京都大学
福井謙一記念研究センター

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Fukui Institute for Fundamental Chemistry Kyoto University

年 報
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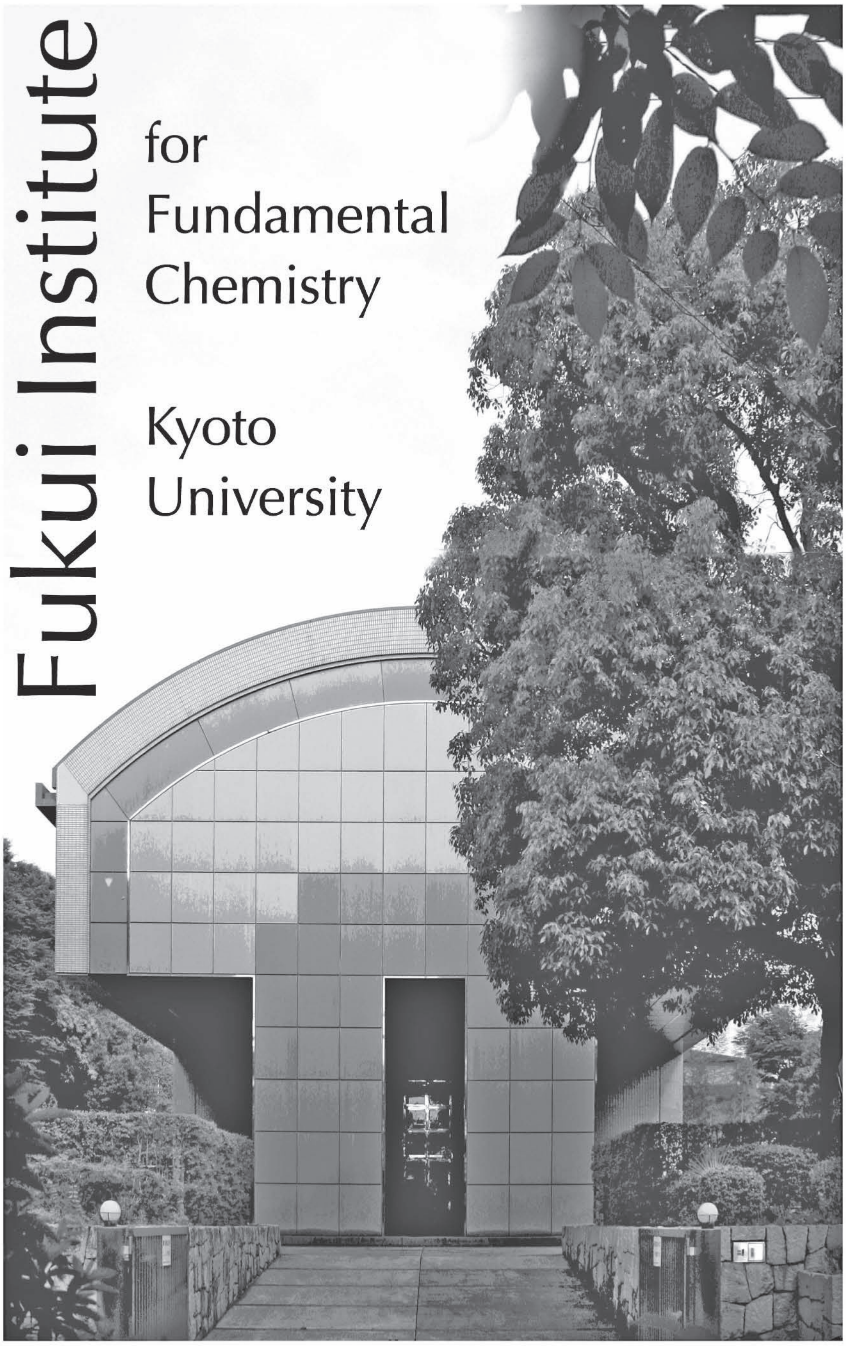

京都大学
福井謙一記念研究センター

はじめに

2015年度（平成27年度）の京都大学福井謙一記念研究センターの活動をまとめた年報をお届けします。本センターは、京都大学本部構内の北、約1キロの高野川沿いの静かな住宅街に独立して位置しております。専任教員は理論研究部門と総合研究部門に准教授各1名を持っているに過ぎませんが、センター長のほか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12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。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の雇用で、自分自身のアイデアで一定期間、自由闊達に研究できる身分を保証しています。

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

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

本センターは、国際活動も活発で、2005年（平成17年）よりチェコおよびスロバキアと理論化学・計算化学シンポジウムを定期的に開催しております。2011年（平成23年）には国内外（主にドイツ、東欧、中国、韓国）から第一線の研究者を招き、第1回福井センター理論化学・計算化学国際シンポジウムを開催しました。こうした国際連携活動をさらに活性化するという観点から、2016年（平成28年）2月に国際連携研究室を設置し、その運営上必要となるコーディネーター役として、特定助教1名を配置しました。本センターは、今後も、理論化学・計算化学分野におけるわが国の研究拠点の役割を果たし、国際連携活動を展開して行きたいと考えております。

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

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

また、現在本センターの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、本センターの名を大い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、研究活動は極めて活発です。今後も、京都大学あるいは国内外との共同研究を積極的に進めて行きたいと考えております。とくに実験科学者との共同研究は重要であり、そのような連携研究をさらに活発化したいと考えております。

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

平成28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/wp-content/themes/fifc/pdf/AnnualReport2015.pdf）

Ⅰ　専任教員・スーパーバイザー

1．教員組織

平成２７年度

職名		氏名	備考
センター長		赤木 和夫	工学研究科高分子化学専攻
副センター長		八尾 誠	理学研究科物理学・宇宙物理学専攻
副センター長		田中 勝久	工学研究科材料化学専攻
副センター長		池田 昌司	専任
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	森脇 淳	理学研究科数学・数理解析専攻
	化学研究所長	時任 宣博	化学研究所物質創製化学研究系
総合研究部門 スーパーバイザー	教授	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	佐藤 啓文	工学研究科分子工学専攻
	教授	佐々 真一	理学研究科物理学・宇宙物理学専攻
	教授	渡辺 宏	化学研究所分子レオロジー
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
	准教授	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)	
国際学術連携研究室	特定助教	水野 英如	専任
永瀬グループ	FIFC リサーチフェロー	永瀬 茂	研究員
諸熊グループ	FIFC リサーチフェロー	諸熊 奎治	研究員
榊グループ	リサーチリーダー	榊 茂好	研究員
田中グループ	シニアリサーチフェロー	田中 一義	研究員

２．教員プロフィール

(1) センター長

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【研究分野】	高分子化学、液晶化学、物質化学
【現在の研究課題】	導電性、液晶性、発光性、階層らせん性の共役系高分子の合成と性質
【研究内容キーワード】	導電性高分子、液晶性共役高分子、不斉液晶反応場、階層構造制御
【最終学歴】	京都大工学研究科博士後期課程
【学位】	工学博士
【略歴】	福井大工助手、筑波大物質工講師、助教授、教授、同大学院数理物質科学研究科教授、学際物質科学研究センター長
【在外研究歴】	カリフォルニア大サンタバーバラ校交換研究員、コーネル大客員研究員
【所属学会】	日本化学会、高分子学会、日本液晶学会、アメリカ化学会
【学会活動】	文部科学省科研費（特定領域研究、2005-2008）「次世代共役ポリマーの超階層制御と革新機能」領域代表、Chair of International Conference on Science and Technology of Synthetic Metals (2010).
【主な著書、学術論文】 （過去 5 年以内）	1. 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）

⑵　副センター長

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【研究分野】	不規則系物理学
【現在の研究課題】	X 線自由電子レーザー・放射光利用の不規則系実験研究
【研究内容キーワード】	液体、クラスター、分子、X 線自由電子レーザー、シンクロトロン放射光、金属・非金属転移、ナノプラズマ、プラズモン／エキシトン、超高速電荷・エネルギー移動、クーロン爆発、電子分光／イオン分光、密度汎関数法
【学歴】	1980 年　3 月　京都大学大学院理学研究科博士後期課程 研究指導認定 1982 年　3 月　京都大学理学博士 学位取得
【学位】	京都大学理学博士
【略歴】	1985 年　8 月　京都大学理学部 助手 採用 1990 年 12 月　京都大学理学部 講師 昇任 1993 年　3 月　京都大学理学部 助教授 昇任 2003 年　6 月　京都大学大学院理学研究科 教授 昇任、現在に至る
【所属学会】	日本物理学会、日本中性子科学会、日本放射光学会、国際教育学会
【学会活動】	国際教育学会理事
【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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【現在の研究課題】	新規酸化物固体の合成と磁気的・誘電的・光学的性質
【研究内容キーワード】	酸化物、磁気的性質、誘電的性質、光学的性質
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【主な著書、学術論文】（過去 5 年以内）	1. 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. 2. 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. 3. 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. 4. H. Akamatsu, K. Fujita, T. Kuge, A. S. Gupta, A. Togo, S. Lei, F. Xue, G. Stone, J. M Rondinelli, L. Chen, I. Tanaka, V. Gopalan, and K. Tanaka, “Inversion symmetry breaking by oxygen octahedral rotations in Ruddlesden-Popper NaRETiO$_4$ family”, *Physical Review Letters* **112** (2014) 187602-1-5. 5. 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. 6. 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. 7. T. Yajima, F. Takeiri, K. Aidzu, H. Akamatsu, K. Fujita, M. Ohkura, W. Yoshimune, S. Lei, V. Gopalan, K. Tanaka, C. M. Brown, M. A. Green, T. Yamamoto, Y.i Kobayashi, and H. Kageyama, “A labile hydride strategy to synthesize heavily nitridized BaTiO$_3$”, *Nature Chemistry* **7** (2015) 1017-1023.
【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. 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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【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.
【学術関係の受賞】	1. 2002年 第19回日本化学会学術賞 2. 2007年 Earl L. Muetterties Memorial Lectureship (University of California, Berkeley)、平成19年度錯体化学会賞 3. 2008年 Humboldt Research Award, Germany 4. 2009年 第61回日本化学会賞 5. 2010年 トムソン・ロイター引用栄誉賞受賞 6. 2011年 平成23年度科学技術分野の文部科学大臣表彰研究部門、The Honorary Fellowship of the Council of the Chemical Research Society of India (CRSI)、平成23年春の紫綬褒章、京都新聞大賞文化学術賞、第22期日本学術会議会員 7. 2013年 The RSC de Gennes Prize、第10回江崎玲於奈賞、平成25年度京都大学孜孜賞、The fellow of the UK Royal Society of Chemistry (RSC) 8. 2014年 2014 Thomson Reuters Highly Cited Researcher 9. 2015年 マルコ・ポーロ イタリア科学賞 10. 2016年 平成28年度日本学士院賞

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【在外研究歴】	2004年6月-2004年12月 連合王国Oxford大学PTCL訪問研究員（Paul A. Madden教授）
【所属学会】	日本化学会、分子科学会、理論化学研究会、溶液化学研究会、イオン液体研究会
【学会活動】	日本化学会　理論化学・情報化学・計算化学ディビジョン幹事（2011年度-）、副主査（2015年度-） 理論化学研究会　第三期世話人（2009年-） 分子科学会　幹事（2012年度-2013年度）、運営委員（2012年度-） 溶液化学研究会　運営委員（2015年度-）
【主な著書、学術論文】 （過去5年以内）	1. Maxim Shishkin and Hirofumi Sato, “Self-consistent parametrization of DFT+U framework using linear response approach: Application to evaluation of redox potentials of battery cathodes” *Phys. Rev. B* **93**(8), 085135 (2016). 2. Yoshihiro Matsumura and Hirofumi Sato, “An integral equation theory for solvation effects on the molecular structural fluctuation” *J. Chem. Phys.* **143**(1), 014104 (2015). 3. Kento Kasahara and Hirofumi Sato, “Development of three-dimensional site-site Smoluchowski-Vlasov equation and application to electrolyte solutions” *J. Chem. Phys.* **140**(24), 244110 (2014). 4. Seigo Hayaki, Yoshifumi Kimura, and Hirofumi Sato, “Ab Initio Study on an Excited-State Intramolecular Proton-Transfer Reaction in Ionic Liquid” *J. Phys. Chem. B* **117**(22), 6759- 6767 (2013). 5. Hirofumi Sato, “A modern solvation theory: quantum chemistry and statistical chemistry” *Phys. Chem. Chem. Phys.* **15**(20), 7450-7465 (2013).
【学術関係の受賞】	日本化学会・進歩賞（2002年） 分子構造総合討論会奨励賞（2006年） 公益信託分子科学研究奨励森野基金（2008年） 溶液化学研究会学術賞（2009年）

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【主な著書、学術論文】 （過去 5 年以内）	1. Thermodynamic entropy as a Noether invariant, S.-I. Sasa, Yuki Yokokura, *Phys. Rev. Lett* **116** 140601/1-140601/6（2016） 2. Replica symmetry breaking in trajectories of a driven Brownian particle, Masahiko Ueda, S.-I. Sasa, *Phys. Rev. Lett* **115** 080605/1-080605/5（2015） 3. Derivation of Hydrodynamics from the Hamiltonian Description of Particle Systems, S.-I. Sasa, *Phys. Rev. Lett* **112** 100602/1-100602/5（2014） 4. Computation of large deviation statistics via iterative measurement-and-feedback procedure, T. Nemoto, S.-I. Sasa, *Phys. Rev. Lett* **112** 090602/1-090602/5（2014） 5. Pure glass in finite dimensions, S.-I. Sasa, *Phys. Rev. Lett* **109** 165702/1-165702/4（2012）

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【主な著書、学術論文】（過去 5 年以内）	1. Y. Matsumiya and H. Watanabe , "Nonlinear Stress Relaxation of Miscible Polyisoprene/Poly(p-tert-butyl Styrene) Blends in Pseudo-monodisperse State", *Macromolecules*, **49**, 4544-4556 (2016). 2. Youngdon Kwon, Yumi Matsumiya, and Hiroshi Wtanabe, Viscoelastic and Orientational Relaxation of Linear and Ring Rouse Chains undergoing Reversible End-Association and Dissociation", *Macromolecules*, **49**, 3593-3607 (2016). 3. Y. Matsumiya, N. Rakkapao, and H. Watanabe, "Entanglement Length in Miscible Blends of cis-Polyisoprene and Poly(p-tert-butylstyrene)", *Macromolecules*, **48**, 7889-7908 (2015). 4. K. Timachova, H. Watanabe, and N. P. Balsara, "Effect of molecular weight and salt concentration on ion transport and the transference number in polymer electrolytes", *Macromolecules*, **48**, 7882-7888 (2015). 5. H. Watanabe, Y. Matsumiya , Y. Masubuchi ,O. Urakawa, and T. Inoue, "Viscoelastic Relaxation of Rouse Chains undergoing Head-to-Head Association and Dissociation: Motional Coupling through Chemical Equilibrium", *Macromolecules*, **48**, 3014–3030 (2015). 6. Y. Masubuchi and H. Watanabe, "Origin of Stress Overshoot under Start-up Shear in Primitive Chain Network Simulation", *ACS MACRO Letters*, **3**, 1183-1186 (2014). 3, 1183-1186 7. E. van Ruymbeke, V. Shchetnikava, Y. Matsumiya, and H. Watanabe, "Dynamic dilution effect in binary blends of linear polymers with well-separated molecular weights", *Macromolecules*, **47**, 7653-7665 (2014). 8. Y. Matsumiya, Y. Masubuchi, T. Inoue, O. Urakawa, C.-Y. Liu, E. van Ruymbeke, and H. Watanabe, "Dielectric and Viscoelastic Behavior of Star-branched Polyisoprene: Two Coarse-Grained Length Scales in Dynamic Tube Dilation",

Macromolecules, **47**, 7637-7652 (2014).

9. Y. Masubuchi, Y. Matsumiya, and H. Watanabe,"Test of orientation/stretch-induced reduction of friction via primitive chain network simulations for polystyrene, polyisoprene and poly-n-buthylacrylate ", *Macromolecules*, **47**, 6768-6775 (2014).
10. Y. Masubuchi, Y. Matsumiya, H. Watanabe, G. Marrucci, and G. Ianniruberto, "Primitive Chain Network Simulations for Pom-pom Polymers in Uniaxial Elongational Flows", *Macromolecules*, **47**, 3511-3519 (2014).
11. K. Horio, T.Uneyama, Y. Matsumiya, Y.Masubuchi, and H.Watanabe, "Rheo-Dielectric Responses of Entangled cis-Polyisoprene under Uniform Steady Shear and LAOS", *Macromolecules*, **47**, 246-255 (2014).
12. H. Watanabe, Y. Matsumiya, and E. van Ruymbeke, "Component relaxation times in entangled binary blends of linear chains: Reptation/CLF along partially or fully dilated tube", *Macromolecules*, **46**, 9296-9312 (2013).
13. Q. Huang, N. J. Alvarez, Y. Matsumiya, H. K. Rasmussen, H. Watanabe, and O. Hassager, "Extensional Rheology of Entangled Polystyrene Solutions Suggests Importance of Nematic Interactions", *ACS Macro Letters*, **2**, 741-744 (2013).
14. Y. Matsumiya, K. Kumazawa, M. Nagao, O. Urakawa, and H. Watanabe, "Dielectric Relaxation of Monodisperse Linear Polyisoprene: Contribution of Constraint Release", *Macromolecules*, **46**, 6067-6080 (2013).
15. S. Suzuki, T. Uneyama, and H. Watanabe, "Concentration Dependence of Nonlinear Rheological Properties of Hydrophobically Modified Ethoxylated Urethane (HEUR) Aqueous Solutions ", *Macromolecules*, **46**, 3497-3504 (2013).
16. Y. Matsumiya, H. Watanabe, A. Takano, and Y. Takahashi, "Uniaxial Extensional Behavior of (SIS)p-type Multiblock Copolymer Systems: Structural Origin of High Extensibility", *Macromolecules*, **46**, 2681–2695 (2013).
17. T. Uneyama, S. Suzuki, and H. Watanabe, "Concentration Dependence of Rheological Properties of Telechelic Associative Polymer Solutions", *Phys. Rev. E*, **86**, 031802 (2012).
18. Y. Matsumiya, Q. Chen, A. Uno, H. Watanabe, A. Takano, K. Matsuoka, and Y. Matsushita, "Dielectric behavior of Styrene-Isoprene (SI) diblock and SIIS triblock copolymers: Global dynamics of I blocks in spherical and cylindrical domains embedded in glassy S matrix", *Macromolecules*, **45**, 7050-7060, (2012).
19. E. Tamura, Y. Kawai, T. Inoue, and H. Watanabe, "Rheo-Optical Study of Viscoelastic Relaxation Modes in Block Copolymer Micellar Lattice System", *Macromolecules*, **45**, 6580-6586 (2012).
20. Q. Chen, Y. Matsumiya, T. Iwamoto, K. Nishida, T. Kanaya, H. Watanabe, A. Takano, K. Matsuoka, and Y. Matsushita, "Dielectric Behavior of Guest cis-Polyisoprene Confined in Spherical Microdomain of Triblock Copolymer", *Macromolecules*, **45**, 2809–2819 (2012).
21. T. Yaoita, T. Isaki, Y. Masubuchi, H. Watanabe, G. Ianniruberto, and G. Marrucci, "Primitive Chain Network Simulation of Elongational Flows of Entangled Linear Chains: Stretch/Orientation-induced Reduction of Monomeric Friction", *Macromolecules*, **45**, 2773–2782 (2012).
22. E. van Ruymbeke, Y. Masubuchi, and H. Watanabe, "Effective Value of the Dynamic Dilution Exponent in Bidisperse Linear Polymers: from 1 to 4/3", *Macromolecules*, **45**, 2085-2098 (2012).
23. S. Suzuki, T. Uneyama, T. Inoue, and H. Watanabe, "Nonlinear Rheology of Telechelic Associative Polymer Networks: Shear Thickening and Thinning Behavior of Hydrophobically Modified Ethoxylated Urethane (HEUR) in Aqueous Solution", *Macromolecules*, **45**, 888-898 (2012).
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【主な著書、学術論文】（過去5年以内）	1. H. Mizuno and R. Yamamoto, “General Constitutive Model for Supercooled Liquids: Anomalous Transverse Wave Propagation”, *Physical Review Letters*, Vol.**110**, p.095901 (5pages), 2013. 2. H. Mizuno, S. Mossa, and J.-L. Barrat, “Elastic heterogeneity, vibrational states, and thermal conductivity across an amorphisation transition”, *Europhysics Letters (EPL)*, Vol.**104**, p.56001 (6pages), 2013. 3. H. Mizuno, S. Mossa, and J.-L. Barrat, “Acoustic excitations and elastic heterogeneities in disordered solids”, *Proceedings of the National Academy of Sciences of the United States of America*, Vol.**111**, p.11949-11954 (6pages), 2014. 4. H. Mizuno, S. Mossa, and J.-L. Barrat, “Beating the amorphous limit in thermal conductivity by superlattices design”, *Scientific Reports*, Vol.**5**, p.14116 (15pages), 2015.

