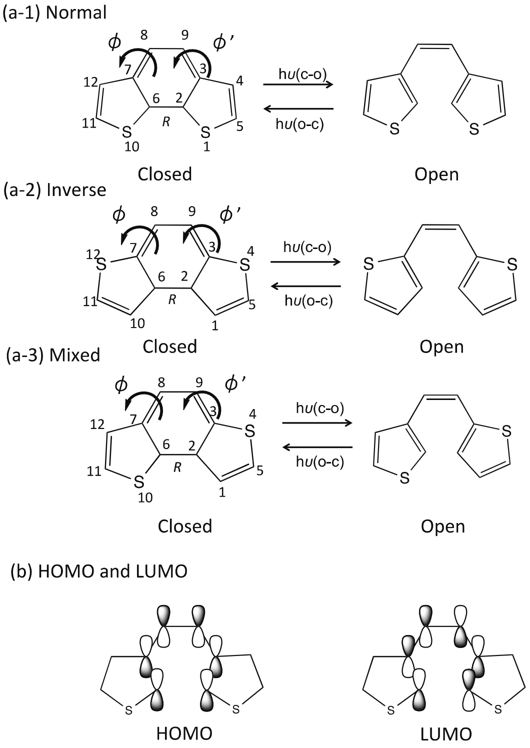


Figure 1. Ring opening-closing transformation with conrotatory motion for (a-1) normal, (a-2) inverse, and (a-3) mixed type of 1,2-dithienylethene, with atomic labels and definition of R, Φ and Φ'. (b). HOMO and LUMO of the open normal form.

The potential energy characteristics including minimum energy conical intersection reveals the origin of different product preference of the three isomers.

(1) For the normal type, the Frank-Condon state excited from either open or closed form of the ground state reaches the same minimum on the excited state and decays to the closed form of the ground state though the same conical intersection.

N-S$_1$-FC1 (Closed), **N-S$_1$-FC2** (Open) → **N-S$_1$-MIN4** → **N-S$_1$/S$_0$-CI1** → **N-S$_0$-MIN1** (Closed),

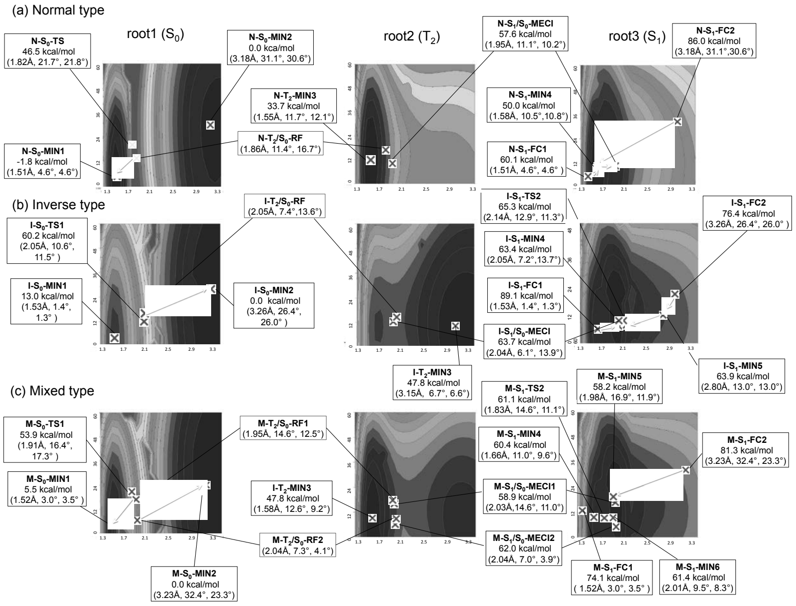
(2) For the inverse type, both forms of FC states reach the same excited state minimum and decay to the open form of the ground state via the same conical intersection,

I-S$_1$-FC1 (Closed), **I-S$_1$-FC2** (Open) → **I-S$_1$-MIN4** → **I-S$_1$/S$_0$-CI1** → **I-S$_0$-MIN2** (Open)

The above findings provide the reason why the experimentally observed quantum yield is large for the closed from in the normal type, and for the open form in the inverse type.

(3) In the mixed type, the observation of both open and closed form in the product is due to the existence of two distinctive conical intersections with different nature and rather easy interconversion between the two pathways.

M-S$_1$-FC1 (Closed) → **M-S$_1$-MIN4** → **M-S$_1$-MIN5** → (a) **M-S$_1$/S$_0$-CI1** → **M-S$_0$-MIN1** (Closed)
(b) M-S$_1$-MIN6 → **M-S$_1$/S$_0$-CI2** → **M-S$_0$-MIN2** (Open)
(b) **M-S$_1$-FC2** (Open) → **M-S$_1$-MIN5** → **(a) M-S$_1$/S$_0$-CI2** → **M-S$_0$-MIN1** (Closed)
(b) M-S$_1$-MIN6 → **M-S$_1$/S$_0$-CI2** → **M-S$_0$-MIN2** (Open)



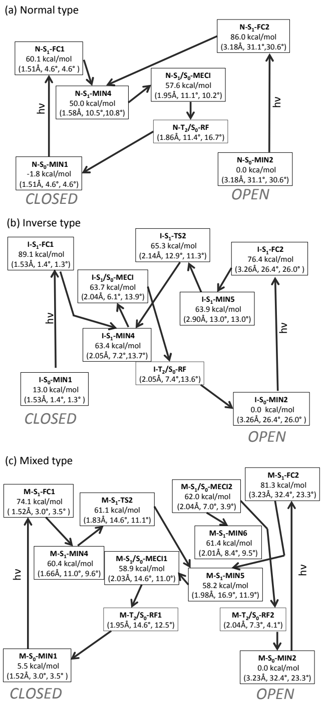


Figure 2. 2D Contour map of potential surfaces of S$_0$ (root 1, left), T$_2$ (root 2, middle) and S$_1$ (root 3, right). Position of critical points on this map is given with the energy and selected geometrical parameters (*R*, *Φ* and *Φ'*).

Figure 3. Summary of ring open-closed isomerization mechanism for (a) normal, (b) mixed, and (c) inverse type.

The present results should be considered qualitative due to the limited reliability of SF-TDDFT. The SF-TDDFT, on the other hand, is applicable to large molecules that are typically used in experiments for efficient photofunctional materials. To raise the accuracy, more reliable CASPT2 level of calculation with the large active-space is required as a future study. In addition, dynamic simulation including multiple potential energy surfaces is required to obtain quantitatively branching ratio for nonadiabatic processes.

Original paper

Photochemical Ring Opening and Closing of Three Isomers of Diarylethene: Spin-Flip Time Dependent Density Functional Study, M. Isegawa and K. Morokuma, *J. Phys. Chem. A.* **119**, 4191 (2015)

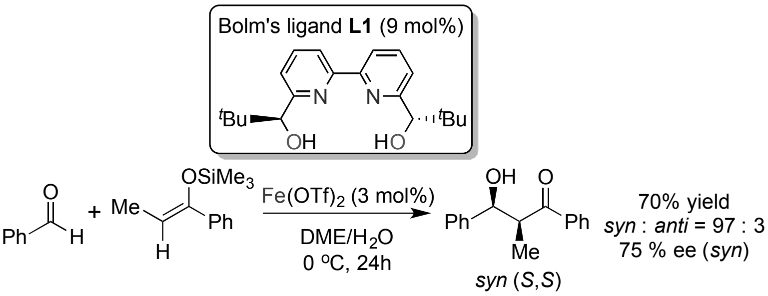
W. M. C. Sameera

JSPS Postdoctoral Fellow, Fukui Kenichi Memorial Research Group 1

1. Summary of the research

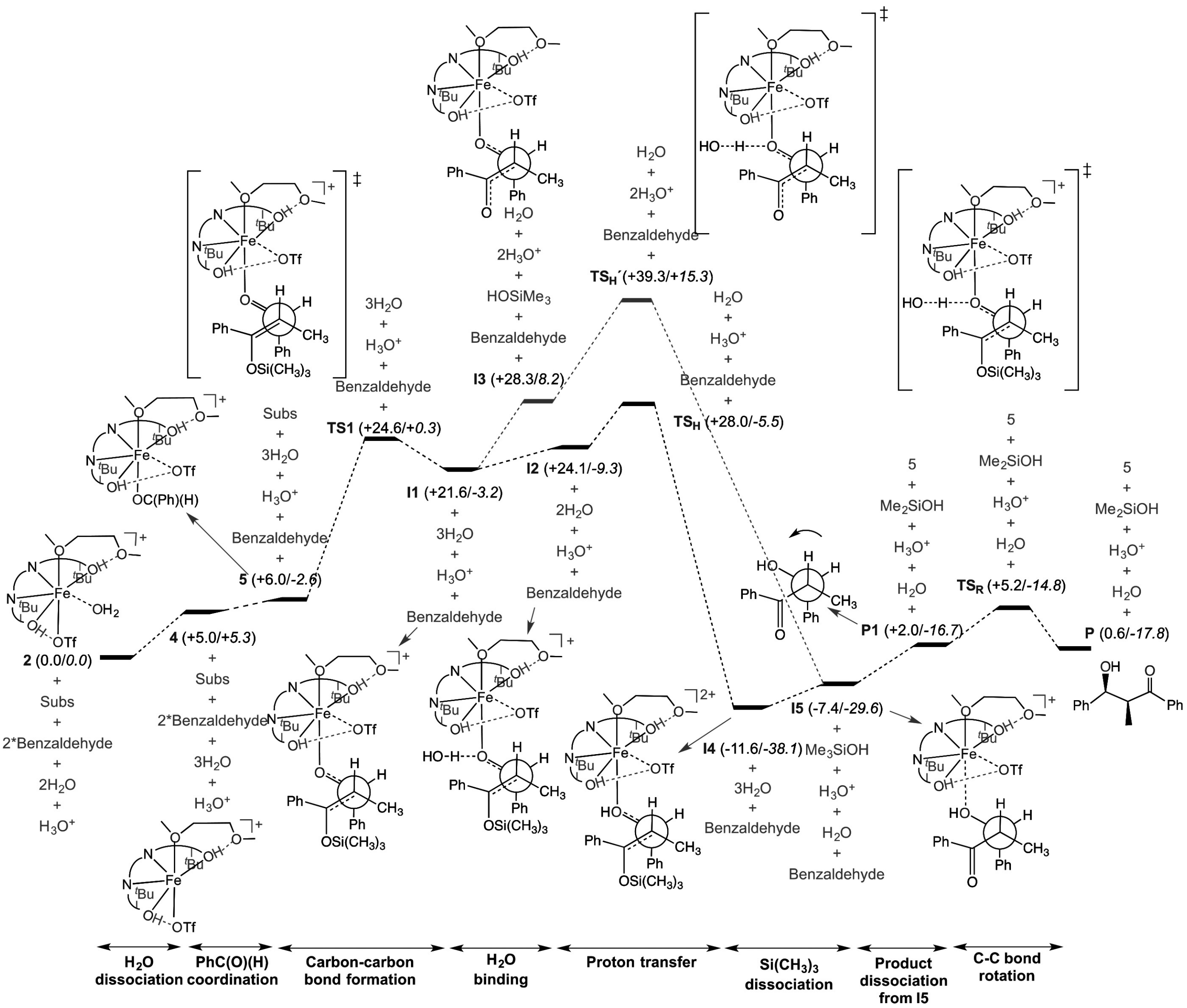
Mukaiyama aldol reactions catalyzed by a chiral Fe(II) complex

I used density functional theory (DFT), combined with the artificial force-induced reaction (AFIR) method, to establish the mechanism of the aqueous Mukaiyama aldol reactions catalyzed by a chiral Fe(II) complex (Scheme 1). In this reaction, 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. This reaction proceeds in the presence of water at 0 ^{0}C.



Scheme 1. Aqueous Mukaiyama aldol reaction of silyl enol ethers with aldehydes catalyzed by Fe(II) with Bolm’s ligand (L1).

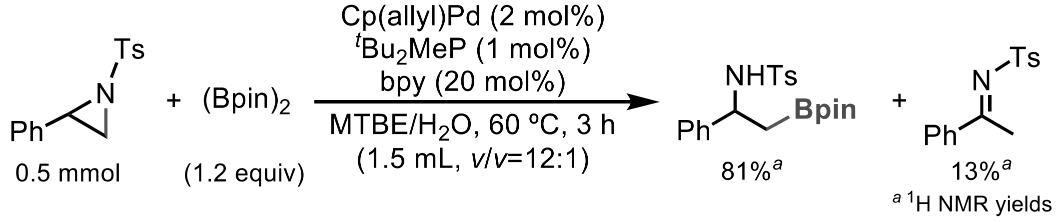
On the bases of the calculations, we identified several thermodynamically stable six- or seven-coordinate complexes in the solution, where the high-spin quintet state is the ground state. Therefore, the overall mechanism operates on the quintet state (Scheme 2). Several complexes are possible in the solution. Of these, seven-coordinate $[(L1)Fe(II)(OTf)(DME)(H_2O)]^+$ complex (**2**) is the thermodynamically most stable complex, and $[(L1)Fe(II)(OTf)(DME)(PhC(O)H)]^+$ (**5**) is the most stable *active* species for the carbon-carbon bond formation. In **5**, a dangling OTf ligand is found, which is attached to the –OH group of L1 *via* hydrogen binding. This feature helps to stabilize **5** in solution and lower the barrier for the carbon-carbon bond formation. The carbon-carbon bond formation is the selectivity-determining step of the reaction, while the proton transfer between solvent (H_2O) and of the carbonyl group of aldehyde is the rate-determining step. The remaining steps of the mechanism are relatively straightforward. The MC-AFIR results identified important competing reaction pathways for the selectivity-determining carbon-carbon bond formation. Calculated enantioselectivity and diastereoselectivity are in good agreement with the experimental results. Overall, the proposed mechanism is consistent with the experiments. This study will guide the design of transition metal catalysts for Mukaiyama aldol reactions in aqueous media.



Scheme 2. Free energy profile (kcal mol^{-1}) for the Mukaiyama aldol reaction of silicon enolates with aldehydes catalyzed by a chiral Fe(II) complexes in aqueous media (ΔG values are in plane text, ΔE values are in italics).

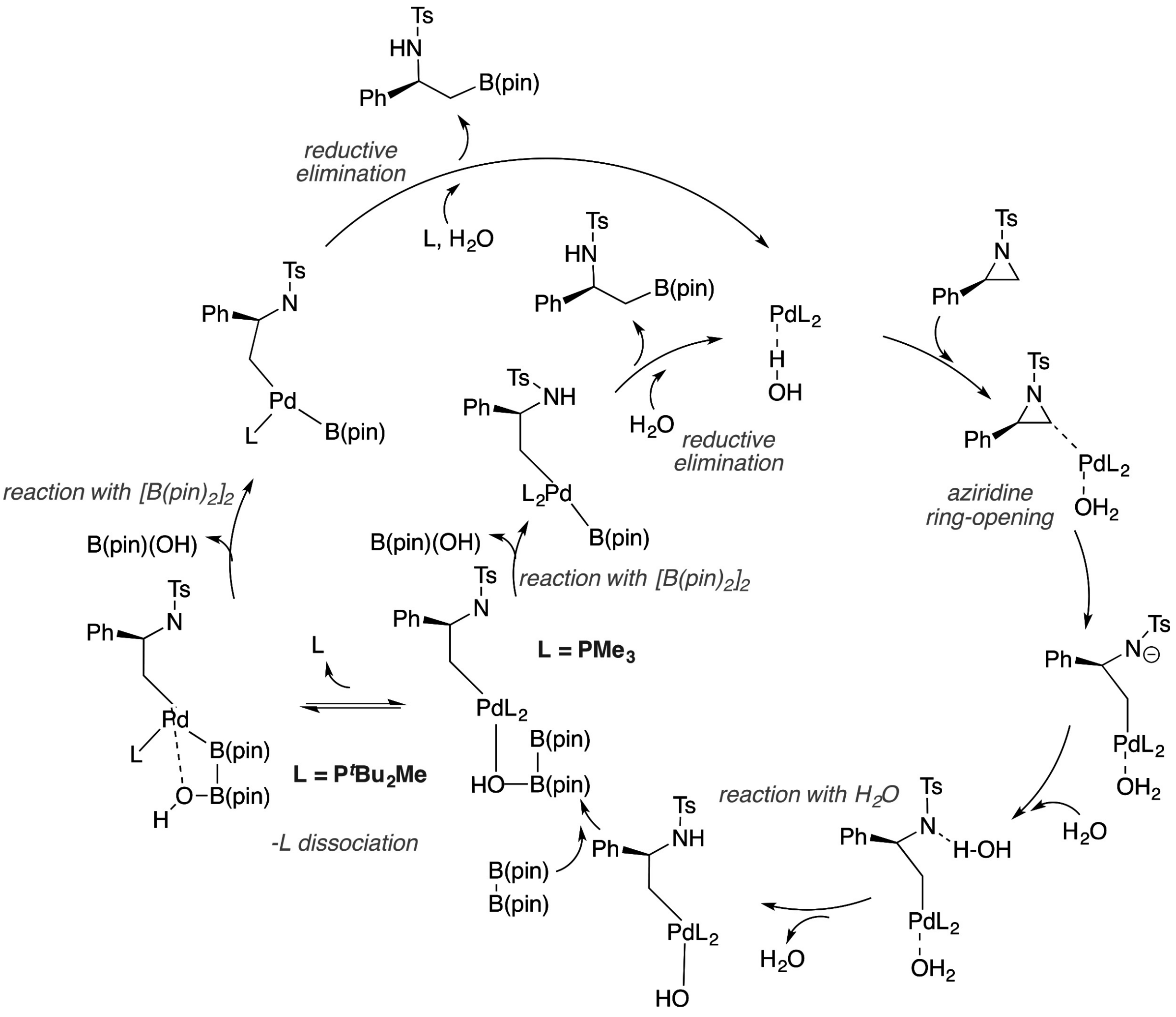
Pd-catalysed borylation of 2-arylaziridines

Pd-catalyzed borylation reactions are well-known in the literature. The Miyaura borylation is a Pd-catalysed conversion of an aryl or alkenyl halide to the corresponding boronic ester. The mechanism of this reaction is related to the Suzuki–Miyaura coupling, and undergoes the Pd(0)/Pd(II) manifold: (a) oxidative addition of the organohalide, (b) reaction with base, (c) transmetalation with the diboron reagent, (d) reductive elimination.



Scheme 3. Pd-catalysed borylation of 2-arylaziridines shown in the scheme 3.

My interest is the Pd-catalysed borylation of 2-arylaziridines shown in scheme 3. This reaction works without a base, and aziridine ring opening occurs at the less hindered carbon. It is important to note that H_2O is very important for this reaction. In the absence of H_2O, reaction does not work. We have used DFT combined with the MC-AFIR method to establish the mechanism of this reaction (Scheme 3).



Scheme 4. Catalytic cycle from computational studies.

We have systematically studied the possible pre-reacted complexes in solution, and identified the thermodynamically most stable complex, which is $PdL_2(H_2O)$. Starting from this complex, next step is the rate determining aziridine ring-opening. We have performed MC-AFIR to rationalized the possible transition states, and confirmed that the ring-opening at the less-hindered carbon centre is favourable. The resulting intermediate reacts with water, giving rise to a PdL_2-OH complex. This species acts as the active species to react with $[B(pin)]_2$, the transmetalation process. This step is however sensitive to the steric effects of the ligand, L. For instance, in the presence of a bulky –$P(^tBu)_2Me$ ligand, transmetalation is difficult to start from PdL_2-OH due to steric repulsions, and therefore one of two –$P(^tBu)_2Me$ (L) of PdL_2-OH intermediate must be dissociated. After the transmetalation step, *cis*/*trans* isomerisation lead to the reductive elimination, and the $PdL_2(H_2O)$ can be recovered for the next catalytic cycle.

2. List of original papers

1. L. W. Chung, W. M. C. Sameera, R. Ramozzi, A. J. Page, M. Hatanaka, G. P. Petrova, T. V. Harris, X. Li, Z. Ke, F. Liu, H-B. Li, L. Ding and K. Morokuma, "The ONIOM Method and its Applications", *Chem. Rev.* 2015, 115, 5678-5796.
2. W. M. C. Sameera, M. Hatanaka, T. Kitanosono, S. Kobayashi, K. Morokuma. "The Mechanism of Iron(II)-catalyzed Asymmetric Mukaiyama Aldol Reaction in Aqueous Media: Density Functional Theory and Artificial Force-Induced Reaction Study". *J. Am. Chem. Soc.* (*Submitted*)
3. M. Besora, A. A. C. Braga, W. M. C. Sameera, J. Urbano, M. R. Fructos, P. J. Pe_rez, F. Maseras, "A computational view on the reactions of hydrocarbons with coinage metal complexes", *J. Organomet. Chem.* 2015, 784, 2-12.
4. 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.
5. 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, 43, 11269-11276. [This article is part of themed collection: Synergy between Experiment and Theory]
6. W. M. C. Sameera, Bethmini Senevirathne, Stefan Andersson, Feliu Maseras and Gunnar Nyman, Binding energies and binding preference of OH, HCO, and CH_3 radicals on hexagonal ice: an ONIOM(QM:AMOEBA09) study. *J. Chem. Phy.* (*Submitted*)
7. F. Castro-Gómez, W. M. C. Sameera, G. Nyman, A. W. Kleij and C. Bo, "DFT Studies on the Al(III) Catalyzed Formation of Cyclic Carbonates from CO_2 and Epoxides: Towards Quantitative Evaluation of the Catalytic Activity". *ACS Catal.* (*Submitted*)
8. D. Sharma, W. M. C Sameera, S. Andersson, G. Nyman, M. J. Paterson, "Computational study of the interactions between benzene and crystalline ice I_h: Ground and excited states". *Phys. Chem. Chem. Phys.* (*Submitted*)

3. List of presentations at meetings.

1. W. M. C. Sameera and Keiji Morokuma**,** *Computational studies of transition metal catalyzed*

carbon-carbon bond formation reactions, the 15th ICQC meeting, China (*Poster*).