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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. M. Yamada, T. Akasaka, and S. Nagase, Endohedral Metal Atoms in Pristine and Functionalized Fullerene Cages, *Acc. Chem. Res.*, **43**, 92-102 (2010). 2. X. Lu, L. Feng, T. Akasaka, and S. Nagase, Current Statues and Future Developments of Endohedral Metallofullerenes, *Chem. Soc. Rev.*, **41**, 7723-7760 (2012). 3. S. Nagase, Multiple Bonds between Lead Atoms and Short Bonds between Transition Metals, *Pure Appl. Chem.*, **85**, 649-659 (2013). 4. X. Lu, T. Akasaka, and S. Nagase, Carbide Cluster Metallofullerenes: Structure, Properties, and Possible Origin, *Acc. Chem. Res.*, **46**, 1627-1635 (2013). 5. M. Yamada, T. Akasaka, and S. Nagase, Carbene Additions to Fullerenes, *Chem. Rev.*, **113**, 7209-7264 (2013). 6. 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). 7. J. –D. Guo, D. J. Liptrot, S. Nagase, and P. P. Power, The Multiple Bonding in Heavier Group 14 Element Alkene Analogues is Stabilized Mainly by Dispersion Force Effects, *Chem. Sci.* **6**, 6235-6244 (2015).
【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
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【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 D_1 and D_0 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

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【現在の研究課題】	遷移金属元素を含む複合電子系の構造、電子状態、反応過程の理論化学
【研究内容キーワード】	電子状態・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、錯体化学会
【主な著書、学術論文】 （過去5年以内）	1. 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). 2. 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). 3. 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). 4. 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). 5. Catalytic Transfer Hydrogenation by Trivalent Phosphorus Compound: Phosphorus-Ligand Cooperation Pathway or PIII/PV Redox Pathway? G. Zeng, S. Maeda, T. Taketsugu, and S. Sakaki,, *Angew. Chem. Int. Ed.*, **128**, 4721-4725 (2014). 6. 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). 7. How Can We Understand Au_8 Cores and Entangled Ligands of Selenolate- and Thiolate-Protected Gold Nanoclusters $Au_{24}(ER)_{20}$ and $Au_{20}(ER)_{16}$ (E = Se, S; R = Ph, Me)? A Theoretical Study, N. Takagi, K. Ishimura, M. Matsui, R. Fukuda, T. Matsui, T. Nakajima, M. Ehara, and S. Sakaki, *J. Am. Chem. Soc.*, **137**, 8593-8602 (2015). 8. 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, M. Nakagaki and S. Sakaki, *Phys. Chem. Chem. Phys.*, **17**, 16294-16305 (2015). 9. Theoretical and Computational Study of a Complex System Consisting of Transition Metal Element(s): How to Understand and Predict Its Geometry, Bonding Nature, Molecular Property, and Reaction Behavior, S. Sakaki, *Bull. Chem. Soc. Jpn.*, **88**, 889-938 (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)

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【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
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【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） 4. 元素ブロック材料の基礎と実用化のための理論化学 ,「中條善樹監修 , 元素ブロック高分子−有機・無機ハイブリッド材料の新概念−」(共著 , シーエムシー , 2015) 5. ボール物理化学 第2版（上）（監訳ならびに共訳，化学同人，2015） 6. ボール物理化学 第2版（下）（監訳ならびに共訳，化学同人，2016） （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).
8. スズ版グラフェン“スタネン”がつくられた！（単著）化学 , **71**, No. 1, 21-26 (2016).

（以上和文総説）

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2. 1,3,5-Benzenetriamine Double- and Triple-Decker Molecules (D. Sakamaki, A. Ito, K. Tanaka, K. Furukawa, T. Kato, and M. Shiro) *Angew. Chem. Int. Ed.*, **51**, 8281-8285 (2012).
3. Electronic Spectra of Cycl[3.3.2]azine and Related Compounds: Solvent Effect on Vibronic Couplings (Y. Shigemitsu, M. Uejima, T. Sato, K. Tanaka, and Y. Tominaga) *J. Phys. Chem. A*, **116**, 9100-9109 (2012).
4. A Triphenylamine Double-Decker: From a Delocalized Radical Cation to a Diradical Dication with an Excited Triplet State (Y. Yokoyama, D. Sakamaki, A. Ito, K. Tanaka, and M. Shiro) *Angew. Chem. Int. Ed.*, **51**, 9403-9406 (2012).
5. Mechanisms of Localization in Isotope-Substitutes Dynamical Jahn-Teller Systems (N. Iwahara, T. Sato, K. Tanaka, and L. F. Chibotaru) *Eur. Phys. Lett.*, **100**, 43001 1-6 (2012).
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).
7. A Polymacrocyclic Oligoarylamine with a Pseudobeltane Motif: Towards a Cylindrical Multispin System (D. Sakamaki, A. Ito, K. Furukawa, T. Kato, M. Shiro, and K. Tanaka) *Angew. Chem. Int. Ed.*, **51**, 12776-12781 (2012).
8. Meta-Para-Linked Octaaza[18]cyclophanes and Their Polycationic States (D. Sakamaki, A. Ito, K. Furukawa, T. Kato, and K. Tanaka) *J. Org. Chem.*, **78**, 2947-2956 (2013).
9. Vibronic Couplings in Cycloadditions to Fullerenes (N. Haruta, T. Sato, N. Iwahara, and K. Tanaka) *J. Phys. C: Conf. Ser.*, **428**, 012003 1-7 (2013).
10. Vibronic Coupling Density and Related Concepts (T. Sato, M. Uejima, N. Iwahara, N. Haruta, K. Shizu, and K. Tanaka) *J. Phys. C: Conf. Ser.*, **428**, 012010 1-19 (2013).
11. Vibronically Induced Activation Mechanism in Photocatalysis of Highly Dispersed Vanadium Oxide Supported on Silica, V_2O_5/SiO_2: Evidence in Phosphorescence Spectra (N. Iwahara, T. Sato, K. Tanaka, and T. Tanaka) *Chem. Phys. Lett.*, **584**, 63-66 (2013).
12. Reaction Mechanism in the Mechanochemical Synthesis of Dibenzophenazine: Application of Vibronic Coupling Density Analysis (N. Haruta, T. Sato, K. Tanaka, and M. Baron) *Tetrahedron Lett.*, **54**, 5920-5923 (2013).
13. Redox Modulation of *para*-Phenylenediamine by Substituted Nitronyl Nitroxide Groups and Their Spin States (A. Ito, R. Kurata, D. Sakamaki, S. Yano, Y. Kono, Y. Nakano, K. Furukawa, T. Kato, and K. Tanaka) *J. Phys. Chem. A*, **117**, 12858-12867 (2013).
14. Vibronic Couplings in C_{60} Derivatives for Organic Photovoltaics (N. Iwahara, T. Sato, K. Tanaka, and H. Kaji) *Chem. Phys. Lett.*, **590**, 169-174 (2013).
15. Preparation of D-A Polymer with Disilanobithiophene as New Donor Component and Application to High-voltage Bulk Heterojunction Polymer Solar Cell (J. Ohshita, M. Nakashima, D. Tanaka, Y. Morihara, H. Fueno, and K. Tanaka) *Polym. Chem.*, **5**, 346-349 (2014).

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17. Pseudo Jahn-Teller Origin of Distortion in [6]Cycloparaphenylene (Y. Kameoka, T. Sato, T. Koyama, K. Tanaka, and T. Kato) *Chem. Phys. Lett.*, **598**, 69-74 (2014).
18. Highly Coplanar (*E*)-1,2-Di(1-naphthyl)disilene Involving a Distinct CH-π Interaction with the Perpendicularly Oriented Protecting Eind Group (M. Kobayashi, N. Hayakawa, K. Nakabayashi, T. Matsuo, D. Hashizume, H. Fueno, K. Tanaka, and K. Tamao) *Chem. Lett.*, **43**, 432-434 (2014).
19. A Designed Fluorescent Anthracene Derivative: Theory, Calculation, Synthesis, and Characterization (M. Uejima, T. Sato, M. Detani, A. Wakamiya, F. Suzuki, H. Suzuki, T. Fukushima, K. Tanaka, Y. Murata, C. Adachi, and H. Kaji) *Chem. Phys. Lett.*, **602**, 80-83 (2014).
20. Quantum Yield in Blue-Emitting Anthracene Derivatives: Vibronic Coupling Density and Transition Dipole Moment Density (M. Uejima, T. Sato, D. Yokoyama, K. Tanaka, and J. –W. Park) *Phys. Chem. Chem. Phys.*, **16**, 14244-14256 (2014).
21. Synthesis and Polymerization of a para-Disubstituted T8-caged Hexaisobutyl-POSS Monomer (T. Maegawa, Y. Irie, H. Fueno, K. Tanaka, and K. Naka) *Chem. Lett.*, **43**, 1532-1534 (2014).
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23. Electronic Structure of Tetraaza[1.1.1.1]o, *p, o, p*-Cyclophane and Its Oxidized States (D. Sakamaki, A. Ito, T. Matsumoto, and K. Tanaka) *RSC Adv.*, **4**, 39476-39483 (2014).
24. Synthesis of Conjugated Polymers Containing Gallium Atoms and Evaluation of Conju gation through Four-Coordinate Gallium Atoms (T. Matsumoto, Y. Onishi, K. Tanaka, H. Fueno, K. Tanaka, and Y. Chujo) *Chem. Commun.*, **50**, 15740-15743 (2014).
25. Reactivity of Endohedral Metallofullerene $La_2@C_{80}$ in Nucleophilic and Electrophilic Attacks: Vibronic Coupling Density Approach (N. Haruta, T. Sato, and K. Tanaka) *J. Org. Chem.*, **80**, 141-147 (2014).
26. Fluorescent Triphenylamine Derivative: Theoretical Design Based on Reduced Vibronic Coupling (Y. Kameoka, M. Uebe, A. Ito, T. Sato, and K. Tanaka) *Chem. Phys. Lett.*, **615**, 44-49 (2015).
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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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).
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35. New Tris- and Pentakis-Fused Donors Containing Extended Tetrathiafulvalenes: New Positive Electrode Materials for Reachargeable Batteries (S. Iwamoto, Y. Inatomi, D. Ogi, S. Shibayama, Y. Murakami, M. Kato, K. Takahashi, K. Tanaka, N. Hojo, and Y. Misaki) *Beilstein J. Org. Chem.*, **11**, 1136-1147 (2015).
36. Fluorescence Enhancement of Non-Fluorescent Triphenylamine: A Recipe to Utilize Carborane Cluster Substituents (M. Uebe, A. Ito, Y. Kameoka, T. Sato, and K. Tanaka) *Chem. Phys. Lett.*, **633**, 190-194 (2015).
37. Highly Efficient Blue Electroluminescence Using Delayed-Fluorescence Emitters with Large Overlap Density between Luminescent and Ground States (K. Shizu, H. Noda, H. Tanaka, M. Taneda, M. Uejima, T. Sato, K. Tanaka, H. Kaji, and C. Adachi) *J. Phys. Chem. C*, **119**, 26283-26289 (2015).
38. para-Bisvinylhexaisobutyl-Substituted T_8 Caged Monomer: Synthesis and Hydrosilylation Polymerization (T. Maegawa, Y. Irie, H. Imoto, H. Fueno, K. Tanaka, and K. Naka) *Polym. Chem.*, **6**, 7500-7504 (2015).
39. Coplanar Oligo(*p*-phenylenedisilenylene)s as Si=Si Analogues of Oligo(*p*-phenylenevinylene)s: Evidence for Extended π-Conjugation through the Carbon-Silicon π-Frameworks (L. Li, T. Matsuo, D. Hashizume, H. Fueno, K. Tanaka, and K. Tamao) *J. Am. Chem. Soc.*, **137**, 15026-15035 (2015).
40. Isolation and Characterization of Persistent Radical Cation and Dication of 2,7-Bis(dianisylamino)pyrene (R. Kurata, K. Tanaka, and A. Ito) *J. Org. Chem.*, **81**, 137-145 (2016).
41. (Z)-1,2-Di(1-pyrenyl)disilene: Synthesis, Structure, and Intramolecular Charge-Transfer Emission (M. Kobayashi, N. Hayakawa, T. Matsuo, B. Li, T. Fukunaga, D. Hashizume, H. Fueno, K. Tanaka, and K. Tamao) *J. Am. Chem. Soc.*, **138**, 758-761 (2016).
42. Synthesis and Characterization of 6,13-Diamino-Substituted Pentacenes (A. Ito, M. Uebe, K. Takahashi, H. Ishikawa, D. Sakamaki, H. Sato, T. Matsumoto, and K. Tanaka) *Chem. Eur. J.*, **22**, 2165-2170 (2016).
43. O_2-Triggered Directional Switching of Photocurrent in Self-Assembled Monolayer Composed of Porphyrin- and Fullerene-Terminated Helical Peptides on Gold (H. Uji, K. Tanaka, and S. Kimura) *J. Phys. Chem. C*, **120**, 3684-3689 (2016).

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【主な著書、学術論文】（過去 5 年以内）	1. M. Tarama, Y. Itino, A.M. Menzel, and T. Ohta, “Individual and collective dynamics of self-propelled soft particles”, *Eur. Phys. J. Special Topics* **223**, 121–139 (2014). 2. M. Tarama, A.M. Menzel, and H. Löwen, “Deformable microswimmer in a swirl: Capturing and scattering dynamics”, *Phys. Rev. E* **90**, 032907 (2014). 3. M. Tarama, P. Cremer, D.Y. Borin, S. Odenbach H. Löwen, and A.M. Menzel, “Tunable dynamic response of magnetic gels: Impact of structural properties and magnetic fields”, *Phys. Rev. E* **90**, 042311 (2014). 4. T. Ohta, M. Tarama and M. Sano, “Simple model of cell crawling”, *Physica D* **318-319**, 3-11 (2016). 5. M. Tarama and T. Ohta, “Reciprocating motion of active deformable particles”, *Europhys. Lett.* **114**, 30002 (2016).
【学術関係の受賞など】	Research Fellow of Japan Society for the Promotion of Science (DC1) (Apr. 2012 - Mar. 2015) ポスター発表 優秀賞（平成24年度未踏科学サマー道場、Aug. 2014） the Richard M. Noyes Fund Fellowship (Jul. 2014)

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【主な著書、学術論文】（過去5年以内）	1. Nishimoto, Y. “DFTB/PCM Applied to Ground and Excited State Potential Energy Surfaces”, *J. Phys. Chem. A* 2016, **120**, 771-784. 2. Nishimoto, Y.; Nakata, H.; Fedorov, D. G.; Irle, S. “Large-Scale Quantum-Mechanical Molecular Dynamics Simulations Using Density-Functional Tight-Binding Combined with the Fragment Molecular Orbital Method”, *J. Phys. Chem. Lett*. 2015, **6**, 5034-5039. 3. Nishimoto, Y. “Time-dependent density-functional tight-binding method with the third-order expansion of electron density”, *J. Chem. Phys*. 2015, **143**, 094108. 4. Nishimoto, Y.; Fedorov, D. G.; Irle, S. “Third-order density-functional tight-binding combined with the fragment molecular orbital method”, *Chem. Phys. Lett*. 2015, **636**, 90-96. 5. Nishimoto, Y.; Fedorov, D. G.; Irle, S. “Density-Functional Tight-Binding Combined with the Fragment Molecular Orbital Method”, *J. Chem. Theory Comput*. 2014, **10**, 4801-4812.
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【主な著書、学術論文】（過去 5 年以内）	1. 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). 2. 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). 3. Complete active space second order perturbation theory (CASPT2) study of $N(^2D)$ + 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). 4. 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). 5. Ionization Energies and Aqueous Redox Potentials of Small Organic Molecules: Capabilities and Limitations of Modern Methods, M. Isegawa, D. A. Pantazis, F. Neese, *J. Chem. Theory Comput.* **12**, 2272 (2016).

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【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, S. Maeda, K. Morokuma, Exploration of Quenching Pathways of Multiluminescent Acenes Using the GRRM Method with the SF-TDDFT Method, *J. Phys. Chem. A*, **119** pp 11479–11487 (2015) 3. S.Sasaki, S.Suzuki, W.M.C. Sameera, K. Igawa, K. Morokuma, G. Konishi, Highly twisted N, N-dialkylamines as a design strategy to tune simple aromatic hydrocarbons as steric environment-sensitive fluorophores, *J. Am. Chem. Phys.*, in press
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【主な著書、学術論文】 （過去 5 年以内）	1. Aurelie Perveaux, Pedro J. Castro, Mar Reguero, Hans-Dieter Meyer, Fabien Gatti, Benjamin Lasorne, David Lauvergnat. *Springer Proceedings In Physics* **162**, 2015, p.386–390. 2. Aurelie Perveaux, Pedro J. Castro, David Lauvergnat, Mar Reguero, and Benjamin Lasorne. *J. Phys. Chem. Lett.* 2015, **6**, 1316–1320 3. Isabel Gómez, Pedro J. Castro and Mar Reguero. *J. Phys. Chem. A* 2015, **119**, 1983–1995. 4. V. José Cotuá, Sandra Cotes, Fernando Castro and Pedro J. Castro. *Journal of Basic & Applied Sciences*, 2013, **9**, 16-20. 5. Pedro J. Castro, Isabel Gomez, Maurizio Cossi and Mar Reguero. *The Journal of Physical Chemistry A*, **116**(31), p.8148–8158, 2012.

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【職名】	特定研究員
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【研究分野】	溶液化学・計算化学・理論化学
【現在の研究課題】	溶液中の遷移金属錯体の化学反応の理論的解析
【研究内容キーワード】	3D-RISM-SCF 法、平均場 QM/MM 法、自由エネルギー解析、溶媒和構造解析、周期的結晶解析
【学歴】	2010 年 3 月　京都大学大学院理学研究科化学専攻博士後期課程 研究指導認定退学
【学位】	2010 年 9 月　理学博士（京都大学）
【略歴】	2010 年 4 月　京都大学大学院理学研究科化学専攻 研修員 2010 年 5 月　京都大学 物質 - 細胞統合システム拠点 教務補佐員 2010 年 10 月　京都大学 物質 - 細胞統合システム拠点 特定研究員 2011 年 4 月　京都大学 福井謙一記念研究センター 特定研究員 2015 年 4 月　京都大学 福井謙一記念研究センター フェロー（榊研）
【所属学会】	日本分子化学会
【主な著書、学術論文】（過去 5 年以内）	1. Aono S., Mori T., and Sakaki S., “3D-RISM-MP2 Approach to Hydration Structure of Pt(II) and Pd(II) Complexes: Unusual H-Ahead Mode vs Usual O-Ahead One” *J. Chem. Theory Comput.* **12** 1189-1206 (2016). [Cover] 2. Aono S., Nakagaki M., Kurahashi T., Fujii H., and Sakaki S., “Theoretical Study of One-Electron Oxidized Mn(III)− and Ni(II)−Salen Complexes: Localized vs Delocalized Ground and Excited States in Solution” *J. Chem. Theory Comput.* **10** 1062 (2014). 3. Aono S., Hosoya T., and Sakaki S., “A 3D-RISM-SCF method with dual solvent boxes for a highly polarized system: application to 1,6-anhydrosugar formation reaction of phenyl alpha- and beta-D-glucosides under basic conditions” *Phys. Chem. Chem. Phys.* **17** 6368 (2013) 4. Aono S. and Sakaki S., “Evaluation Procedure of Electrostatic Potential in 3D-RISM-SCF Method and Its Application to Hydrolyses of Cis- and Transplatin Complexes” *J. Phys. Chem. B* **116** 13045 (2012) 5. Aono S. and Sakaki S., “Proposal of new QM/MM approach for geometry optimization of periodic molecular crystal: Self-consistent point charge representation for crystalline effect on target QM molecule” *Chem. Phys. Lett.* **544** 77 (2012). 6. Aono S., Yamamoto T. and Kato S. “Solution reaction space Hamiltonian based on an electrostatic potential representation of solvent dynamics” *J. Chem. Phys.* **134** 144108 (2011).

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【研究分野】	Computational Chemistry
【現在の研究課題】	Electronic Structure of Inverted Sandwich Type Complexes
【研究内容キーワード】	Electronic Structure of Metal Complex, Multireference Theory
【学歴】	March 2005, Master of Sci., Graduate School of Science, Kyushu University March 2009, Doctor of Sci., Graduate School of Science, Kyushu University
【学位】	Doctor of Science from Kyushu University
【略歴】	Apr. 2009, Postdoctoral Fellow, Kyushu University
【所属学会】	Japan Society for Molecular Science The Chemical Society of Japan
【主な著書、学術論文】（過去 5 年以内）	1. Masayuki Nakagaki and Shigeyoshi Sakaki “Inverse Sandwich-Type Dinitrogen Complexes of Hetero-Dinuclear 3d Metals: Theoretical Prediction of Characteristic Features of Geometry and Spin Multiplicity” Submitting to *Phys. Chem. Chem. Phys.* 2. 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) 3. Masayuki Nakagaki and Shigeyoshi Sakaki “CASPT2 Study of Inverse Sandwich-Type Dinuclear Cr(I) and Fe(I) Complexes of the Dinitrogen Molecule: Significant Differences in Spin Multiplicity and Coordination Structure between These Two Complexes” *J. Phys. Chem. A*, **118**, 1247-1257 (2014) 4. Shinji Aono, Masayuki Nakagaki, Takuya Kurahashi, Hiroshi Fujii, and Shigeyoshi Sakaki “Theoretical Study of One-Electron Oxidized Mn(III)– and Ni(II)–Salen Complexes: Localized vs Delocalized Ground and Excited States in Solution” *J. Chem. Theory Comput.*, **10** 1062-1073 (2014)

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【研究分野】	Computational Quantum Chemistry
【現在の研究課題】	Nickel catalyzed hydroarylation of linear olefin
【研究内容キーワード】	Nickel, Lewis Acid, linear olefin, NHC
【学歴】	June 2011, Faculty of Chemistry, Northeast Normal University, P.R. China
【学位】	Ph.D. in Physical Chemistry
【略歴】	July 2011-Present, Faculty of Chemistry, Northeast Normal University, Changchun, P.R. China. August 2014-Present, Postdoctoral Fellow, Kyoto University.
【所属学会】	Chinese Chemical Society Membership
【主な著書、学術論文】（過去 5 年以内）	1. Li Y.; Zhang, J.; Yang, F.; Liang, J.; Sun, H.; Tang, S.W.; Wang R. *Phys. Chem. Chem. Phys.* 2014, **16**, 24604-24609. 2. Wang, F. D.; Wang, F.; Zhang, N.; Li, Y.; Tang, S.W.; Sun, H.; Chang, Y.; Wang, R. *Chem. Phys. Lett.* 2013, **555**, 212-216. 3. Tang, S.W.; Wang, F.D.; Zhang, N.; Chang, Y.; Sun, H.; Zhang, J.; Xie, H.; Qiu, Y.; Wang, R. *Phys. Chem. Chem. Phys.* 2012, **14**, 16476-16485. 4. Tang, S.W.; Feng, J.; Qiu, Y.; Sun, H.; Wang, F.; Su, Z.; Chang, Y.; Wang, R. *J. Comput. Chem.* 2011, **32**, 658-667.

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【研究分野】	Computational chemistry
【現在の研究課題】	Theoretical Study of Cross-coupling Reaction between Pd(II)-X and Co(I)-R Complexes
【研究内容キーワード】	Transition state and electronic property of cross-coupling reaction
【学歴】	December 2012, School of Science, Xi'an Jiaotong University
【学位】	Doctor of Materials Physics and Chemistry, Xi'an Jiaotong University
【略歴】	July 2014, Postdoctoral Fellow, Kyoto University
【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) 7. H. Zheng, X. Zhao, S. Sakaki, Reaction of Fullerene with Dinuclear Ruthenium Complex: Theoretical Understanding and Prediction, in submission.