2. W. M. C. Sameera, Fengyi Liu, Satoshi Maeda, and Keiji Morokuma, *Spin-flip time-dependent density functional theory (SF-TDDFT) study of TokyoMagenta (TM) and TokyoGreen (TG)*, The 12th Kenichi Fukui Memorial Research Center Symposium, Kyoto University, Japan (*Poster*).
3. W. M. C. Sameera, Miho Hatanaka, Keiji Morokuma, *On the mechanism of Fe(II) catalyzed asymmetric Mukaiyama-Aldol reaction in aqueous media*, The 2nd international symposium for young chemists, Osaka University, Japan. (*Poster*)
4. W. M. C. Sameera and Keiji Morokuma, *Computational studies of the carbon-carbon bond formation reactions*, Conference on C-C bond cleavage, Kyoto University, Japan. (*Poster*)
5. W. M. C. Sameera, Miho Hatanaka, Keiji Morokuma, *A computational study of the asymmetric Mukaiyama-Aldol reaction*. Conference on the new aspects of reactive organometallic complexes of transition metals, Osaka University, Japan. (*Poster*)
6. M. Hatanaka, J. Jian, R. Romazzi, W. M. C. Sameera, and S. Suzuki, *Explore the world of chemistry reactions by computers*, Conversation with the researchers in the academic day of the Kyoto University, Japan. (*Poster*)
7. W. M. C. Sameera, Bethmini Senevirathne, Muhsen Al-Ibadi, Stefan Andersson, Gunnar Nyman, *Interstellar radical species binding on ices: a hybrid QM/MM approach*, Icy Grain Chemistry for Formation of Complex Organic Molecules: From Molecular Clouds to Protoplanetary Disks, Comets and Meteorites, Tokyo Institute and Technology, Japan (*Talk*).
8. W. M. C. Sameera, Stefan Andersson, Gunnar Nyman, *Hybrid QM/MM Methods for Interstellar Chemistry*, MOLEC 2014 meeting, University of Gothenburg, Sweden. (*Poster*)

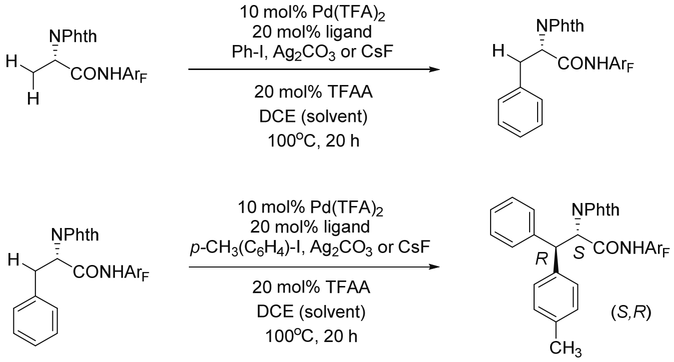
Julong Jiang

SPR Fellow (March 1st 2014 to February 28th 2015)

Research Topics

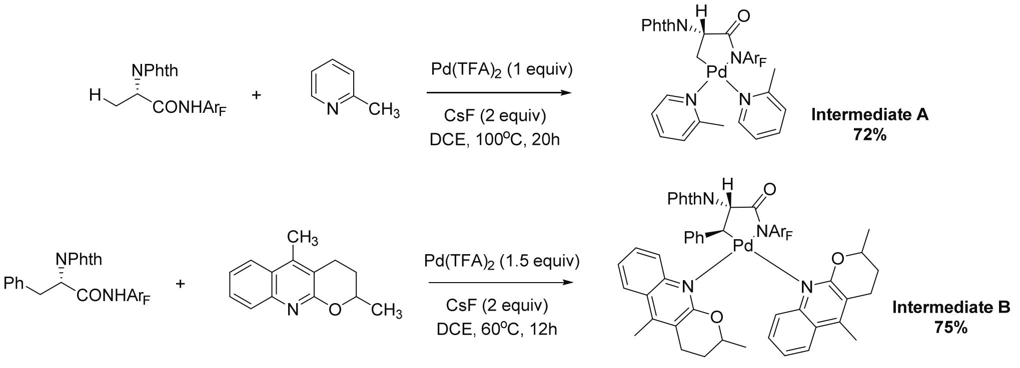
1. **Theoretical investigation on the Pd-catalyzed C(sp^3)-H activation in the synthesis of unnatural amino acids**

   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 specific substrate should be synthesized prior to the subsequent cross-coupling reaction. It should be noted that these special substrates are not always easy to be prepared, and sometimes suffer from the decomposition due to the instability. In recent years, people turned their 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 directed C-H activation on sp^3 carbons. (Yu *et al.*, *Science*, **2014**, *343*, 1216)



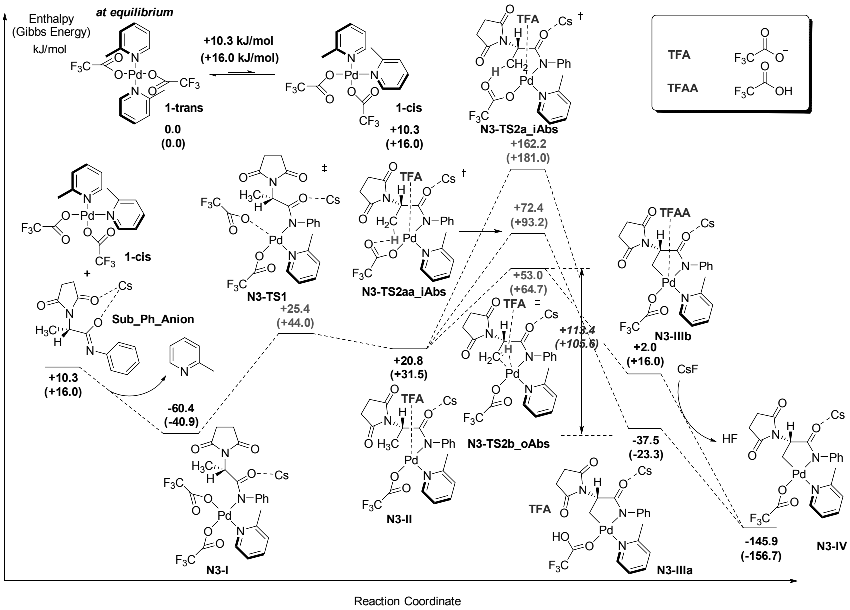
Scheme 1. Palladium-catalyzed C(sp3)-H activation and subsequent arylation

More interestingly, as shown in Scheme 2, the intermediates A and B generated through C-H activation have been successfully isolated and characterized. 2-Methylpyridine (2-picoline) was found as an appropriate ligand for the primary C(sp3)-H activation, whereas an electron-rich ligand (2-alkoxylquinoline) was used for the secondary C(sp3)-H bond. The reaction conditions become much milder with the help of 2-alkoxylquinoline.



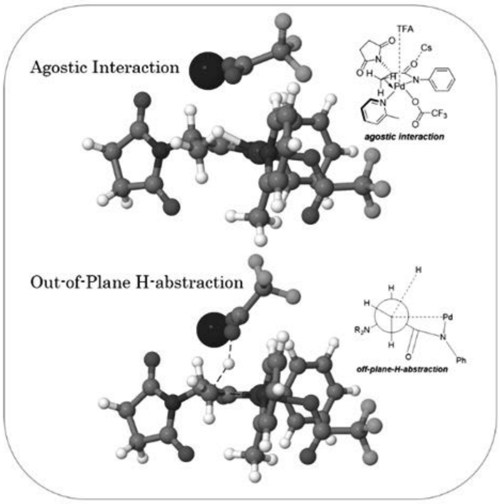
Scheme 2. Generation of intermediate A and intermediate B

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 detailed mechanism of this one-pot C-H activation and arylation reaction. The calculations were performed on DFT level of theory (B3LYP-GD3). Interestingly, as a result, we found that the conventional CMD mechanism (or AMLA mechanism), in which the base is a carboxylate ligand directly coordinating to the central metal atom, does not apply to this reaction.



Scheme 3. Enthalpy profile for Pathway N3, in which both L2 and L3 positions are occupied by TFA ligands

The H-abstraction in this reaction is actually conducted by an *out-of-plane* TFA which has no covalent interaction with the Pd(II) atom. Inspection of the corresponding transition states shows that the conformation of the sp^3-C atom is distorted in the TS which follows the traditional CMD mechanism. Based on our findings, the minimum energy pathway was located as **Pathway N7**. Moreover, our calculations suggested that agostic interaction is crucial in weakening the C-H bond based on the inspection of the pre-reaction complex.

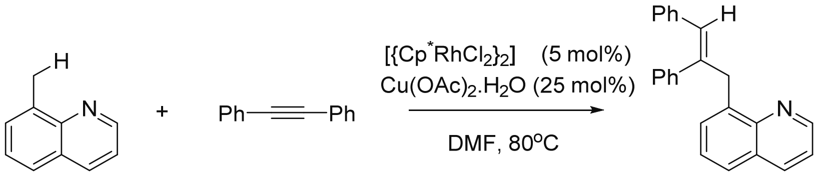


Scheme 4. Agostic interaction and out-of-plane H-abstraction

The Origin of the stereoselectivity in the secondary C(sp^3)-H bond functionalization was found to be the energy gap between two transition states at the secondary C(sp3)-H activation step. The steric repulsion between the phenyl group and the succinimide moiety is crucial to the selectivity. The size of the aryl halide for the C-H bond functionalization is irrelevant to the selectivity, since the stereochemistry of the final product is determined at the C-H activation step rather than the oxidative addition step. More kinds of amino acids may be prepared in this way. Some other aspects that affect the C-H activation, such as the solvent effect and the ligand effect, were also studied by us. The details were discussed in the published paper.

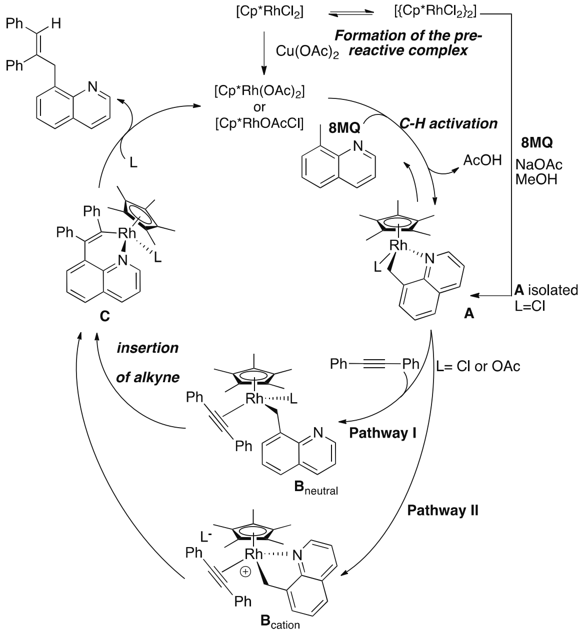
2. Rh(III)-Catalyzed C(sp3)-H Bond Activation via an External Base Metalation Deprotonation Mechanism: A Theoretical Study

Recently, the Wang group from Nankai University reported a novel Rh(III)-catalyzed C(sp3)-H activation of 8-methylquinoline followed by the insertion of an alkyne (see **Scheme 5**) in DMF. (B. Liu, T. Zhou, B. Li, S. Xu, H. Song, B. Wang *Angew. Chem. Int. Ed.* **2014**, *53*, 4191-4195.) Since 8-methylquinoline is the parent moiety of a series of bioactive compounds, this method has a potential application in future's drug discovery.



Scheme 5. C-H activation and insertion reactions for 8-methylquinoline

The mechanism proposed by Wang *et al.* is shown in **Scheme 6**. After dissociation of the rhodium dimer and exchange of ligand with the Cu(II) acetate, the first step is the C-H activation, which results in the formation of the intermediate A. This intermediate bears a rare Rh-C(sp3) bond, which can go through further functionalization. After dissociation of the heterocyclic moiety and chelation of the alkyne (intermediate **Bneutral**), the alkyne insertion is proposed to give the intermediate C. The final product is then generated with a proton source. The intermediate **A** has been isolated and fully characterized experimentally using free acetate anion in methanol.



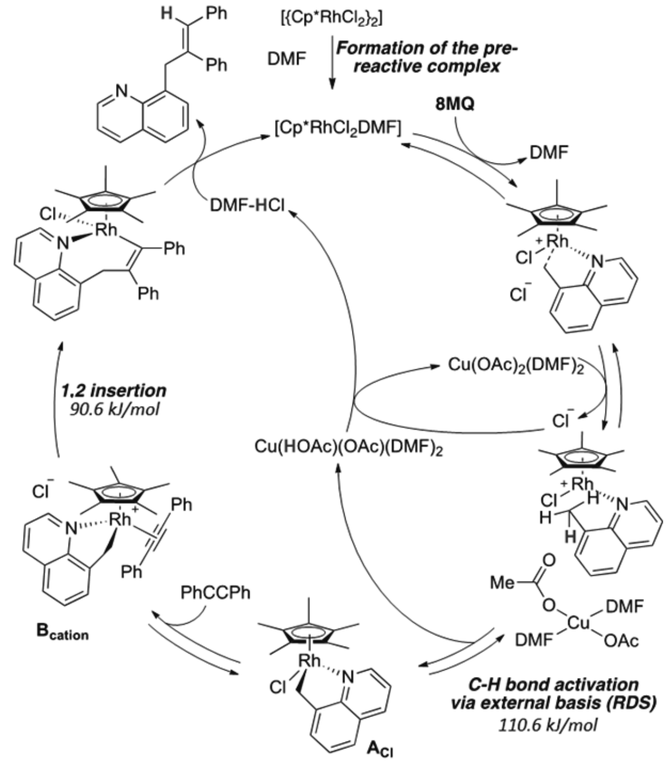
Scheme 6. Proposed mechanism by Wang et al. via Bneutral (Pathway I) and alternative mechanism Bcation (Pathway II).

Herein, we wish to shed new lights on the reaction mechanism based on DFT calculations. What is the pre-reactive complex activating the C-H bond and more particularly what is the role of the copper acetate in the formation of the intermediate A? How does the alkyne insertion to A occur? Why the reaction cannot proceed to the alkyne insertion product with free acetate? To answer these questions, pathways involving free and complexed acetate ligand will be considered. Finally, the insertion of the alkyne will be studied by considering both neutral and cationic pathways. All of the calculations were carried out at DFT level of theory (B3LYP) with an empirical dispersion correction (GD3).

If free acetate anion is used as the base, the C-H bond activation step is irreversible and should proceed in a rapid way, according to our calculation results. The traditional intramolecular CMD mechanism, which is widely used for C-H bond activation reactions, is no longer valid in this case. Indeed, the excess of free acetate anions permits to deprotonate easily the methyl of the reactant due to the better basicity of the free acetate than the ligated one.

For the full catalytic process, the copper (II) acetate is used as the base. The presence of copper prohibits the release of free acetate and thus a traditional intramolecular CMD mechanism involving an acetate ligand on the rhodium center is not possible. Therefore, the external base CMD mechanism involving the copper (II) acetate occurs. The deprotonation is found reversible in these conditions as observed experimentally. According to our results, the copper(II) center is not directly involved the C-H activation reaction since it is fully coordinated by ligands, and one of the ligated acetate ligands activates the C-H bond. The copper (II) complex with a protonated acetate, [Cu(HOAc)(OAc)(DMF)2]+, releases the proton to solution. This fact makes the H-D exchange feasible so that deuterium can be detected from the products. Moreover, the use of non-free acetate plays a critical role to ensure the feasibility of the next step as the alkyne insertion. The original proposed pathway

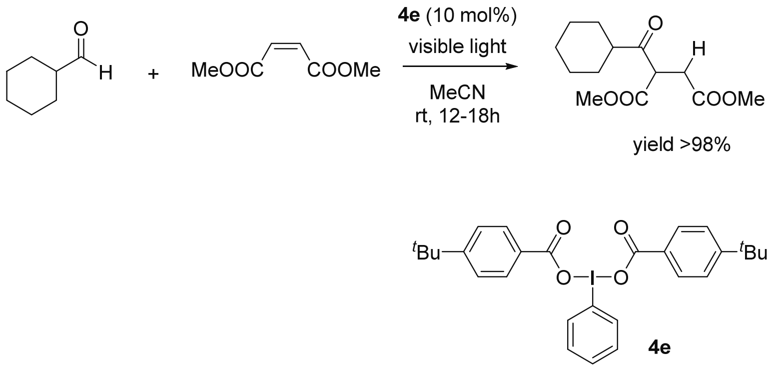
(**Pathway I**) was found inconsistent with the experiments and was proved to be less favored in energy than the newly suggested cationic mechanism (**Pathway II**). This new pathway starts with a relatively easy Rh-Cl bond breaking to give a stable cationic complex after coordination of the diphenylacetylene. The DMF promotes this process as a polar solvent, which could explain why the reaction is failing in less polar solvents. The 1,2-insertion reaction can be treated as a nucleophilic attack from the methylene group on the quinoline ring to the C-C triple bond of the diphenylacetylene. The insertion reaction is followed by a metathesis reaction to give the final product. The insertion and metathesis steps are extremely exothermic and thus irreversible. By considering the overall reaction, the C(sp3)-H activation is the rate-determining step since it has the highest effective barrier of +110.6 kJ/mol. Therefore, the kinetic isotope effect (KIE) can be observed if a deuterated substrate is employed as showed by Wang *et al*. Based on our newly findings, we proposed a revised mechanism for this reaction, which is shown in **Scheme 7**.



Scheme 7. Revised catalytic cycle based on our DFT calculations

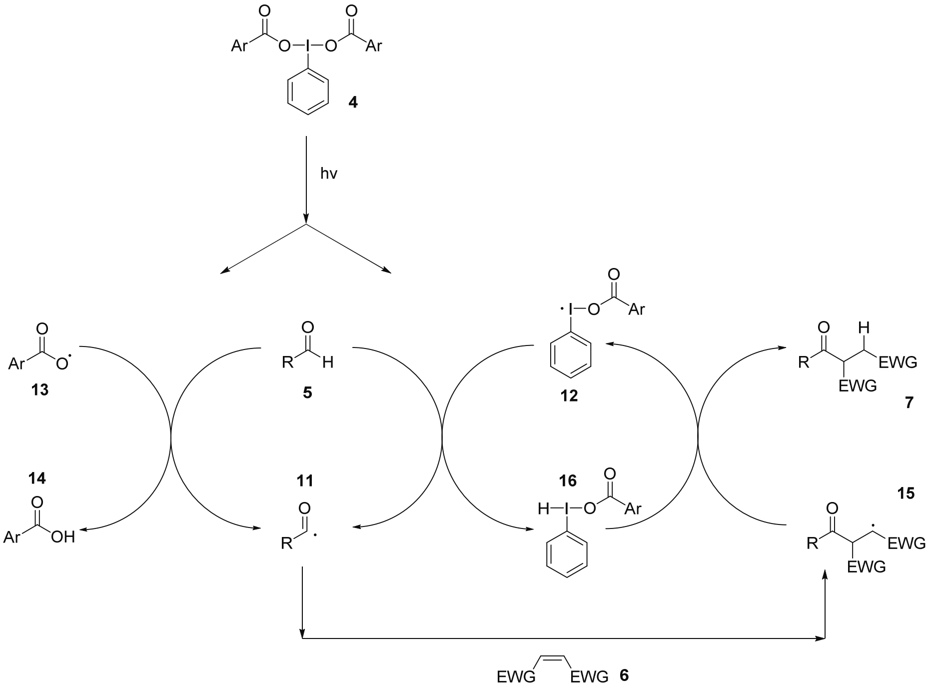
3. The Mechanism of Metal-Free C-H Activation of Branched Aldehydes and Acylation of Alkenes Using Hypervalent Iodine Compound: A Theoretical Study

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. Recently, the Maruoka group reported a C-H activation reaction of the branched aldehydes under mild conditions, in which a hypervalent iodine(III) reagent was proposed as the catalyst (see **Scheme 8**).17 This reaction led to the generation of acyl radical, which can be subsequently trapped by an electron-deficient alkene without the common side-reaction of decarbonylation. This kind of reaction has been called hydroacylation, which was usually assisted by a transition-metal as catalyst.



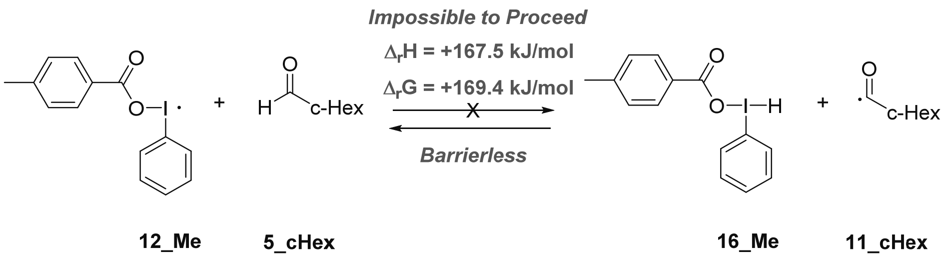
Scheme 8. The C-H activation of aldehydes catalyzed by the hypervalent iodine (III) reagent 4e

A variety of experimental studies have been carried out for clarification of the reaction mechanism. The initiation step of this reaction is the photon-assisted homolytic cleavage of the O-I bond in the iodine(III) reagent **4e**, which generates a carboxyl radical and an iodonyl radical accordingly. To test whether the carboxyl radical is responsible for abstracting hydrogen atom from the aldehyde, the deuterated carboxylic acid was added to the mixture as an additive, given the fact that the deuterium should appear in the product if the carboxyl radical is the H-atom carrier. However, only trace amount of deuterated product was detected at the end of reaction. Therefore, a mechanism based on these experimental observations was originally proposed, as shown in **Scheme 9**.



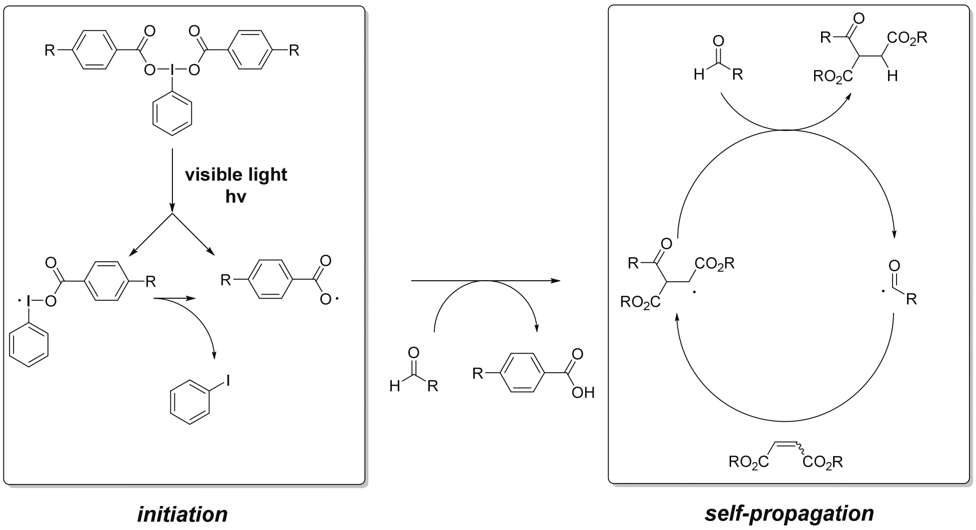
Scheme 9. Proposed mechanism in which an iodonyl radical acts as a catalyst

To fully understand this reaction mechanism and to improve the reaction systematically in the near future, we decided to perform theoretical investigations on this hydroacylation reaction. With the help of DFT calculations, we can confirm that the iodonyl radical **12_Me** is impossible to abstract H atom from the aldehyde, as shown in **Scheme 10**.



Scheme 10. Energy change for the H-abstraction by the iodonyl radical 12_Me

This finding disagrees completely with the initially proposed iodonyl mechanism, and prompted us to re-examine the mechanism of this metal-free hydroacylation reaction. Our extra calculations have shown that the hypervalent iodine reagent is actually an initiator rather than a reactive catalyst. After initiation, the reaction proceeds via a chain propagation mechanism through the addition reaction of an acyl radical to the electron-deficient alkene, followed by a hydrogen abstraction from the aldehyde by the resultant carbon-centered radical species. Our theoretical investigations led to a completely new mechanism shown in **Scheme 11**.



Scheme 11. Mechanism of the C-H activation and acylation reaction based on our theoretical studies

Publications

1. Julong Jiang, Jin-Quan Yu, Keiji Morokuma, “Mechanism and Stereoselectivity of Directed C(sp^3)-H Activation and Arylation Catalyzed by Pd(II) with Pyridine Ligand and TFA. A Computational Study”, *ACS Catal.* **2015**, *5*, 3648-3661.
2. Julong Jiang, Romain Ramozzi, Keiji Morokuma, “Rh(III)-Catalyzed C(sp3)-H Bond Activation via an External Base Metalation/Deprotonation Mechanism: A Theoretical Study”, *Chem. Eur. J.* **2015**, Accepted.
3. Julong Jiang, Romain Ramozzi, Shin Moteki, Asuka Usui, Keiji Maruoka, Keiji Morokuma, “The Mechanism of Metal-Free C-H Activation of Branched Aldehydes and Acylation of Alkenes Using Hypervalent Iodine Compound: A Theoretical Study”, *J. Org. Chem.* Submitted.

Others

Poster presentation in "Conversation with Researchers" in the Academic Day of Kyoto University

Title: Explore the world of chemistry reactions by computers

Authors: Morokuma Group (Miho Hatanaka, Julong Jiang, Romain Romazzi, WMC Sameera, and Satoshi Suzuki), Fukui Institute for Fundamental Chemistry, Kyoto University

Date and Place: September 28 (Sunday), 2014. Clock Tower Centennial Hall, Kyoto University

Shinichi Yamabe

FIFC Fellow, Kenichi Fukui Memorial Research group 2

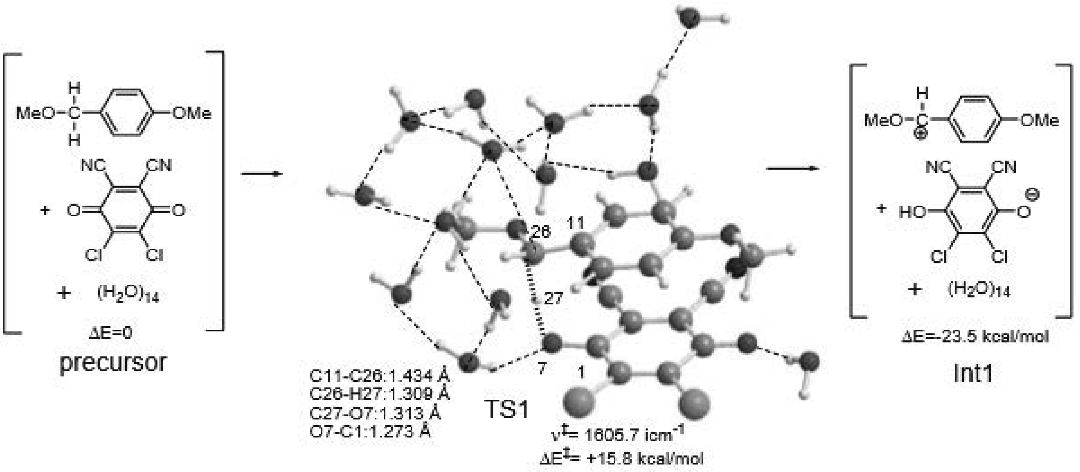
1. Summary of the research of the year

(1-1) A DFT Study of Hydride Transfers to the Carbonyl Oxygen of DDQ

Hydride-transfer reactions between benzylic substrates and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) were investigated by DFT calculations. The lowest unoccupied molecular orbitals of DDQ has the largest extension on two carbonyl oxygens, which comes from two-step mixing of antisymmetric orbitals of fragment pi MOs.

Transition-state (TS) geometries and activation energies of reactions of four benzylic substrates R2-CH2-para-C6H4-R1 (R1,R2 = H and/or OCH3) with DDQ were calculated. B3LYP, BHandH, M06-2X and wB97xD B3LYP methods were used. The basis sets employed were 6-31G(d), 6-311(+*)G(d), 6-311++G(d,p) and 6311++G(3df,2pd), where "6-311(+*)G(d)" means that a diffuse and a polarization functions are added only to the migrating hydrogen(hydride). This was found to be a practical computational method, giving energies and geometries similar to those of M06-2X/6-311++G(3df,2pd) and wB97xD/6311++G(3df,2pd). For toluene (R1=R2=H), an initiation-propagation model was suggested, and the calculated kinetic isotope effect k(H)/k(D) = 5.0 with the tunnel correction at the propagating step is in good agreement with the experimental value 5.2.

A reaction of para-MeO-C6H4-CH2(OMe) + DDQ + (H2O)14 -> para-MeO-C6H4-C(=O)H + HOMe + DDQH2 + (H2O)13 was investigated by M06-2X/6-311(+)G*. TS1 is for the hydride transfer, leading to the ion pair intermediate (Int1). From Int1, the hemiacetal intermediate (Int2) is generated via TS2. Int2 is hydrolyzed via TS3 into Int3 consisting of para-methoxybenzaldehyde and methanol. The change of Int3 → TS4 → product is the neutralization of DDQH- to DDQH2. Thus, four elementary processes were found and the hydride transfer (TS1) is the rate-determining step. The hydride transfer was promoted by association with the water cluster.
The size of the water cluster, (H2O)n, at TS1 was examined. Three models of n = 14, 20, and 26 were found to give similar activation energies.
Metal-free neutral hydride transfers from activated benzylic substrates to DDQ were proposed to be ready processes both kinetically and thermodynamically.



(1-2) Frontier orbitals and transition states in the oxidation and degradation of L-ascorbic acid.

DFT calculations were carried out to investigate reaction paths of L-ascorbic acid (AAH2), hydroxyl radical and water clusters. Frontier-orbital analyses were also made to examine the regioselectivity of the OH(.) addition. Transition states of the electrolytic dissociation of AAH2 and intermediate carboxylic acids were found to have very small activation energies through proton transfers along hydrogen bonds. The ionized species (anions) are subject to the electrophilic attack of OH(.). The process of AAH2 -> AA.- -> dehydroascrobic acid -> diketogulonic acid -> theronic acid was discussed on thebasis of the calculated elementary processes. These of dehydroascrobic acid -> a bicyclic hemiketal were also examined as a side-chain participating reaction. The oxidation and degradation of vitamin C up to threonic acid were summarized to be a donor(AAH2)-acceptor(OH.) reaction.

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(3) "SN1-SN2 and SN2-SN3 mechanistic changes revealed by transition
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International Journal of Quantum Chemistry, in press.

2. Presentation at academic conference

"Frontier orbitals and transition states in the oxidation and degradation of L-ascorbic acid: a DFT study"
第１２回 福井謙一記念研究センター シンポジウム（２０１５年１月２３日）
At Fukui Institute for Fundamental Chemistry, Kyoto University

土方　優

FIFC フェロー

1. 今年度（半期）の研究の要約

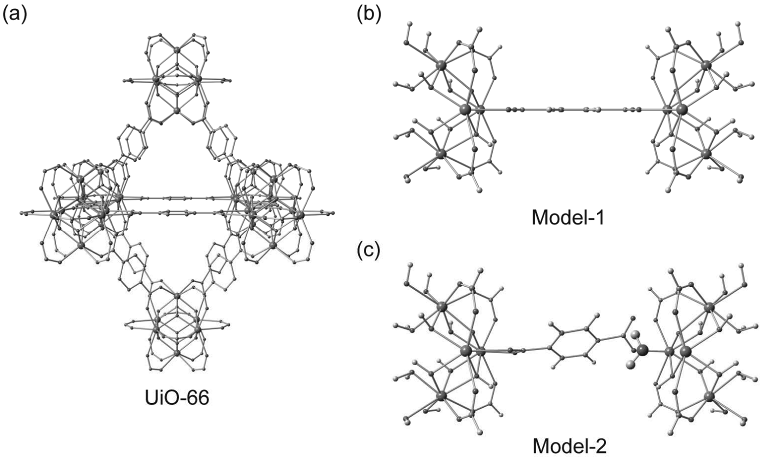
今年度は配位高分子における、骨格構造の安定性に関する研究を行った。

【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。これら新規材料としての応用を考えた際に重要となるのが、水の存在、つまり PCP の耐水性であり、近年では耐水性に関する実験研究も多く報告されている。特に通常の単核錯体と異なり、三次元骨格を組んだ場合は金属–配位子館結合だけでなく、骨格を崩壊させるためのエネルギーも考慮する必要があると考えられる。そこで骨格中における水との反応からその安定性についての知見を得ることを目的とした。

【計算、結果、考察】

図１に示した Zr_4O_6 クラスターからなる UiO-66 と呼ばれる骨格 $[Zr_4O_6(OH)_4(L)]_n$（L=OOC-Ph-COO）と配位子の異なる類似の構造（L= OOC-(Ph)$_2$-COO, OOC-(Ph)$_3$-COO, , OOC-bpy-COO）について、水付加による不安定化の評価を行った。３次元骨格構造内における水付加を想定しmodelにおけるZrクラスター部分の距離は固定して行った。得られた結果を表１にまとめる。



（図 1）UiO-66 の細孔構造と model 構造

（表１）H2O 付加による不安定化と各寄与(kcal/mol)

L の種類	H_2O 付加	L	framework のみの
OOC-Ph-COO	0.9	3.3	32.1
OOC-(Ph)$_2$-COO	-4.6	3.2	29.8
OOC-bpy-COO	-3.2	3.9	30.5
OOC-(Ph)$_3$-COO	-2.8	5.2	32.8

L = OOC-Ph-COO の方が L = OOC-(Ph)$_2$-COO に比べ水付加による不安定化が小さい、つまり耐水性が高いという結果が得られた。これは実験結果とも一致している。一方で、L = OOC-(Ph)$_3$-COO は L = OOC-(Ph)$_2$-COO に比べ安定性が高いという結果となり、これは実験結果に一致していない。この理由については現在検討中である。

2. 論文

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(2) Yuh Hijikata and Shigeyoshi Sakaki
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“Porous light metal coordination polymers with charge-polarized neutral ligand”
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4. 書籍

1. 錯体化学選書 10「金属錯体の量子・計算化学」
4.4 章　PCPs/MOFs の構造と機能発現（4－4－1 から 4－4－6 担当）
土方　優 三共出版　2014 年 10 月 10 日

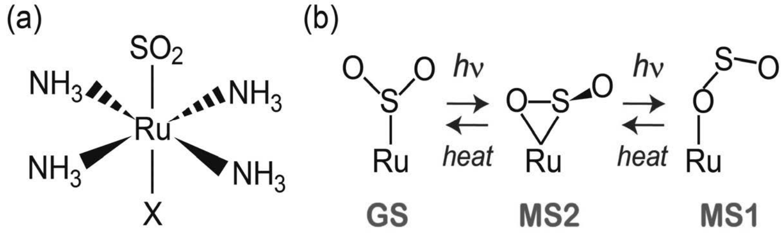
青野　信治

センターフェロー（榊研）

1. 今年度の研究の要約

【序】 d^6 金属の Ru(II)と SO_2 により構成される八面体型 Ru(II)-SO_2 錯体 [$Ru^{II}(NH_3)_4(SO_2)X$]Y は、基底状態において SO_2 の S 原子が Ru(II)に配位したη^1 型の安定構造（GS 構造）を持つ。この結晶に低温中で可視光を照射すると光異性化反応が起こり、GS 構造から O と S 原子が Ru(II)に配位したη^2 型の準安定構造（MS2 構造）および O 原子が配位したη^1 型の準安定構造（MS1 構造）へ変化する。光反応後に温度を上昇させ、逆に MS1 構造から MS2 構造へ、MS2 構造から GS 構造へ戻す事が可能であり、この錯体は分子デバイスとしての利用が期待されている（Scheme 1）[1]。

光異性化反応後の GS、MS1、MS2 の存在比は Ru(II)-SO_2 錯体のトランス位の配位子 X の種類のみならず対イオン Y の種類や温度により大きく異なる事が実験で観測されている。従って、この異性化反応に対する周囲の分子からの影響を明らかにする事は分子デバイスの設計・制御の上でも重要である。

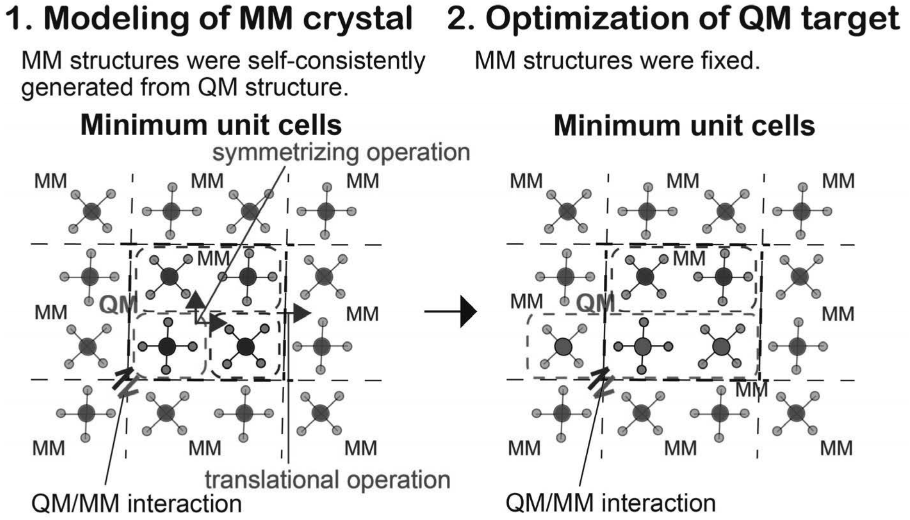


Scheme 1: Ru(II)-SO_2 の異性化反応

本研究では光異性化反応後の熱異性化過程について注目し、まず単分子レベルでのトランス位の配位子効果を調べる為に配位子 X が Cl^-、H_2O、pyridine の場合に対して遷移状態構造を最適化し、そのエネルギー変化を求め、気相中と水中での周囲の環境の違いについて比較・検討した。また X=pyridine、Y=2Cl^-・H_2O の場合に対して QM/MM 法を用いて遷移状態構造とポテンシャルエネルギー変化を求め、Ru(II)-SO_2 錯体の異性化反応への結晶効果とその温度依存性を検討した。

【方法】 構造最適化およびエネルギー計算には B3PW91 汎関数による DFT 法を用いた。Ru の原子価電子には(311111/22111/411)基底を用い、内殻電子は Stuttgart グループの ECP で置き換えた。また O、S、Cl 原子には 6-311G++(2df, 2pd)基底、C、N 原子には 6-311++G**基底、H 原子には 6-31++G**基底を用いた。水中の溶媒効果は PCM 法により考慮し、結晶効果は周期境界条件に基づく QM/MM 法により取り入れた [2]。

本研究での QM/MM 法に基づく結晶中の構造決定は、次のような二段階で構築されている（Scheme 2）。反応中心以外の部分は MM 領域として点電荷と LJ 変数によるモデル化を行う。ここでは対称操作と格子ベクトルによる並進操作を用いる事で全結晶部分を再構成できる最小限の領域（参照領域）を QM 領域として選び、計算された RESP 電荷を MM 領域に再分布させる事で自己無撞着に MM 領域の構造と点電荷を決定した [2]。 得られた MM 領域を固定した条件下で、式(1)のエネルギー E_{crystal} が最少となるように反応中心部分の構造最適化を行った。



Scheme 2: QM/MM 法による結晶中の構造決定

$$E_{\text{crystal}} = E_{\text{QM}} + E_{\text{QM/MM}} = \left\langle \Phi_{\text{QM}} \middle| \hat{H}^{\text{gas}} \middle| \Phi_{\text{QM}} \right\rangle + \left(E_{\text{ES}} + E_{\text{LJ}} \right) \qquad \text{式(1)}$$

ここで MM 領域を固定した条件下では MM 分子の内部エネルギーと MM-MM 間の相互作用エネルギーが一定であると見做すと、変化量Δ E_{crystal} は反応中心（QM 領域）の構造変化に伴う全結晶のポテンシャルエネルギーの変化量に相当する事になる。

[$\text{Ru}^{\text{II}}(\text{NH}_3)_4(\text{SO}_2)(\text{pyridine})$] ($2\text{Cl}^-$・$\text{H}_2\text{O}$)の場合、単量体を QM 領域に選び、MM 領域は全て GS 構造、全て MS1 構造、全て MS2 構造であると仮定した３通りの MM モデルを構築した。特に MS2 構造において SO_2 分子がすべて同じ向きとなる結晶構造を仮定したが、それに加えて１層ごとに逆の向きとなる晶構造も MS2'構造として考えた。その後、QM 領域には異性化反応を起こす単量体とそれに隣接する２分子からなる合計３分子を選び、MM 領域の構造と電荷分布を固定して、結晶中での構造変化とエネルギー変化Δ E_{crystal} を計算した。構造最適化の際、着目する単量体の Ru 原子の位置は固定した。また本研究では、温度の違いは格子ベクトルの違いとしてエネルギー変化に反映されており、格子ベクトルは実験結果から引用した。

【結果】 気相中の GS→MS1 の異性化反応の構造変化では GS 構造と MS1 構造の間に MS2 構造が存在し、Ru と結合を作らない O 原子（O_{free}）が面外に回り込むように移動する（図 1）。Ru と結合を作る O 原子（O_{bond}）との距離 $r(\text{Ru-O}_{\text{bond}})$が短くなり、S との距離 $r(\text{Ru-S})$が長くなるが、それらは複雑な変化を示す事から、１次元の反応座標としては距離の差 $q = r(\text{Ru-O}_{\text{free}}) - r(\text{Ru-S})$ が有用である。この特徴は気相中のみならず溶液中、結晶中でも共通である。

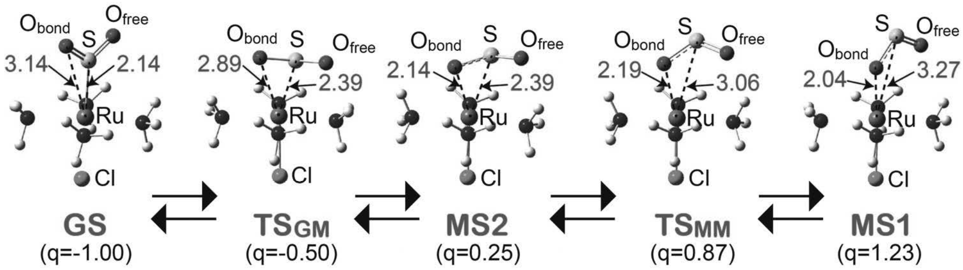


図 1: 気相中での異性化反応の構造変化（配位子 X = Cl）

配位子 X が Cl^-、H_2O、pyridine の場合について、気相中でのエネルギー E_{gas} および水中での自由

エネルギーΔA の変化には、大きな配位子効果と溶媒効果が確認された（図 2)。特に気相中ではトランス位の配位子 X が中性の H_2O や pyridine の場合は MS1 構造と GS 構造のエネルギー差は僅かであるのに対し、アニオン性の Cl^-の場合は MS1 構造が 10 kcal/mol 以上も不安定となる。この相違は配位子 X の種類による $Ru\text{-}SO_2$ 結合エネルギーの変化や X の電子供与・逆供与性や電荷の違いによると考えられ、検討する必要がある。また水中では配位子 X の種類による自由エネルギー変化の違いは小さくなるが、$X=H_2O$、pyridine の場合でさえ MS1 構造が GS 構造よりも 20 kcal/mol も不安定となり、エネルギー変化は気相中と大きく異なる。これは異性化反応に伴う内部エネルギーの変化だけでなく、反応中心と周囲分子との相互作用エネルギーの変化も重要である事を示唆する。結晶中でも同様のエネルギー差がみられる。

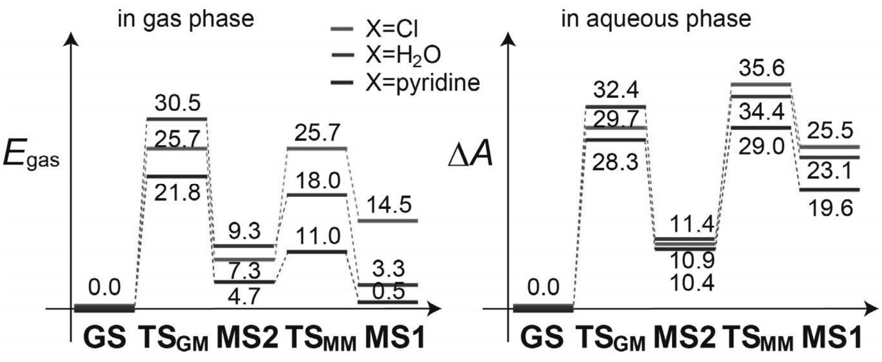


図 2: 気相中での E_{gas} および水中でのΔA の変化

反応中心以外の結晶分子が全て GS 構造である場合、全て MS1 構造である場合、全て MS2 構造である場合のいずれにおいても、水中の場合と同様に MS1 構造が GS 構造よりも大きく不安定化される事を示している（図 3)。ポテンシャルエネルギーの変化の形状は、MS1→MS2 の構造変化における障壁より MS2→GS の構造変化における障壁の方が高く、低温中では MS1 からの構造緩和が GS まで戻らず、MS2 で長時間存在する事を示唆する。特に MS2 構造と MS1 構造の間のポテンシャルエネルギー変化は周囲分子や温度に依存しており、MS1→MS2 の構造変化の障壁は周囲分子が GS 構造である場合よりも MS2 構造である場合の方が低く、また温度の上昇に伴い低くなる点も示唆している。この結果は、実験において熱を加える事で MS1 からの構造緩和が生じる点や、100K →140K 程度の温度上昇では MS2 の存在比が増加するものの GS の存在比は変化しない点などの傾向に一致している。

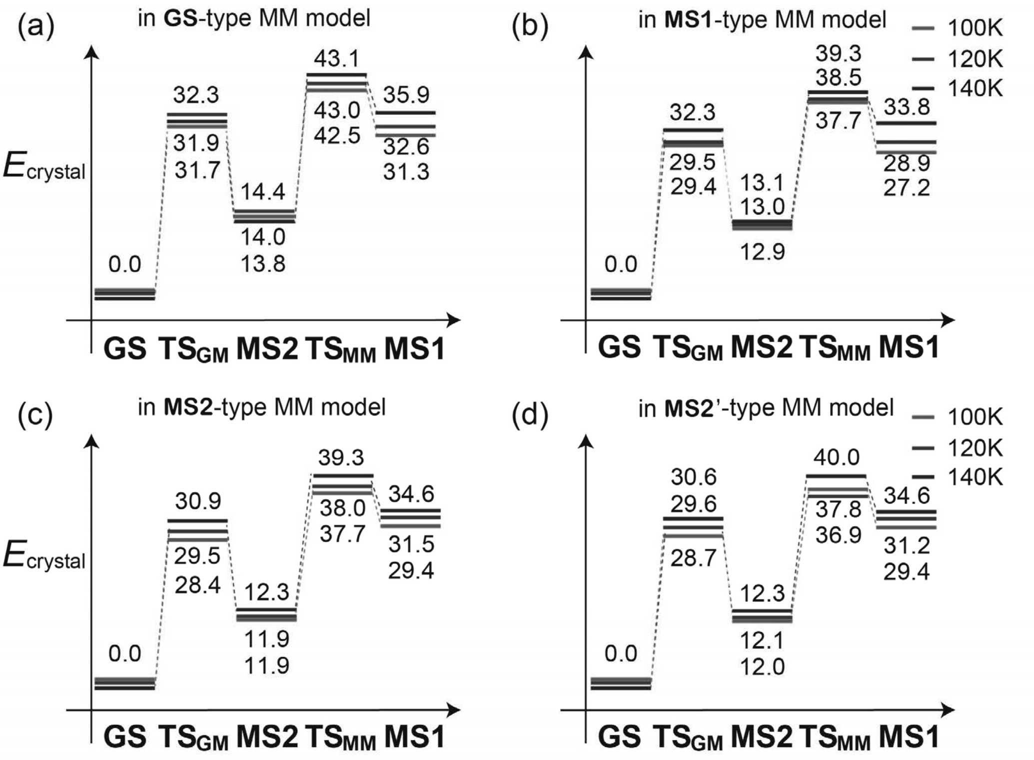


図 3: 結晶中での E_{crystal} の変化

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第8回分子科学討論会　広島　2014/9/21　1P122

4. その他

(1) 「結晶中におけるRu(II)-SO2錯体の異性化反応：配位子および結晶効果」福井謙一
京都大学第12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
2015/1/23　P46

Guixiang Zeng（會　桂香）

SPR Fellow, SAKAKI Group

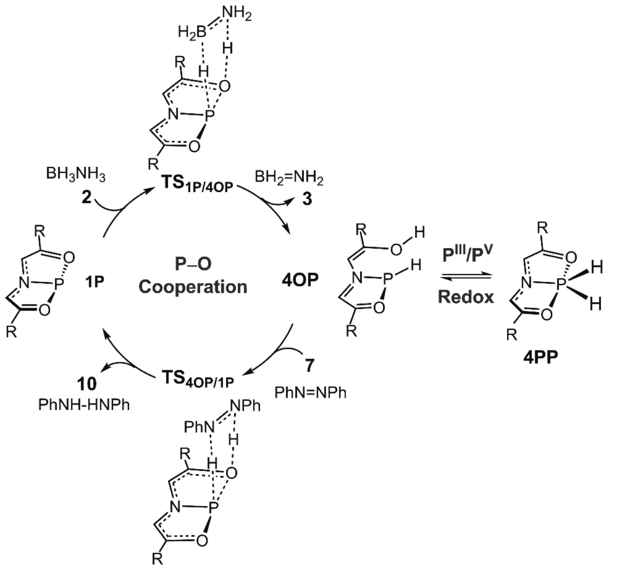
1. Summary of the research of the year

Catalytic Transfer Hydrogenation by Trivalent Phosphorus Compound: Electronic Process, Ligand Influence, and Prediction [1]

Due to the desire for cheaper and environmentally friendly catalysis, main-group element catalysts attract increasing interest in the past decade for their excellent reactivities similar to those of transition metal complexes. However, catalytic cycles performed by main-group element compounds are limited. Constructing catalytic cycles in the chemistry of main group element compounds are interesting, which would provide new possibilities in the catalyses. The reaction mode of the E−ligand (E=main group element) cooperation has not been reported for the main-group element compound until recently. In 2012, a trivalent phosphorus compound ADPO (**1P**) was reported to be able to catalyze the transfer hydrogenation reaction of azobenzene with NH_3BH_3; see Eq. 1.

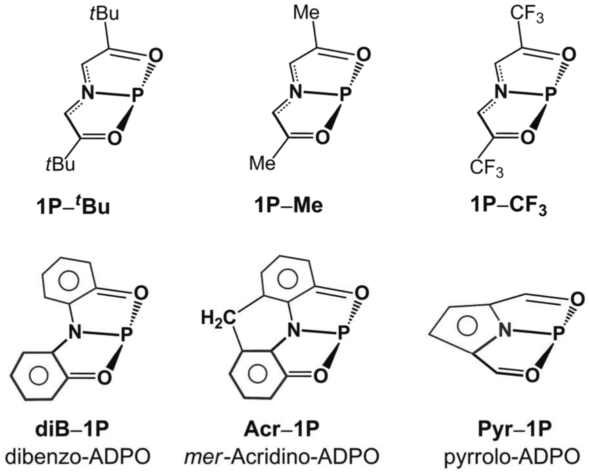
(1)

We found that the reaction occurs through an unprecedented phosphorus−ligand cooperation pathway, which resembles the metal−ligand cooperation; see Scheme 1. In the reaction, the structure around the phosphorus atom dramatically changes from a planar T-shaped geometry to a tetrahedral one. However, the electronic processes along such significant geometry changes are still ambiguous. Such information bodes well for our deeper understanding of the E-ligand cooperation reaction. Constructing new and more efficient main group element compounds is also of great importance for the development of the non-metal catalysis.