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【研究分野】	Computational Chemistry
【現在の研究課題】	Computational investigation on the bonding and reactivity of transition metal complexes
【研究内容キーワード】	DFT, transition metal complexes, σ -bond activation
【学歴】	Master of Science, University of Kerala, Trivandrum, India (2008)
【学位】	Ph.D., Academy of Scientific and Innovative research, India (2015)
【主な著書、学術論文】 （過去 5 年以内）	1. Nishamol Kuriakose, Shantanu Kadam, and Kumar Vanka,* (2012), A theoretical study of metal–metal cooperativity in the homogeneous water gas shift reaction, *Inorg. Chem.*, **51**, 1, 377–385. 2. Nishamol Kuriakose and Kumar Vanka,* (2013), Can molecular cages be effective at small molecule activation? A computational investigation, *Inorg. Chem.*, **52**, 8, 4238–4243. 3. Nishamol Kuriakose and Kumar Vanka,* (2014), New insights into small molecule activation byacyclic silylenes: a computational investigation, *Dalton Trans.*, **43**, 2194-2201. 4. Vaishali S. Shende,a Savita K. Shingote,a Sudhindra H. Deshpande,a Nishamol Kuriakose,b Kumar Vanka,b* Ashutosh A. Kelkara* (2014), Asymmetric transfer hydrogenation of imines in water/methanol co-solvent system and mechanistic investigation by DFT study, *RSC Adv.*, **4**, 46351–46356. 5. Nishamol Kuriakose and Kumar Vanka,* (2015), Can substituted allenes be highly efficient leaving groups in catalytic processes? A computational investigation, *J. Comput. Chem.*, **36**, 795–804. 6. Nishamol Kuriakose and Kumar Vanka,* (2016), Can main group systems act as superior catalysts for dehydrogenation reactions in comparison to transition metal based systems? A computational investigation, *Dalton Trans.*, Advance Article, DOI: 10.1039/C5DT01058F. 7. Teruhiko Saito, Nishamol Kuriakose, Shigeyoshi Sakaki,* Yoshiaki Nakaoa* Synthesis of neutral and anionic Aluminum containing Rhodium complexes and their reactivity toward cleavage of srong σ–bonds. *(communicated).*
【学術関係の受賞など】	Shell India Computational Talent Prize - India – 2013: Honorable Mention Award for the paper “Can Molecular Cages Be Effective at Small Molecule Activation? A Computational Investigation.

４．共同研究員プロフィール

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【研究分野】	Computational Chemistry
【現在の研究課題】	Hybrid QM/MM methods, theoretical inorganic chemistry, florescent probs.
【学歴】	July 2005, BSc (Hons), University of Sri Jayewardenepura, Sri Lanka.
【学位】	PhD, University of Glasgow, United Kingdom.
【略歴】	Postdoctoral Fellow, University of Oxford (2010). Posdoctoral Fellow, Institute of Chemical Research of Catalonia, Spain (2011).
【所属学会】	Marie Curie Fellowship, University of Gothenburg, Sweden (2013) JSPS postdoctoral fellow, FIFC, Kyoto University. Japan (2014)
【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, “Transition metal catalysis by density functional theory and density functional theory molecular mechanics”, *WIREs Comput. Mol. Sci.*, Wiley-VCH, 2012, **2**, 375-380. 2. L. Maestre, W. M. C. Sameera, M. M. Díaz-Requejo, F. Maseras, P. J. Pérez. “A General Mechanism for the Copper- and Silver-Catalyzed olefin aziridination reactions: concomitant involvement of the singlet and triplet pathways”, *J. Am. Chem. Soc.* 2013, **135**, 1338-1348. 3. 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, K. Morokuma, “The ONIOM Method and its Applications”, *Chem. Rev.* 2015, **115**, 5678-5796. 4. W. M. C. Sameera, M. Hatanaka, T. Kitanasono, 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.* 2015, **137**, 11085-11094. 5. W. M. C. Sameera, S. Maeda, K. Morokuma, “Computational catalysis using the artificial force induced reaction (AFIR) method”, *Acc. Chem. Res.* 2016, **49**, 763-773.
【学術関係の受賞など】	Assistant professor, Hokkaido University, Japan. (2016) 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】	Molecular Spectroscopy and Computational Chemistry
【現在の研究課題】	Reaction of photo-functional molecules
【研究内容キーワード】	Excited State Proton Transfer Theoretical Study by GRRM
【学歴】	Sept. 2000, Master of Sci., Department of Chemistry, Hebei Normal University, China Sept. 2004, Doctor of Sci., Department of Chemistry, Fudan University, China
【学位】	Doctor of Science from Fudan University, China
【略歴】	October. 2007, Assistant Professor, Associate Professor, Zhejiang Sci-Tech University, China
【所属学会】	Chemical Society of China
【主な著書、学術論文】（過去 5 年以内）	1. Chen Xiao, Zhao Yanying*, Zhang Haibo, Xue jiadan, Zheng Xuming* Excited state proton transfer dynamics of thioacetamide in S_2(π-π*) state: resonance Raman spectroscopic and quantum mechanical calculations study. *J. Phys. Chem. A* **119**, 832-842(2015) 2. Zhao Yanying, Xu Qiang* Chapter 15, Metal-organic frameworks as platforms for hydrogen generation from chemical hydrides in Organometallics and Related Molecules for Energy Conversion, Green Chemistry and Sustainable Technology. *Springer-Verlag Berlin Heidelberg* 421-467(2015). W.-Y. Wong (ed.), DOI 10.1007/978-3-662-46054-2_15. 3. Li Dan, Zhao Yanying*, Xue Jia-Dan, Zheng Xuming Structural dynamics of 4-formaldehyde imidazole and imidazole in light absorbing S_2(π-π*) state *Journal of Raman Sepctroscopy* **46**(3), 293-301(2015). 4. Zhao Yanying*, Zhang Yuchen, Liu Xin, Zheng Xuming Formation, characterization, structure and bonding analysis of the metal-carbon bond OM-(η^6-C_6H_6) (M = Sc, Ti) complexes in solid matrix: Infrared spectroscopic and theoretical study. *J. Orgmet. Chem.* **777**, 25-30(2015) 5. Zhao Yanying*, Fan Kexue, Huang Yongfei, Zheng Xuming Matrix isolation infrared spectra, assignment and DFT investigation on reactions of iron and manganese monoxides with CH_3C1. *Spectrochimica Acta Part A-Molecular and Biomolecular Spectroscopy* **116**, 96-101(2013) 6. Zhao Yanying* C-Cl Activation by Group IV Metal Oxides in Solid Argon Matrixes: Matrix Isolation Infrared Spectroscopy and Theoretical Investigations of the Reactions of MOx (M = Ti, Zr; x=1, 2) with CH_3Cl. *J. Phys. Chem. A* **117**(27), 5664-5674(2013)
【学術関係の受賞など】	Project Grants 521 521 Talents Cultivation, Zhejiang Sci-Tech University, Zhejiang, Zhejiang, 2012~Present

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【研究分野】	Computational Chemistry
【現在の研究課題】	Theoretical study of catalytic reaction
【研究内容キーワード】	Fullerene-Transition metal complexes
【学歴】	June 2006, Master's degree., National Taiwan University January 2012, Philosophy's degree, National Tsing Hua University
【学位】	Philosophy's degree from National Tsing Hua University
【略歴】	Postdoctoral Fellow, Applied Chemistry Department, Chiayi University
【主な著書、学術論文】 （過去5年以内）	1. Ming-Chung Yang, Ming-Der Su, The addition reactions between N-heterocyclic carbenes and fullerenes (C_{60} and C_{70}): a density functional study, *Theoretical Chemistry Accounts*, 2015, **134**, 38. 2. Ming-Chung Yang, Tsung-Wei Shih, Yu-Chi Li, Jia-Ying Ma, and Ming-Der Su, A Model Study on Molecular Properties and Mechanistic Investigations of P=C=E14 Molecules, *European Journal of Inorganic Chemistry*, 2015, 1795-1803. 3. Tsung-Wei Shih, Ming-Chung Yang, and Ming-Der Su, Doubly Bonded E13=P and B=E15 Molecules and Their Reactions with H_2, Acetonitrile, Benzophenone, and 2,3-Dimethylbutadiene, *Inorganic Chemistry*, 2015, **54**, 5154. 4. Ming-Chung Yang, Ming-Der Su, Theoretical Designs for Fullerene Carbenes, C_{60}-E-C_{60} and C_{70}-E-C_{70} (E = Group 14 Elements): A Target for Experimental Studies, *J. Phys. Chem. C*, 2015, **119**, 12668.

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13回　京都大学福井謙一記念研究センターシンポジウム

日　　時　2016年（平成28年）2月5日

場　　所　京都大学福井謙一記念研究センター（3F大会議室）

講　　演　田中　一義（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）
「発光性分子材料の理論化学的設計」
10:15－11:15

西森　秀稔（東京工業大学 大学院理工学研究科 教授）
「量子アニーリング理論とD-Waveマシン」
11:30－12:30

永谷　清信（京都大学 大学院理学研究科 助教）
「Ｘ線自由電子レーザーとの付き合い方」
（八尾誠先生の都合により、代講）
14:00－15:00

― 休 憩 ―

ポスターセッション　15:30－17:20

懇親会（１Ｆ多目的ルーム）　17:30－19:00

２．福井センターセミナー

第13回　福井センターセミナー

日　　時　2015年（平成27年）9月26日　15:00－17:20

場　　所　京都大学福井謙一記念研究センター（1F多目的室）

15:00 〜 15:40　W.M.C.SAMEERA　(FIFC)
“Artificial force induced reaction method for mechanisms involving Transition metal complexes and clusters”

15:40 〜 16:20　Takuya SAITO　(FIFC)
“Driven Anomalous Diffusion in Polymer Stretching”

16:30 〜 17:20　Masayuki OHZEKI　(Kyoto Univ.)
“Accelerated Langevin Dynamics and its application to machine learning”

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) 榊　茂好　リサーチリーダー
滋賀県立膳所高等学校　2015年（平成27年）5月9日

(2) 諸熊　奎治　FIFCリサーチフェロー 他
京都大学アカデミックディ　2015年（平成27年）10月4日

(3) W.M.C. SAMEERA 他
私立市川高等学校（千葉県）　2015年（平成27年）10月14日

(4) 榊　茂好　リサーチリーダー
京都府立南陽高等学校　2015年（平成27年）11月6日

(5) 榊　茂好　リサーチリーダー
私立星陵高等学校（静岡県）　2015年（平成27年）12月9日

(6) 田中　一義　シニアリサーチフェロー
京都市成長産業創造センター　2015年（平成27年）12月17日

５．その他（報告）

諸熊 奎治FIFCリサーチフェローは、巨大分子の化学反応の計算方法を構築した功績により日本学士院会員に選出された（平成27年12月14日開催の第1094回総会）。

また、第34回京都府文化賞の特別功労賞を受賞。量子化学の第一人者として、電子計算機を駆使した分子の構造と機能の予測、その反応設計の功績が認められた（平成28年2月9日）。

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)

Equilibrium phase diagram of a randomly pinned glass-former

Upon cooling, glass-forming liquids show a dramatic increase of their viscosities and relaxation times before they eventually fall out of equilibrium at low temperatures. This laboratory glass transition is a purely kinetic effect since it occurs at the temperature at which the relaxation time of the system crosses the time scale imposed by the experiment, e.g. via the cooling rate. Despite the intensive theoretical, numerical, and experimental studies of the last five decades, the mechanism responsible for the slowing down and thus for the (kinetic) glass transition is still under debate and hence a topic of intense research. From a fundamental point of view the ultimate goal of these studies is to find an answer to the big question in the field: Does there exist a finite temperature at which the dynamics truly freezes and, if it does, whether this ideal glass transition is associated with a thermodynamic singularity or whether it is of kinetic origin.

Support for the existence of a kinetic transition comes from certain lattice gas models with a ``facilitated dynamics". In these models, the dynamics is due to the presence of ``defects" and hence for such systems the freezing is not related to any thermodynamic singularity. However, the first evidence that there does indeed exist a thermodynamic singularity goes already back to Kauzmann who found that the residual entropy (the difference of the entropy of the liquid state from that of the crystalline state) vanishes at a finite temperature TK if it is extrapolated to temperatures below the laboratory glass transition. Subsequently many theoretical scenarios that invoke the presence of a thermodynamic transition have been proposed. One of these is the so-called ``random first order transition" (RFOT) theory which, inspired by the exact solution of a mean-field spin glass, predicts that at T_K the glass-former does indeed undergo a thermodynamic transition at which the residual, or configurational entropy S_c (the logarithm of the number of the states which are available to the system) vanishes and concomitantly breaks the replica symmetry. A further appealing feature of RFOT is that it seems to reconcile in a natural way the (free) energy-landscape scenario and mode-coupling theory (MCT), a highly successful theory that describes the relaxation dynamics at intermediate temperatures.

Despite all these advances, the arguments put forward in the various papers must be considered as phenomenological since compelling and undisputed experimental or numerical evidence to prove or disprove any of these theories and scenarios is still lacking. The only exception are hard spheres in infinite dimensions, for which mean-field theory should become exact, but even in this case some unexpected problems are present. This lack of understanding is mainly due to the steep increase of the relaxation times which hampeirs the access to the transition point of thermally equilibrated systems and hence most of the efforts to identifying the transition point, if it exists, resort on unreliable extrapolation.

In the present work, we use computer simulation to determine for a canonical glass-former with pinned particles the ideal glass transition temperature T_K as a point at which S_c vanishes. For the first time this is done without invoking any kind of extrapolation. Fig. 1(a) shows the entropy per (unpinned) particle as a function of the fraction of pinned particles at several temperatures T and we recognize that with increasing c the entropy decreases rapidly. For all temperatures this decrease is linear at small *c* but then the curves bend at intermediate *c* and follow a weaker c-dependence. For T < 0.5 this bent becomes sharp, strongly indicating that a thermodynamic glass transition takes place. This becomes more evident by evaluating the configurational entropy obtained by subtracting from S the vibrational entropy S_{vib}. In order to estimate S_{vib}, we have determined the inherent structures and calculated the eigenfrequencies. Using the harmonic approximation, one can calculate S_{vib} which is shown in Fig.1(a) as well (solid lines) and we see that it shows basically a linear decrease with c, a trend which is due to the suppression of the low frequency modes in the density of states. We can now estimate the configurational entropy S_c as the difference $S_c = S - S_{\mathrm{vib}}$ and in Fig.1(b) we show the c-dependence of Sc for various temperatures. This figure shows that, for T < 0.5, S_c quickly decreases with increasing *c* and becomes basically zero at a finite value of *c*, indicating that the system has entered the ideal glass state in which the entropy is basically due to harmonic vibrations. For T > 0.55, the approach of S_c to zero is milder and the bent is less sharp, indicating that the transition becomes a crossover.

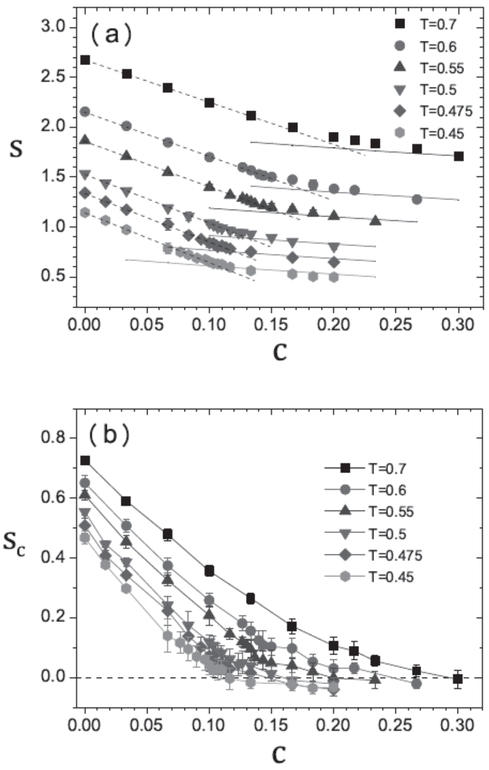

Fig. 1 (a): Entropy of the system, s, as evaluated from the thermodynamic integration, as a function of c (symbols). The entropies of the disordered solid states Svib, obtained using the harmonic approximation, are drawn as solid lines. The dashed lines are a linear extrapolation from the low c sides. (b): The configurational entropy $S_c = S - S_{\mathrm{vib}}$. The error bars have been estimated from the sample to sample fluctuations..

Thermal fluctuations, mechanical response, and hyperuniformity in jammed solids

Jamming is a geometric phase transition occurring in dense particle systems in the absence of temperature. We use computer simulations to analyze the effect of thermal fluctuations on several signatures of the transition. We show that scaling laws for bulk and shear moduli only become relevant when thermal fluctuations are extremely small, and propose their relative ratio as a quantitative signature of jamming criticality. Despite the nonequilibrium nature of the transition, we find that thermally induced fluctuations andmechanical responses obey equilibrium fluctuation-dissipation relations near jamming, provided the appropriate fluctuating component of the particle displacements is analyzed. This shows that mechanical moduli can be directly measured from particle positions in mechanically unperturbed packings, and suggests that the definition of a “nonequilibrium index” is unnecessary for amorphous materials.We find that fluctuations of particle displacements are spatially correlated, and define a transverse and a longitudinal correlation length scale which both diverge as the jamming transition is approached. We analyze the frozen component of density fluctuations and find that it displays signatures of nearly hyperuniform behavior at large length scales. This demonstrates that hyperuniformity in jammed packings is unrelated to a vanishing compressibility and explains why it appears remarkably robust against temperature and density variations. Differently from jamming criticality, obstacles preventing the observation of hyperuniformity in colloidal systems do not originate from thermal fluctuations.

One-dimensional Kac model of dense amorphous hard spheres

We considered an one-dimensional chain of the d-dimensional boxes each of which contains *N* hard spheres as a model system of liquids under confinement. By focusing on the large dimensional limit, we analytically computed the phase diagram of the model. From the chain length dependence of the transition densities, we derived the critical behavior of the two relevant length scales of the glass transition.

We summarize the results in Fig 2. The upper panel is the phase diagram of the glass transition of the confined liquid, where phi is the normalized density and *L* is the distance between the boundaries. There are the two relevant length scales ξ_{d} and ξ_{K}, which diverge as $\xi_{\mathrm{d}} \sim (\varphi_{\mathrm{d}} - \varphi)^{-1/4}$ and $\xi_{\mathrm{K}} \sim (\varphi_{\mathrm{K}} - \varphi)^{-1}$, respectively. When $L > \xi_{\mathrm{d}}$, the system holds the ergodicity and is in the liquid phase. For $\xi_{\mathrm{K}} < L < \xi_{\mathrm{d}}$, the phase space splits into the many sub-spaces and the ergodicity of the system is broken at least in the large dimensional limit. In $L < \xi_{\mathrm{K}}$ region, the number of the sub-spaces becomes sub-exponential and no longer contributes to the entropy. Thus the equilibrium phase transition from the liquid phase to the ideal glass phase occurs. These results are consistent with the results for the p-spin mean-field spin glass model, where the critical behaviors $\xi_{\mathrm{d}} \sim (T - T_d)^{-1/4}$ and $\xi_{\mathrm{K}} \sim (T - T_K)^{-1}$ are observed. This confirms that the proposed model is considered to be a hard sphere extension of the p-spin mean-field spin glass model under confinement. The result for ξ_{d} is also consistent with the prediction of the inhomogeneous mode-coupling theory for the dynamic correlation length diverging at the mode-coupling transition point. The lower panel of Fig. 2 is the phase diagram of the jamming transition. There are the two relevant length scales ξ_{th} and ξ_{GCP} which diverge as $\xi_{\mathrm{th}} \sim (\varphi_{\mathrm{th}} - \varphi)^{-1/4}$ and

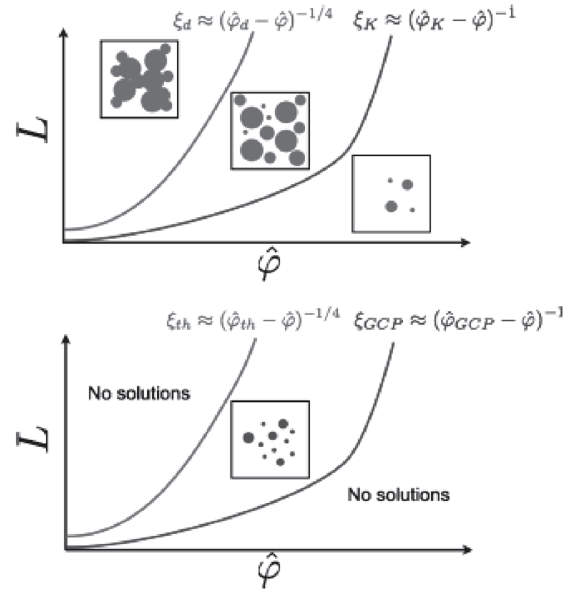

Fig. 2 Schematic phase diagram of our model.

$\xi_{\mathrm{GCP}} \sim (\varphi_{\mathrm{GCP}} - \varphi)^{-1}$, respectively. When $L > \xi_{\mathrm{th}}$, there are no jammed states. For $\xi_{\mathrm{GCP}} < L < \xi_{\mathrm{th}}$, there exist exponentially many jammed states. The number of the jammed states decreases with L, and becomes sub-exponential when $L < \xi_{\mathrm{GCP}}$.

The decoupling of the glass transitions in the two-component p-spin spherical model

Binary mixtures of large and small particles with disparate size ratio exhibit a rich phenomenology at their glass transition points. In order to gain insights on such systems, we introduce and study a two-component version of the p-spin spherical spin glass model. The model is composed of strongly interacting spins (strong spins) and weakly interacting spins (weak spins), which mimic the glass forming binary mixtures of large and small particles with disparate size ratio.