Scheme 1. Reaction Mechanism of the Reaction Shown in Eq. 1.

Here, we examined the substituent effect, framework effect and electronic processes of the reaction to explain these two effects. The catalysts examined in this work are shown in Scheme 2.



Scheme 2. Catalysts examined in this work.

First, the substituent influence on the reactivity of **1P** was examined. As shown in Figure 1, the Gibbs energy barriers ($\Delta G^{0\neq}$) of the NH_3BH_3 dehydrogenation step decreases in the order 27.1 kcal/mol (R=*t*Bu) > 26.6 kcal/mol (R=Me) > 20.9 kcal/mol (R=CF_3), indicating that the electron withdrawing (EWD) substituent is favorable for the dehydrogenation step. The EWD substituent (R=CF_3) also significantly stabilizes the intermediate **4OP** by 8.3 kcal/mol as compared with the R=*t*Bu case. For the transfer hydrogenation step, when **4OP** was taken as the reference, the $\Delta G^{0\neq}$ increases in the order 14.6 kcal/mol (R=*t*Bu) < 18.0 kcal/mol (R=Me) < 18.3 kcal/mol (R=CF_3). It indicates that the EWD substituent is unfavorable for this reaction step. However, if we take the initial reactants, that is more stable than **4OP**, as the energy reference, the $\Delta G^{0\neq}$ decreases in the order 30.1 kcal/mol (R= Me) > 28.1 kcal/mol (R=*t*Bu) > 23.5 kcal/mol (R=CF_3). It indicates that the EWD substituent facilitates the transfer hydrogenation step through its large stabilization of **4OP**.

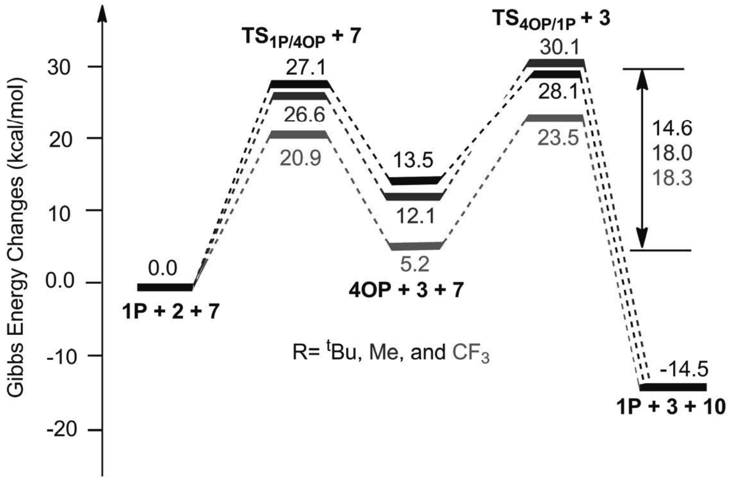


Figure 1. Reaction profile for the transfer hydrogenation reaction by **1P** with the substituents of *t*Bu, Me, and CF_3.

Second, we explored the framework effect on the reactivity of **1P**. As shown in Figure 2, the larger conjugate framework significantly enhances the activity of **1P**, where the $\Delta G^{0\neq}$ values considerably decrease from 26.6 and 30.1 kcal/mol (**1P−Me**) to 19.1 and 22.9 kcal/mol (**diB−1P**), respectively. More interesting thing is that the dehydrogenation step is exothermic by -4.7 kcal/mol whereas it is endothermic by 12.1 kcal/mol in the **1P−Me** catalyzed reaction. We will explain why **4OP** was stabilized by the dibenzo-ONO ligand so much below. Furthermore, when the benzene ringing in **diB−1P** was connected with a CH_2 linkage, $\Delta G^{0\neq}$ values further decrease to 13.9 and 17.5 kcal/mol, respectively. These calculation results indicate that the activity of **1P** was further enhanced.

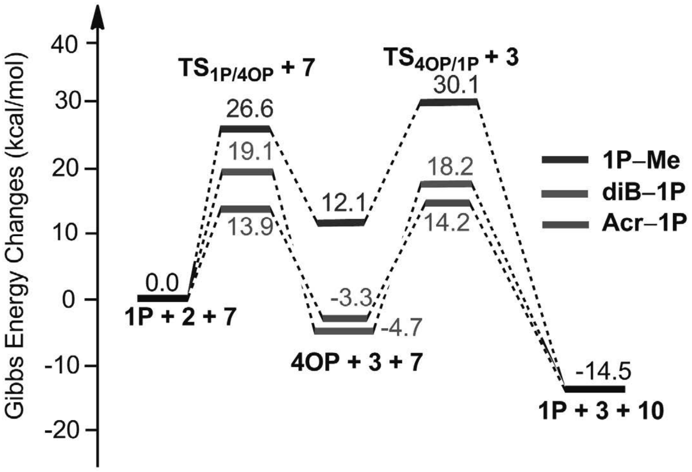


Figure 2. Reaction profile for the transfer hydrogenation reaction by **1P−Me**, **diB−1P**, and **Acr−1P**.

Third, we explored the electronic processed to explain the substituent and framework effects. In the dehydrogenation step, the population of each part of the ligand increases and the ligand population reaches to maximum in the intermediate **4OP**; see Figure 3. This is why the EWD substituent as well as the larger conjugated framework facilitate the dehydrogenation step and stabilizes **4OP**.

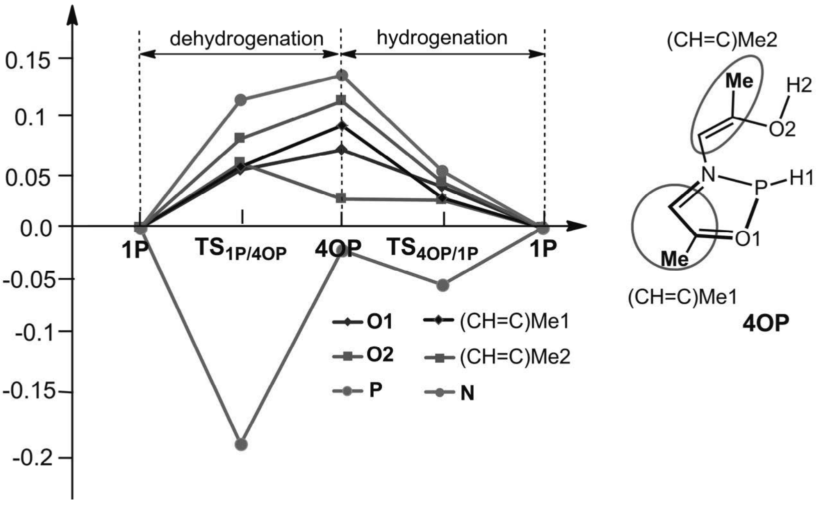
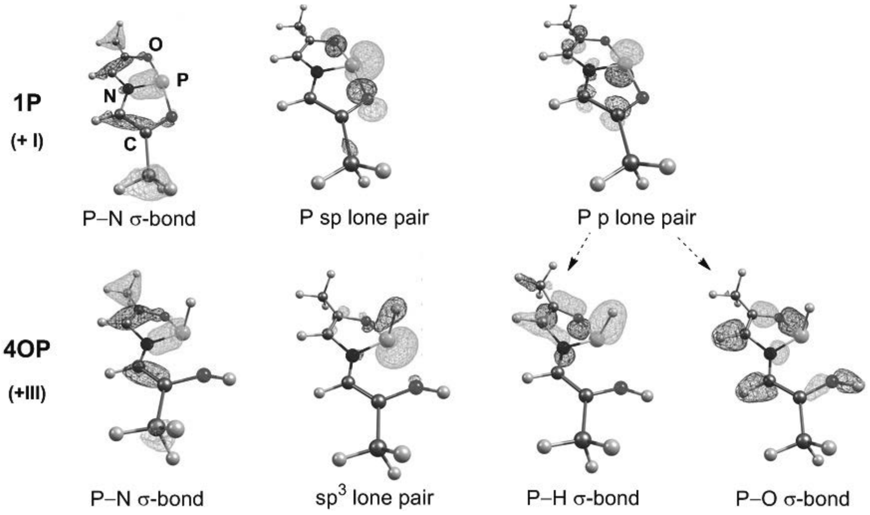


Figure 3. NBO analysis along the transfer hydrogenation reaction by **1P**.

Finally, we clarified the oxidation state of the phosphorus central atom. In **1P**, there is a hybrid sp lone pair orbital, a P−N σ−bonding orbital, a P−N π-bonding orbital and a P−N π* anti-bonding orbital around the phosphorus center; see the upper half of Scheme 3. In **4OP**, the P−N σ−bonding orbital, the hybrid sp lone pair orbital of the phosphorus element, and the nitrogen p lone pair orbital are retained; see the lower half of Scheme 3. However, the phosphorus p lone pair orbital disappears. Instead, one P−H σ-bonding orbital and one P–O σ-bonding orbital appear. Comparing the orbitals of **1P** and **4OP**, we come to the following conclusion: the phosphorus p lone pair was consumed to form the P−H and P−O σ-bonds when going from **1P** to **4OP** (the dehydrogenation step). As a result, the phosphorus oxidation state should increase by 2 in this reaction step. Note that the phosphorus center bears a typical tetrahedral geometry in **4OP**, indicating that the oxidation state of the phosphorus center is +III as well known. This interpretation is consistent with the presence of tree σ-bonding orbitals (P−N, P−O, and P−H) around the phosphorus center in **4OP**. Reversely, the phosphorus oxidation state would decrease by 2 when going from **4OP** to **1P** in the transfer hydrogenation step, indicating that the oxidation state of the phosphorus center in **1P** is +I. This understanding is also consistent with previous interpretation of the phosphorus oxidation state in **1P**.



Scheme 3. Important Kohn-Sham orbitals of **1P** and **4OP**.

In brief, transfer hydrogenation of azobenzene with NH3BH3 mediated by a trivalent phosphorus compound **1P** occurs through a phosphorus-ligand cooperation catalytic cycle. In this cooperation catalytic cycle, the phosphorus oxidation state changes between +I and +III. This is completely different from the transition metal-ligand cooperation catalytic cycle, where the metal oxidation state does not change. The reactivity of the phosphorus compound can be improved by a) electron withdrawing substituent; b) extending the C=C double bonds on the framework to large conjugated benzene rings (**diBen−1P**); c) Connecting the two benzene rings in **diBen−1P** with a CH_2 linkage (**Acr−1P**); d) Constructing a pyrrole ring around the apical atom. Larger conjugated framework promoted phosphorus compound is much more efficient than the electron withdrawing substituent promoted one.

Original papers

[1] Guixiang ZENG, Satoshi MAEDA, Tetsuya TAKETSUGU, and Shigeyoshi SAKSKI "Catalytic Transfer Hydrogenation by Trivalent Phosphorus Compound: Electronic Process, Ligand Influence, and Prediction" *In preparation.*

2. Presentation at academic conferences

Guixiang ZENG, Satoshi MAEDA, Tetsuya TAKETSUGU, and Shigeyoshi SAKSKI "Catalytic Transfer Hydrogenation by Trivalent Phosphorus Compound: Combination of Phosphorus-Ligand Cooperation and PI/PIII Redox" The 15th International Congress of Quantum Chemistry, Beijing June 8~13, **2015**

3. Others

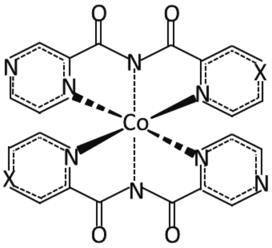
Guixiang ZENG, Satoshi MAEDA, Tetsuya TAKETSUGU, and Shigeyoshi SAKSKI "Mechanistic Study on C-H Alkylation of Alkenes with Alcohols Catalyzed by a Cationic Ru(II) Hydride Complex: Direct C-O Bond Activation" The 12th symposium of Fukui Institute for Fundamental Chemistry, Kyoto, January. 23, **2015**.

中垣　雅之

FIFC フェロー

1. 今年度の研究の要約（A4 3-5 ページ、図・表なども適宜挿入する）

【緒言】 Co(II)と 2 つのピラジン環をもつイミド配位子との錯体 $[Co(dpzca)_2]$ (スキーム 1)は、高温領域で 4 重項、低温領域で 2 重項をとり、スピンクロスオーバー現象を示す[1]。一方、ピラジン環の 1 つをピリジン環に置き換えた類似体 $[Co(pypzca)_2]$ は、低温においても高スピン状態のみをとる[2]。このような僅かな配位子の差によるスピンクロスオーバー現象の違いは興味深く、その起源の解明には金属錯体の電子状態と分子間相互作用の双方を正しく評価する詳細な理論研究が不可欠である。本研究では、結晶中でのスピン状態のエネルギー変化に着目し、スピンクロスオーバーに関する振る舞いの異なる２つの金属錯体について比較を行った。



$[Co(dpzca)_2]$: X=N
$[Co(pypzca)_2]$: X=C

スキーム 1

【計算方法】 $[Co(dpzca)_2]$ 及び $[Co(pypzca)_2]$ 錯体について、孤立分子及び結晶中での各スピン状態の構造と相対エネルギーを求めた。構造最適化には密度汎関数法を用い、QM/MM 法[3]を用いて周囲の分子の影響を考慮した。相対エネルギーは複数の計算法により評価した後、B3LYP-D 法及び GMC-QDPT 法で求めた。GMC-QDPT 法の参照関数には、Co に配位した N 原子の lone pair 軌道、Co 原子の 3d 及び 4d 軌道を活性軌道とした RASSCF(11e,12o)波動関数を用いた。遷移金属の内殻電子は Stuttgart-Dresden-Born の ECP で置き換え、原子価軌道には triple-zeta 基底関数を用いた。Co 原子に隣接した 6 つの N 原子には aug-cc-pVDZ を、その他の原子には cc-pVDZ を用いた。

【結果及び考察】 2 重項及び 4 重項状態の最適化構造は、それぞれ 90K 及び 298K における結晶構造とよい一致を示した(表 1)。Co 原子と配位する N 原子との結合長は、孤立系での計算においても実験値に近い値が得られたが、結晶内では平均誤差 0.01 Å で実験値によく一致した。また、カルボニル基の二面角で示される配位子の歪みは結晶中の分子間相互作用由来であり、QM/MM 法でのみ実験値に近い値が得られた。

表１． 最適化構造及び X 線結晶構造の構造パラメータ

	最適化構造				X 線結晶構造	
	2 重項 $^{a)}$		4 重項		90K$^{a)}$	298K
	孤立系	QM/MM	孤立系	QM/MM		
r(Co-N$_{ca}$) / Å	1.921 / 1.953	1.917 / 1.945	1.999	2.075	1.913 / 1.945	2.050
r(Co-N$_{pz}$) / Å	2.001 / 2.170	1.970 / 2.197	2.157	2.150	1.971 / 2.188	2.146
r(Co-N$_{pz}$) / Å	2.001 / 2.170	1.982 / 2.216	2.157	2.150	1.991 / 2.198	2.146
a(N$_{pz}$-Co-N$_{pz}$) / deg.	165.7 / 161.4	165.2 / 158.8	157.0	154.8	165.1 / 159.4	155.0
d(O-C-C-O) / deg.	0.0 / 0.0	3.7 / 18.6	4.5	21.2	2.4 / 18.6	18.4

a) 2 つの配位子が異なる値をもつ

表２に示すように、スピン状態間のエネルギー差は、密度汎関数法では用いる汎関数に大きく依存する。また、MP4(SDQ)法では 17.1 kcal/mol とかなり大きくなり、MP4 法はこの種の錯体には使用できない。GMC-QDPT 法では 4.3 kcal/mol であり、スピン転移が起こる実験事実を考慮すると妥当な値であると考えられる。また、M06L を除くすべての計算で 4 重項の方が 2 重項よりも安定であることから、低温結晶中の 2 重項状態の安定化は主に結晶中の分子間相互作用に起因していると考えられる。

表 2. [Co(dpzca)$_2$]のスピン状態間のエネルギー差⊿E(2et-4et) (kcal/mol)

method	⊿E	method	⊿E
PBE0	7.1	HF	49.1
B3LYP	2.4	MP2	16.6
B3LYP-D	0.7	MP3	26.7
M06	7.1	MP4(SDQ)	17.1
M06L	−1.8	RASSCF	23.8
		GMC-QDPT	4.3

分子間相互作用エネルギーの評価のため、結晶構造を用いたピラジン二量体のモデル計算を行い、CCSD(T)法の値と比較したところ、B3LYP-D 法が CCSD(T)と近い値を与えることから、QM/MM 法の計算には B3LYP-D 汎関数を用いた。

図 1 に示すように、[Co(dpzca)$_2$]の結晶中のスピン状態のエネルギー差は B3LYP-D 法を用いた計算では、低温結晶中の 2 重項状態が最も安定であり、高温結晶では 4 重項状態が 2 重項状態よりも安定である。QM 部分を GMC-QDPT 法で計算した場合はスピン状態の逆転は見られなかったが、高温結晶構造では低スピン状態が高スピン状態より 7.0 kcal/mol 不安定であるのに対して、低温結晶構造では 2.8 kcal/mol しか不安定とならず、低温構造における低スピン状態の安定性の増大という傾向は実験と一致している。

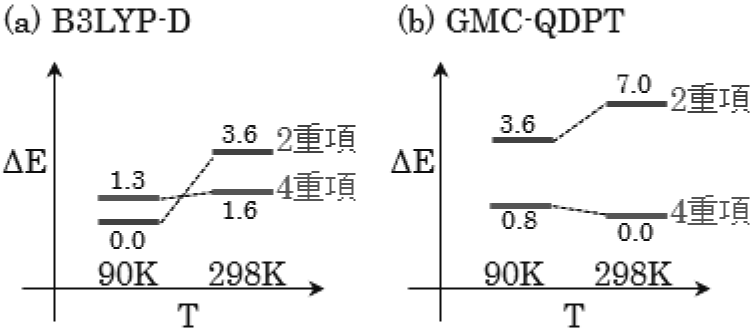


図 1 [Co(dpzca)$_2$]の結晶中のスピン状態のエネルギー差 (kcal/mol)

[Co(pypzca)$_2$]は、孤立分子の計算では構造,スピン状態のエネルギー差共に[Co(dpzca)$_2$]との違いは見いだせなかった。一方、結晶条件下の計算では、低温結晶構造における 2 重項状態の安定化が[Co(dpzca)$_2$]よりも小さく、B3LYP-D 法の結果ではどちらの結晶構造においても 4 重項が基底状

態として得られた(図 2)。この結果は[Co(pypzca)$_2$]ではスピンクロスオーバーが観測されないという実験結果に矛盾しない。

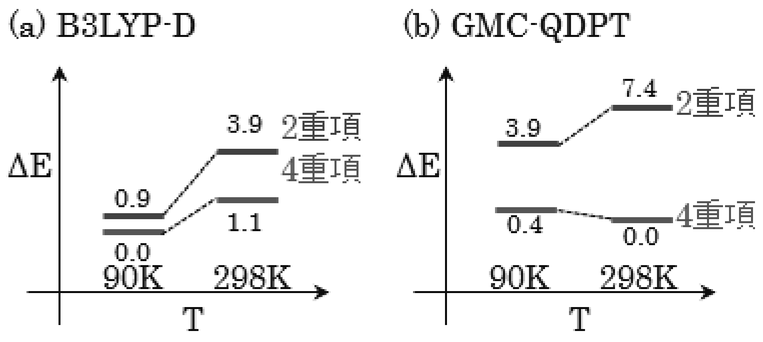
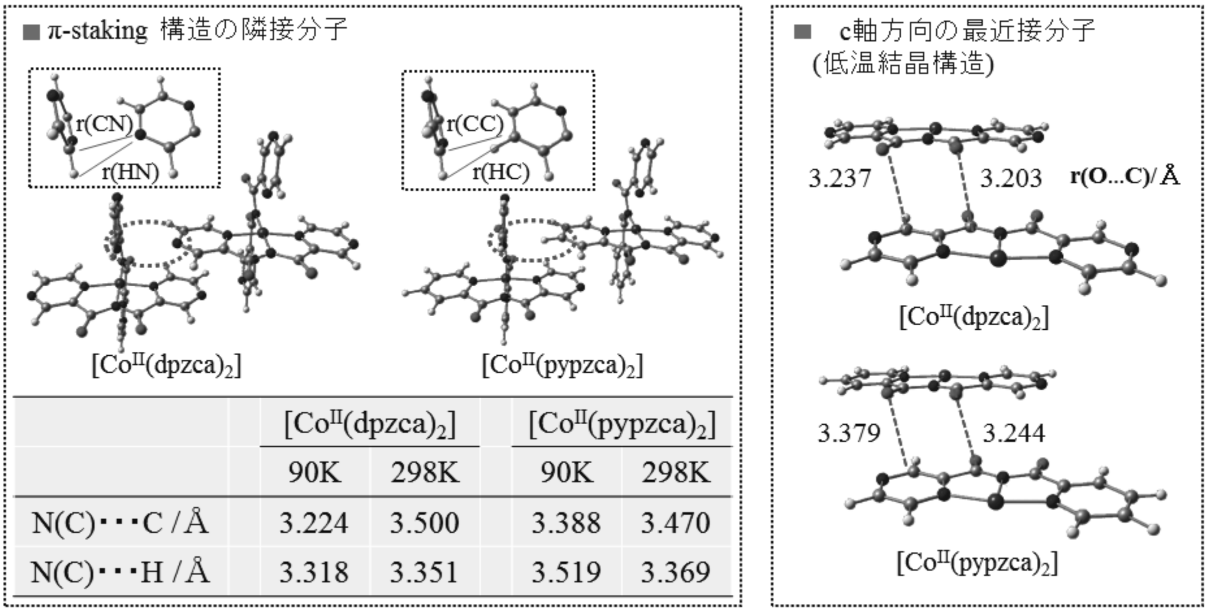


図 2 [Co(pypzca)$_2$]の結晶中のスピン状態のエネルギー差 (kcal/mol)

２つの錯体のスピン状態のエネルギー差の違いが結晶中でのみ見られることから、両者の結晶構造に関して比較を行った。[Co(dpzca)$_2$]では実験・計算結果の双方において、低温結晶構造の格子ベクトルが高温結晶構造よりも短い。一方、QM/MM 法で求められた[Co(pypzca)$_2$]の低温結晶構造の格子ベクトルは、高温結晶構造よりも長い。

[Co(dpzca)$_2$]結晶では低温結晶構造でピラジン環が垂直方向のピラジン環に近づき密なπ-staking 構造を形成する。一方、[Co(pypzca)$_2$] 結晶ではピリジン環の水素原子の立体反発が、隣接分子に近づくことを阻害している(図 3)。また、c 軸方向の隣接分子との間の分子間相互作用は主にカルボニル基によるπ-π及び CH-π相互作用である。[Co(dpzca)$_2$]の低温結晶構造ではカルボニル基が１つの隣接分子と相互作用に有利な様に近接する(図 3)。一方、[Co(pypzca)$_2$] 結晶では制限された構造変化によって、カルボニル基と隣接分子との距離が増加し分子間相互作用が減少する。



	[Co^{II}(dpzca)$_2$]		[Co^{II}(pypzca)$_2$]	
	90K	298K	90K	298K
N(C)･･･C /Å	3.224	3.500	3.388	3.470
N(C)･･･H /Å	3.318	3.351	3.519	3.369

図 3. QM/MM 結晶構造中の隣接分子との原子間距離

以上の結果から、[Co(dpzca)$_2$]と[Co(pypzca)$_2$]錯体の違いは電子状態ではなく分子間相互作用に由来し

【文献】

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[2] M. G. Cowan and S. Brooker, *Dalton Trans.*, **2012**, 41, 1465
[3] S. Aono and S. Sakaki, *Chem. Phys. Lett.* **2012**, 544, 77

2. 論文

(1) Masayuki Nakagaki, Shigeyoshi Sakaki
“CASPT2 study of inverse sandwich-type dinuclear 3d transition metal complexes of ethylene and dinitrogen molecules: similarities and differences in geometry, electronic structure, and spin multiplicity”
Phys. Chem. Chem. Phys. 17, 16294-16305(2015).