We have found that when the strengths of the interactions of the weak and strong spins are not widely separated, the model has only one glass phase. This glass phase is the frozen state of both the strong and weak spins and is described by the conventional 1RSB solution. On the other hand when the strengths of the interactions are well separated, the model exhibits the decoupling of the glass transitions of the weak and strong spins and, as a result, there appear the three distinct glass phases. We referred to them as the 1RSB(1), the 1RSB(2), and the 2RSB glass phases. The 1RSB(1) glass phase appears in the region where the number fraction of the strong spins is very small. This glass phase is the frozen state of both the strong and weak spins, although the transition into this phase is driven mainly by the freezing of the weak spins. The 1RSB(2) glass phase appears in the region where the number fraction of the strong spins is large. In this glass phase, only the strong spins are frozen while the weak spins are left mobile. By cooling the 1RSB(2) glass further, the 2RSB glass phase is obtained, in which the weak spins are also frozen. The 2RSB glass phase is characterized by the two-step hierarchical structure of the free energy landscape. The 2RSB glass transition becomes ether discontinuous or continuous depending on the number fraction of the strong spins. The discontinuous 2RSB thermodynamic transition is accompanied with the jump of the second order derivative of the free energy, namely the heat capacity. On the other hand, for the continuous 2RSB thermodynamic

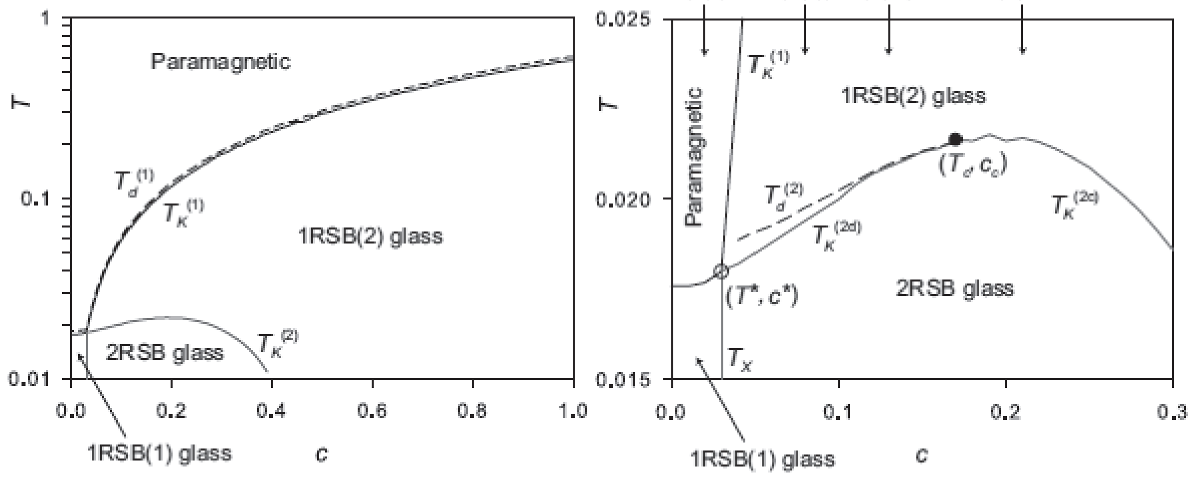

Fig. 4 The phase diagram of the two-component p-spin spherical model.

transition, the heat capacity changes continuously while the third order derivative of the free energy jumps discontinuously. Based on the results, we have discussed the connection of the present model to the randomly pinned PSM. The phase diagram of the present model appears to be similar to that of the randomly pinned PSM. We have analytically showed that the free energy of the two-component PSM becomes exactly identical to that of the randomly pinned PSM in the small limit of the ratio between the strengths of the interactions of the weak and strong spins. We have also discussed the implications of the present results for the MCT for binary mixtures of large and small particles with disparate size ratio. We have found that the 1RSB solution can not correctly describe the 2RSB glass phase although it can capture a trace of the 2RSB transitions for a certain range of parameters, which may leave questionable the applicability of the MCT to describe the decoupling of the glass transitions in binary mixtures with disparate size ratio. for the glass transitions of binary mixtures.

2. Original papers

(1) “Equilibrium phase diagram of a randomly pinned glass-former”
Misaki Ozawa, Walter Kob, Atsushi Ikeda, Kunimasa Miyazaki
Proc. Natl. Acad. Sci. USA 112, 6914 (2015).
(2) “Reply to Chakrabarty et al.: Particles move even in ideal glasses”
Misaki Ozawa, Walter Kob, Atsushi Ikeda, Kunimasa Miyazaki
Proc. Natl. Acad. Sci. USA 112, E4821 (2015).
(3) “Thermal fluctuations, mechanical response, and hyperuniformity in jammed solids”
Atsushi Ikeda, Ludovic Berthier
Phys. Rev. E 92, 012309 (2015).
(4) “One-dimensional Kac model of dense amorphous hard spheres”
Harukuni Ikeda, Atsushi Ikeda
EPL 111, 40007 (2015).

3. Presentation at academic conferences

(1) Atsushi Ikeda
Replica theory analysis of the glass transitions of complicated systems: Network-formers and ellipsoids
International Workshop on Dynamics in Viscous Liquids, 2015/5/4-5/7, Montpellier, France
(2) 池田 昌司
「少し複雑な系のガラス転移：レプリカ理論によるアプローチ」
東大物性研短期研究会「ガラス転移と周辺分野の科学」，2015 年 7 月 30 日-8 月 1 日，柏 （招待講演）

(3) Atsushi Ikeda
Thermal fluctuations, mechanical response, and hyperuniformity in jammed solids
Japan-France Joint Seminar "New Frontiers in Non-equilibrium Physics of Glassy Materials", 2015/8/11-14, Kyoto (Invited talk)

(4) 池田 昌司
「ガラス転移の統計力学：理想ガラスは存在するか？」
日本セラミックス協会 第29回秋季シンポジウム，2015年9月16日-9月18日，富山（招待講演）

(5) Atsushi Ikeda
Thermodynamic glass transition of a randomly pinned glass-former
Third East Asia Joint Seminar on Statistical Physics, 2015/10/14-17, Seul, Korea (Invited talk)

(6) 池田 昌司
「過冷却液体のエネルギーランドスケープについて」
第３８回溶液化学シンポジウム・プレシンポジウム, 2015年10月20日，高知 （招待講演）

4. Others

(1) 池田 昌司
「ガラス転移のエネルギー曲面」
研究会「化学反応のポテンシャル曲面とダイナミックス」, 2016年3月28日，京都 (invited)

Hideyuki Mizuno

Assistant Professor

1. Summary of the research of the year (2015)

Elastic Moduli and Vibrational Modes Close to the Jamming Transition
- From Disordered to Ordered Jammed Particulate Systems -

Abstract

Recent studies have well established peculiar mechanical and vibrational properties of jammed particulate solids close to the jamming transition point. The elastic moduli follow power-law scalings with the packing pressure, and the vibrational density of states (vDOS) exhibits a plateau regime above the characteristic frequency ω*. Those features can be explained by “isostaticity” coming from the marginal stability close to the jamming transition, where the contact number is a central parameter to describe the material properties [1]. Previous works have paid attention mainly on “disordered” jammed systems, where the constituent particles are packed in a random, disordered structure. In the present work, we focus on more “ordered” jammed systems with ordered structures. We demonstrate that close to the jamming transition point, even the ordered systems exhibit the similar mechanical and vibrational properties as those of disordered systems. Our results suggest that physics of isostaticity is valid for disordered to ordered systems close to the jamming transition and can determine the material properties of marginally stable solids, regardless of their static structures.

From disordered to ordered jammed particulate systems

We have studied the jammed particulate systems. The constituent particles interact via a finite-range, purely repulsive, harmonic potential, which has been often employed in many previous numerical works. Following the procedure proposed in Ref. [2], we have prepared the jammed particulate systems with several different structures, which are distinguished by the value of the orientational order parameter, Q_6 = 0.0, 0.1, 0.2, 0.3, 0.4, and 0.5.

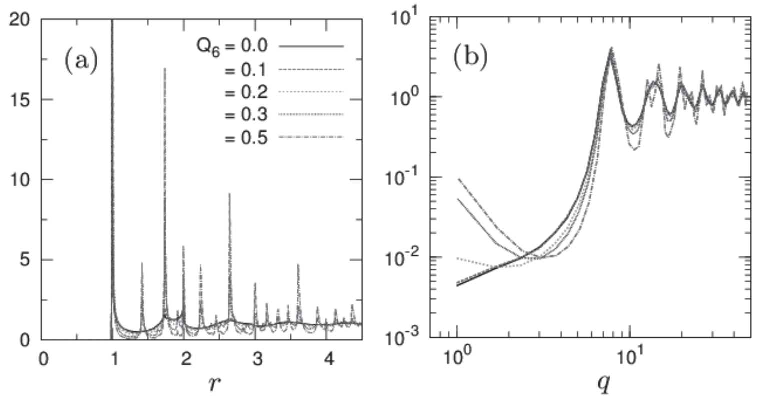

Fig. 1: Static structure of the system for different Q_6 values. We plot the radial distribution function g(r) in (a) and the static structure factor S(q) in (b).

Figure 1 shows the radial distribution function g(r) and the static structure factor S(q) for different Q_6 values. In the case of $Q_6 = 0.0$, we see the highly disordered structure which has been intensively studied by many previous works. On the other side, as Q_6 increases towards 0.5, the system becomes more ordered state. For $Q_6 = 0.5$, we can observe the crystalline-like, ordered, lattice structure. In addition, S(q) shows the clear enhancement of the long-range spatial correlation at small wavenumbers q. A main goal of the present study is to unveil the mechanical and vibrational properties for those more ordered systems close to the jamming transition point.

Power-law scalings with packing pressure, in elastic moduli, contact number, frequency ω*

Figure 2 plots the elastic moduli (bulk K and shear G moduli), excess contact number $\Delta z = z - z_c$ ($z_c = 2d$ is the critical value, d =3 is the spatial dimension), and the characteristic frequency ω*, as functions of the packing pressure p. We have well established the following power-law scalings in those quantities, which are all independent of the static structural properties, i.e., the values of Q_6:

$$\begin{gathered} \Delta z \sim p^{1/2}, \\ K - K_c \sim \Delta z, \quad G - G_c \sim \Delta z, \quad \omega^* \sim \Delta z. \end{gathered} \tag{1}$$

Remarkably the excess contact number Δz follows the same power-law scaling with p, independently of Q_6 values, suggesting that the physics of isostaticity can work for not only disordered systems but also ordered ones. Indeed, in the following, we will show the mechanical and vibrational properties are controlled by the isostaticity, regardless of static structures, even in the ordered systems.

For the elastic moduli K and G, we observe that (i) their dependences on p are controlled by the excess contact number Δz only, independently of Q_6 values, whereas (ii) the critical values of K_c and G_c depend on the static structure, the Q_6 value. Particularly the zero shear modulus value of $G_c = 0$ is a special feature to the “disordered” packings, as has been discussed at some length in Ref. [3]. On the other side, the more ordered packing shows the larger, positive, finite value of G_c.

The characteristic frequency ω*, above which the vDOS shows the

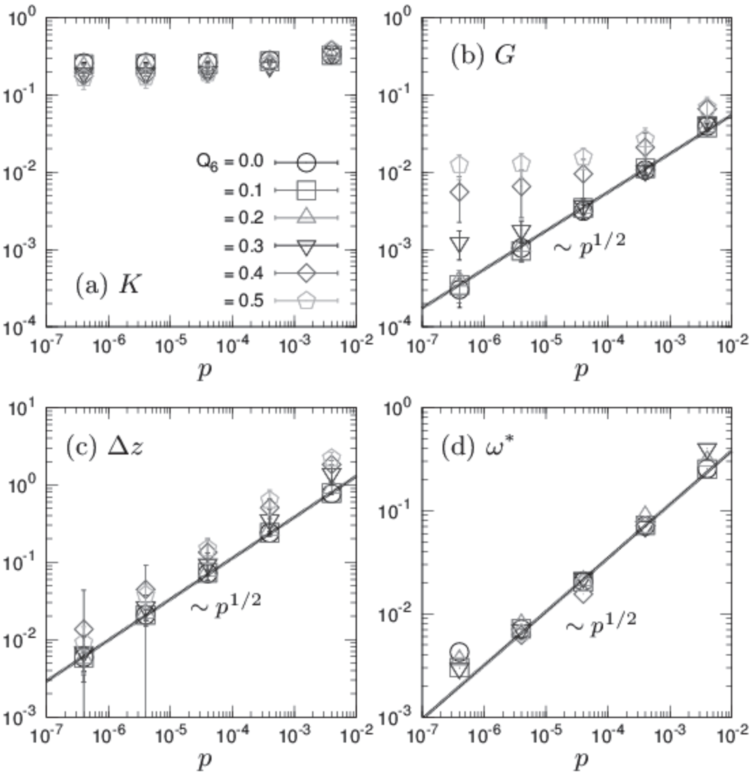

Fig. 2: Dependences on the packing pressure p of the quantities for different Q_6 values: The (a) bulk modulus K, (b) shear modulus G, (c) excess contact number $\Delta z = z - z_c$, and the (d) characteristic frequency ω*.

peculiar plateau regime, is also controlled by Δz, independently of the Q6 values. This result suggests that “anomalous” vibrational modes in the plateau regime are also determined by the isostaticity, for both the disordered and ordered systems, which will be discussed next.

Vibrational modes in disordered to ordered jammed systems

We have analyzed the vibrational eigenmodes of jammed systems, in the same way as has been done in Ref. [3]. We have calculated the vDOS g(ω), and the vibrational amplitudes (compressional/stretching $e^{k\parallel}$, sliding $e^{k\perp}$, and net $e^{k\parallel}_{net}$) and the mode energies (compressional/stretching $\delta E^{k\parallel}$ and sliding $\delta E^{k\perp}$) of all the vibrational modes k. Figure 3 shows those quantities as functions of the eigenfrequency ω for different Q_6 values of $Q_6 = 0.0$ to 0.5. We have already reported the results of the disordered case, $Q_6 = 0.0$, in Ref. [3]. The vDOS shows a crossover from the Debye-like scaling to the plateau behavior at the characteristic frequency ω*. The crossover at ω* is characterized by the competition between the compressional/stretching $\delta E^{k\parallel}$ and sliding $\delta E^{k\perp}$ vibrational energies: $\delta E^{k\parallel}$ dominates the total vibrational

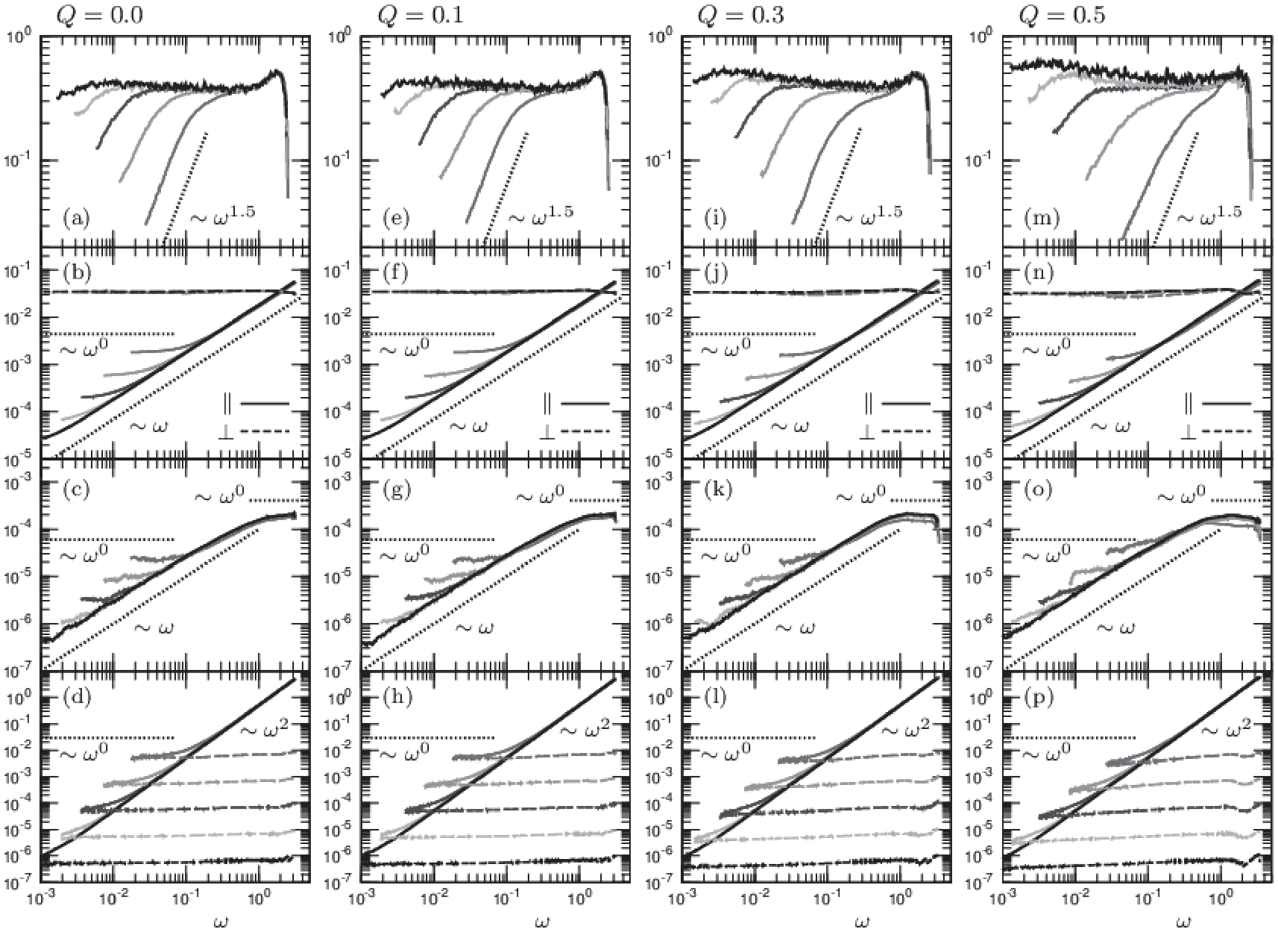

Fig. 3: Vibrational eigenmodes of the system for different Q_6 values. The vDOS g(ω) in (a),(e),(i),(m), the vibrational amplitudes $e^{k\parallel}$(solid lines), $e^{k\perp}$(dashed lines) in (b),(f),(j),(n), the net amplitude $e^{k\parallel}_{net}$ in (c),(g),(k),(o), and the mode energies $\delta E^{k\parallel}$(solid lines), $\delta E^{k\perp}$(dashed lines) in (d),(h),(l),(p) are plotted as functions of the eigenfrequency ω. The different lines indicate different packing pressures, p = $4*10^{-3}$ (red), $4*10^{-4}$ (green), $4*10^{-5}$ (blue), $4*10^{-6}$ (orange), $4*10^{-7}$ (black), from right to left or from top to bottom.

energy above ω^*, whereas $\delta E^{k\perp}$ is comparable to $\delta E^{k\parallel}$ and play a role in the total energy below ω^*. Here we make an important note that “anomalous” modes in the plateau regime can be featured by the dominant compressional/stretching energy, where the constraint in the sliding direction is negligible and the vibrational motions show very large sliding component of $e^{k\perp}$, as well observed in Fig. 3.

Remarkably those vibrational features observed in the disordered packing, $Q_6 = 0.0$, persist to the more ordered cases up to $Q_6 = 0.5$. We naturally expect that the vibrational modes in the Debye-like regime at $\omega < \omega^*$ and the spring-dynamics regime at $\omega > \omega^h$ (=1) should be different between different structures. However, here we demonstrate that the vibrational natures in the plateau regime above ω^* and below ω^h are independent of the static structural properties, controlled by the excess contact number only, i.e., the isostaticity. We have also performed the eigenmode decomposition of nonaffine elastic moduli, in the same way as was done in Ref. [3] for disordered packings, and confirmed that the eigenmode decomposition in the plateau regime is also insensitive to the static structural properties.

Conclusion

In the present work, we have studied elastic moduli and vibrational modes in marginally stable jammed packings with several different static structures. We have showed that the peculiar features observed in the disordered packings also persist to even more ordered particulate systems. Particularly the same power-law scalings with packing pressure, in elastic moduli, contact number, characteristic frequency ω^*, hold for the disordered to ordered systems. In addition, anomalous vibrational natures in the plateau regime are controlled by the isostaticity, regardless of static structural properties. Our results suggest the universal aspect of physics of isostaticity which can explain the material properties of marginal stable solids close to the jamming transition point, independently of their static structures.

Acknowledgement

This work is a collaboration during 2015 with Kuniyasu Saitoh (Tohoku University) and Leonardo E. Silbert (Southern Illinois University Carbondale). A manuscript to present the results is now in preparation.

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[3] H. Mizuno, K. Saitoh, and L. E. Silbert, *Physical Review E* **93**, 062905 (2016).

2. Original papers

(1) A. Nicolas, F. Puosi, H. Mizuno, and J.-L. Barrat, “Elastic consequences of a single plastic event: Towards a realistic account of structural disorder and shear wave propagation in models of flowing amorphous solids”,
Journal of the Mechanics and Physics of Solids, Vol.78, p.333-351 (19pages), 2015.

(2) H. Mizuno, S. Mossa, and J.-L. Barrat, “Beating the amorphous limit in thermal conductivity by superlattices design”,
Scientific Reports, Vol.5, p.14116 (15pages), 2015.

3. Presentation at academic conferences

(1) L. E. Silbert, H. Mizuno, and M. Sperl, “Shear modulus heterogeneities in disordered frictionless particle packings”,
American Physical Society March Meeting 2015, San Antonio, TX, USA, 2015/03/02-06.

(2) A. Nicolas, J. Rottler, F. Puosi, H. Mizuno, and J.-L. Barrat, “Local rearrangements in the flow of disordered solids: long-range elastic interactions and spatio-temporal correlations, from atomistic simulations to coarse-grained models”,
The 10th Annual European Rheology Conference, Nantes, France, 2015/04/14-17.

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The 9th European Solid Mechanics Conference, Madrid, Spain, 2015/07/06-10.

4. Others

(1) H. Mizuno, S. Mossa, and J.-L. Barrat, “Acoustic excitations and elastic heterogeneities in disordered solids”,
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(2) H. Mizuno, S. Mossa, and J.-L. Barrat, “Crystalline super-networks for super thermal insulation”,
Minatec. Newsletter (Monthly journal of MinaTec, the Grenoble hub for nanotechnology), Vol.37, p.1, December 2015.

２．FIFC リサーチフェロー

Shigeru Nagase

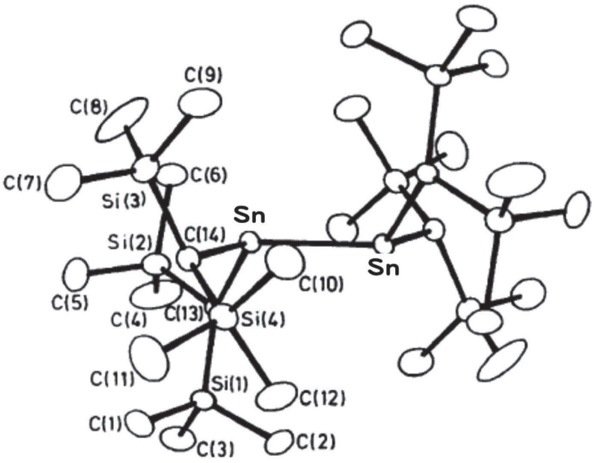
FIFC Research Fellow

1. Summary of the Research of the Year

The bonding between heavier main group atoms in sterically crowded molecules are investigated. In addition, the interesting properties of endohedral metallofullerenes are investigated.

(a) The Multiple Bonding in Heavier Group 14 Analogues ($R_2E{=}ER_2$, E = Ge, Sn, Pb) of Alkenes, Which is Stabilized by Dispersion Force Effects

Since the first successful synthesis of a double bond between Sn atoms (Figure 1), heavier analogues of alkenes have attracted special interest in main group chemistry. The structures and bonding in $[(SiMe_3)_2CH]_2E{=}E[CH(SiMe_3)_2]_2$ and $[(SiMe_3)_2NH]_2E{=}E[NH(SiMe_3)_2]_2$ (E = Ge, Sn, or Pb) and their dissociation into $:E[CH(SiMe_3)_2]_2$ and $:E[NH(SiMe_3)_2]_2$ monomers were theoretically studied using hybrid density functional theory (DFT) at the B3PW91 level with basis set superposition error and zero point energy corrections. The structures were also optimized with the dispersion-corrected B3PW91-D3 method to yield dispersion force effects. The calculations generally reproduced the experimental structural data for the tetraalkyls with a few angular exceptions. Without dispersion corrections, the dissociation energies of $[(SiMe_3)_2CH]_2E{=}E[CH(SiMe_3)_2]_2$ were calculated to be -2.3 (Ge), +2.1 (Sn), and -0.6 (Pb) kcal/mol, which indicate that the dimeric E-E bonded structure is favored only for tin. However, when dispersion force effects are included, much higher dissociation energies of 28.7 (Ge), 26.3 (Sn), and 15.2 (Pb) kcal/mol were calculated, indicating that all three E-E bonded dimers are favored. Calculated thermodynamic data at 25 °C and 1 atm for the dissociation of the alkyls yield ΔG values of 9.4 (Ge), 7.1 (Sn), and -1.7 (Pb) kcal/mol, indicating that the dimers of Ge and Sn, but not Pb, are favored. These results are in harmony with experimental data. The dissociation energies of $[(SiMe_3)_2NH]_2E{=}E[NH(SiMe_3)_2]_2$ without dispersion correction are -7.0 (Ge), -7.4 (Sn), and -4.8 (Pb) kcal/mol, showing that the monomers are favored in all cases. Inclusion of the dispersion correction yields the values 3.6 (Ge), 11.7 (Sn), and 11.8 (Pb) kcal/mol, showing that dimerization is favored but less strongly so than in the alkyls. The calculated thermodynamic data for the amido germanium, tin, and lead dissociation yield ΔG values of -12.2, -3.7, and -3.6 kcal/mol at 25 °C and 1 atm, consistent with the observation of monomeric structures.



$[(SiMe_3)_2HC]_2Sn{=}Sn[CH(SiMe_3)_2]_2$

Fig. 1 The first example of Sn-Sn double bonding

Overall, these data indicate that, in these sterically crowded molecules, dispersion force attraction between the ligands is of greater importance than group 14 element-element bonding, and is mainly responsible for the dimerization of the metallanediyls species to give the dimetallenes. Calculations on the non-dissociating distannene $(^tBu_2MeSi)_2Sn{=}Sn(SiMe^tBu_2)_2$ also show that attractive dispersion forces are key to its stability, though the bonding between the central Sn atoms has been emphasized (Figure 2).

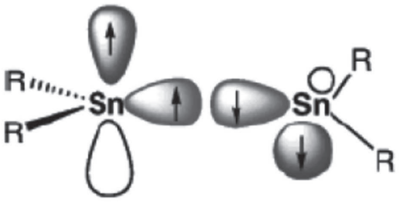


Fig. 2 Orbital interactions between Sn atoms

(b) Dispersion Force Effects on the Dissociation of "Jack-in-the-Box" Diphosphanes (R_2P-PR_2) and Diarsanes (R_2As-AsR_2)

The dissociation of sterically-crowded diphosphanes (R_2P-PR_2) and diarsanes (R_2As-AsR_2) (R = $[CH(SiMe_3)_2]_2$ and $[NH(SiMe_3)_2]_2$) into PR_2 and AsR_2 radical monomers was theoretically studied using hybrid density functional theory at the B3PW91 and dispersion-corrected B3PW91-D3 levels. The calculations reproduced the experimental structural data for the teraalkyls with good accuracy. Without the dispersion correction, negative dissociation energies of -10.3 and -6.5 kcal/mol were calculated for the phosphorus and arsenic tetraalkyls, indicating that the radical monomers are more stable. In contrast, the incorporation of dispersion force effects afforded high, positive dissociation energies of +37.6 and +37.1 kcal/mol that favored dimeric structures. The dissociation energies (without dispersion) calculated for the tetraamido-substituted dimer are also negative, but changed to positive values of +29.3 and +32.5 kcal/mol upon optimization with the D3 dispersion term. In contrast to earlier calculations, which indicated that the release of accumulated strain energy within the tetraalkyl dimers was the driving force for dissociation to monomers (i.e. the Jack-in-the-box molecular model), the present calculations show that dispersion force attractive interactions exceed those of ligand relaxation and stabilize the dimeric structures. Single-point MP2 (Second-order Møller-Plesset Perturbation Theory) calculations including dispersion effects afforded dissociation energies of 30.4 and 30.8 kcal/mol for the tetraalkyl species, suggesting that the addition of the D3 dispersion term to the B3PW91 functional may overestimate such forces by 7-8 kcal/mol. It is concluded that the balance of dispersion forces and entropic effects are the major determinants of the dissociation equilibria.

(c) (2 + 2) Cycloaddition of Benzyne to Endohedral Metakkofullerenes $M_3N@C_{80}$ (M = Sc, Y): A Rotating-Intermediate Mechanism

The reaction mechanism and origin of regioselectivity of (2 + 2) cycloadditions of benzyne to endohedral metallofullerenes $M_3N@C_{80}$ (M = Sc, Y) were investigated with density functional calculations. The reaction was demonstrated to follow a diradical mechanism rather than a carbene mechanism, in which the formation of the diradical intermediate is the rate-determining step. Through rotation of benzyne moiety on the fullerene surface, the diradical intermediate on 566 site could isomerize to two new diradical intermediates which give rise to two distinct [5,6] and [6,6] benzoadducts, respectively. However, the diradical intermediate on 666 site only produces the [6,6] benzoadduct. The nature of the endohedral cluster not only influences the regioselectivity, but also determines the cycloadduct geometry. For $Sc_3N@C_{80}$, the [5,6] benzoadduct is preferred kinetically and thermodynamically, whereas in the case of $Y_3N@C_{80}$, both [5,6] and [6,6] benzoadducts are favorable. In contrast to closed-cage benzoadducts of $Sc_3N@C_{80}$, $Y_3N@C_{80}$ affords open-cage benzoadducts, making it the first example that the endohedral cluster could alter cycloadducts from the closed cage to open cage. With further analysis, it is revealed that the origin of regioselectivity results from the local strain energy of the fullerene cage.

(d) Warning to Theoretical Structure Elucidation of Endohedral Metallofullerenes

Endohedral scandium fullerenes have attracted substantial interest since they were synthesized and isolated in 1992. The Sc_2C_{74} series including both $Sc_2@C_{74}$ and $Sc_2C_2@C_{72}$ forms were thoroughly investigated with density functional theory (DFT) methods including B3LYP, CAM-B3LYP, M06-2X, wB97XD, and some other DFT methods combined with statistical mechanics in the present work. Among all the Sc_2C_{74} isomers, $Sc_2C_2@C_s(10528)\text{-}C_{72}$ is the most thermodynamically stable, and it is overwhelming at the temperature region of fullerene formation, which is very consistent with experiments. A deviation that the B3LYP method as well as other DFT methods without long-range corrections tends to overestimate energies of $Sc_2C_2@C_{72}$ series was exposed for the first time to our best knowledge, and this deviation may not only be restricted to the $Sc_2C_2@C_{72}$ series but also apply to other scandium carbide fullerenes $Sc_2C_2@C_{2n}$ ($2n \neq 72$) and even other metal carbide fullerenes. Misleading conclusions will be drawn on the basis of inaccurate energies calculated with B3LYP method and other DFT methods without long-range corrections. As B3LYP, BP86, PBE, etc. are fairly widely used methods in theoretical studies of endohedral metallofullerenes, our work is an instructive warning to these studies.

(e) Other Research Subjects

(1) "Synthesis and Characterization of a 1,2-Digermabenzene", (2) "Ring Expansion to 1-Bromo-1-alumacyclonona-2,4,6,8-tetraene by Insertion of Two Alkyne Molecules into the Al-C Bonds", (3) "Theoretical Insight into the Ambiguous Endohedral Metallofullerene Er_3C_{74}: Covalent Interactions among Three Lanthanide Atoms", (4) "Reaction of a Diaryldigermyne with Ethylene", (5) "Quasi-Three-Coordinate Iron and Cobalt Terphenoxide Complexes $\{Ar^{iPr8}OM(/\text{-}O)\}_2$ (Ar^{iPr8} = $C_6H\text{-}2,6\text{-}(C_6H_2\text{-}2,4,6\text{-}{}^{i}Pr_3)_2\text{-}3,5\text{-}iPr_2$; M = Fe or Co) with $M(III)_2(/\text{-}O)_2$ Core Structures and the Peroxide Dimer of 2-Oxepinoxyl Relevant to Benzene Oxidation","Synthesis, (6) Synthesis, Structure, and Reactivities of Iminosulfane- and Phosphane-Stabilized Carbones Exhibiting Four-Electron Donor Ability", (7) "Preparation, Structural Determination, and Characterization of Electronic Properties of Bis-Silylated and Bis-Germylated $Lu_3N@I_h\text{-}C_{80}$", (8) "Diverse Coordination Modes in Tin Analogues of a Cyclopentadienyl Anion Depending on the Substituents on the Tin Atom", (9) "Effective Derivatization and Extraction of Insoluble Missing Lanthanum

Metallofullerenes La@C_{2n} (n = 36-38) with Iodobenzene ", (10) "Calculations of the Water-Dimer Encapsulated into C_{84}", (11) "Selenium-Substituted Phosphaalkenes Obtained through 1, 2-Elimination of Chlorosilanes from Selenenylchlorophines" (12) "Computational Picture of Silyl Transfer from Silylsilatranes to Arylpalladium Chloride", and (13) "Crystal Structure of 4-methybenzenecarbothioic Acid and Computational Investigations of Benzenecarbochlcogenoic Acids (C_6H_5COEH and C_6H_5CEOH, E = S, Se, Te)".

2. Original papers

(1) J. –D. Guo, S. Nagase, and P. P. Power, "Dispersion Force Effects on the Dissociation of “Jack-in-the–Box” Diphosphanes and Diarsanes", *Organometallic*s, **34**, 2028-2033 (2015).

(2) T. Yang, S. Nagase, T. Akasaka, J. M. Poblet, K. N. Houk, M. Ehara, and X. Zhao,"(2+2) Cycloaddition of Benzyne to Endohedral Metallofullerenes M_3N@C_{80} (M = Sc, Y): A Rotating-Intermediate Mechanism", *J. Am. Chem. Soc.*, **137**, 6820-6828 (2015).

(3) T. Sasamori, T. Sugahara, T. Agou, J. –D. Guo, S. Nagase, R. Streubel, and N. Tokitoh, "Synthesis and Characterization of a 1,2-Digermabenzene", *Organometallics*, **34**, 2106-2109 (2015).

(4) T. Agou, T. Wasano, T. Sasamori, J. –D. Guo, S. Nagase, and N. Tokitoh, "Ring Expansion to 1-Bromo-1-alumacyclonona-2,4,6,8-tetraene by Insertion of Two Alkyne Molecules into the Al-C Bonds", *Angew. Chem. Int. Ed.*, **54**, 9568-9571 (2015).

(5) Y. –J. Guo, H. Zheng, T. Yang, S. Nagase, and X. Zhao, "Theoretical Insight into the Ambiguous Endohedral Metallofullerene Er_3C_{74}: Covalent Interactions among Three Lanthanide Atoms", *Inorg. Chem.*, **54**, 8066-8076 (2015).

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3. Review articles

(1) 山田道夫、赤阪　健、永瀬　茂、「不飽和直線状トリキナン構造をもつ金属内包フラーレン$Sc_2@C_{66}$」、*固体物理*、**50**, 189-194 (2015).

(2) 鈴木光明、前田　優、永瀬　茂、赤阪　健、「金属内包フラーレンの構造決定」、*日本結晶学会誌*、**58**, 73-78 (2016).

4. Books

(1) M. Yamada, S. Sato, Y. Takano, L. Feng, S. Nagase, and T. Akasaka, Endohedral Metallofullerenes: From Chemical Reactivity to Material Performance", In *Chemical Science of π-Electron Systems* (Eds. T. Akasaka, A. Osuka, S. Fukuzumi, H. Kandori, and Y. Aso), Springer, Chapter 9, pp. 133-153 (2015).

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３．リサーチリーダー

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1. Summary of the research of 2015

The complex systems consisting of transition metal element(s), heavy main-group element(s), organic group(s) are attractive research targets in wide areas of modern chemistry. For instance, such complex systems play important roles as metal enzymes, catalysts, photo-sensitizer, molecular switch, luminescence material and so on. Also, they are important research target in the physical chemistry and molecular science, because they exhibit a variety of geometry, molecular property, bonding nature, reactivity, and catalysis. These features attract a lot of interests in theoretical and computational chemistry. All these features deeply relate to their electronic structures. In this regard, the theoretical and computational studies of the electronic structures of the complex systems are indispensable in further development of chemistry.

These complex systems are challenging research targets from the point of view of theoretical/computational chemistry, because their electronic structures are not simple but complicated in many cases. One good example is to incorporate large electron correlation effects in theoretical calculation of such system, which is still not easy even nowadays.

Our group is theoretically investigating the complex systems bearing complicated electronic structure with electronic structure theory. In 2015, we performed several theoretical studies, as follows: (i) CASPT2 study of inverse sandwich-type dinuclear 3d transition metal complexes of ethylene and dinitrogen molecules, (ii) Theoretical Study of $Pd_{11}Si_6$ Nanosheet Compounds Including Seven-Coordinated Si Species and Its Ge Analogues, (iii) Au_8 Cores and Entangled Ligands of Selenolate- and Thiolate-Protected Gold Nanoclusters $Au_{24}(ER)_{20}$ and $Au_{20}(ER)_{16}$ (E = Se, S; R = Ph, Me), (iv) Characterization of $AlPO_4(110)$ Surface in Adsorption of Rh Dimer and Its Comparison with γ-$Al_2O_3(100)$ Surface, (v) Heterolytic Activation of Dihydrogen Molecule by Hydroxo-/Sulfido-Bridged Ruthenium−Germanium Dinuclear Complex, (vi) Activation of Strong Boron–Fluorine and Silicon–Fluorine σ-Bonds: Theoretical Understanding and Prediction, and (vii) 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, below.

(i) 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

The spin multiplicity of transition metal complexes has attracted a lot of interest recently because spin multiplicity is closely related to single-molecule magnets, spin-crossover complexes, spin catalysis, and so on. In this regard, it is of considerable interest to obtain theoretical knowledge of how to understand spin multiplicity and how to control it. In general, it is said that a strong ligand field leads to the presence of a low-spin state and a weak ligand field leads to the presence of

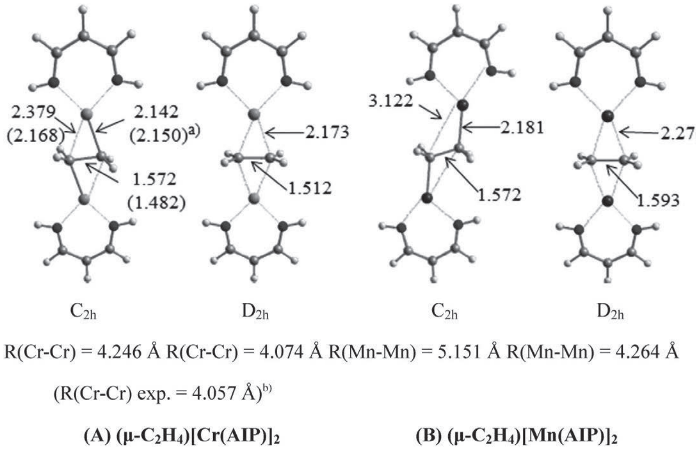


Figure 1. CASSCF-optimized geometry of Mn and Cr ISTCs of ethylene

a high-spin state. However, the story is not so simple in dinuclear transition metal complexes, because of the presence of interaction between the two metal centers. Recently, inverse sandwich-type dinuclear transition metal complexes (ISTCs) were synthesized. In ISTCs, an organic moiety is sandwiched by two metal moieties in contrast to the usual sandwich-type complex in which a metal is sandwiched by two organic moieties. ISTCs attract great interests in coordination chemistry, organometallic chemistry, and physical chemistry because of their characteristic geometries, bonding natures, and molecular properties. For instance, benzene and toluene ISTCs of Cr have a septet ground state and those of V(I) have a quintet ground state, which are unusually high spin multiplicities. In our previous theoretical study of benzene ISTCs, we found that the spin multiplicity of the ground state monotonically increases from a closed-shell singlet to a nonet when going from Sc to Mn but suddenly decreases to an open-shell singlet in Fe. Hence, it is of considerable interest to systematically investigate the spin multiplicity of ethylene and dinitrogen ISTCs of all first-row transition metal elements and elucidate how the spin multiplicity changes along the first-row transition metal elements.

Table 1. Stable geometry and relative energies of various spin multiplicity

(A) Dinitrogen complex

Spin	**Sc**		**Ti**		**V**		**Cr**		**Mn**		**Fe**		**Co**		**Ni**	
	C_{2h}	D_{2h}	C_{2h}	D_{2h}	C_{2h}	D_{2h}	C_{2h}	D_{2h}	C_{2h}	D_{2h}	C_{2h}	D_{2h}	C_{2h}	D_{2h}	C_{2h}	D_{2h}
11									1.8	29.4						
9							5.5	5.8	1.4	28.4	1.2	24.1				
7					2.2	2.7	4.1	3.8	1.0	26.8	0.9	21.2	0.8	15.6		
5			12.4	1.2	1.4	1.5	2.8	2.0	0.6	25.6	0.6	18.1	0.6	11.1	0.1	21.3
3	7.4	0.3	11.9	0.5	0.7	0.6	1.8	0.8	0.3	24.7	0.3	16.3	0.3	7.7	0.1	11.1
1	7.3	0.0	11.6	0.0	0.3	0.0	1.2	0.0	0.0	24.1	0.0	15.1	0.0	5.8	0.0	6.9

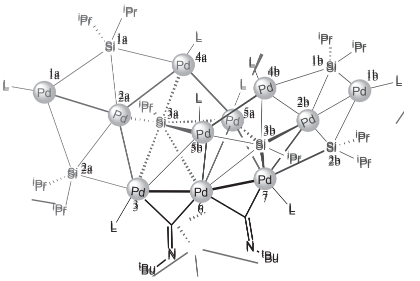
(B) Ethylene complex

Spin	**Sc**		**Ti**		**V**		**Cr**		**Mn**		**Fe**		**Co**		**Ni**	
	η^2	η^1	η^2	η^1	η^2	η^1	η^2	η^1	η^2	η^1	η^2	η^1	η^2	η^1	η^2	η^1
9							3.1	24.6	0.0	0.2						
7					1.4	35.2	2.1	19.9	5.0	5.2	3.9	0.0				
5			1.7	20.8	0.9	21.4	1.2	15.3	9.4	9.6	10.0	7.3	4.8	0.0		
3	0.4	21.6	0.8	19.9	0.4	17.5	0.4	12.2	13.9	13.9	15.9	14.2	13.9	11.3	15.1	0.0
1	0.0	19.3	0.0	18.1	0.0	15.9	0.0	10.5	18.7	18.4	22.3	21.9	24.3	24.4	47.8	30.5

In this work, we theoretically investigated ethylene and dinitrogen ISTCs of Sc to Ni. The spin multiplicities and coordination structures of inverse sandwich-type complexes (ISTCs) of ethylene and dinitrogen molecules with 3d transition metal elements (Sc to Ni), (μ-C_2H_4)[M(AIP)]$_2$ and (μ-N_2)[M(AIP)]$_2$ (AIPH = (Z)-1-amino-3-iminoprop-1-ene; M = Sc to Ni) were investigated by the CASPT2 method. In both ethylene and dinitrogen ISTCs of the early 3d transition metals (Sc to Cr), sandwiched ethylene and dinitrogen ligands coordinate with two metal atoms in an η^2-side-on form and their ground states have an open-shell singlet spin multiplicity. The η^1-end-on coordination structure of dinitrogen ISTCs is considerably less stable than the η^2-side-on form in these metals. For the late 3d transition metals (Mn to Ni), ethylene and dinitrogen ISTCs exhibit interesting similarities and differences in spin multiplicity and structure as follows: in ethylene ISTCs of Mn to Ni, the ground state has an open-shell singlet spin multiplicity like those of the ISTCs of early transition metals. However, the ethylene ligand is considerably distorted, in which the ethylene carbon atoms have a tetrahedral-like structure similar to sp^3 carbon and each of them coordinates with one metal in a μ-η^1: η^1 structure. These geometrical features are completely different from those of ISTCs of the early transition metals. In dinitrogen ISTCs of Mn to Ni, on the other hand, the ground state has a high spin multiplicity from nonet (Mn) to triplet (Ni). The η^2-side-on coordination structure of the dinitrogen ligand is as stable as the η^1-end-on form in the Mn complex but the η^1-end-on structure is more stable than the η^2-side-on form in the Fe to Ni complexes. All these interesting similarities and differences between ethylene and dinitrogen ISTCs and between the early and late transition metal elements arise from the occupation of several important molecular orbitals.