3. 学会発表

(1) 中垣 雅之，青野信治，榊 茂好
「Co(II)錯体の電子状態と分子間相互作用: スピンクロスオーバーの制御因子」
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(2) 中垣 雅之，青野信治，榊 茂好
「スピンクロスオーバーを示すCo(II)錯体の電子状態と結晶内分子間相互作用」
第 8 回分子科学討論会 2014 東広島　広島　2013/9/21-24 4P103 ポスター

4. その他

(1) 中垣 雅之，青野信治，榊 茂好
スピンクロスオーバーを示すCo(II)錯体の電子状態と結晶内分子間相互作用」
第12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 2015/1/23

Yue Chen

SPR Fellow

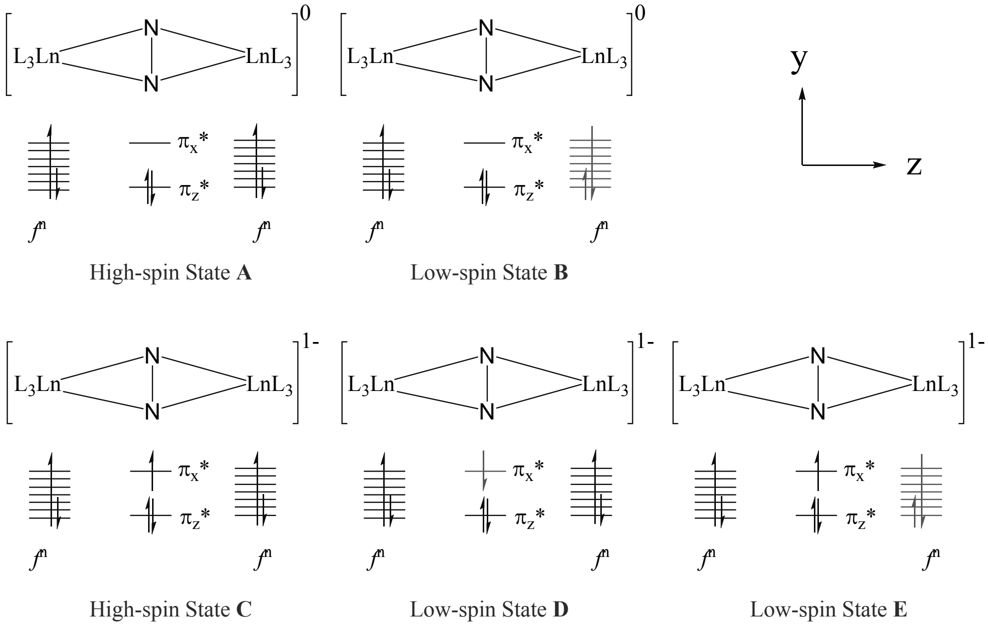
1. Summary of the research of the year

The Interaction between f Orbital and Radical N$_2$-bridge Ligand in Single-Molecule Magnet

Since the discovery of the magnetic relaxation properties of the Mn$_{12}$-acetate cluster, pursuing the efficient single-molecule magnet (SMM) that functions at higher temperature is still a grand challenge. A substantial spin reversal barrier $\boldsymbol{U}$ of the total spin S is essential for the magnetic property of SMM. Because the behavior of SMM is related to the total spin and the axial anisotropy $\boldsymbol{D}$ and U can be simply estimated by $\boldsymbol{U}=|\boldsymbol{D}|\boldsymbol{S}^2$, two strategies are expected to useful for designing the SMM with high $\boldsymbol{U}$ value. One is to maximize the total spin $\boldsymbol{S}$ by synthesis of high-nuclearity clusters. However, the clusters with many exchange-coupled transition metals can achieve large $\boldsymbol{S}$ value but is accompanied by low $\boldsymbol{D}$ value that induces finally low $\boldsymbol{U}$ value. This is likely due to the complicated interrelationship between $\boldsymbol{S}$ and $\boldsymbol{D}$. Therefore, in recent years, considerable attention has focused on the other strategy: designing SMM with large anisotropy barriers. Lanthanide ions are commonly employed in the SMM because its unquenched *f* orbital moments and strong spin-orbit coupling can produce high anisotropy. In 2003, Ishikawa et al. developed first mono-lanthanide SMM [LnPc$_2$]^n (Ln = Tb^{3+} and Dy^{3+}; H$_2$Pc = phthalocyanine; n = -1, 0, +1) which present considerably greater U value (260 cm^{-1}) than the reported 3*d*-SMM; see Scheme 1. Furthermore, the some polymetallic lanthanide complexes have been reported to possess clear SMM property and large U value. The understanding of magnetic interaction between lanthanide ions and between lanthanide and ligand is useful for improving the polymetallic lanthanide SMM. Recently, Long et al. found the radical bridge ligand can affect the SMM property significantly in dinuclear lanthanide complexes. For example, the N$_2^{3-}$ radical bridged lanthanide complex {[(Me$_3$Si)$_2$N]$_2$Ln(THF)(μ-η^2:η^2-N$_2$)(THF)Ln[(Me$_3$Si)$_2$N]$_2$}$^{1-}$ (abbreviated as [Ln(N$_2$)Ln]$^{1-}$, Ln = Gd, Tb, Dy, Ho, Er) have remarkable electronic structure. In Gd complex, a strong intramolecular exchange coupling (J = -27 cm^{-1}) was observed. The Tb complex is marked as the most successful SMM to date due a record blocking temperature T$_B$ of 14 K for M(H) hysteresis, and the Dy complex also shows T$_B$ of 8.4 K. However, the Ho and Er complexes do not show any M(H) hysteresis. Because these complexes has quite similar geometries in which the N-N bond length is between 1.394 and 1.408Å, the difference of Ln properties influence the SMM properties significantly. In this work, we theoretically analyzed the electronic structure of [Ln(N$_2$)Ln]$^{1-}$ (Ln = Gd, Tb, Dy, Ho, Er) and revealed the interaction between N$_2$-birdged and lanthanide.

Because the Gd^{3+} has f^7 electronic configuration, the electronic structure of [L$_3$Gd(N$_2$)GdL$_3$]^n (n = 0, -1) is more simple than other lanthanide analogues. We firstly analyzed the electronic structure of Gd complexes, and then revealed the similarity and difference with other lanthanide complexes. In the neutral [L$_3$Gd(N$_2$)GdL$_3$], the N^2-bridge ligand is expected to be N$_2^{2-}$ in which the π_x^* is empty and π_z^* is doubly occupied. The two Gd center can couple via two manner high-spin state (State **A**) and low-spin state (State

B); see Scheme 1. Since the one additional electron in $[L_3Gd(N_2)GdL_3]^{1-}$ is supposed in π_x^* of N_2^{3-} bridge-ligand, the three spin centers (two Gd^{3+} and N_2^{3-}) can couple into three spin states; see high-spin state **C**, low-spin state **D**, and low-spin state **E** in Scheme 1. The difference in geometry is tiny between state **A** and **B**. The N1-N2 bond length of bridged N_2 ligand is 1.234 Å that agrees well with experimental value of 1.278 Å. In state **A**, the spin density on Gd1, N_2, and Gd3 are 7.07, -0.05, and 7.07, respectively, while they are 7.08, 0.00, and -7.08 in state **B**. In both state **A** and **B**, the π_x^* is empty and π_x^* is doubly occupied, indicating that the electronic structure of N_2-bridge ligand is N_2^{2-}; see Figure S1. The energies of state **A** and **B** are nearly the same; see Table 1. The same geometry and energy indicates that the two Gd atoms in state **A** and **B** have little exchange correlation to each other. For anionic complex $[L_3Gd(N_2)GdL_3]^{1-}$, the low-spin state **D** and **E** is lower than the high-spin state C but their geometries have little difference; see Figure 1. The geometries of state **A-D** are Ci symmetrical but state **E** is C1 symmetrical. For Tb, Dy, Ho, and Er systems, the similar case in the geometry was found. The state **A** and **B** are nearly degenerate, but the energies of state **D** is not always the lowest one.



High-spin State **A** Low-spin State **B**

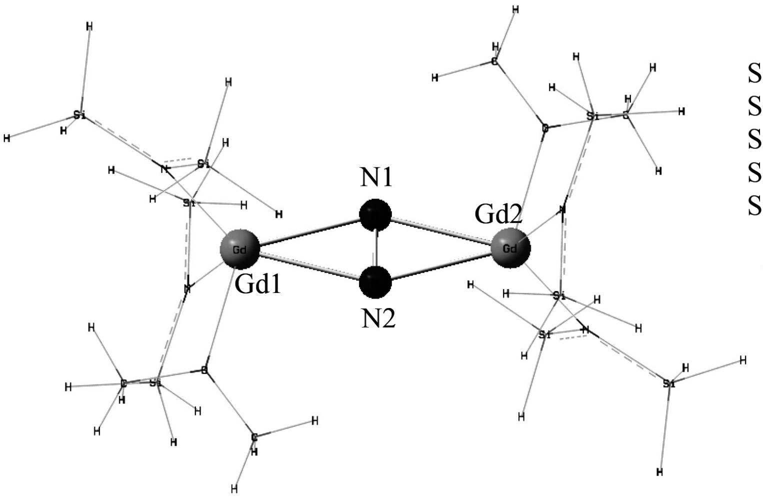
High-spin State **C** Low-spin State **D** Low-spin State **E**

Scheme 1. Different spin-coupling states.

Table 1. The energies of different spin states calculated by DFT.

	Gd	Tb	Dy	Ho	Er
State A	22.5	22.2	21.0	23.0	27.8
State B	22.5	22.2	21.0	23.0	26.2
State C	0.0	0.0	0.0	0.0	0.0
State D	-1.6	0.4	0.0	-0.4	-1.9
State E	-0.8	-1.0	-3.0	0.0	-1.0

Unit: kcal/mol.



	Gd1-N1	Gd2-N1	N1-N2	Gd1-N2	Gd2-N2
State A	2.335	2.348	1.234	2.348	2.335
State B	2.335	2.348	1.234	2.348	2.335
State C	2.210	2.217	1.385	2.217	2.210
State D	2.209	2.215	1.388	2.215	2.209
State E	2.209	2.218	1.386	2.214	2.211

Figure 1. The geometries of different states optimized by DFT.

Since the little influence of ligand field on the splitting *f* orbitals, these systems have strong multi-configuration character. The electronic structures of state **C** and **D** are analyzed by CASPT2/CASSCF method. The 14 *f* orbitals of two lanthanide atoms and the π_x^* of N_2 moiety were included in the CASSCF calculation; see Figure 2. The π_z^* of N_2 moiety was not involved in the calculation of Tb-Er because it is always doubly occupied. For Gd complexes, because CASSCF calculation of state **C** (16-tet) requires 16 orbitals at least, π_z^* of N_2 moiety was involved.

Since Gd has f^7 configuration, the state **C** and **D** are 16-tet and 14-tet, respectively. Four 16-tet states and four 14-tet states were calculated by CASPT2/CASSCF(17e,16o). Among these states, there are three low-lying energy state ($X^{14}Au$, $a^{16}Au$, and $A^{14}Ag$) and five high energy states. The ground state is $X^{14}Au$, and $a^{16}Au$ and $A^{14}Ag$ are only 0.6 and 0.7 kcal/mol above $X^{14}Au$, but the high energy states are above the ground state by 49 kcal/mol at least. Because only these low-lying states are crucial to the magnetic properties of Gd complex, the detailed electronic structure of these states were present here but the high energy states were presented in supporting information.

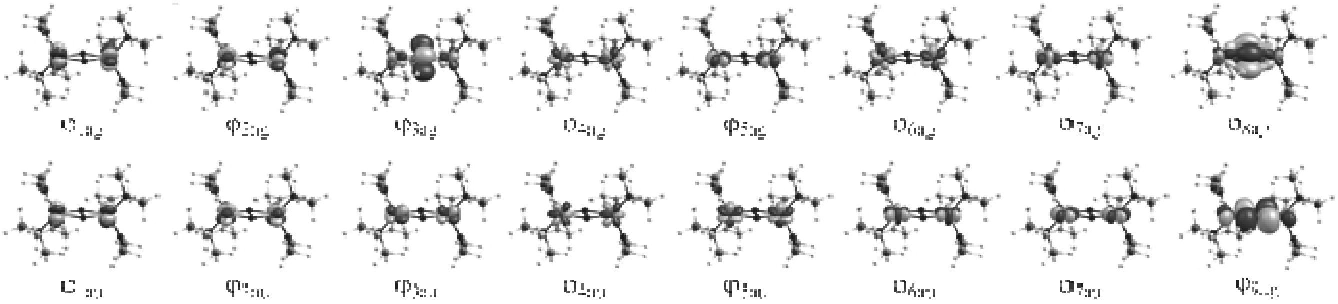


Figure 2. The active orbitals involved in the casscf calculation.

In $X^{14}Au$, four configurations $\varphi_{3ag}^{2}\varphi_{8ag}^{0}$, $\varphi_{3ag}^{0}\varphi_{8ag}^{2}$, $\varphi_{3ag}^{\alpha}\varphi_{8ag}^{\beta}$, and $\varphi_{3ag}^{\beta}\varphi_{8ag}^{\alpha}$ with respective weight of 30%, 24%, 18%, and 18% contribute most.[30] The φ_{3ag} is the bonding orbital between $\delta_{f_{xyz}}$ of Ln_2 moiety and π_x^* of N_2 moiety, and the φ_{8ag} is the anti-bonding orbital; see Figure 3. There results indicate a weak bonding interaction between f_{xyz} of Gd and π_x^* of N_2 moiety. The Mulliken spin population on Gd_1, N_2 moiety, and Gd_2 are 6.91, -0.81, and 6.91, respectively. It seems like there is one β-spin electron localized on N_2 moiety which couples with seven α-spin electron of each Gd atoms formally. Actually, the negative spin population on N_2 moiety arises from the spin polarization of φ_{8ag} induced by the α-spin electrons of Gd atoms; see Figure 3. Therefore, the formally anti-spin coupling state low-spin state **D** is the outcome of spin-polarization.

Table 2. The Mulliken spin population of the Ln and N_2 moiety in the ground state

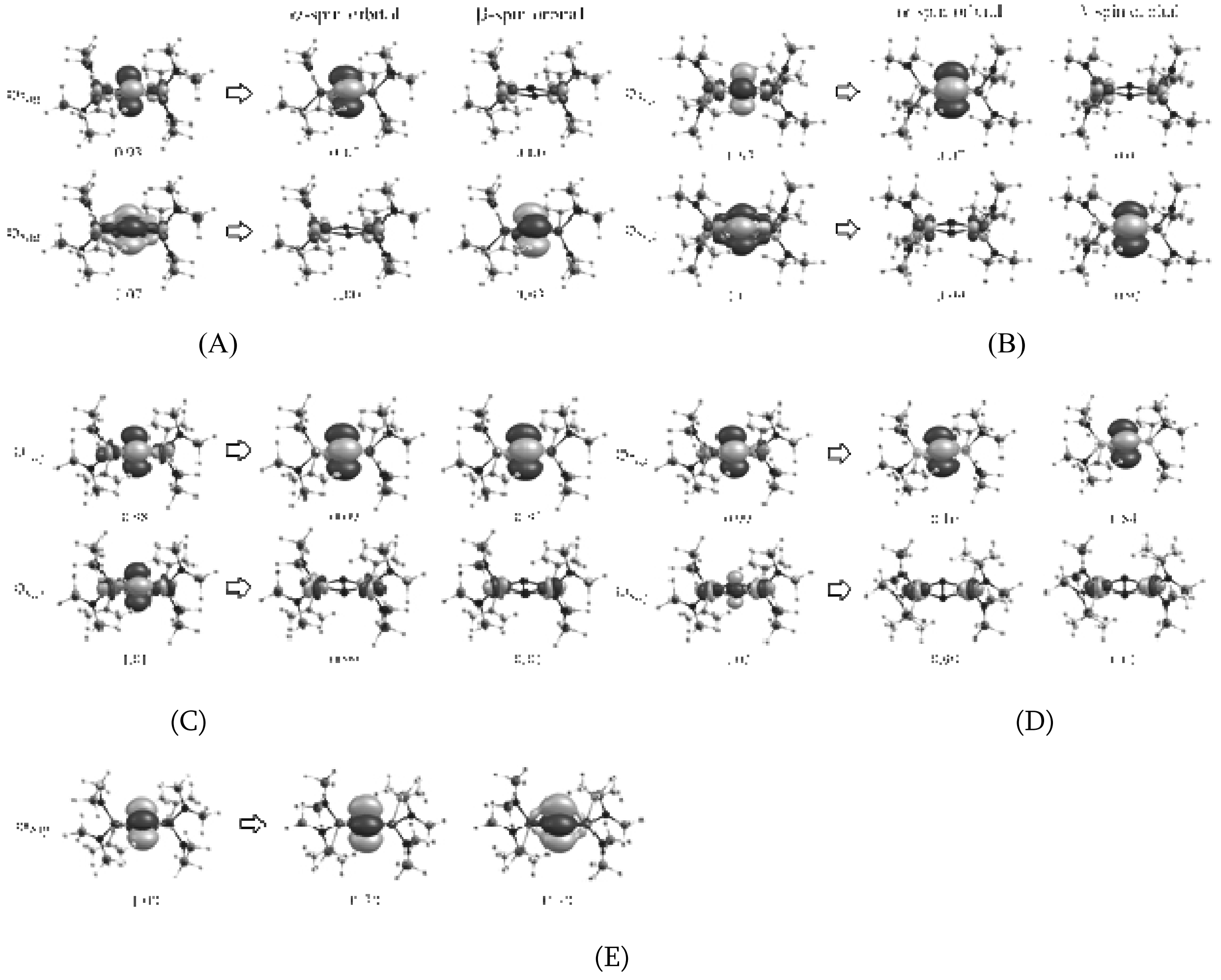
	Ground state	Gd	N_2
$Gd(N_2)Gd$	$X^{14}Au$	6.91	-0.81
$Tb(N_2)Tb$	$X^{12}Ag$	5.90	-0.79
$Dy(N_2)Dy$	$X^{10}Au$	4.88	-0.76
$Ho(N_2)Ho$	$X^{8}Ag$	3.81	-0.62
$Er(N_2)Er$	$X^{6}Au$	2.79	-0.58

In $a^{14}Ag$, there is no dominant configuration but 16 important configurations contributes nearly 100%, and they are $\varphi_{iag}^{2}\varphi_{iau}^{0}$, $\varphi_{iag}^{0}\varphi_{iau}^{2}$, $\varphi_{3ag}^{2}\varphi_{8ag}^{0}$, and $\varphi_{3ag}^{0}\varphi_{8ag}^{2}$ (i = 1-7) where the φ_{iau} and φ_{iag} correspond to the Ag and Au symmetrical molecular orbital composed mainly of the same atomic *f* orbital of Gd.[30] The Mulliken spin population on Gd_1, N_2 moiety, and Gd_2 are 6.03, 0.93, and 6.03, respectively, which is different from that in $X^{14}Au$. The lower spin population on Gd is induced by the exchange coupling between two Gd atoms and coupling between N_2 moiety and Gd.

As expected, $A^{16}Au$ has one main configuration with weight of nearly 100%, in which the π_z^* (φ_{ag8}) are double occupied and π_x^* (φ_{ag9}) is singly occupied and the rest *f* orbitals are singly occupied. The Mulliken spin population on Gd_1, N_2 moiety, and Gd_2 are 7.03, 0.92, and 7.03, respectively. This state is the well-known high-spin coupled state. In $A^{16}Au$, the f_{xyz} of Gd and π_z^* of N_2 moiety do not have bonding overlap unlike that in the ground state $X^{14}Au$.

It is apparent that the low-spin state $X^{14}Au$ is more stable than the high-spin state $A^{16}Au$, which is consistent with the experimental observation. The δ-type bonding overlap between f_{xyz} of Gd and π_x^* of N_2 moiety is crucial to the stability of $X^{14}Au$ and expected to be responsible for the single magnet manner.
Though Tb(III) has only one more electron than Gd(III), the electronic structure of Tb complex becomes more complicated. The energy differences among of the ten states (five 14-tet states and five12-tet state) are less than 3.0 kcal/mol. Similar to Gd complex, the ground state of Tb complex is low-spin state $X^{12}Ag$ instead of high-spin 14-tet state. The lowest two excited 12-tet states ($A^{12}Au$ and $B^{12}Ag$) are 0.3 and 1.1 kcal/mol above the ground state, and the lowest two excited 14-tet states ($a^{14}Au$ and $b^{14}Ag$) are both about 1.3 kcal/mol higher. Similar to the ground state $X^{14}Au$ of Gd complex, there no dominant configuration in $X^{12}Ag$ of Tb complex, but four configurations $\varphi_{1ag}^{2}\varphi_{1au}^{\alpha}\varphi_{2ag}^{\alpha}\varphi_{2au}^{2}\varphi_{3ag}^{2}\varphi_{8ag}^{0}$, $\varphi_{1ag}^{\alpha}\varphi_{1au}^{2}\varphi_{2ag}^{2}\varphi_{2au}^{2}\varphi_{3ag}^{2}\varphi_{8ag}^{0}$, $\varphi_{1ag}^{2}\varphi_{1au}^{\alpha}\varphi_{2ag}^{\alpha}\varphi_{2au}^{2}\varphi_{3ag}^{0}\varphi_{8ag}^{2}$, and $\varphi_{1ag}^{\alpha}\varphi_{1au}^{2}\varphi_{2ag}^{2}\varphi_{2au}^{2}\varphi_{3ag}^{0}\varphi_{8ag}^{2}$ contribute significantly with total weight of 55%, indicating important role of the bonding interaction (φ_{3au} and φ_{8ag}) between f_{xyz} of Tb and π_z^* of N_2 moiety. The Mulliken spin population on Tb and N_2 moiety are 5.90 and -0.79, respectively. The negative spin population on N_2 moiety should also arise from the spin polarization; see Figure 3. The first excited 12-tet state $A^{12}Au$ has nearly the same occupation numbers and spin population but different irreducible representation to the ground state. The $a^{14}Au$ contains two configurations $\varphi_{1ag}^{\alpha}\varphi_{1au}^{2}\varphi_{2ag}^{\alpha}\varphi_{2au}^{2}$ and $\varphi_{1ag}^{2}\varphi_{1au}^{\alpha}\varphi_{2ag}^{2}\varphi_{2au}^{\alpha}$ with weight of 50% and 50%, and $b^{14}Ag$ contains two configurations $\varphi_{1ag}^{2}\varphi_{1au}^{\alpha}\varphi_{2ag}^{\alpha}\varphi_{2au}^{2}$ and $\varphi_{1ag}^{\alpha}\varphi_{1au}^{2}\varphi_{2ag}^{2}\varphi_{2au}^{\alpha}$ with weight of both 50%.

The a^{14}Au and b^{14}Ag both have similar occupation numbers to the ground state but the positive spin population (0.93) on N_2 moiety. However, the bonding overlap between f_{xyz} of Tb and π_x^* of N_2 moiety was not found, like the case in the high-spin state A^{16}Au of Gd complex.


(A) (B)

(C) (D)

(E)

Figure 3. Spin polarization in the ground state of Gd complex (A), Tb complex (B), Dy complex (C), Ho complex (D), and Er complex (E).

The ground state of Dy complex is how-spin 10-tet and nearly triply degenerate (X^{10}Au, X'^{10}Au, and X''^{10}Au). There are six low-lying excited 10-tet states that are 0.3-0.5 kcal/mol above the ground state. The energies of all the calculated excited state are among 0.3 and 1.3 kcal/mol relative to ground state. Different from the ground states of Gd and Dy complex, there is no bonding overlap between f_{xyz} of Dy and π_x^* of N_2 moiety but the overlap between f_{yz^2} of Dy and π_x^* of N_2; see Figure 3. The spin distribution on Dy and N_2 are 4.88 and -0.76, respectively, where the negative spin population on N_2 moiety is also attributed to the spin polarization.

The Ho has a low-spin ground state X^8Ag and the Er complex has a low-spin ground state X^6Au. In both states, there is no bonding overlap between f_{xyz} of Dy and π_x^* of N_2 moiety but weaker overlap between f_{xyz} of Ln and π_x^* of N_2 moiety; see Figure 3. The Mulliken spin population on the N_2 moiety in Ho and Er complexes are -0.62 and -0.58, respectively; see Table 2. Meanwhile, there are a lot of low-lying excited state, including both high-spin and low-spin states.

From Gd to Er complex, there are some similarities. (1) All the ground states are the low-spin coupled state, where the N_2 has negative spin population. (2) The multi-reference character is significant since many configurations contribute comparably to the ground state; (3) There are a lot of low-lying excited states. (4) The high-spin state and low-spin state have little difference in geometry. Meanwhile, the differences are important. (1) In Gd and Tb complexes, the f_{xyz} of Ln and π_x^* of N_2 can form a δ-type bonding and anti-bonding orbitals. However, only the overlap between f_{yz^2} of Ln and π_x^* of N_2 instead of δ-type bonding overlap above was observed in Dy, Ho, and Er complexes; see Figure 3. In addition, the overlap between f_{yz^2} of Ln and π_x^* of N_2 becomes weak from Dy to Er. (2) From Gd to Er, the number of low-lying excited states increases because of the increasing of *f*-electrons. (3) The spin population of N_2 on the ground state becomes less negative from Gd to Er.