(ii) Theoretical Study of $Pd_{11}Si_6$ Nanosheet Compounds Including Seven-Coordinated Si Species and Its Ge Analogues:

Nanoscale metal particles have attracted a lot of interests in the last decade, because such metal particles exhibit new properties, which are considerably different from those of bulk metals and large metal particles. One good example is the new field of catalysis by using gold nanoparticles, which was first found by Haruta and coworkers. In almost all cases, such metal particles have three-dimensional structures. On the other hand, the reports on two-dimensional metal plate compounds have been limited so far. Although ultrafine palladium, rhodium, and ruthenium nanoplate materials have been reported recently, the thickness is approximately 1–2 nm, indicating that these materials are much thicker than graphene, which is one of the typical plate materials. Considering that graphene exhibits very different properties from those of multi-layers graphite, one can expect that very fine nanosheet materials, like graphene, are of considerable interest. Actually, monolayer materials of molybdenum disulfide and boron nitride exhibit considerably different properties from those of bulk compounds. In this regard, monolayer nanosheet compounds of metals attract a lot of interests and various planar clusters have been synthesized. However, the examples have been limited. Recently, much larger palladium nanosheet compounds, that is, $Pd_{11}(Si\textit{i}Pr)_2(Si\textit{i}Pr_2)_4(CNR)_{10}$ (**1** for R=*t*Bu and **2** for R=2,4,6-Me_3-C_6H_2) were synthesized by Nagashima, and coworkers, as shown in Scheme 1. These completely new compounds are of considerable interest. In the present theoretical work, we investigated the Pd_{11} monolayer nanosheet compounds $Pd_{11}(SiMe)_2(SiMe_2)4(CNMe)_{10}$ **1Si** and **2Si**, and their Ge analogues **1Ge** and **2Ge** with the DFT method, where compounds **1Si** and **2Si** are models of **1** and **2**, respectively. All Pd atoms are somewhat positively charged and the electron density is accumulated between the Pd and Si atoms, indicating that a charge transfer (CT) occurs from the Pd to the Si atoms of the $SiMe_2$ and SiMe groups. Negative regions of the Laplacian of the electron density were found between the Pd and Si atoms. A model of a seven-coordinated Si species, that is, Pd_5(Pd-SiMe), is predicted to be a stable pentagonal bipyramidal molecule. Five Pd atoms in the equatorial plane form bonding overlaps with two 3p orbitals of the Si atom. This is a new type of hypervalency. The Ge analogues have geometry and an electronic structure similar to those of the Si compounds. But their formation energies are smaller than those of the Si analogues. The use of the element Si is crucial to synthesize these nanoplate compounds.



Scheme 1. Structure of $Pd_{11}Si_6$ nanosheet compound

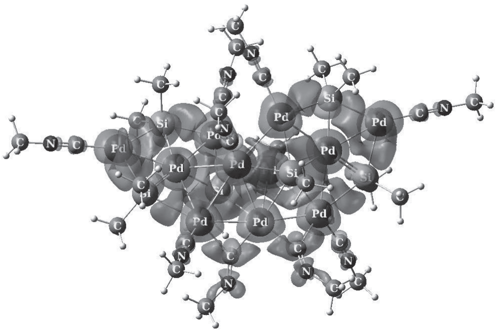
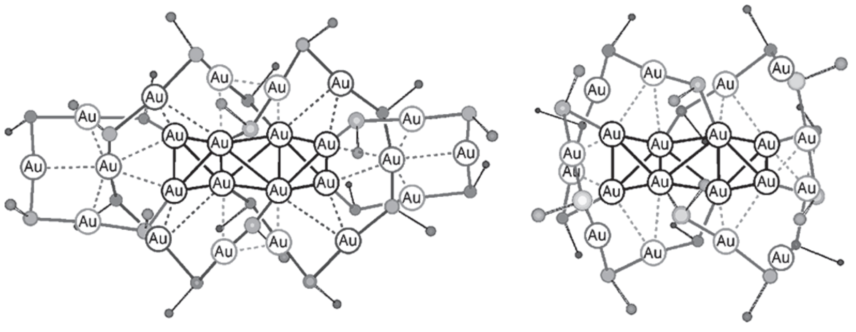


Figure 2. Difference density of $Pd_{11}Si_6$ nanosheet compound from Pd(0), $SiMe_2$, and MeCN. Blue; decrease in density, orange; increase in density

(iii) Au_8 Cores and Entangled Ligands of Selenolate- and Thiolate-Protected Gold Nanoclusters $Au_{24}(ER)_{20}$ and $Au_{20}(ER)_{16}$ (E = Se, S; R = Ph, Me)

Gold nanoclusters protected by organic ligands attract much interests as a building block of novel functional materials such as catalysts, photonics, and molecular electronics, because metal nanoclusters exhibit unusual physicochemical properties and chemical reactivity different from bulk metals. Among them, thiolate-protected gold clusters, which are represented with a general $Au_n(SR)_m$ formula, have been widely known. In those compounds, an Au_n core is surrounded by organothiolate (SR) ligands. In many cases, the Au_n core has a highly symmetrical geometry with a closed-shell singlet ground state. Recently, novel thiolate-protected gold clusters $Au_{20}(SR)_{16}$ and $Au_{24}(SR)_{20}$ (R = CH_2CH_2Ph) have been synthesized. Though their crystal structures have not been reported yet, experimental reports suggest that the Au_8 core is surrounded by four organothiolate ligands such as $Au_3(SR)_4$ and $Au_5(SR)_6$. This type of Au_8 core has never been observed before. Very recently, the first X-ray analysis of a similar selenolate-protected Au nanocluster compound $Au_{24}(SeR)_{20}$ (R = Ph) **1-SePh** was successfully made. Very recently, the first X-ray analysis of a similar selenolateprotected Au nanocluster compound $Au_{24}(SeR)_{20}$ (R = Ph) **1-SePh** was successfully made. **1-SePh** consists of an Au_8 core with two $Au_3(SeR)_4$ and two $Au_5(SeR)_6$ staple-like chain ligands. Despite of these interesting geometries, no theoretical study has been presented on these clusters.

In this work, we theoretically investigated the geometries and the electronic structures of $Au_{24}(SeR)_{20}$ **1-SeR**, $Au_{20}(SeR)_{16}$ **2-SeR** (R = Ph and Me; Scheme 2). The geometries and electronic structures of selenolate-protected Au nanoclusters, $Au_{24}(SeR)_{20}$ and $Au_{20}(SeR)_{16}$, and their thiolate analogues are theoretically investigated with DFT and SCS-MP2 methods, to elucidate the electronic structure of their unusual Au_8 core and the reason why they have the unusual entangled "staple-like" chain ligands. The Au_8 core is understood to be an $[Au_4]^{2+}$ dimer in which the $[Au_4]^{2+}$ species has a tetrahedral geometry with a closed-shell singlet ground state. The SCS-MP2 method successfully reproduced the distance between two $[Au_4]^{2+}$ moieties, but the DFT with various functionals failed it, suggesting that the dispersion interaction is crucial between these two $[Au_4]^{2+}$ moieties. The SCS-MP2-calculated formation energies of these nanocluster compounds indicate that the thiolate staple-like chain ligands are more stable than the selenolate ones, but the Au8 core more strongly coordinates with the selenolate staple-like chain ligands than with the thiolate ones. Though $Au_{20}(SeR)_{16}$ has not been reported yet, its formation energy is calculated to be large, suggesting that this compound can be synthesized as a stable species if the concentration of Au(SeR) is well adjusted. The aurophilic interactions between the staple-like chain ligands and between the Au_8 core and the staple-like chain ligand play an important role for the stability of these compounds. Because of the presence of this autophilic interaction, $Au_{24}(SeR)_{20}$ is more stable than $Au_{20}(SeR)_{16}$ and the unusual entangled ligands are involved in these compounds.



Scheme 2. Structures of $Au_{24}(ER)_{20}$ and $Au_{20}(ER)_{16}$ (E = S or Se; R=Ph) .

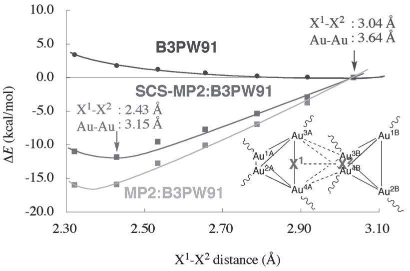


Figure 3. Potential energy surface against X1-X2 distance of $Au_{24}(SeR)_{20}$

(iv) Characterization of $AlPO_4$(110) Surface in Adsorption of Rh Dimer and Its Comparison with γ-Al_2O_3(100) Surface

Metal elements of groups 9 and 10 such as Pt, Pd, and Rh are used now in many three-way catalysts for automobiles. Particularly, these metals play crucial roles in NO−CO and NO−hydrocarbon reactions. Considering that these metals are not abundant on the earth, it is of considerable importance to reduce the content of these metals in catalysts. In general, these metals are used as dispersed nanoparticles combined with the surface of the support to suppress sintering and maintain dispersion of small metal particles. Actually, almost all excellent state-of-the art catalysts consist of metal nanoparticles and appropriate supports. Recently, Machida and co-workers found that the use of tridymite-type aluminum orthophosphate ($AlPO_4$) as a support can markedly decrease the quantity of Rh in the three-way catalyst because thermally stable and highly dispersed Rh nanoparticles are anchored well on the phosphate surface. Considering that $AlPO_4$ is a robust and cheap material, their finding is of considerable importance in constructing a low-cost but effective catalyst. To elucidate the reasons this $AlPO_4$ exhibits such an excellent anchoring effect, it is necessary to ascertain where the Rh adsorption occurs, how strong the interaction between the Rh particle and the surface is, and to clarify the origin of the interaction.

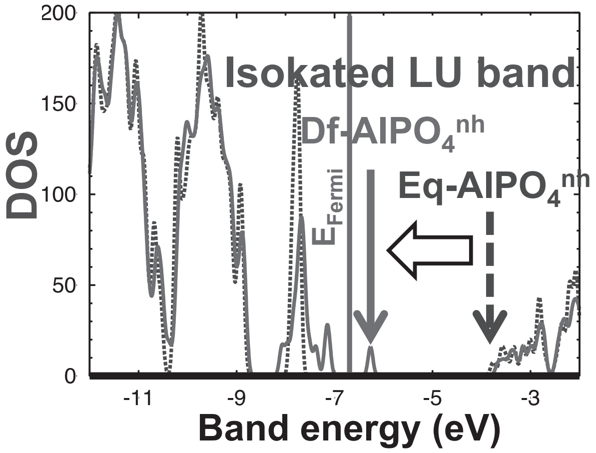
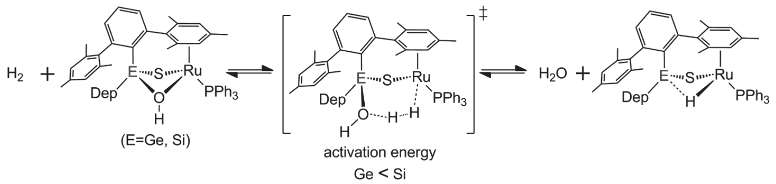


Figure 4. Change in band structure of non-hydrated $AlPO_4$ by the interaction with Rh_2.

Adsorption of Rh dimer on $AlPO_4$(110) and γ-Al_2O_3(100) surfaces was theoretically investigated by periodic DFT calculation with a slab model to elucidate characteristic features of the $AlPO_4$ surface in comparison with the γ-Al_2O_3 surface. The adsorption at the PO site is the most favorable in both nonhydrated and hydrated $AlPO_4$ surfaces, which is consistent with the experimental finding. The adsorption at the AlO site is the least favorable. The adsorption energy at the PO site of the $AlPO_4$ surface is considerably larger than that at the γ-Al_2O_3 surface. One important reason is that the deformation energy of the γ-Al_2O_3 surface is much larger than that of the $AlPO_4$ surface. Bader charge analysis, difference electron density map, and projected density of states (p-DOS) clearly disclose that the charge transfer (CT) occurs from the Rh dimer to the $AlPO_4$ surface (Figure 4). This CT is stronger than in the adsorption on the γ-Al_2O_3 surface. The lowest unoccupied band (LU band in conduction band) plays a crucial role as an electron-acceptor orbital in this CT interaction. The LU band of the $AlPO_4$ exists at a lower energy than that of γ-Al_2O_3. Therefore, the CT from the Rh dimer to the $AlPO_4$ surface is considerably larger than that to the γ-Al_2O_3 surface. These results show that the presence of the isolated LU band at a low energy and the flexible $AlPO_4$ structure are important factors for the anchoring effect, which achieves outstanding thermal stability of the supported Rh nanoparticles on the $AlPO_4$ surface and therefore enables a reduction in quantity of Rh in the three-way catalyst using $AlPO_4$.

(v) Heterolytic Activation of Dihydrogen Molecule by Hydroxo-/Sulfido-Bridged Ruthenium−Germanium Dinuclear Complex.

Heterolytic H−H σ-bond activation of dihydrogen molecule (H_2) with transition metal complex is one of the most important research subjects in biochemistry and inorganic chemistry, because the heterolytic activation of H_2 is involved as a key step in hydrogen metabolism by hydrogenases. To explore and mimic its catalysis, many experiments have been



Scheme 3. Reaction scheme of H2 activation by Ru-Ge dinuclear complex

carried out to synthesize good models of [NiFe]-hydrogenase, and the activation reactions of H_2 with such hydrogenase models as Ir−Ir, Rh−Rh, Mo−Mo, W−Ir, W−Ru, Ru−Ni, and Fe−Ni dinuclear complexes have been reported. Recently, Matsumoto, Tatsumi, and their co-workers synthesized a hydroxo-/sulfido-bridged Ru−Ge dinuclear complex $[Dmp(Dep)Ge(\mu\text{-}S)(\mu\text{-}OH)Ru(PPh_3)]^+(BArF_4)^-$ (Dmp = 2,6-dimesitylphenyl, Dep = 2,6-diethylphenyl, ArF_4 =3,5-$(CF_3)_2C_6H_3$) and reported its interesting reactions (Scheme 3), as follows: (1) This complex performs σ-bond activation of H_2 at room temperature to afford H_2O and $[Dmp(Dep)Ge(\mu\text{-}S)Ru(H)(PPh_3)]^+(BArF_4)^-$, which is similar to the activation reaction of H_2 by hydrogenase, and (2) addition of H_2O to the product induces the reverse reaction to afford H_2 and the original Ru−Ge complex, indicating that the reversible reaction is successfully performed by this Ru−Ge complex.

In this theoretical work, we investigated the H−H σ-bond activation of H_2 to afford H_2O promoted by the hydroxo-/sulfido-bridged Ru−Ge dinuclear complex $[Dmp(Dep)Ge(\mu\text{-}S)(\mu\text{-}OH)Ru(PPh_3)]^+$ (1). Heterolytic activation of dihydrogen molecule (H_2) by hydroxo-/sulfido-bridged ruthenium−germanium dinuclear complex $[Dmp(Dep)Ge(\mu\text{-}S)(\mu\text{-}OH)Ru(PPh_3)]^+$ (**1**) (Dmp = 2,6-dimesitylphenyl, Dep = 2,6-diethylphenyl) is theoretically investigated with the ONIOM(DFT:MM) method. H_2 approaches **1** to afford an intermediate $[Dmp(Dep)(HO)Ge(\mu\text{-}S)Ru(PPh_3)]^+\text{-}(H_2)$ (**2**). In **2**, the Ru−OH coordinate bond is broken but H_2 does not yet coordinate with the Ru center. Then, the H_2 further approaches the Ru center through a transition state **TS2−3** to afford a dihydrogen σ-complex $[Dmp(Dep)(HO)Ge(\mu\text{-}S)Ru(\eta^2\text{-}H_2)(PPh_3)]^+$ (**3**). Starting from **3**, the H−H σ-bond is cleaved by the Ru and Ge−OH moieties to form $[Dmp(Dep)(H_2O)Ge(\mu\text{-}S)Ru(H)(PPh_3)]^+$ (**4**). In **4**, hydride and H_2O coordinate with the Ru and Ge centers, respectively. Electron population changes clearly indicate that this H−H σ-bond cleavage occurs in a heterolytic manner like H_2 activation by hydrogenase. Finally, the H_2O dissociates from the Ge center to afford $[Dmp(Dep)Ge(\mu\text{-}S)Ru(H)(PPh_3)]^+$ (**PRD**). This step is rate-determining. The activation energy of the backward reaction is moderately smaller than that of the forward reaction, which is consistent with the experimental result that PRD reacts with H_2O to form **1** and H_2. In the Si analogue $[Dmp(Dep)Si(\mu\text{-}S)(\mu\text{-}OH)Ru(PPh_3)]^+$ (**1Si**), the isomerization of **1Si** to **2Si** easily occurs with a small activation energy, while the dissociation of H_2O from the Si center needs a considerably large activation energy. Based on these computational findings, it is emphasized that the reaction of **1** resembles well that of hydrogenase and the use of Ge in **1** is crucial for this heterolytic H−H σ-bond activation.

(vi) Activation of Strong Boron–Fluorine and Silicon–Fluorine σ-Bonds: Theoretical Understanding and Prediction

The σ-bond cleavage by transition-metal complexes, such as oxidative addition and σ-bond metathesis, is the first step in almost all homogeneous catalytic reactions. To date, the B-F bond in boranes and Si-F bond in silanes have been alien to such bond activation reactions, precluding their direct catalytic transformation. This is because B-F and Si-F σ-bonds are two of the strongest σ-bonds (bond dissociation energies of B-F and Si-F σ-bonds are 183 and 129 kcal mol^{-1}, respectively) owing to strong bonding interaction between electropositive atom and electronegative fluoride. Activation of these σ-bonds by a transition metal, if readily achieved, would open a new door to synthesis of novel organic fluoroboron and fluorosilicon compounds, which are potentially valuable functional materials. Recently, Braunschweig and co-workers made a remarkable breakthrough when they reported the first example of B-F σ-bond activation via oxidative addition. In their reaction, the B-F σ-bond of BF_3 is cleaved by a platinum(0) bis(phosphine) complex.

Herein, we report a detailed theoretical study on B-X σ-bond activation (X=F, Cl) and similar Si-F σ-bond activation by a Pt^0 complex. Our purposes are to elucidate the reason why the strong B-F σ-bond can be easily cleaved by a Pt^0 complex under mild conditions and to present theoretical prediction how to activate the similarly strong Si-F σ-bond of SiF_4 by a Pt^0 complex. The oxidative addition of BF_3 to a platinum(0) bis(phosphine) complex $[Pt(PMe_3)_2]$ (**1**) was investigated by density functional calculations. Both the cis and trans pathways for the oxidative addition of BF_3 to **1** are endergonic (ΔG°=26.8 and 35.7 kcal mol^{-1}, respectively) and require large Gibbs activation energies ($\Delta G^{\circ\ddagger}$ =56.3 and 38.9 kcal mol^{-1}, respectively). A second borane plays crucial roles in accelerating the activation; the trans oxidative addition of BF_3 to **1** in the presence of a second BF_3 molecule occurs with $\Delta G^{\circ\ddagger}$ and ΔG° values of 10.1 and -4.7 kcal mol^{-1}, respectively. $\Delta G^{\circ\ddagger}$ becomes very small and ΔG° becomes negative. A charge transfer (CT) occurs from the dissociating fluoride to the second non-coordinated BF_3. This CT interaction stabilizes both the transition state and the product. The B-F σ-bond cleavage of BF_2Ar^F (Ar^F=3,5-bis(trifluoromethyl) phenyl) and the B-Cl σ-bond cleavage of BCl_3 by **1** are accelerated by the participation of the second borane. The calculations predict that trans oxidative addition of SiF_4 to **1** easily occurs in the presence of a second SiF_4 molecule via the formation of a hypervalent Si species.

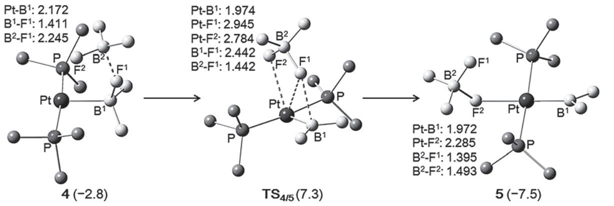
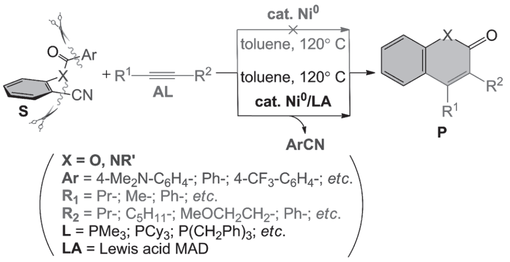


Figure 5. Geometry and energy changes in the B-F σ-bond cleavage by Pt(0) complex in the presence of the second BF_3

(vii) Reasons Two Nonstrained C−C σ-Bonds Can Be Easily Cleaved in Decyanative [4 + 2] Cycloaddition Catalyzed by Nickel(0)/Lewis Acid Systems. Theoretical Insight



Scheme 4. Ni^0/LA-catalyzed [4 + 2] cycloaddition of oarylcarboxybenzonitrile with alkyne

The selective activation of nonstrained inert C−C σ-bonds has attracted much attention because of its powerful and wide application to organic syntheses and catalytic reactions. This process is not only helpful for the construction of complex molecular skeletons from simple starting materials but also satisfies atom economy. However, the process still faces tremendous challenges due to the inertness of the nonstrained C−C σ-bond, considering that the C−C σ-bond cleavage is more difficult than C−H σ-bond cleavage because both sp^3 orbitals of two carbon atoms extend well toward each other in the C−C σ-bond and thereby an incoming metal center cannot interact well with these sp^3 orbitals.