Based on the results above, the interaction between Ln and N_2 moiety among these five complexes can be categorized into two types. The first is the δ-bonding type that includes Gd and Tb complexes, and the second is general orbital overlap type that includes Dy, Ho, and Er complexes. These two different types are related to two factors: *f*-orbital splitting and *f*-orbital energy. Even though *f*-orbital is inner-shell and not affected by the ligand field significantly, the small splitting of *f*-orbital has crucial role to the magnetic properties at very low temperature. The splitting of *f*-orbital can be reflected by the change of *f*-orbital occupation number on the ground state from Gd to Er. In Gd complex, the $\varphi_{1au}(f_{x(x^2-3y^2)})$, $\varphi_{2au}(f_{y(3x^2-y^2)})$, $\varphi_{3au}(f_{xyz})$, $\varphi_{4au}(f_{z(x^2-y^2)})$, $\varphi_{5au}(f_{z^3})$, $\varphi_{6au}(f_{xz^2})$, and $\varphi_{7au}(f_{yz^2})$ are all singly occupied,[31] where the term in parenthesis is the major component of corresponding φ_i. With the increase of one electron from Gd to Tb, the occupation numbers of φ_{2au} and φ_{3au} increase to about 1.5, whereas the other orbitals are still singly occupied. From Tb to Dy, the occupation number of φ_{3au} to φ_{4au} increase to about 1.5 too, but φ_{5au} to φ_{7au} are still singly occupied. From Dy to Ho to Er, only the φ_{7au} is still singly occupied. We can deduce that the *f*-orbital energy order in these complexes is $f_{x(x^2-3y^2)} \sim f_{y(3x^2-y^2)} < f_{xyz} \sim f_{z(x^2-y^2)} < f_{z^3} < f_{xz^2} < f_{yz^2}$, but the orbital splitting is small. Among 7 *f*-orbital, only f_{xyz} can form δ-bonding overlap with π_x^* of N_2. From Tb to Dy, the disappearance of δ-bonding overlap is likely due to the decrease of f_{xyz} of Dy since the π_x^* energy changes little. Because (1) the f_{yz^2} is the highest *f*-orbital, (2) the occupation number of f_{xyz} increases, and (3) orbital lobes of f_{yz^2} extends towards π_x^*, the overlap between f_{yz^2} and π_x^* occurs. From Dy to Er, the f_{yz^2} energy decreases continuously, the overlap degree between f_{yz^2} and π_x^* decreases.

2. Original papers

(1) **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. 43, 11478-11492(2014)

(2) Shubin Yang, Changlun Chen, Yue Chen, Jiaxing Li, Dongqi Wang, Xiangke Wang
"Competitive Adsorption of PbII, NiII, and SrII Ions on Graphene Oxides: A Combined Experimental and Theoretical Study”
ChemPlusChem 80(3),480–484 (2015)

3. Presentation at academic conferences

(1) Yue Chen, Shigeyoshi Sakaki
“Catalysis of Mo-Mo Quintuple Bond in Synthesis of Benzene from Alkyne. A Theoretical Study”
The XXVI International Conference on Organometallic Chemistry (ICOMC 2014), July 13 to 18, 2014, Sapporo, Japan

4. Others

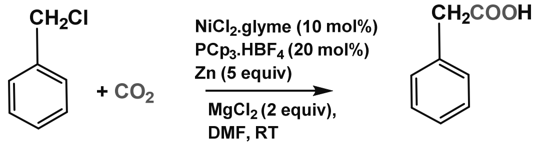
(1) Yue Chen, Shigeyoshi Sakaki
“Theoretical Study on the H2 and X-H bond Activation by Mo-Mo quintuple bond”
第12回京都大学福井謙一記念研究センターシンポジウム -諸熊奎治先生傘寿記念-, Kyoto. Jan. 23, 2015

Sayyed Fareed Bhasha

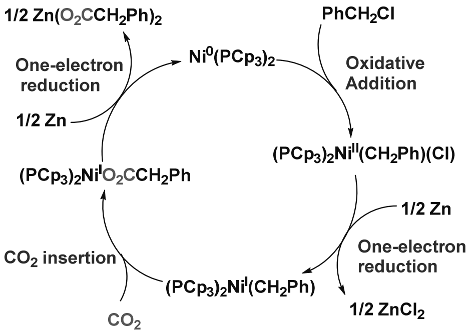
Advanced Scientist

1. Summary of the research of the year

The increase of carbon dioxide (CO_2) content in the atmosphere is a serious threat to the environment. The development of the transformation of CO_2 into useful chemicals has been one of the important topics in the last decade. In this regard, various attempts have been made using transition-metal complexes. Among various CO_2 transformations, direct carboxylation of organic halide with CO_2 has been elusive until recently, though such direct carboxylation is attractive because of the importance of carboxylic acids for valuable applications. Martin and co-workers introduced the transformation of benzyl halide to phenylacetic acid with CO_2 using a Ni catalyst (Scheme 1). This Ni-catalytic system contains Zn powder and $MgCl_2$. If Zn powder is absent, no catalytic conversion occurs. If $MgCl_2$is not added, the yield is very low. The experimentally proposed reaction mechanism suggests that a Ni^I intermediate might be crucial in the catalytic cycle, as shown in Scheme 2. However, mysterious is the role of $MgCl_2$; it is not clear why $MgCl_2$ plays a crucial role in providing good yield of the product. We theoretically investigated this Ni-catalyzed carboxylation of benzyl chloride to phenylacetic acid to elucidate the role of $MgCl_2$. All the calculations were carried out with the B3LYP-D functional using Gaussian 09 package.



Scheme 1. Ni-catalyzed carboxylation of $PhCH_2Cl$ with CO_2.



Scheme 2. Plausible mechanism for the Ni-catalyzed carboxylation reaction of $PhCH_2Cl$ with CO_2.

In this reaction, it is likely that the catalytic cycle begins with the oxidative addition of benzyl chloride **1** to $Ni(PCp_3)_2$ **2** (Cp = cyclopentyl); see scheme 2. Starting from **3**, the oxidative addition of the $PhCH_2$-Cl bond occurs to afford a four-coordinated Ni^{II}-intermediate *cis*-$Ni^{II}(Cl)(CH_2Ph)(PCp_3)_2$ **4** via a transition state $\mathbf{TS_{3\text{-}4}}$. The $\Delta G^{\circ\ddagger}$ is 9.3 kcal/mol, indicating that the oxidative addition easily occurs (Fig 1). The complex **4** isomerizes to a more stable trans-form $Ni^{II}(Cl)(CH_2Ph)(PCp_3)_2$ **5**.

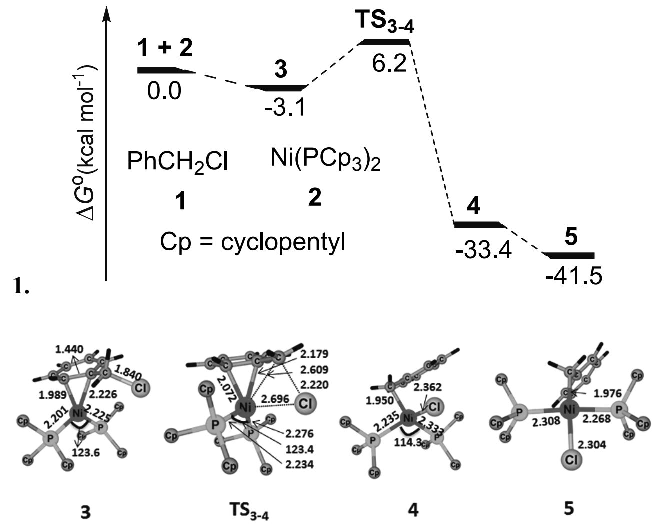


Fig. 1 Changes in the Gibbs energy and geometry by the oxidative addition of 1 to 2. Cp represent cyclopentyl group. Bond lengths are in Å and angles in degree.

$MgCl_2$ interacts with the CO_2 moiety of Ni(I) species formed after the one-electron reduction of **5** to form an adduct $Ni(CH_2Ph)(PCp_3)_2(\eta^1\text{-}CO_2)(MgCl_2)$. The Mg-O distance (1.951 Å) and the O-C-O angle (133.6°) which is smaller than in Ni(I)-CO_2 adduct. These geometrical features indicate that the Mg-O and Ni-CO_2 interactions are considerably stronger in $Ni(CH_2Ph)(PCp_3)_2(\eta^1\text{-}CO_2)(MgCl_2)$ than. The $\Delta\Delta G^{0\ddagger}$ ($\Delta G^{0\ddagger}$($\mathbf{TS_{8\text{-}9}}$)-$\Delta G^{0\ddagger}$($\mathbf{TS_{12\text{-}13}}$)) value (12.0 kcal/mol) strongly suggests that $MgCl_2$ accelerates the CO_2 insertion into the Ni-CH_2Ph bond as a non-innocent additive.

The final step is the one-electron reduction of **13** with Zn. The calculated ΔG^0 value for this step is -12.4 kcal/mol. The anion exchange between $Zn(O_2CCH_2Ph)_2$ and $MgCl_2$ occurs with a considerably negative ΔG^0 of -15.4 kcal/mol, indicating that the formation of $Mg(O_2CCH_2Ph)_2$ is thermodynamically more favourable. These results suggest that $MgCl_2$ also assists the one-electron reduction. Because $MgCl_2$ is consumed in the reaction, two-equivalent of $MgCl_2$ to benzyl chloride is necessary (Scheme 1).[7] The Gibbs free energy profile for the total catalytic cycle clearly indicates that $MgCl_2$ promotes the carboxylation of benzyl chloride with CO_2.

In conclusion, we proposed that $MgCl_2$ plays crucial roles in the CO_2 insertion as a non-innocent additive and one-electron reduction process. To the best of our knowledge, this is the first report that recognizes these roles of $MgCl_2$ and provides correct understanding of the roles in the CO_2 conversion reaction.

3. List of original papers

1. Sayyed, F. B.; Sakaki, S. "The Crucial Roles of MgCl2 as a Non-innocent Additive in the Ni-Catalyzed Carboxylation of Benzyl Halide with CO2". Chem.Commun. 2014, 50, 13026-13029.

4. 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).

5. List of presentations at meetings

(1) The Crucial role of Ni(I) species in Ni-catalyzed Carboxylation of Aryl Halides with CO2: Theoretical Study. F. B. Sayyed, Y. Tsuji and S. Sakaki, ICOMC2014, July13-17, Sapporo

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、昨年度に引き続き、長時間に亘って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】

われわれが目指してゆく低炭素社会に向けた、次世代エネルギーの 1 つである水素ガスは、入手可能な天然資源として大量には存在しない。そこで、近年、遷移金属錯体の存在下において、電気化学的な酸化還元反応による水素ガスの生成が注目されている[1]。

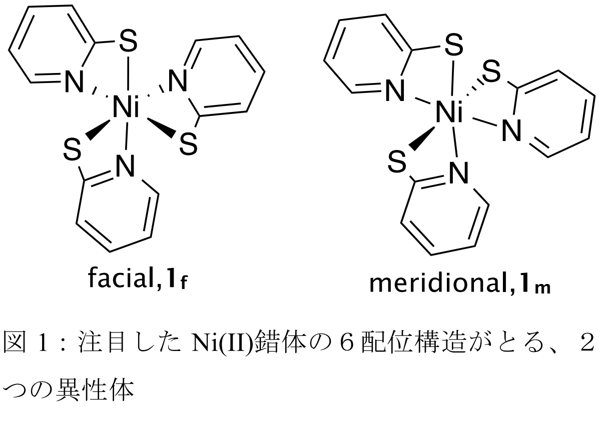
水 1 分子の分解(式 1)は吸熱反応であり、必要なエネルギーは 2.46 eV である。この反応を進行させるために必要なエネルギーとして、化石燃料の代わりに、太陽光や風力などを用いる。つまり、この反応を用いることによって、自然エネルギーを、化学エネルギーに変換し、水素ガスとして蓄えることができる。式 1 の逆反応である水素ガスの酸化(燃焼)では、二酸化炭素(CO_2)は発生せず、2.46 eV のエネルギーが得られることが分かる。

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

可能な限り少ないエネルギーによる水素ガスの生成を目的とした、プロトン還元活性をもつ遷移金属触媒の報告が、多くの実験研究によって行われている。特に、コスト面から Pt といった貴金属ではなく、Co や Ni、Mo など卑金属を用いた触媒の提案が盛んである。本研究では、これまで提案されてきた触媒のなかで、長時間に亘って高い水素発生活性を示す Ni(II)錯体[2]を取り上げた。その錯体における 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に取り組んできた。

【計算方法】

DFT (B3PW91 汎関数) 法を使用し、溶媒分子を連続誘電体として扱う CPCM 法で溶媒効果を考慮して構造最適化を行った。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 における EtOH:H2O=1:1 の混合溶媒を用い



facial,1_f　　meridional,1_m

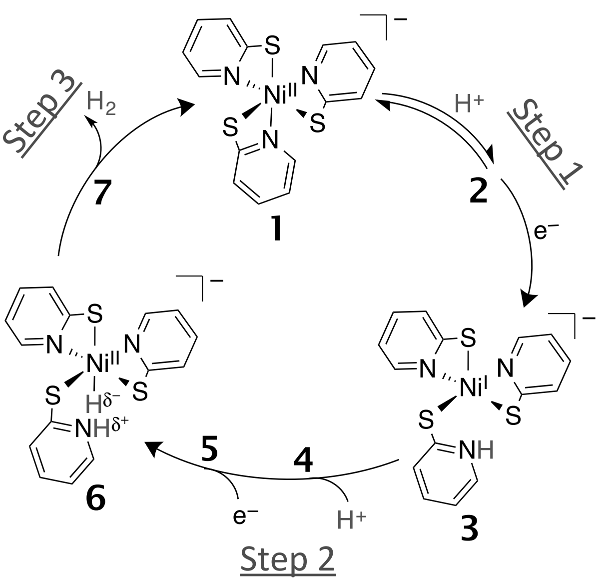
図 1：注目した Ni(II)錯体の 6 配位構造がとる、2 つの異性体

た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から決定した。

【結果と考察】

取り上げた Ni(II)錯体の６配位構造(**1**)には、図１に示すような facial 型($\mathbf{1_f}$)と meridional 型($\mathbf{1_m}$)の異性体が存在する。X 線結晶解析で観測できるのは $\mathbf{1_m}$ のみであるが、計算によると溶液中では 0.8 kcal/mol だけ、わずかに $\mathbf{1_f}$ が安定である結果が得られた。また、両異性体とも三重項状態が安定となった。

スキーム１に **1** から、実験から提案されている始まる水素発生サイクルを示す。このサイクルは、プロトン付加→１電子還元→プロトン付加→１電子還元の順序で進行する（CECE 機構）。



スキーム１

Step 1 では、プロトンはピリジン環の N に付加する場合、$\mathbf{1_m}$ から３つの異性体が生じるので、**2** には合計４つの異性体が存在する。続いて生じる１電子還元に掛かる還元電位の計算結果は、実験を概ね再現した。一方、**1** で１電子還元が起こる場合を考えると、その還元電位の計算値は実験値と大きく異なっている。これらの結果は、Step 1 はプロトン付加→１電子還元の順序で進むことを支持している。

Step 2 において、**3** に対するプロトン付加は、Ni(I)に付加するのではなく、ピリジン環の N への付加(**4**)が約 20 kcal/mol が安定であった。１電子還元は、ピリジン環の π 性反結合性軌道で起こり(**5**)、それに連続してピリジン環の N から Ni(I)へのプロトン移動による異性化反応が生じる(**6**、図２)。ただし、この順序とは逆に、プロトン付加に先んじて１電子還元が起こる可能性を、現在の計算結果からだけでは否定できない。

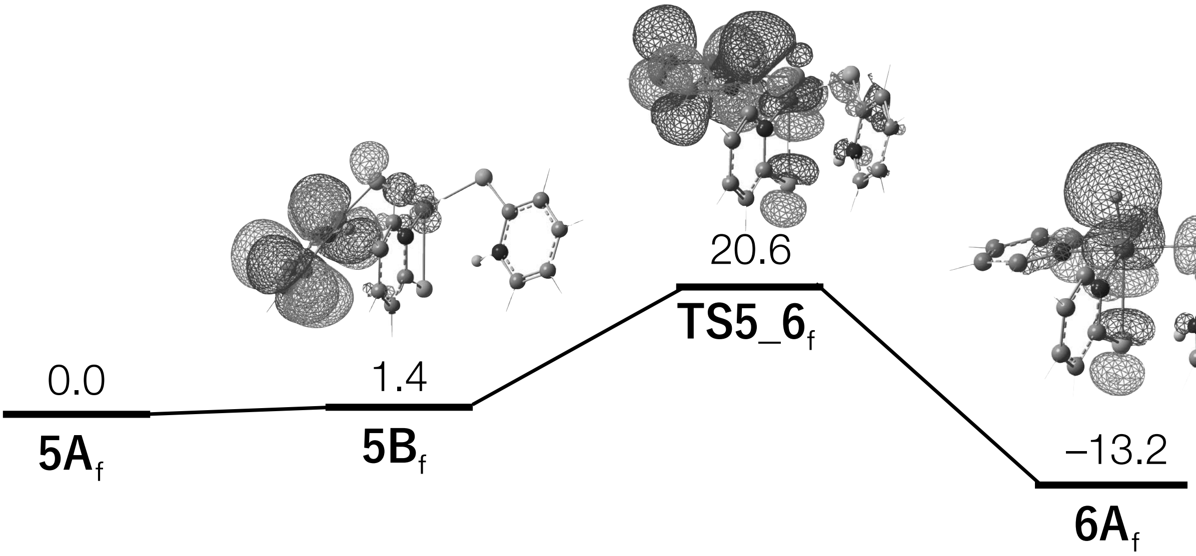


図２：Step 2 における、１電子還元体(**5**)からプロトンが移動する異性化反応のエネルギープロファイルと、そのときの SOMO の変化。図中の数字の単位は、kcal/mol である。

Step 3 は、Ni(II)–H とピリジル環の N–H 間のカップリングを経由して、水素ガスが発生する反応である（図３）。この反応の障壁は 0.6 kcal/mol と非常に低く、**7** からの H_2 の解離には障壁を見つけられなかった。これらは、本研究で取り上げた Ni(II)触媒が高い水素発生活性をもつ理由であると考えられる。また、この低い反応障壁は、H_2 になる２つの H 以外の幾何構造が大きく変化せず、$H^{\delta-}\cdots H^{\delta+}–N$ が直線状構造になることで、遷移状態が安定化することに起因する。

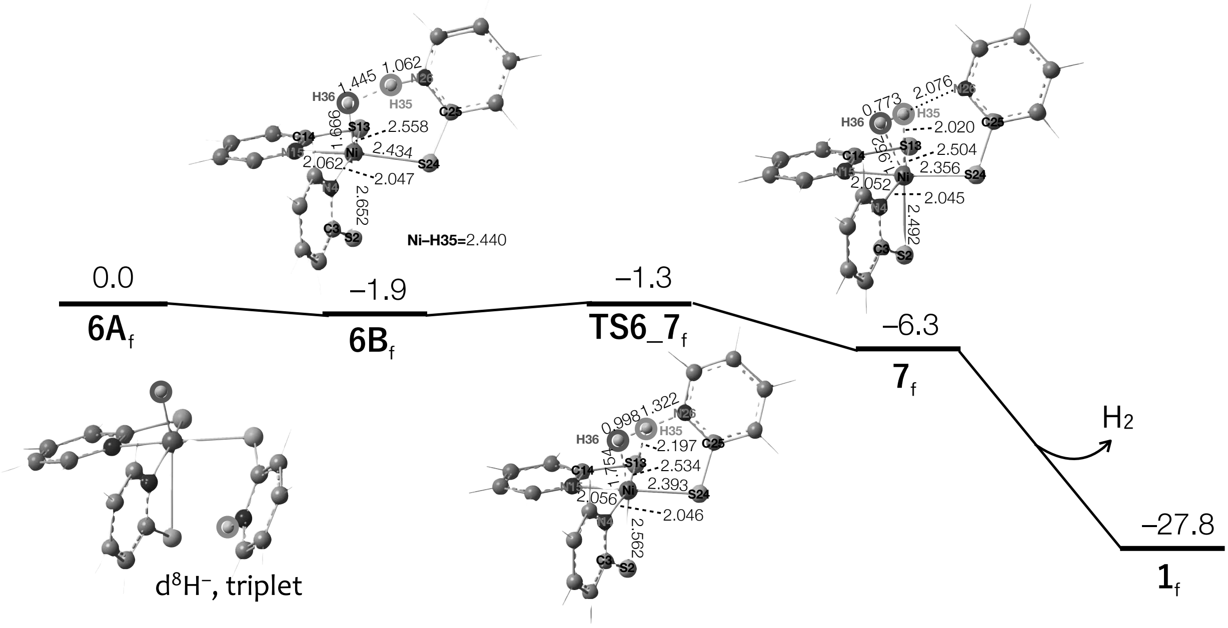


図３：Step 3 における、**6** から水素ガスが発生する反応のエネルギープロファイルと、そのときの幾何構造の変化。図中の数値の単位は、kcal/mol と Å である。

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2．論文

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4．その他

1. 〇山田健太、榊茂好

   「プロトン還元活性を示すNi(II)錯体による触媒反応機構に関する理論的研究」第12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　2015/01/23　P51

Shuwei Tang

SPR Fellow

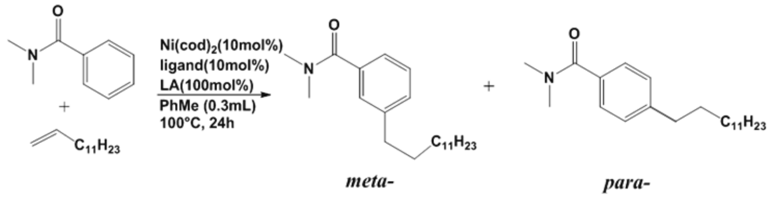
1. Summary of the research of the year

Reaction Mechanism and Regioselectivity of [Ni(NHC)/AlMe$_3$]-Catalyzed Olefin Hydroarylation through C−H Activation

The hydroarylation of unsaturated olefins through direct functionalization of aromatic C-H bond is a typical delegate in the class of C-C bond formation reaction. However, current metal catalyzed hydroarylation that generating linear products still faces many deficiencies, such as requiring directing groups, occurring with specific heteroarenes, or occurring with modest preference for linear over the branched product. An efficient cooperation of transition metals (TMs) with Lewis acids (LAs) is expected to be a powerful implement for such aromatic C-H bond activation. Recently, Nakao and co-workers reported a combination of nickel, Lewis acid, and N-heterocyclic carbene (NHC) ligand directly catalyzed the aromatic C-H bond of *N, N*-dimethylbenzamide with good to excellent yields and broad substrate applicability. However, the mechanistic details and the origins of regioselectivity about this reaction are not elucidated at present. Also, the role of LA in the Ni-catalyzed aromatic C-H activation is not clear at all.

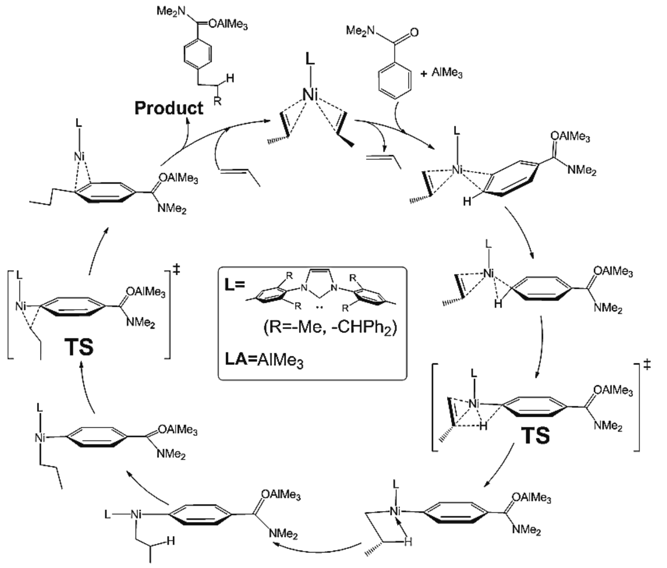
Here, we theoretically investigated the Ni^0(NHC)/LA catalyzed hydroarylation of linear olefins using DFT method with M06 functional (**Scheme 1**).

Scheme 1



(1) The most favorable catalysis cycle of this reaction consists four key elementary steps：coordination of *N, N*-dimethylbenzamide to the nickel (0) center, C-H bond activation of aryl group, isomerization of alkylation production, and C-C bond reductive elimination, as presented in **Scheme 2**. In the C-H activation process, the H transfer occurs from aryl group to alkene without forming a Ni-hydride intermediate, which is understood to be the oxidative addition to the metal-ligand moiety. In the C-C reductive elimination step, the TS without propene coordination is more favorable.

Scheme 2



(2) In the comparison of various ligands [small (IMes) vs. bulky ligand (IPr*)], the reaction mechanisms are same to each other, and the C-C reductive elimination is the rate determining step. Compared to the IMes ligand case, the activation barriers in bulky ligand system decrease 1~2kcal/mol, see Figure 1. In the part of ratio calculation of para- and meta-products, our result is *p/m*=60:40, which is in good agreement with the experimental value (*p/m*=58:42).

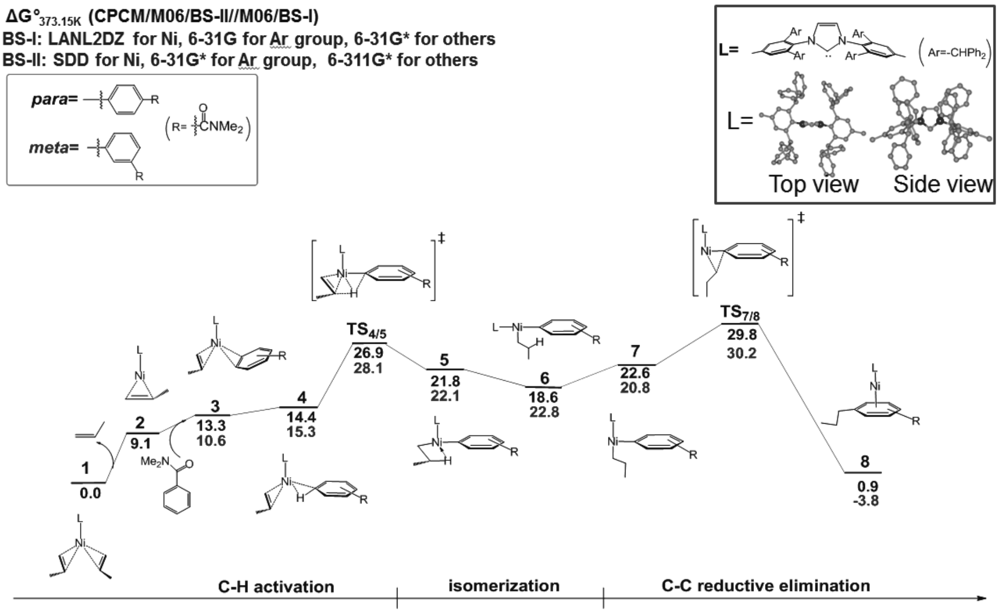


Figure 1. Energy profiles ($\Delta G^{\circ}_{373.15K}$) of the hydroarylation of olefin without LA.

(3) In order to understand the role of LA in the reaction mechanism, we investigated the reaction in bulky NHC ligand (IPr*) that catalyzed by nickel and $AlMe_3$. In our calculation, the LA prefers to coordinate with amide part of *N, N*-dimethylbenzamide. Figure 2 presents the Gibbs energy profile of hydroarylation of olefin with LA case. Due to the charge transfer from aryl group to LA, the activation barriers considerably decrease in comparison with the situation without LA. Moreover, the presence of LA changes the rate determining step, namely, from reductive elimination of C-C bond to C-H activation step. For the ratio calculation for para- and meta-products, we have got a data of *p/m*=72:28, significantly high than the situation with LA participation, and also in a good agreement with experimental data of *p/m*=81:19 in qualitative. Therefore, the presence of Lewis acid increases the regioselectivity of reaction.

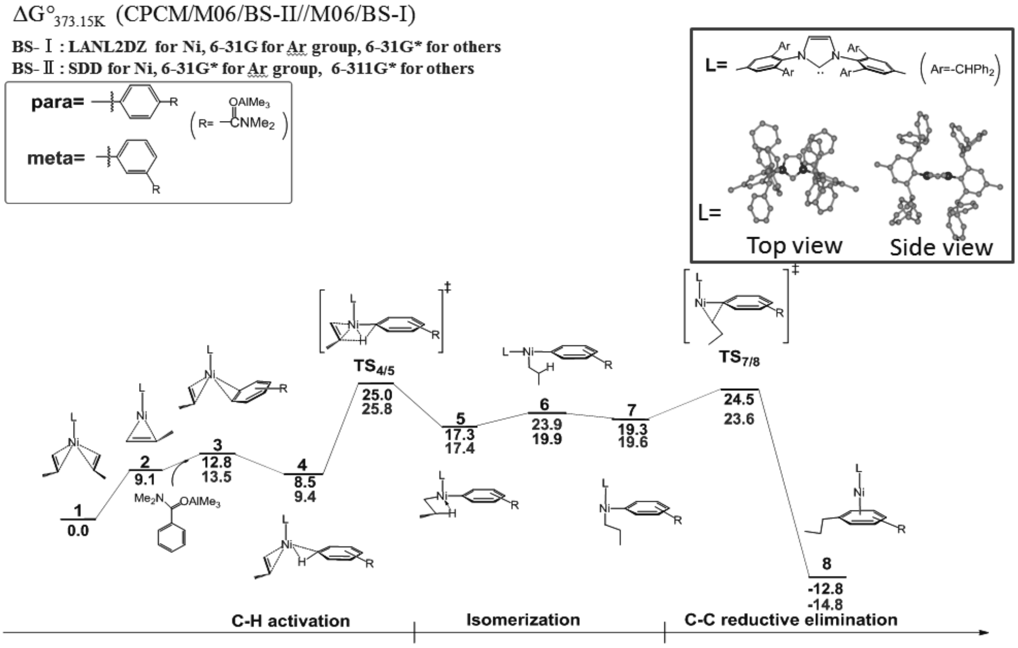
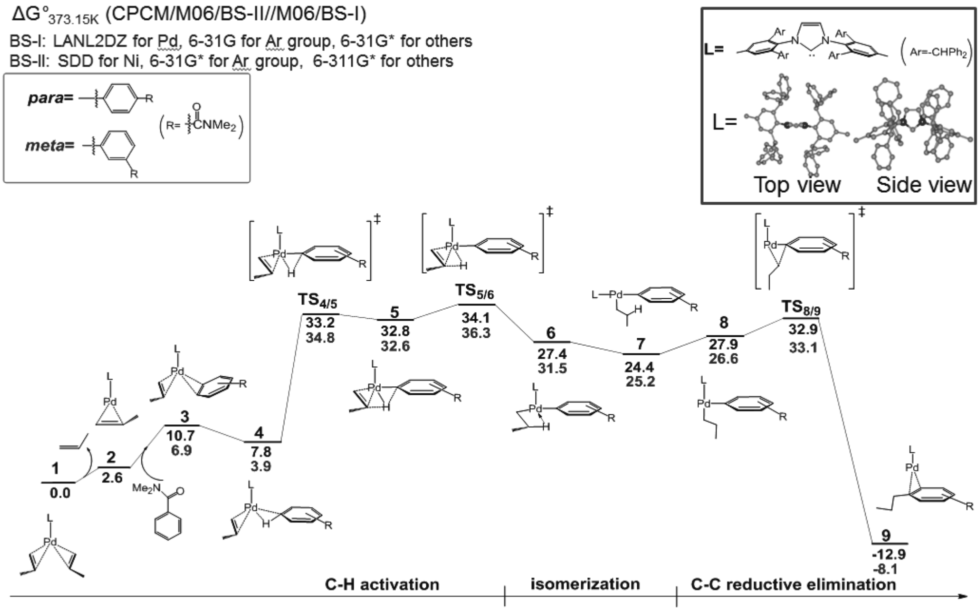


Figure 2. Energy profiles ($\Delta G°_{373.15K}$) of the hydroarylation of olefin with LA.

(4) In order to get insight into the dependence of different M (M=Ni, Pd, Pt) on the reaction mechanism, we take the reaction promoted by Pd without LA case as an example. Figure 3 describes the Gibbs energy profile of hydroarylation of olefin promoted by Pd. Apparently, the mechanism is significant different from the Ni case, because a Pd-hydride intermediate is located with high energy. Moreover, the rate determining step changes from C-C bond elimination step to hydrolation process, and the activation barriers are

considerably higher (~5 kcal/mol) than the Ni case. This may be one reason for the truth that Pd is not suitable for hydroarylation of linear olefins.



2. Original papers

(1) Shuwei Tang, Shogo Okumura, Yoshiaki Nakao, and Shigeyoshi Sakaki, “Reaction Mechanism and Regioselectivity of [Ni(NHC)/AlMe$_3$]-Catalyzed Olefin Hydroarylation through C-H Activation: A computational study”, *in preparation*.

(2) Shuwei Tang, Shogo Okumura, Yoshiaki Nakao, and Shigeyoshi Sakaki, “Alkylation Reaction of Aromatics via C-H Activation Process: Theoretical Study of Metal and Ligand Effects”, *in preparation*.

3. Presentation at academic conferences

Shuwei Tang, Shogo Okumura, Yoshiaki Nakao, and Shigeyoshi Sakaki, “Reaction Mechanism and Regioselectivity of [Ni(NHC)/AlMe$_3$]-Catalyzed Olefin Hydroarylation through C-H Activation: A computational study”, 第2回 中尾 T CREST 合同研究会について, Tokyo, March 29, 2015.

4. Others

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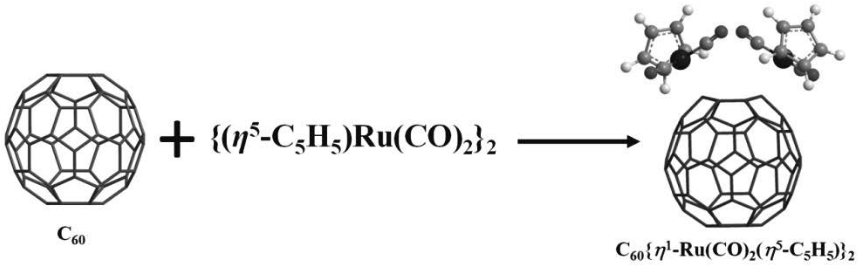
Hong Zheng

SPR Fellow

1. Summary of the research of the year

Addition of Dinuclear Ruthenium Complex to Fullerene: Theoretical Study of Reaction mechanism and Prediction

In the light of unique properties of transition-metal complex and fullerene, a large number of transition-metal complexes of fullerene have been synthesized and are expected to be new materials for their novel properties. However, most of transition-metal complexes of fullerene are of η^2-coordination or η^5-coordination, while very few cases involve η^1-coordination and deeper interpretation on them is still destitute. Recently, a new kind of transition-metal complexes of fullerene $C_{60}\{\eta^1\text{-Ru(CO)}_2(\eta^5\text{-}C_5H_5)\}_2$, which is recognized as the first kind of pure η^1-coordination between transition metal and fullerene, was discovered.



Scheme 1. Reaction between $\{(\eta^5\text{-}C_5H_5)\text{Ru(CO)}_2\}_2$ and C_{60}-I_h.

In this work, extensive theoretical study on the formation mechanism and electronic structure of $C_{60}\{\eta^1\text{-Ru(CO)}_2(\eta^5\text{-}C_5H_5)\}_2$ were performed. The reaction mechanism between $\{(\eta^5\text{-}C_5H_5)\text{Ru(CO)}_2\}_2$ and C_{60} was comprehensively investigated considering all possible pathways. As the product was obtained with a small yield after a long period (4~6 months), implying a large energy barrier and maybe a small reaction energy, one Li^+ cation was introduced into the C_{60} cage for the purpose of refining the reaction mechanism. Specially, the mechanism of excited state, corresponding to the photo irradiation in experiment, was probed and compared to the experimental proposal.

Reaction mechanism of singlet surface. When the Ru complex approaches the fullerene cage, three types of reaction pathways arise, in which the C_{60} cage exhibits different orientations. Among all the reaction patterns, pathA has the smallest activation barrier ($\Delta G^{\ddagger}$= 45.80 kcal/mol) and hence becomes the most probable mechanism (Fig 1). The Ru-Ru distance has been dramatically enlarged (from 2.77 Å to 3.85 Å) after the first peak and no direct orbital overlap between the Ru atoms exists in the intermediate state (INTA), in which the Ru centers are linked barely by a bridging carbonyl and the Ru-C_{60} bonding feature is of η^2-fasion. Then, along with the cleavage of another Ru-CO bond, the two Ru centers in INTA will move to the para sites of one six-member ring of the carbon cage and finally reach the product (PRO) geometry through the second transition state (TSA2). TSA2, in which the Ru-Ru distance is furtherly elongated to 4.20

Å and one Ru center is attached to the cage in the form of η^1-coordination while the other one is 3.32 Å away from the addition site, lies 9.68 kcal/mol above TSA1 in Gibbs energy and evidently is of the most importance in the whole reaction process.

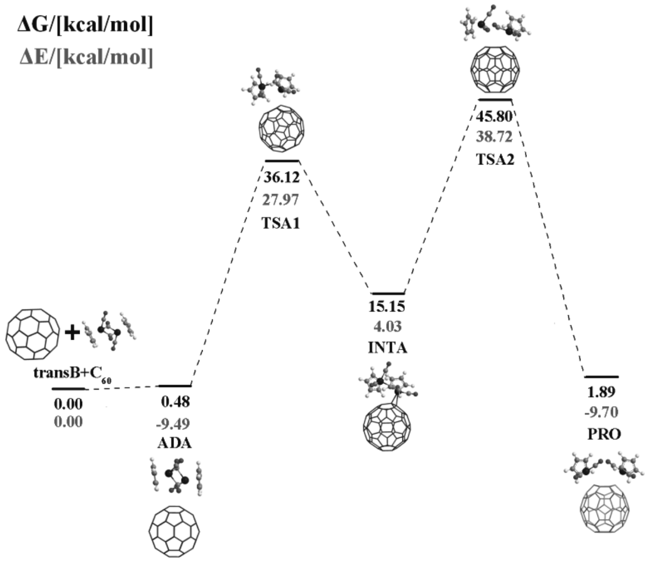


Fig 1. Gibbs energy profiles of the optimum reaction pathway (pathA). The relative potential energies are also presented in red color.

Reaction between {(η^5-C_5H_5)Ru(CO)$_2$}$_2$ and Li$^+$@C_{60}. Two types of reaction mechanisms between the Ru complex and Li$^+$@C_{60} were investigated and the better pathway is displayed in Fig 2. The Ru complex can interact with Li$^+$@C_{60} easier than C_{60} thanks to a negative reaction energy and a lower activation barrier. The situation is rather ambiguous when the first Ru center reacts with the cage, whereas the reaction of the second Ru center brings in a sharp barrier. The fact that the geometry structure of Li$^+$-TSA2 is alike to TSA2 implies the lowered activation energies would essentially originate from the change of electronic feature.

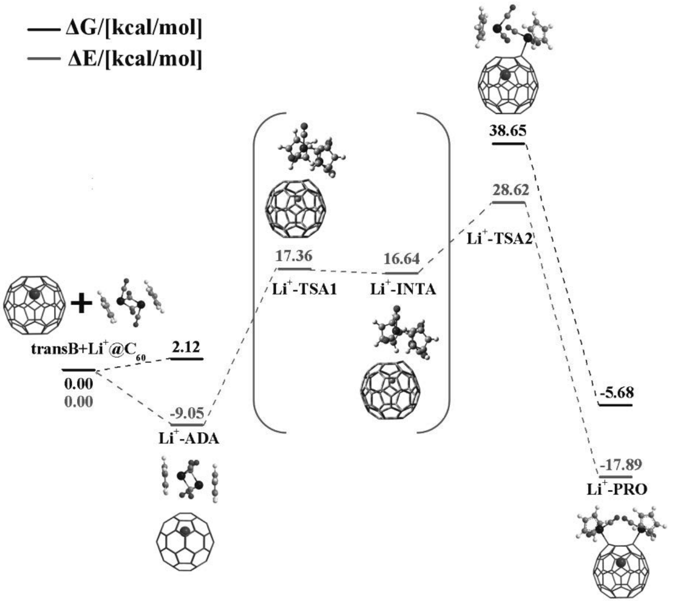


Fig 2. Energy profiles of Li$^+$-pathA.

Further analyses of electron populations of pathA and Li$^+$-pathA recover significant differences of electron transfer between the two reactions: In pathA, the carbonyls donating about 0.3 e to the fullerene cage plays the most important role during the electron transfer process, while the Cp rings show rather an inert performance; In Li$^+$-pathA, not only the carbonyls but also the Cp rings donate electron to C_{60}. Evidently the Li$^+$ cation can draw more charge from the Cp rings to promote electron transfer and thus the reaction will be efficiently smoothed.

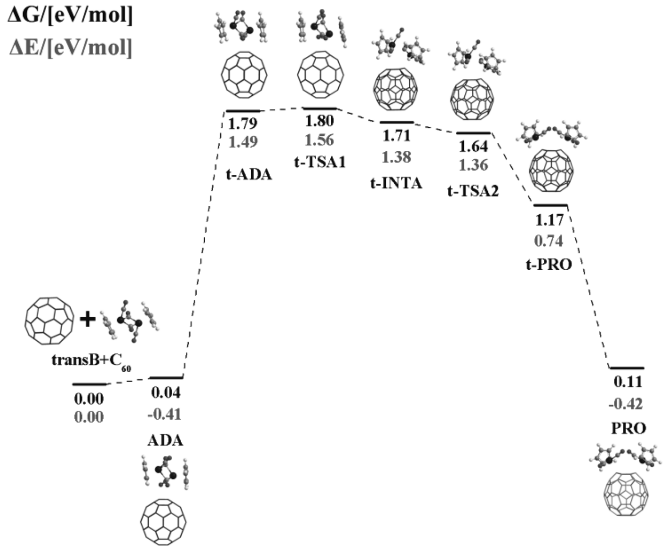


Fig 3. Energy profiles of t-pathA.

Reaction mechanisms including photo irradiation. The multi-step reaction pathways in the presence of photo irradiation were simulated and t-pathA with the same orientation of fullerene cage as pathA is determined to be the optimum mechanism (Fig 3). As depicted in Fig 3, the energy changes of triplet surfaces are rather flat and intensive tendency of forward reaction can be expected since the triplet product t-PRO is much more stable than the triplet reagents t-ADA. As comparison, the excited Ru complexes of all tautomeric forms and the further decomposition product (two (η^5-C_5H_5)Ru(CO)$_2$ radicals) have been calculated. It is found that the decomposition of the most stable triplet Ru complex is endothermic and hence such cleavage of Ru-Ru bond assumed in previous report is actually unreasonable.

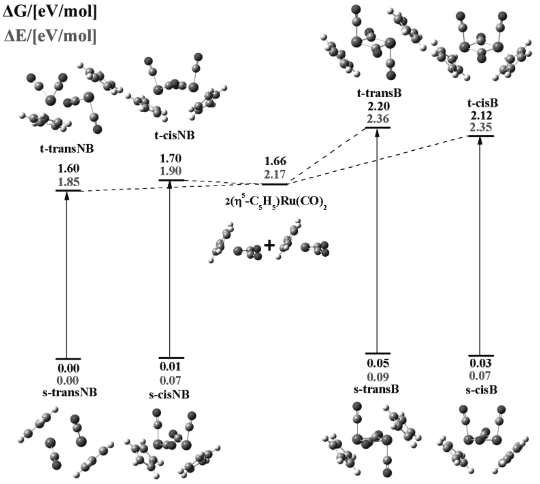


Fig 4. Gibbs and potential energy differences among singlet and triplet dinuclear Ru complexes and double Ru-centered radicals.

In this work, systematical theoretical study on the reaction between dinuclear Ru complex and C_{60} under various conditions were performed. The multi-step reaction between $\{(\eta^5\text{-}C_5H_5)Ru(CO)_2\}_2$ and C_{60} is slightly endothermic and needs a very large activation energy, which is consistent with the very low yield experimentally reported. Also, being different from the rough reaction on the C_{60} cage, Li^+-encapsulated C_{60} can easily react with the dinuclear Ru complex to afford $Li^+@C_{60}\{\eta^1\text{-}Ru(CO)_2(\eta^5\text{-}C_5H_5)\}_2$ through a smaller activation energy of 38 kcal/mol. It is revealed that not only carbonyls but also Cp rings donate electron to the $Li^+@C_{60}$ species and therefore more electron transfer occurs within this Li^+-included reaction. In particular, the reaction at the triplet excited state happens with nearly no-barrier and negative reaction energy, which is also consistent with the experimental result. The previous assumption of producing Ru-centered radicals by means of cleaving Ru-Ru bond in the presence of photo irradiation has been excluded due to an unreasonably endothermic cleavage process of the dinuclear Ru complex.

2. Original papers

(1) Hong Zheng, Xiang Zhao, Shigeyoshi Sakaki,
"Addition of Dinuclear Ruthenium Complex to Fullerene: Theoretical Study of Reaction mechanism and Prediction" *In preperation*.

3. Others

(1) Hong Zheng, Shigeyoshi Sakaki,
"Theoretical Study on Crowded Organometallic Fullerene $C_{60}\{\eta^1\text{-}Ru(CO)_2(\eta^5\text{-}C_5H_5)\}_2$" The 11th symposium of Fukui Institute for Fundamental Chemistry, Kyoto, January 23, 2015

５．共同研究員

Maneeporn Puripat

Visiting Researcher

1. Summary of the research of the year

Theoretical Study of Biginelli Reaction

The Biginelli reaction is a three-component reaction which was firstly published by the Italian chemist Pietro Biginelli in 1893. Typically, it is the condensation of a benzaldehyde, an acetoacetate and an (thio) urea and leads to dihydropyrimidines as product. It involves numerous researches in the drug development programs for many pharmacological advantages such as antihypertensive agents, potassium channel antagonists, anti-HIV agents, antitumor activity, anti-epileptics, anti-malarials, anti-microbials, anti-inflammatories, anti-tubercular activity, anti-bacterial activity and so forth. To enhance the efficiency of processes, several reports dealt with catalyst variations which are Brϕnsted acids, Lewis acids, ionic liquids, biocatalysts and organocatalysts.

In theoretical study of Biginelli reaction, finding transition state structures is essential missions to analyze and predict its mechanisms. This knowledge is advantages for the design of a more effective process. Presently, there are numerous methods which were developed for searching minimum energy reaction path automatically. One of them is the artificial force induced reaction (AFIR) method which was developed in 2010. It was applied to various organic reactions. Its ability is to be able automatically and systematically explore all probable reaction pathways including unexpected reaction paths.

Nevertheless, the mechanism of the Biginelli reaction is still not concluded. Thus, the Biginelli reaction mechanisms should be studied so that it can provide more understanding about roles of catalysts. In this research, the plausible pathways of the Biginelli reaction using AFIR method have been purposed.

For scope of the study, a benzaldehyde, an ethyl acetoacetate and a urea will be used as the model for Biginelli Reaction. The transition structures will be located by means of AFIR using the density functional theory (DFT) at M06-2X with 3-21G basic set for the initial search and their energies will be recomputed with higher accurate methods 6-31+G(d) for final results. The polarized continuum model (PCM) was employed in all calculations with the dielectric constant of 24.9 and 2.4 for ethanol and toluene, respectively. Moreover, the explicit solvent molecule(s) in ethanol have been considered in the proton transfer steps to determine the effect of solvent proticity.

The intrinsic reaction coordinate (IRC) was employed to confirm the reaction pathway. In all calculations, the first, and the second energy derivatives were calculated by the Gaussian09 program. The Global Reaction Route Mapping (GRRM) program was utilized to optimizations and IRC calculations.

In this research, the entire reaction mechanism of the Biginelli reaction starting from benzaldehyde, urea, and ethyl acetoacetate as reactants by using the recently-developed artificial force induced reaction (AFIR) method combined with DFT calculations have been investigated. The most favorable pathway starts with the condensation of the urea and benzaldehyde, followed by the addition of ethyl acetoacetate. Contrary to common believe, the rate-determining step of this reaction is the cyclization step (C-N bond formation) with 21.5 kcal mol^{-1} activation energy. Surprisingly, an extra urea can catalyze nearly all steps of all the routes. The role of the extra urea is to stabilize the molecules and reserve a proton as proton donors and proton acceptors during the process. Thus, we can say that the Biginelli reaction is urea-catalyzed multicomponent reaction. Also, the reaction mechanism was found to be identical in ethanol and toluene.

2. Original papers

- Puripat, M.; Ramozzi , R.; Hatanaka, M.; Parasuk, W.; Parasuk, V.; Morokuma, K, *J. Org. Chem.* **2015**, Just Accepted.

3. Presentation at academic conferences

- The 12th FIFC Symposium, Kyoto, Japan, January 23rd, 2015.
- The 16th International Conference on Density Functional Theory and its Applications in Debrecen, Hungary, August 31st- September 4th, 2015.