In the present work, we theoretically investigated the full catalytic cycle of the Ni^0/LA-catalyzed [4 + 2] cycloaddition of oarylcarboxybenzonitrile with alkyne (Scheme 4) by density functional theory (DFT). Two constrained C−C σ-bonds are cleaved in a novel nickel(0)/LA-catalyzed decyanative [4 + 2] cycloaddition of o-arylcarboxybenzonitrile with alkyne, where LA represents a Lewis acid such as methylaluminum bis(2,6-ditert-butyl-4-methylphenoxide). The catalytic cycle of this reaction is systematically investigated here by DFT method to clarify the reasons two nonstrained C−C σ-bonds are successfully cleaved in this reaction. DFT calculations indicate that this reaction occurs via the oxidative addition of the C−CN σ-bond of o-arylcarboxybenzonitrile to the Ni(0) center, alkyne insertion into the Ni(II)−aryl bond, C−C coupling between the vinyl carbon and the carboxyl carbon atoms, and β-aryl elimination followed by reductive elimination. One LA interacts with the cyano nitrogen atom of o-arylcarboxybenzonitrile to accelerate the oxidative addition by stabilizing the unoccupied σ* + π* C−CN antibonding orbital. One more LA interacts with the carbonyl oxygen of o-arylcarboxybenzonitrile. This LA enhances the electrophilic nature of the carbonyl carbon to accelerate the C−C coupling, because this step occurs through the nucleophilic attack of the vinyl carbon at the carbonyl carbon atom. The second C−C σ-bond activation occurs via β-aryl elimination, the transition state of which is stabilized by the interaction between LA and the carbonyl oxygen atom. These results lead to the clear conclusion that the presence of two LA molecules is crucial to achieve the dual C−C σ-bond cleavages. The reasons LA accelerates the oxidative addition of the C−CN σ-bond to the nickel(0) center and the C−C coupling followed by the β-aryl elimination are discussed in detail.

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“Reasons Two Nonstrained C-C σ-Bonds Can Be Easily Cleaved in Decyanative [4+2] Cycloaddition Catalyzed by Nickel(0)/Lewis Acid Systems. Theoretical Insight”
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(7) Masafuyu Matsui, Masato Machida, Shigeyoshi Sakaki,
“Characterization of $AlPO_4$(110) Surface in Adsorption of Rh Dimer and Its Comparison with gamma-Al_2O_3(100) Surface: A Theoretical Study”
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(8) Hajime Kameo, Shigeyoshi Sakaki
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(10) Shinichi Yamabe, Shoko Yamazaki, and Shigeyoshi Sakaki,,
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(11) Masayuki Nakagaki and Shigeyoshi Sakaki
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3. Presentation at academic conferences

(1) Yue Chen, Masayuki Nakagaki, Shigeyoshi Sakaki,
"Bonding Nature, Reactivity and Catalysis of M-M Multiple Bond: Theoretical Study"
The 6th JCS(Japan-Czech-Slovakia)-Joint Symposium, Oct.11-14, 2015, Somlenice, Slovakia, (Invited)

(2) Shigeyoshi Sakaki
"Theoretical understanding of catalysis by transition metal complex with unusual valence"
X Pacifichem2015, Dec. 15 – 20, Honolulu, USA. (Invited)

(3) Shigeyoshi Sakaki
"Theoretical Study of Complex System Consisting of Transition Metal Element(s)",
The Seven-th Asia-Pacific Confernece on Theoretical and Computational Chemistry, Jan. 25 to 28, 2016, Kaoshiung, Taiwan. (Plenary)

(4) 榊　茂好
"遷移金属元素とケイ素化学種の相互作用と反応過程の理論研究: 面白さと難しさ".
第１９回ケイ素化学シンポジウム　2015年10月23-24日　琵琶湖ラフォーレ、守山 (Invited)

(5) 榊　茂好
"複合金属微粒子の構造と電子状態"
分子研・研究会「触媒の分子科学」2016年　3月9-10日、岡崎

(6) 榊　茂好
"理論化学・計算化学の未来：展望と期待"
計算分子科学研究拠点　第6回研究会　2016年3月14-15日、岡崎

(7) S. Aono, S. Sakaki
"Isomerization of ruthenium(II) sulfur dioxide complex in crystal; Theoretical study with QM/MM approach"
The Seven-th Asia-Pacific Confernece on Theoretical and Computational Chemistry, Jan. 25 to 28, 2016, Kaoshiung, Taiwan.

4. Others

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４．シニアリサーチフェロー

田中　一義

シニアリサーチフェロー

１．　今年度の研究の要約

有機 EL 素子の発光メカニズムには大きく分けて、(1) $S_1 \rightarrow S_0$ 遷移を利用する蛍光発光、(2) $T_1 \rightarrow S_0$ 遷移を利用するリン光発光、そして(3) $S_1 \rightarrow S_0$ 遷移と $T_1 \rightarrow S_1 \rightarrow S_0$ 遷移すなわち熱活性型遅延蛍光 (Thermally activated delayed fluorescence: TADF)があり、TADF をさらに拡張したものとして T_1 の代わりに T_2 の利用を考えることもある。今年度は $T_1 \rightarrow S_1 \rightarrow S_0$ 遷移による TADF を実現するために向けた分子ブロック設計を行った。

【始めに】第三世代の有機電界発光素子(OLED)として、熱活性型遅延蛍光(TADF)に興味が持たれている(Chart 1)。これは電界発光効率の改善のために、S_1 以上の一重項状態から項間交差によっていったん T_1 に移った励起子を熱活性化によって再度 S_1 に戻して（逆項間交差）S_1 励起子とし、その蛍光発光を利用するものである。特に OLED では S_1 励起子が 25%生成するのに対して、T_1 励起子が 75%生成することが分かっている 1)。したがって通常有機物を用いる OLED では無輻射遷移でこの 75%の T_1 励起子が消えるために、何らかの形でこれを有効利用することは重要な課題となる 2)。ここでは高効率 TADF のための理論的な設計指針を提案し、実際に分子の合成を行って構築した OLED からの発光効率（外部量子効率）を測定した 3)。

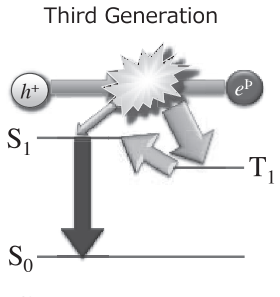

Chart 1

【TADF の設計指針】TADF に関わる詳細な機構(Figure 1)の検討によって、高効率 TADF の設計にとっては以下のような３点の考慮が重要であることが分かる。

(i)$T_1 \rightarrow S_1$ の逆項間交差速度 k_{RISC} が $T_1 \rightarrow S_0$ の無輻射遷移速度 k_{nr}' よりも大きいこと

$$k_{\mathrm{RISC}} > k_{\mathrm{nr}}'$$

(ii)$T_1 \rightarrow S_0$ のりん光発光速度 k_{P} が小さいこと

$$k_{\mathrm{P}} \simeq 0$$

(iii)$S_1 \rightarrow S_0$ の蛍光発光速度 k_{F} が、同じく $S_1 \rightarrow S_0$ の無輻射遷移速度 k_{nr} よりも大きいこと

$$k_{\mathrm{F}} > k_{\mathrm{nr}}$$

上記(i)で現れた k_{RISC} については以下の関係が利用できる。

$$k_{\mathrm{RISC}} \propto \exp\left[-\Delta E_{\mathrm{ST}}\right] \quad \text{および} \quad \Delta E_{\mathrm{ST}} = 2K_{ij} = 2\langle ij|ji\rangle \propto S_{ij}^{2} \qquad (1)$$

ここで ΔE_{ST} は S_1 と T_1 のエネルギー差、K_{ij}, S_{ij} はそれぞれ MO i, j 間の交換積分と重なり積分である。S_1 と T_1 の電子配置が主に S_0 の HOMO i と LUMO j で決まると考えれば、S_{ij} は HOMO–LUMO 間の重なり積分である。次に上記(ii)は通常の有機分子では満たされている（ほとんどりん光は出な

い)。さらに(iii)で現れた k_F については

$$k_F \propto {\mu_{10}}^2\;;\;{\mu_{ij}}^2\;;\;{S_{ij}}^2 \qquad (2)$$

の関係が利用できる。ここで μ_{10} は S_0–S_1 状態間の遷移双極子モーメントであり、i, j は上と同じく HOMO、LUMO で近似できる。すなわち k_F も HOMO–LUMO 間の重なり積分 S_{ij} の二乗で表すことができる。

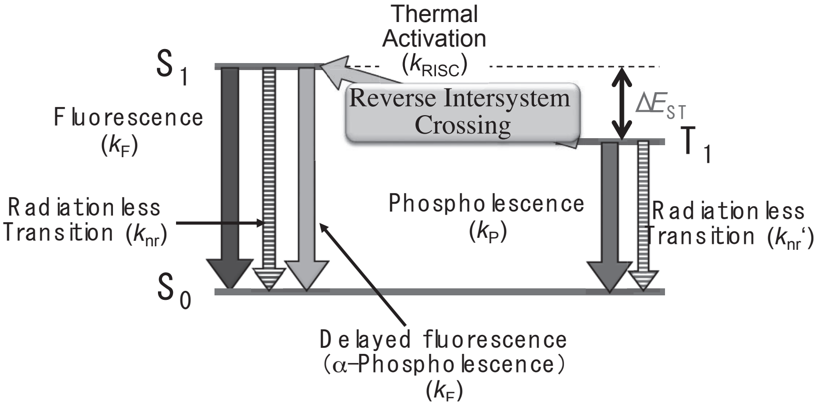

Figure 1. Mechanism of TADF related with S_0, S_1, and T_1.

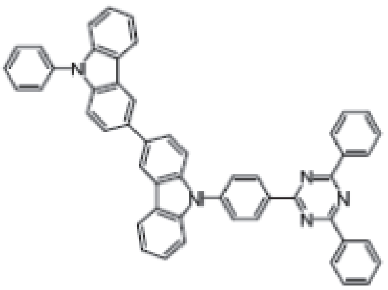

Figure 2. BCzT designed in the present study.

以上から、ΔE_{ST} を小さくするには S_{ij} を小さくし、k_F を大きくするには S_{ij} を大きくする必要があり、S_{ij} の値にはトレードオフの関係があることになる。しかしここで、式(2)は近似的なもので遷移双極子モーメント μ_{ij} は重なり積分と完全な比例関係にあるわけではないことに注意する。このことを使うとトレードオフ関係は少し弱められるので、これに注意しながら極力上記３点を満たすように新規に設計した分子 BCzT (9-(4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)-9'-phenyl-9H,9'H-3,3'-bicarbazole) を Figure 2 に示す。この分子の DFT 計算 (CAM -B3LYP/cc-pVDZ)によると、右側のトリアジン環はかなり捻じれており、これによって ΔE_{ST} を下げることができた（実験値 0.29-0.33 eV）。一方で S_0–S_1 状態間の遷移双極子モーメントを稼ぐことにより S_1 からの無輻射遷移は低減できる。またこの分子は分子内電荷移動を起こしやすい構造になっており、左側のカルバゾール部分がドナー、右側のトリアジン環がアクセプターとなっている。

この分子を実際に合成し、DPEPO (bis(2-(diphenylphosphino)phenyl)ether oxide) をホスト材とする OLED を作製して 483 nm 発光の外部量子効率を測定したところ、従来の限界値とされる 5 - 7.5 %の 3-4 倍である 21.7 %の値を達成した。460 nm の化学発光（387 nm 励起）の蛍光量子収率は 300 K において 95.6 %であった。

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1. 今年度の研究の要約

今年度は、(1)PRODANの分子内電荷移動反応の自由エネルギー解析および(2)スピン反転型時間依存密度汎関数法（SF-TDDFT）による非断熱分子動力学シミュレーション手法の開発を行った。

【PRODANの分子内電荷移動反応の自由エネルギー解析】

溶液における光化学反応のメカニズムを理解するうえで、電子励起状態の自由エネルギーは重要な役割を与える。私は過去の研究において、励起状態の電子状態計算であるTDDFT法と、溶液の積分方程式理論 (RISM) と組み合わせた計算方法を提案している[1]。この論文では、励起状態の自由エネルギーおよびその解析的な微分を使って、励起状態プロトン移動反応を自由エネルギー面で解析を行った。この研究の発展として、励起状態の電子状態が基底状態のそれとは大きく異なる、分子内電荷移動反応をとりあげた。この反応の場合、自由エネルギーで記述するためには、励起状態に対応した溶媒和を明示的に取り込むことが必要不可欠であることを示した[2]。

本年度の研究では、その応用として 6-propionyl-(*N,N*-dimethylamino)naphthalene (PRODAN) 分子 (図 1) を対象とした。この分子は、電子供与性のジメチルアミノ基と電子吸引性のプロピオニル基をもち、分子内電荷移動状態からの蛍光が確認されている。

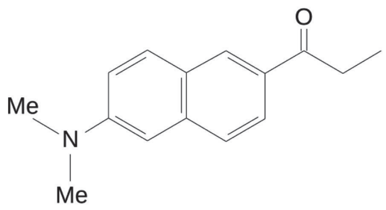

図 1: PRODAN 分子

電荷移動状態における分子構造として、平面型 (PICT) あるいはジメチルアミノ基がねじれた構造 (TICT) のいずれかが考えられる。PRODAN分子に対して、メタノール溶液中における分子内電荷移動反応について自由エネルギー面による解析を行った。過去の研究では、電荷移動状態の溶媒和を明示的に取り込む必要があることを示されている[2]。分子が大きく、計算コストがかかるが、同程度の精度を得られる自由エネルギーの補正を加える[2]ことで解決した。

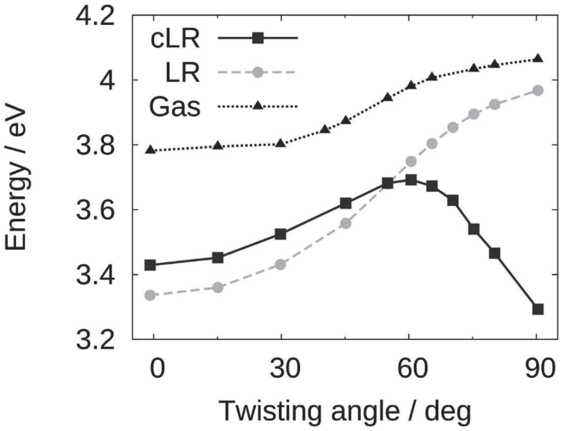

図 2: PRODAN 分子の電荷移動状態のエネルギー曲線

図 2 に、孤立分子およびメタノール溶液中の PRODAN 分子のエネルギー曲線を示した。計算条件として、TD-CAMB3LYP/DH+(d)を採用した。気相中のポテンシャルエネルギー曲線 (Gas) は、ねじれに対して吸熱的である。溶液中では、補正がない自由エネルギー (LR) では平面型 (PICT) だけが見られ、ねじれに対して吸熱的である。対照的に、補正項を加えた自由エネルギー曲線 (cLR) では PICT および TICT のいずれも安定な構造をあたえる。両者の間には反応障壁が存在するため、おそらく前者が有利であると考えられる。この反応障壁は溶媒の極性に依存することが予想される。したがって、PICT と TICT の生成比や蛍光寿命について、現在の計算手法で定性的にではあるが議論できると考えている。

【SF-TDDFT 法による非断熱分子動力学シミュレーション手法の開発】

光励起後の分子の動的過程は、蛍光や燐光といった発光だけでなく、無輻射遷移による基底状態への緩和や化学反応など様々な経路をたどる。これらの複雑で競争的な過程を説明し、光機能材料などの新規分子設計に寄与することが、理論化学計算には求められている。中でも無輻射遷移では、エネルギーの近接した複数のポテンシャル面が関与し、それらの間の遷移が重要な役割を果たす。近年、超高速の時間分解スペクトルによる測定が可能となり、励起状態の分子の反応過程が追跡可能となりつつある。したがって、理論計算においてもこうした実験結果を説明するために実時間に対応した動的過程を解析する手法が求められている。

過去の研究で、スピン反転型時間依存密度汎関数法 (SF-TDDFT) が励起状態と基底状態のポテンシャル面の交差が定量的に記述できることを報告した[3]。本研究では、方法論の自然な拡張として、SF-TDDFT 法を非断熱分子動力学シミュレーションと組み合わせた。その結果、電子励起状態からの緩和過程の詳細を明らかにすることが可能となった。本研究では、非断熱分子動力学シミュ

レーションのアルゴリズムとして Tully [4] の fewest switch surface hopping (FSSH) の手法を採用した。この方法は、状態間の遷移の計算に非断熱カップリングが必要とするが、今回 SF-TDDFT レベルの解析的なもの[5]を実装した。SF-TDDFT 計算および断熱分子動力学シミュレーションは電子状態計算プログラム GAMESS を用い、独自の FSSH プログラムと連結した。

テスト計算として、アゾメタン (CH$_3$-N=N-CH$_3$) の *Z*→*E* の光異性化を取り上げた。計算レベルは、テスト段階のため SF-BHHLYP/3-21G とやや低くしてある。図 3 に示したように、二成分の緩和が見られた。また、それぞれの成分に対応する代表的なトラジェクトリーを図 4 に示した。速い成分 (<80 fs) は *Z* 体から交差領域に速やかに到達し、基底状態への遷移に一度で成功している。それに対し、遅い成分 (150-250 fs) は円錐交差での一度目の遷移に失敗し、いったん *E* 体を形成している。その後、*E* 体から交差領域に到達し、基底状態への遷移に成功している。

従来のポテンシャル面の解析では、励起状態の極小点や反応障壁あるいは円錐交差の同定にとどまり、遷移のしやすさや遷移後の過程は説明できない。本研究で採用した非断熱分子動力学シミュレーションは、ポテンシャル面の解析を補完する貴重な情報をあたえて

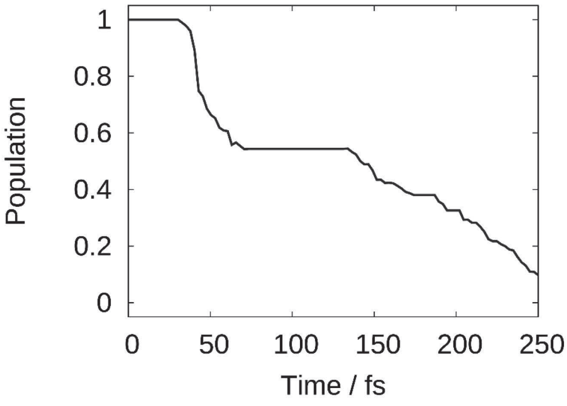

図 3: アゾメタンの S$_1$ 状態の population

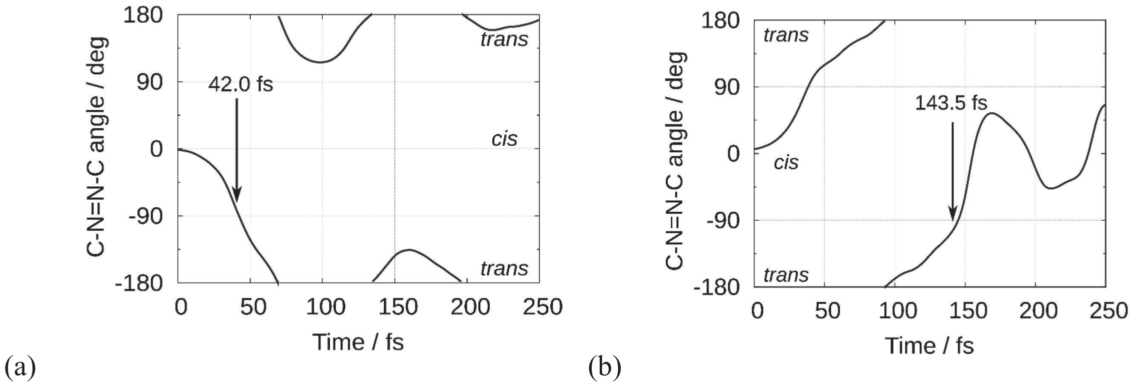

図 4: 典型的なトラジェクトリーにおける C-N=N-C のねじれ角
(a)速い成分および (b)遅い成分

いる。今後の予定として、プログラムの効率化と大規模分子系への応用が期待される。

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Takuya Saito

FIFC Fellow

1. Summary of the research of the year

Driven anomalous diffusion in polymer stretching

Linear polymer suspended in solution takes a fluctuating random coil. We tracked one end called tagged monomer, which undergoes the anomalous diffusion until the characteristic relaxation time. In this study, we investigated driven anomalous diffusion in polymer stretching by pulling tagged monomer.

(i) Force constant

To see the fluctuation characteristics in highly driven situation, we checked the fluctuation-dissipation relation that holds in equilibrium state. If the force is enough weak, the polymer can retain the equilibrium shape. But, if the force is strong, the polymer gets largely deformed and forms the non-equilibrium shape. We first carried out the molecular dynamics simulations under non-equilibrium condition. Repeating the stretching trials, we established the average drift and the positon variance. Examining the ratio of the variance to the average drift, we observed that the ratio deviates from the FDR.

We then constructed the theoretical stochastic descriptions to interpret the FDR deviations on the basis of the mode analysis. Even in the stretching regime, the initial configuration fluctuations remain eventually leading to the deviation.

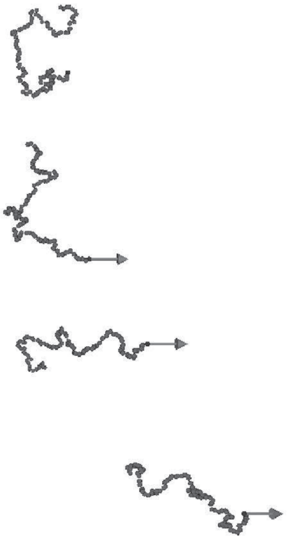

Fig. 1. Snapshots of polymer stretching in MD simulation. One end begins to be pulled at t=0.

(ii) Velocity constant

Pulling one end with constant velocity is fairly feasible in experiments. The generalized Langevin equation formulation discussed at the force constant suggests analogous relations, in which the momentum fluctuations at constant velocity are expected to show the similar results to those at constant force. Indeed, we confirmed the analogous results, which show the normalized ratio of the momentum deviates from the FDR at the high velocity.

The velocity constant, however, makes it difficult to theoretically derive the tagged monomer dynamics from the microscopic viewpoint. Assuming the decoupled modes, we proposed the equation of stochastic motion in momentum space. We first discussed the mode analysis in equilibrium and stretching. Combining them qualitatively reproduces the FDR deviations.