4. Others

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V　資料

1．研究業績一覧（平成 26 年度）

№	Authors	Title	Journal	Volume (Number), first page to last page	year
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80	J. Jiang, R. Ramozzi, K. Morokuma	Rh(III)-Catalyzed C(sp3)-H Bond Activation via an External Base Metalation Deprotonation Mechanism	*Chem. Eur. J.*	accepted	2015
Travis Harris					
81	Lung Wa Chung, W. M. C. Sameera, Romain Ramozzi, Alister J. Page, Miho Hatanaka, Galina P. Petrova, Travis V. Harris, Xin Li, Zhuofeng Ke, Fengyi Liu, Hai-Bei Li, Lina Ding, and Keiji Morokuma	The ONIOM Method and its Applications	*Chem. Rev.*	[Online early access]. DOI: 10.1021/ cr5004419. Published Online: Apr 8, 2015.	2015
伊勢川　美穂					
82	Miho Isegawa, Fengyi Liu, Satoshi Maeda, Keiji Morokuma	Ab initio reaction pathways for photodissociation and isomerization of nitromethane on four singlet potential energy surfaces with three roaming paths	*J. Chem. Phys.*	140, 244310	2014
83	Miho Isegawa, Fengyi Liu, Satoshi Maeda, Keiji Morokuma	Complete active space second order perturbation theory (CASPT2) study of N(2D) + H2O reaction paths on D1 and D0 potential energy surfaces: Direct and roaming pathways	*J. Chem. Phys.*	141, 154303	2014
84	Miho Isegawa, Keiji Morokuma	Photochemical Ring Opening and Closing of Three Isomers of Diarylethene: Spin-Flip Time Dependent Density Functional Study	*J. Phys. Chem. A*	199, 4191-4199	2015
W. M. C. Sameera					
85	L. W. Chung, W. M. C. Sameera, R. Ramozzi, A. J. Page, M. Hatanaka, G. P. Petrova, T. V. Harris, X. Li, Z. Ke, F. Liu, H-B. Li, L. Ding and K. Morokuma	The ONIOM Method and its Applications	*Chem. Rev.*	In press	2015
86	J. Llaveria, Á. Beltrán, W. M. C. Sameera, A. Locati, M. M. Díaz-Requejo, M. I. Matheu, S. Castillón, F. Maseras, P. J. Pérez	A computational view on the reactions of hydrocarbons with coinage metal complexes	*J. Organomet. Chem.*	784, 2-12.	2015

№	Authors	Title	Journal	Volume (Number), first page to last page	year
87	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
88	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, [Fe8(μ4-O)4(μ-4-Cl-pz)12Cl4]–	*Dalton Trans.*	43, 11269-11276.	2014
Julong Jiang					
89	Julong Jiang, Jin-Quan Yu, Keiji Morokuma	Mechanism and Stereoselectivity of Directed C(sp^3)-H Activation and Arylation Catalyzed by Pd(II) with Pyridine Ligand and TFA. A Computational Study	*ACS Catal.*	5, 3648-3661	2015
90	Julong Jiang, Romain Ramozzi, Keiji Morokuma	Rh(III)-Catalyzed C(sp3)-H Bond Activation via an External Base Metalation/Deprotonation Mechanism: A Theoretical Study	*Chem. Eur. J.*	Accepted.	2015
91	Julong Jiang, Romain Ramozzi, Shin Moteki, Asuka Usui, Keiji Maruoka, Keiji Morokuma	The Mechanism of Metal-Free C-H Activation of Branched Aldehydes and Acylation of Alkenes Using Hypervalent Iodine Compound: A Theoretical Study	*J. Org. Chem.*	Submitted	2015
山邊　信一					
92	Shinichi Yamabe, Guixiang Zeng, Wei Guan, Shigeyoshi Sakaki	Substrate dependent reaction channels of the Wolff-Kishner reduction reaction: A theoretical study		10, 259-270	2014
93	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
94	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, 1140-1148	2014
95	Shinichi Yamabe, Guixiang Zeng, Wei Guan, Shigeyoshi Sakaki	Proton Transfers in the Strecker Reactions revealed by DFT calculations	*Beilstein Journal of Organic Chemistry*	vol. 10, 1765-1774	2014
96	Shinichi Yamabe, Guixiang Zeng, Wei Guan, Shigeyoshi Sakaki	A DFT Study on Proton Transfers in Hydrolysis Reactions of Phosphate Di-Anion and Sulfate Mono-Anion	*Journal of Computational Chemistry,*	Volume 35, Issue 30, 2195-2204.	2014
97	D. T. Usmanov, L. C. Chen, Z. Yu, S. Yamabe*, S. Sakaki and K.Hiraoka*	Atmospheric pressure chemical ionization (APCI) of using alternating current corona discharge ion source	*Journal of Mass Spectrometry*	vol. 50, No. 4, 651-710	2015
98	Govinda P. Khanal, Rajendra Parajuli, Elangannan Arunan,Shinichi Yamabe, Kenzo Hiraoka and Eiko Torikai,	Study of structures, energies and vibrational frequencies of (O2)n+(n=2-5) clusters by GGA and meta-GGA density functional methods	*Computational and Theoretical Chemistry*	vol. 1056, 24-36	2015
99	Shinichi Yamabe, Noriko Tsuchida, Shoko Yamazaki and Shigeyoshi Sakaki	Frontier orbitals and transition states in the oxidation and degradation of L-ascorbic acid: a DFT study	*Org. Biomol. Chem*	vol. 13, 4002-4015	2015
100	aokazu Yoshikawa, Shinichi Yamabe, Shigeyoshi Sakaki,	Transition States of the 3MLCT to 3MC Conversion in Ru(bp)2(phen deriveativ)2+ complexes	*Journal of Molecular Structure*	vol. 1094, 98-108	2015

№	Authors	Title	Journal	Volume (Number), first page to last page	year
101	Nobuko Kanehisa, Tsuyoshi Inoue,and Hiroshi Takashima,	A DFT study of hydride transfers to the carbonyl oxygen of DDQ	*International Journal of Quantum Chemistry*	in press	2015
土方　優					
102	Keisuke Kishida, Yumiko Watanabe, Satoshi Horike, Yoshihiro Watanabe, Yoshikuni Okumura, Yuh Hijikata, Shigeyoshi Sakaki, and Susumu Kitagawa	DRIFT and theoretical studies of ethylene/ethane separation on flexible microporosity of [Cu_2($_{2,3}$-pyrazinedicarboxylate)2(pyrazine)]n	*Eur. J. Inorg. Chem.*	2747-2752	2014
103	Ryo Ohtani, Munehiro Inukai, Yuh Hijikata, Tetsuya Ogawa, Mikihito Takenaka, Masaaki Ohba, and Susumu Kitagawa	Sequential synthesis of coordination polymersomes	*Angew. Chem. Int. Ed.*	54, 1139-1143	2015
104	Shin-ichro Noro, Junya Mizutani, Yuh Hijikata, Ryotaro Matsuda, Hiroshi Sato, Susumu Kitagawa, Kunihisa Sugimoto, Yasutaka Inubushi, Kazuya Kubo, and Takayoshi Nakamura	Porous coordination polymers with ubiquitous and biocompatible metals and a neutral bridging ligand	*Nat. Commun.*	6, 5851	2015
青野　信治					
105	Taichi Inagaki, Shiniji Aono, Hiroshi Nakano, and Takeshi Yamamoto	Like-Charge Attraction of Molecular Cations in Water: Subtle Balance between Interionic Interactions and Ionic Solvation Effect	*J. Phys. Chem. B*	118, 5499-5508	2014
Guixiang Zeng（會　桂香）					
106	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
107	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
108	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
109	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
110	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.*	53 (13), 6444-6457	2014
中垣　雅之					
111	Masayuki Nakagaki and Shigeyoshi Sakaki	CASPT2 study of inverse sandwich-type dinuclear 3d transition metal complexes of ethylene and dinitrogen molecules: similarities and differences in geometry, electronic structure, and spin multiplicity	*Phys. Chem. Chem. Phys.*	17, 16294-16305	2015

№	Authors	Title	Journal	Volume (Number), first page to last page	year
Yue Chen					
112	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.*	43, 11478-11492	2014
113	Shubin Yang, Changlun Chen, Yue Chen, Jiaxing Li, Dongqi Wang, Xiangke Wang	Competitive Adsorption of PbII, NiII, and SrII Ions on Graphene Oxides: A Combined Experimental and Theoretical Study	*ChemPlusChem*	80 (3), 480-484	2015
Sayyed Fareed Bhasha					
114	Fareed Bhasha Sayyed and Shigeyoshi Sakaki	The crucial roles of $MgCl_2$ as a non-innocent additive in the Ni-catalyzed carboxylation of benzyl halide with CO_2	*Chem. Commun.*	50, 13026-13029	2014
115	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 (13), 6444-6457	2014
116	Tetsuaki Fujihara, Yuichiro Horimoto, Taiga Mizoe, Fareed Bhasha Sayyed, Yosuke Tani, Jun Terao, Shigeyoshi Sakaki, Yasushi Tsuji	Nickel-Catalyzed Double Carboxylation of Alkynes Employing Carbon Dioxide	*Org. Lett.*	16 (18), 4960-4963	2014
山田　健太					
117	Kenta Yamada, Yukio Kawashima, Masanori Tachikawa	Accurate Prediction of Hyperfine Coupling Constants in Muoniated and Hydrogenated Ethyl Radicals: Ab Initio Path Integral Simulation Study with Density Functional Theory Method	*J. Chem. Theory. Comput.*	10 (5), 2005-2015	2014
118	Takako Mashiko, Kenta Yamada, Shuichi Hiraoka, Umpei Nagashima, Masanori Tachikawa	Molecular dynamics simulation of self-assembled nanocubes in methanol	*Mol. Simul.*	41 (10-12), 845-849	2014
119	Kenta Yamada, Yukio Kawashima, Masanori Tachikawa	Quantum simulation for muoniated and deuterated methyl radicals in implicit water solvent: combined ab initio path integral molecular dynamics and the polarizable continuum model simulation study	*Mol. Simul.*	41 (10-12), 832-839	2014
Maneeporn Puripat					
120	Maneeporn Puripat, Romain Ramozzi, Miho Hatanaka, Waraporn Parasuk, Vudhichai Parasuk, Keiji Morokuma	The Biginelli reaction is a urea-catalyzed organocatalytic multicomponent reaction	*The journal of organic chemistry*	Just Accepted	2015

＊以下に表示の研究業績（論文）は、共著である

No14&69. No15&71. No16&68. No21&72. No31&73. No32&83.

No37&82. No49&112. No50&114. No52&102. No53&116. No57&110.

No74,78,81&85. No76&120. No92&106.

２．共同研究者受入れ状況（平成 26 年度）

受入れ教員	共同研究者名	受入れ身分	受入れ期間	所属機関・職	研究内容
諸熊 奎治	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	Chulalongkorn University（タイ）・ PhD 学生	複雑分子系の理論化学・計算化学
諸熊 奎治	FERNANDEZ A Victor M	外国人 共同研究者	平成 26 年 4 月 1 日～ 平成 26 年 7 月 3 日	Chemical Research of Catalonia（スペイン）・ PhD 学生	複雑分子系の理論化学・計算化学
諸熊 奎治	KAPUKOTUWE WARAWWE, Pulasthika Bethmini	外国人 共同研究者	平成 26 年 5 月 14 日～ 平成 27 年 5 月 13 日	ヨーテボリ大学（スウェーデン）・ PhD 学生	複雑分子系の理論化学・計算化学
永瀬　茂	ZHENG, Jia-Jia	外国人 共同研究者	平成 26 年 8 月 1 日～ 平成 27 年 1 月 31 日	Xi'an Jiaotong University（中国）・ 博士課程学生	塩素化フラーレンおよび金属内包フラーレンの理論的研究
諸熊 奎治	HUDSON, Brandi M.	外国人 共同研究者	平成 26 年 6 月 17 日～ 平成 26 年 8 月 19 日	カリフォルニア大学（アメリカ）・ 大学院研究員	EAPSI：AFIR法を用いたGRRM戦略：テルペン形成経路に対するメチル化の影響予測
榊　茂好	LEI, Ming	招へい 外国人学者	平成 26 年 6 月 28 日～ 平成 26 年 8 月 31 日	Beijing University（中国）・教授	d電子複合系の理論化学
諸熊 奎治	SAMEERA, W.M. C.	外国人 共同研究者	平成 26 年 9 月 16 日～ 平成 28 年 9 月 15 日	日本学術振興会・ 外国人特別研究員	合成キラル金属ポルフィリンの反応機構と選択性の計算化学による研究
諸熊 奎治	POMOGAEVA Anna Vladimirovna	外国人 共同研究者	平成 26 年 11 月 15 日～ 平成 26 年 12 月 23 日	Petersburg State University（ロシア）・ 博士研究員	アルキル金属アミノボランの気相中および凝縮系における反応機構の理論的研究
諸熊 奎治	NGUYEN, Hoa My	招へい 外国人学者	平成 27 年 1 月 6 日～ 平成 27 年 2 月 16 日	ベトナム大学（ベトナム）・講師	計算化学法によるMRSAのβ-ラクタム抗生物質耐性に関する研究
諸熊 奎治	JAMAL, Adeel Ashraf	外国人 共同研究者	平成 27 年 2 月 1 日～ 平成 28 年 1 月 31 日	Emory University（アメリカ）・ 博士研究員	炭化水素の熱分解の第一原理に基づく反応速度論的モデルの構築
諸熊 奎治	鈴木 机倫	共同研究者	平成 27 年 3 月 1 日～ 平成 28 年 2 月 29 日	北海道大学（日本）・ 博士研究員	反応経路自動探索法を基盤とする化学反応の理論設計技術
諸熊 奎治	HEYDEN, Andreas	招へい 外国人学者	平成 27 年 3 月 27 日～ 平成 27 年 8 月 3 日	University of South Carolina（アメリカ）・ 教授	複雑分子系の理論化学

３．海外渡航一覧（平成 26 年度）

職　　名	氏　　名	期間（自）	期間（至）	目 的 地
シニアリサーチフェロー	諸熊　奎治	2014.4.24	2014.5.1	オーストラリア
シニアリサーチフェロー	諸熊　奎治	2014.5.15	2014.5.27	スイス
シニアリサーチフェロー	諸熊　奎治	2014.5.29	2014.6.6	アメリカ合衆国・カナダ
外国人共同研究者	RAMOZZI, Romain Raoul, Marcel	2014.6.27	2014.7.20	フランス
准　教　授	池田　昌司	2014.7.19	2014.7.27	アメリカ合衆国
研究員（学術研究奨励）	榊　　茂好	2014.7.20	2014.7.25	シンガポール
シニアリサーチフェロー	諸熊　奎治	2014.9.13	2014.9.21	ロシア
研究員（学術研究奨励）	永瀬　　茂	2014.10.28	2014.11.3	スウェーデン
シニアリサーチフェロー	諸熊　奎治	2014.10.29	2014.11.2	スウェーデン
研究員（学術研究奨励）	榊　　茂好	2015.2.21	2015.2.27	ドイツ
研究員（学術研究奨励）	永瀬　　茂	2015.3.5	2015.3.11	インド

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12回

京都大学 福井謙一 記念研究センター シンポジウム

諸熊奎治先生傘寿記念

開会式（Opening）

［開会の辞］田中 一義（センター長）　10:00–10:05
［ご 挨 拶］伊藤 紳三郎（工学研究科長）　10:05–10:15

講演会（Lecture session）

北川 進（京都大学 物質ー細胞統合システム拠点）　10:15–11:15
「多孔性金属錯体の化学と応用」

田中 肇（東京大学 生産技術研究所）　11:30–12:30
「水の局所構造化と熱力学異常・結晶化におけるその役割」

– 昼食 –

傘寿記念講演（Memorial lecture）

諸熊 奎治（京都大学 福井謙一記念研究センター）　14:00–15:00
Keiji Morokuma
(Fukui Institute for Fundamental Chemistry, Kyoto University)
「Chemical Theory of Complex Molecular Systems: Discovery and Insights from Computational Studies of Chemical Reactions」

– コーヒーブレイクー

ポスターセッション（Poster session）　15:30–17:20
お祝いの会・懇親会（Celebration, Banquet）　17:30–19:00

平成27年1月23日（金）

会場：京都大学 福井謙一記念研究センター

2015. 1. 23　Fukui Institute for Fundamental Chemistry, Kyoto University

京都大学福井謙一記念研究センター
〒606-8103　京都市左京区高野西開町34-4
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第 12 回京都大学福井謙一記念研究センターシンポジウム
-諸熊奎治先生傘寿記念-

プログラム

日時　平成 27(2015)年 1 月 23 日（金）
場所　京都大学福井謙一記念研究センター

講演会　(3 階大会議室 10:00～12:30)

- 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　**伊藤 紳三郎**（京都大学 工学研究科長）　・・・10:05-10:15

- **北川 進** (京都大学 物質－細胞統合システム拠点)　司会：永瀬 茂（福井センター）
  「多孔性金属錯体の化学と応用」　・・・10:15-11:15

－　休憩　－

- **田中 肇** (東京大学 生産技術研究所)　司会：山本 量一（京大院工）
  「水の局所構造化と熱力学異常・結晶化におけるその役割」　・・・11:30-12:30

－　昼休み　－

傘寿記念講演　(3 階大会議室 14:00～15:00)

- **諸熊 奎治** (京都大学 福井謙一記念研究センター)　司会：榊 茂好（福井センター）
  Keiji Morokuma (Fukui Institute for Fundamental Chemistry, Kyoto University)
  「Chemical Theory of Complex Molecular Systems: Discovery and Insights from Computational Studies of Chemical Reactions」　・・・14:00-15:00

－　休憩　－

ポスターセッション　(3 階大会議室 15:30～17:20)

お祝いの会・懇親会　(1 階多目的ルーム 17:30～19:00)

ポスターリスト (3 階大会議室 15:30～17:20)

- ✓ 番号が奇数の方は前半(15:30-16:25)、番号が偶数の方は後半(16:25-17:20)には、ポスターボードの前で発表するようにしてください。
- ✓ Authors with odd and even poster numbers should be present at the poster during the first half (15:30-16:25) and the second half (16:25-17:30) of the session, respectively.

1. **$(H_2O)_n$ (n<26)クラスター中の水素結合ネットワークの解析**
○岩田 末廣 (慶応大理工)

2. **低障壁水素結合の量子化学 ―多成分系分子理論の応用―**
○立川 仁典 (横浜市大院生命ナノ)

3. **分子を対象とした第一原理経路積分分子動力学法の実装と応用**
○河津 励[1,2]、立川 仁典[1] (横市大生命ナノ[1]、東大総文[2])

4. **基底関数に含まれる軌道指数を用いた解析接続法による光イオン化断面積の変分計算**
森田 将人、松崎 黎、○藪下 聡 (慶大理工)

5. **CS_2 光解離反応の真空紫外サブ 20fs 光電子イメージング**
○堀尾 琢哉、Roman Spesyvtsev, 鈴木 俊法 (京大院理)

6. **GRRM 法による未知化学の探索： H4C4**
○大野 公一[1]、佐藤 寛子[2]、岩本 武明[1] (東北大院理[1]、国立情報学研究所[2])

7. **単成分人工力誘起反応（SC-AFIR）法とその応用**
○前田 理[1], 原渕 佑[1], 武次 徹也[1], 諸熊 奎治[2] (北大院理[1]、京大福井セ[2])

8. **New Insights in Isocyanides Multicomponent Reactions**
○Romain Ramozzi and Keiji Morokuma (FIFC, Kyoto Univ.)

9. **Unveiling the Essence of Pd(II)-Catalyzed C(sp^3)-H Activation: Is the CMD Mechanism Still Applicable?**
○Julong Jiang[1], Jin-Quan Yu[2] and Keiji Morokuma[1] (FIFC, Kyoto Univ.[1], Depart. of Chem., The Scripps Research Institute[2])

10. **The Biginelli Reaction: An Organocatalyzed Multicomponent Reaction**
○ Maneeporn Puripat[1,2], Romain Ramozzi[1], Miho Hatanaka[1], Vudhichai Parasuk[2,3] and Keiji Morokuma[1,4] (FIFC[1], Nanosci. & Tech. Chulalongkorn Univ.[2], Chem. Chulalongkorn Univ.[3], Chem & Emerson Center for Sci. Comp. Emory Univ.[4])

11. **Glucose Transformation to 5-Hydroxymethylfurfural in Acidic Aqueous and Ionic Liquid Solvents**
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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12回
福井センターセミナー
The 12th Fukui Center Seminar

2014年4月8日(火) 14:00-17:30

京都大学福井謙一記念研究センター1F 多目的室 (Room: 1F 106)
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(at FIFC, Kyoto Univ. on April, 8(Tue.), 2014)

14:00～15:00　Yuichi MASUBUCHI　(Kyoto Univ.)

“Modeling and Simulations of Polymer Dynamics”

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(Philipps-Univ. Marburg)
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多数の方のご来場を歓迎いたします
We welcome all of you to join.

６．その他（報告）

日経産業新聞 2014.10.21-22 より抜粋
日本のイノベーター　京都大学：シニアリサーチフェロー　諸熊　奎治
計算機化学（上）分子の反応予測を簡単に、（下）新薬や触媒、応用広がる

京都大学福井謙一記念研究センターのシニアリサーチフェローを務める諸熊奎治は、生命の営みにも関係する化学反応という現象を理論的に解明してきた。

2013年のノーベル化学賞では受賞はかなわなかったが、「重要な貢献をした７人」に名を連ねた。

京大へ進学した諸熊は後にノーベル化学賞を受賞する教授の福井謙一の指導を受けた。1960年代初頭の日本には満足な性能のコンピューターがなかった。

昨年のノーベル化学賞を受けたマーティン・カープラス氏の誘いで、64年に米コロンビア大学へ留学したことで転機が訪れる。同大が使うコンピューターは京大のものより1000倍ほど速かった。「米国で勝負したい」と考えたが、京大の関係者は強く帰国を求めた。ただ一人、福井は「まあいいんじゃないか」と理解を示した。諸熊は退路を断つため京大の助手を辞め、米国に残った。

まず手がけたのは水分子が２つ結合した構造の解析だ。たった２っとはいえコロンビア大の新型計算機でも苦労した。毎週48時間計算し、答えを出すまでに２カ月かかった。利用者が少ない土曜の朝から始め、月曜朝までコンピューターを動かした。「仮眠を取りつつ数時間ごとに紙で打ち出される結果を確認した」と振り返る。結果は当時の定説とは違った。構造は水素と酸素が水素結合で直線状につながっていた。数年後に実験で同じ結果が出て注目を集めた。水の様々な性質の決め手になる基本構造は今では、高校の教科書にも載っている。

米ロチェスター大学の教授だった76年、「エネルギー分割法」と呼ぶ手法を開発した。分子の間には静電気や電子の動きなど様々な力やエネルギーが働く。

諸熊の下で共同開発に取り組んだ神戸大学の北浦和夫特命教授は「分子が多数集また物質を設計できるようになった」と説明する。みずほ情報総酬はエネルギー分割法を使って新薬の候補となる化学物質がたんぱく質と結びつきやすいかどうかを調べるソフトを東京大学と共同開発し昨年４月に販売を始めた。

さらに諸熊は1995年、たんぱく質のような巨大な分子の振る舞いを予測する「ONIOM(オニオム)法」を開発した。80年代以降、コンピューターの性能は飛躍的に向上し、次第に大きな分子を扱えるようになったが、タンパク質のような巨大な分子を計算するのは難しかった。そこで諸熊は分子をいくつかの部分にわけ、反応や機能に重要な役割を果たす中心部は量子力学を駆使して高い精度で計算し、周辺部は簡単な計算で処理して組み合わせる方法を考えた。中心部から何重にも皮が重なるタマネギ（オニオン）を連想させたことから諸熊が育った大阪府南部の名産品タマネギにちなんで名づけた。オニオム法の登場で、化学合成を促す触媒や体内の酵素反応の解明が進んだ。宇部興産は医薬品や合成繊維の原料を合成する触媒の分子構造を解析する研究に生かす。

いま諸熊が注目するのは、化学反応が始まる際の分子の形が変わる様子の解明で、北海道大学と共同研究を進めている。解明できれば、効率的で狙った機能を持つ化学物質の合成が可能になるかもしれない。

京大の助手だった諸熊が最初に米国に渡ってから半世紀がたつ。「マイナーだった計算機化学は今や化学における大きな柱に成長した」と喜ぶ。

一方で分子の世界に残る謎はまだまだ多い。80歳になっても、研究への意欲は衰えない。師である福井謙一（京大名誉教授）の名を冠した研究所で若手研究者を育てながら、今も研究の第一線に残り、次のターゲットを見据えている。

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