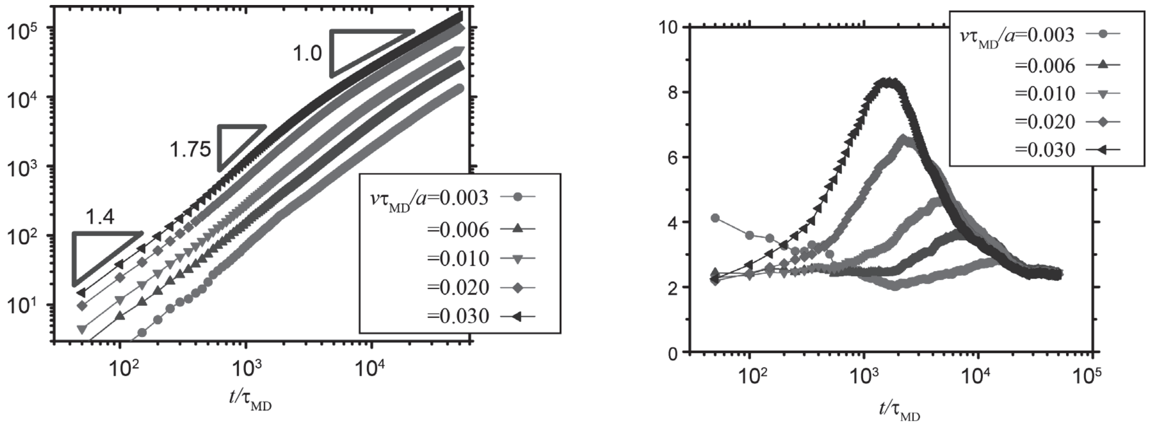

Fig. 2. Numerical results of <p(t)> (left) and the normalized ratio v<Dp^2>/(k_BT<p>) (right) in polymer stretching at constant velocity.

Driven anomalous diffusion in branched polymer

Developing analyses of branched polymers are inevitable for better understanding of biopolymer behavior. One of expected examples is proteins, where folded conformations are often regarded as branched polymers. The spectral dimension associated with the density of state is known as the way to see the connectivity.

We developed our anomalous diffusion theory by including the branched polymer with the spectral dimension in addition to the Flory exponent and dynamical exponents on the basis of the scaling or mode analysis. Compared with the linear one, the diffusion exponents get smaller as the connectivity increase more.

Polymer in athermal noise

Recently, the polymer characteristics in athermal or active noise generated by the energy source have begun to be recognized as the important subjects. If the motion of equation for the objects suspended in solution is written by the Langevin equation, thermal noise is related to the frictional kernel through the fluctuation-dissipation relation. Athermal noise no longer satisfies that. Many theoretical works has reported the unique anomalous diffusion by adopting exponential decay correlation of the noise. In the study, we developed the scaling theory including the exponential decay, but not relying on the noise detail. In addition, we discussed the general polymerized objects with arbitrary connectivity, excluded volume effects and dissipation mechanism in the presence of the athermal noise.

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“Driven anomalous diffusion: An example from polymer stretching”
Phys. Rev. E 92, 012601(2015).

3. Presentation at academic conferences

(1) Takuya Saito
“Driven Anomalous Diffusion in Polymer Stretching”
The 13th Fukui Center seminar,
Fukui Institute for Fundamental Chemistry, Kyoto, Sep. 29, 2015.

(2) 齋藤拓也, 坂上貴洋
“駆動される高分子の標識されたモノマーの異常拡散”
日本物理学会 2015 秋季大会, 関西大学 千里山キャンパス, Sep 17, 2015

(3) 齋藤拓也、坂上貴洋
“伸張させる条件に依存した高分子の揺らぎの特徴”
日本物理学会第 71 回年次大会, 東北学院大学 泉キャンパス, Mar 22, 2016

4. Others

(4) Takuya Saito and Takahiro Sakaue
“Driven Anomalous Diffusion in Polymer Stretching”
The 13th symposium of Fukui Institute for Fundamental Chemistry, Kyoto, Feb. 05, 2016.

Mitsusuke Tarama

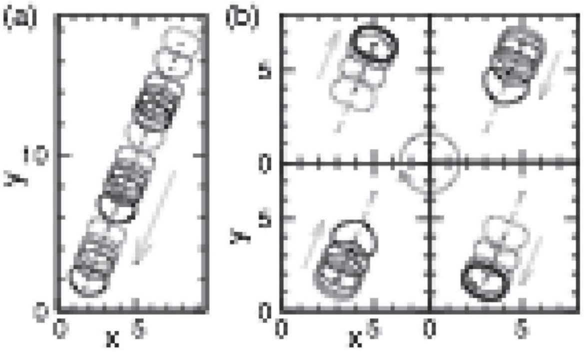
FIFC Fellow

1. Summary of the research of the year

Reciprocating motion of active deformable particles

Active matter is an object that possesses machinery to convert potential energy to kinetic energy and consequently exhibits movement by breaking symmetry. It is a broad concept including both biological and artificial systems. Well-studied active particles are rigid ones, which have prescribed undeformable shape, such as self-propelled camphor particles and active colloids as well as bacteria. There also exist deformable active particles that change their shape during the active movement. Shape deformation is of basic importance for living cells and micro-organisms like eukaryotes. Besides, artificial active particles accompanied by shape deformation are realised in liquid droplets and vesicles. For such active deformable particles, various dynamical states have been obtained even for an isolated single self-propelled object. The theoretical study of such active particles are briefly divided into two approaches. One is a detailed modeling of each specific example, which enables us to clarify the mechanisms and properties of the system. Besides, since the examples of active particles range from biological to artificial systems, it is also important to develop general descriptions to elucidate universal features of miscellaneous active particles. We are interested in the latter aspect and have pushed forwards the development of a general description of active deformable particles.

Quite recently reciprocating motion has been observed in several different systems. By reciprocating motion, we refer to a motion of a particle that moves back and forth periodically along a straight line. One of such systems is an oily droplet floating on aqueous solution. On the surface of the droplet, chemical reactions take place that cause self-propulsion. In a certain condition, it exhibits a reciprocating motion without being affected by the boundary wall [1]. The second example is a vertically vibrated system of a water droplet floating on viscous fluid [2]. Among various dynamical states, a parameter region is found where a droplet undergoes a reciprocating motion without turning around. The third example is a living cell which migrates by blebbing [3]. We note that a run-and-reverse motion has also been observed in some swimming bacteria having front-rear asymmetry [4]. However, the velocity in the forward motion is different from that in the reverse motion, unlike the case that we consider in the present study. As the last example here, we mention that reciprocating motions of an isolated domain have been obtained in numerical simulations of a set of reaction-diffusion equations with global coupling in two dimensions [5]. These are strong implications for which the reciprocating motion in homogeneous media is a generic motility in self-propelled soft systems. Our aim of this research is to develop systematic study of the reciprocating motion of active deformable particles in homogeneous media and to clarify its origin by focusing on the shape deformation.



By taking into account the second- and third-mode deformations, as well as the centre-of-mass velocity, we have introduced a nonlinearly-coupled equations of motion among them from symmetry considerations. By analysing the equations numerically in a two-dimensional space, we found two route to the reciprocating motion. One is a direct appearance from a motionless elliptically-deformed particle. Theoretical analysis revealed that this transition is characterised by the Hopf bifurcation of the trial solution of FitzHugh-Nagumo type equations. The other is more complicated; There is a solution where the particle moves in a straight line with the speed oscillating in time. There also exists its mirror symmetric solution that moves in the opposite direction along the same line. These solutions are represented by limit cycles in the phase space, e.g. the Poincare space of the magnitudes of the velocity and the third-mode deformation. They merge via a saddle point located at the origin of the space, which represents to the trivial motionless solution, to form a large limit cycle around the origin. See Fig. 1. The resulting limit cycle solution corresponds to the reciprocating motion. This bifurcation from the pair of the oscillatory rectilinear motion to the reciprocating motion is characterised by gluing bifurcation. In both cases, the second-mode deformation determines the axis of motion in the homogeneous space. The superposition of the second-mode deformation and the third-mode deformation breaks the front-rear symmetry of the particle shape, which couples to the centre-of-mass velocity vector to achieve the periodic back-and-forth oscillation along the axis.

Fig. 1: Trajectory of the centre-of-mass in real space (dashed line) with some snapshots of the particle (gray solid lines) of (a) the oscillatory rectilinear motion and (b) the reciprocating motion. (c) Time evolution of the magnitude and angle of the centre-of-mass velocity and the second- and third-mode deformations of the reciprocating motion. (d) Attractor in the $\bar{v}$-$\bar{s}_3$ space of the reciprocating motion (solid line) and that of the oscillatory rectilinear motion (dashed line), where the dotted line corresponds to the attractor of the oscillatory rectilinear motion that moves in the opposite direction. The arrows indicate the time-evolution direction. The figure is taken from M. Tarama and T. Ohta, Europhys. Lett. 114, 30002 (2016).

The results of this study have recently been published in Europhys. Lett. 114, 30002 (2016): Mitsusuke Tarama and Takao Ohta, "Reciprocating motion of active deformable particles".

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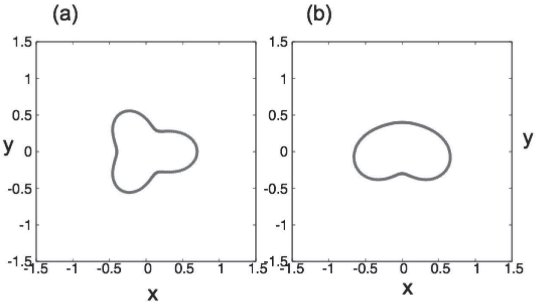
Model of a crawling cell

The migration of a biological cell is classified into two groups. One is a swimming motion in a fluid phase like the motion of bacteria and chlamydomonas, which are two typical examples of swimmers characterised as pusher and puller, respectively. The other is a crawling motion on a substrate. Such crawling motion is found in keratocyte and Dictyostelium cells. These cells exhibit characteristic shape deformation. Keratocyte cells take a crescent shape and moves with the front in the convex side. On the other hand, Dictyostelium cells tend to take triangular shape with the front wider and the rear narrower. See Fig. 2.

Based on symmetry consideration of migration and shape deformations, we have formulated phenomenologically the dynamics of a crawling cell in two dimensions. Forces



are introduced to change the cell shape, which then induce migration of the cell on a substrate. For time-independent forces we show that not only a stationary motion but also a limit cycle oscillation of the migration velocity and the shape occurs as a result of nonlinear coupling between different deformation modes. Besides, time-dependent forces are generated in a stochastic manner by utilizing the so-called coherence resonance of an excitable system. The present coarse-grained model has a flexibility that it can be applied, e.g., both to keratocyte cells and to Dictyostelium cells, which exhibit quite different dynamics from each other. The key factors for the motile behavior inherent in each cell type are identified in our model.

Fig. 2: Stationary shapes of a crawling cell subjected to constant deformation forces that have similar characteristics as that of (a) Dictyostelium cell moving to the left and (b) keratocyte cell migrating upwards. The figure is taken from T. Ohta et al. Physica D 318-319, 3-11 (2016).

We have proposed that the correlation between the deformations and the migration velocity plays an important role in the cell crawling. Such correlation exists even without the nonlinear coupling between the second- and third-mode deformations. The nonlinear coupling yields more persistent motion. That is, the cell tends to migrate without large changes of the direction for the same intensity of the random noises as that in the linear case. Similar dynamics was also observed in the experiment of Dictyostelium cells by Maeda et al. [5]. They have made a systematic comparison of the motility in a starved condition and a vegetative condition. A cell in a starved condition migrates at a larger velocity and elongates in the direction parallel to the migration direction. Its trajectory is much more persistent than in a vegetative condition.

The results obtained in this study are summarized in the paper published as in the Original papers (1).

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Physica D 318-319, 3-11 (2016).

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“Oscillatory motion of active deformable particles”
8th International Conference Engineering of Chemical Complexity, IAS, Technische Universität München, Garching, Müchen, Germany, 23 Jun., 2015 (poster).

(2) Mitsusuke Tarama, and Takao Ohta,
“Oscillation of active deformable particles”
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(3) Mitsusuke Tarama, and Takao Ohta,
“Reciprocating motion of active deformable particles”
Hierarchical Dynamics in Soft Materials and Biological Matter, Kyoto University, Kyoto,

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第５回ソフトマター研究会, 東北大学 青葉山キャンパス, 17 Dec., 2015 (oral: invited).

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Pacifichem 2015: Self-organization in Chemistry (#165) [3A], Honolulu, Hawaii, 18 Dec., 2015 (oral).

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アクティブマター研究会 2016, 九州大学 箱崎キャンパス 国際ホール, 22 Jul., 2016 (oral).

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(3) Mitsusuke Tarama
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“Nonlinear dynamics of active deformable particles”
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“Nonlinear dynamics of active deformable particles”
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Yoshio Nishimoto

FIFC Fellow

1. Summary of the research of the year

Development of the FMO-DFTB Method

I'm developing a large-scale quantum-mechanical method, called FMO-DFTB,[1] these days. FMO-DFTB is a combined method between the fragment molecular orbital approach and the density-functional tight-binding method.

The first development is FMO-DFTB3.[2] Considering the recent progress of the DFTB method, it is of great importance to make FMO-DFTB applicable to polarized or biological systems. The inclusion of the third-order correction modifies both the internal energy and the electrostatic potential (ESP) contributions in fragment calculation. FMO-DFTB3 reproduced relative stabilities and the optimized structures of three polyalanine (α-helix, β-sheet, and extended) isomers obtained with the corresponding full (e.g., without fragmentation) DFTB calculation. FMO-DFTB3 was applied to optimizing a nano flake of cellulose 1β, consisting of 10 944 atoms, and a good agreement with the experimental structure was obtained. For a cellulose sheet containing 1368 atoms, FMO-DFTB was 43.5 times faster than the corresponding full DFTB3 calculation. The binding between sheets and chains in cellulose was elucidated, and two dispersion models were compared. This study has been published on Chemical Physics Letters.[2]

In addition, the fully analytic gradient of FMO-DFTB has been developed.[3] The FMO approach is not a fully variational method, one has to include the orbital response contributions in calculating the derivative of the total energy with respect to nuclei. The previous FMO-DFTB has ignored the contributions, but they must be properly taken into account to perform molecular dynamics (MD) simulations; otherwise energy may not be conserved in NVE ensemble. In order to obtain the fully analytic gradient, although solving the coupled-perturbed equation is seemingly a straightforward approach, one has to solve $3N_{\mathrm{at}}$, where N_{at} is the number of atoms in the whole system, response equations per iteration, and they depend on the size of the entire system. Therefore, the self-consistent Z-vector (SCZV)[4] method was employed instead. The accuracy of the implemented analytic gradient was demonstrated on water clusters and a polypeptide and is reasonably high. For instance, Figure 1 shows the difference between analytic and numerical FMO-DFTB3 gradients for $(H_2O)_{64}$. The error of the analytic gradient, red filled circles, is rather small. The root-mean-square and maximum deviations of gradient are 0.000 002 and 0.000 006 a.u./Bohr with the response contributions, while they are 0.000 140 and 0.000 657 a.u./Bohr otherwise. The cost for SCZV is similar to the monomer self-consistent-charge step. The radial distribution functions (RDFs) obtained with FMO-DFTB are found to be similar to those from conventional DFTB, while the computational cost is greatly reduced: 73.26 and 0.68 s with full DFTB and FMO-DFTB, respectively, showing a speed-up factor of 108 with FMO-DFTB. As a possible application, FMO-DFTB/MD was applied to 100 ps MD simulations (one million step) of liquid hydrogen halides ($(HX)_{1000}$; X = F, Cl, Br, and I). FMO-DFTB calculation takes 1.8 s per MD step, while full

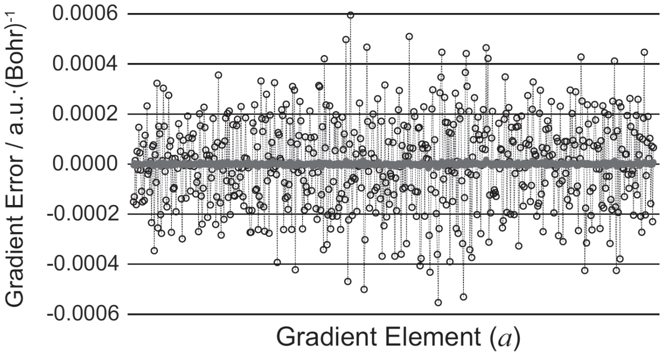

Figure 1. Differences between analytic and numerical FMO-DFTB3 gradients for $(H_2O)_{64}$. Red filled and black empty circles indicate the values (gradient errors) with and without the response terms.

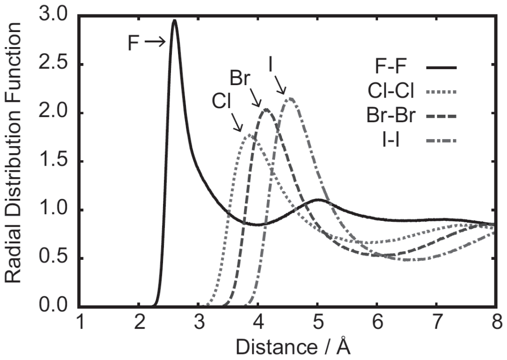

Figure 2. X-X radial distribution functions, shown with black solid (X = F), red dotted (Cl), blue dashed (Br), and purpose dashed-dot (I) lines.

DFTB does 1816 s. The RDFs obtained with the MD simulation are plotted in Figure 2. The method chosen in the study (FMO-DFTB2 with the UFF dispersion correction) gives reasonable RDFs of the hydrogen halides. FMO-DFTB/MD looks like a promising tool for QM/MD simulations of large systems, considering its low computational scaling and high parallel efficiency. This study is published has been published on the Journal of Physical Chemistry Letters.[3]

More recent developments, combination between FMO-DFTB and PCM, were summarized, and the manuscript was submitted.

Development of Excited-State Methods with DFTB

I completed two developments in the time-dependent version of DFTB (TD-DFTB). The first one is the extension of the previous TD-DFTB2 formalism[5] to the recent DFTB3[6] method, named TD-DFTB3.[7] Regarding the formulation, one additional term that comes from the second-order derivative of the third-order energy with respect to the density matrix is needed in computing excitation energies. In computing the analytic gradient with the Z-vector method, the third-order derivative of the third-order energy with respect to the density matrix is required. This term was assumed to be zero in TD-DFTB2. Since the third-order derivative term does not appear in Hartree-Fock, the new term may be viewed as a pseudo-exchange-correlation functional for DFTB. Improvement of DFTB3 for typical small molecules over DFTB2 in adiabatic excitation energy is not notable. Nevertheless, DFTB3 is supposed to be superior to DFTB2 for polar and hydrogen bonded systems, so it is still early to conclude that TD-DFTB3 does not improve excited state properties. Therefore, the absorption and fluorescence energies of cresyl violet, which contains one positive charge, in explicit water molecules have been calculated as a practical test example. The ten structures generated in the study consist of 323-404 atoms (cresyl violet plus 97 to 124 water molecules), so TD-DFT calculation for the systems is rather challenging in terms of the computational cost. The calculated excitation energies are summarized in Table 1. Although the absorption energies were overestimated relative to the experimental result,[8] the agreement of the TD-DFTB3 fluorescence energy with

Table 1. Experimental (ref. 8) and calculated absorption and fluorescence energies (unit in eV) for cresyl violet and oscillator strengths. Calculated energies and oscillator strengths in water are the averages of 10 geometries. Values in parentheses represent lower and upper bounds of 10 energies.

	Excitation energies		Oscillator strength	
Method	Absorption	Fluorescence	Absorption	Fluorescence
TD-DFTB2 (in vacuum)	2.46	2.10	0.452	0.200
TD-DFTB3 (in vacuum)	2.50	2.15	0.429	0.187
TD-DFTB2 (in water)	2.40 (2.35/2.44)	1.93 (1.80/2.03)	0.427	0.175
TD-DFTB3 (in water)	2.46 (2.43/2.49)	1.96 (1.86/2.09)	0.442	0.157
Experiment (in water)	2.12	1.96	N/A	N/A

the experiment was fairly promising.

In addition, (TD-)DFTB/PCM[9] has been developed. In particular, the analytic gradient of TD-DFTB/PCM excitation energy has not been available in any program packages. The benchmark calculation in this study shows that TD-DFTB/PCM is comparable with TD-DFT/PCM using GGA functionals such as PBE and BLYP. However, these methods underestimate absorption and emission energies, compared with experiment. This should be attributed to the lack of long-range corrections. It has been challenging for DFTB to treat biological systems unless fractional occupation numbers or explicit solvent molecules are used, because of the band-gap problem for DFTB and GGA functionals. Solute-solvent electrostatic interactions alleviate the band-gap problem, and thus it is possible for us to apply DFTB to realistic biological systems. In this study, (TD-)DFTB/PCM has been applied to a DNA-TOTO complex, PDB ID: 108D, which consists of 619 atoms, full excited-state calculations with DFT or wavefunction methods are very challenging. Minima on S_0 and excited-state potential energy surfaces were successfully obtained using TD-DFTB/PCM, and it is predicted that the enhancement of fluorescence energy of TOTO is attributed to the prohibition of rotation of TOTO when it is intercalated into the DNA.

All the developed methods are implemented in GAMESS-US and will be available in the next official release of it.

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“Third-order density-functional tight-binding combined with the fragment molecular orbital method”
Chem. Phys. Lett. 636, 90-96 (2015).

(2) Yoshio Nishimoto
"Time-dependent density-functional tight-binding method with the third-order expansion of electron density”
J. Chem. Phys. 143(9), 094108 (2015).

(3) Yoshio Nishimoto, Hiroya Nakata, Dmitri G. Fedorov, and Stephan Irle
“Large-Scale Quantum-Mechanical Molecular Dynamics Simulations Using Density-Functional Tight-Binding Combined with the Fragment Molecular Orbital Method”
J. Phys. Chem. Lett. 6(24), 5034-5039 (2015).

(4) Yoshio Nishimoto
“DFTB/PCM Applied to Ground and Excited State Potential Energy Surfaces”
J. Phys. Chem. A 120(5), 771-784 (2016).

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“Time-dependent density-functional tight-binding method with the third-order expansion term”
The 9th Annual Meeting of Japan Society for Molecular Science (3P114), Tokyo, September 18, 2015

(2) Yoshio Nishimoto
“Method Developments for the Time-Dependent Density-Functional Tight-Binding (TD-DFTB) Method”
The 96th CSJ Annual Meeting (4B4-38), Kyoto, March 27, 2016

4. Others

(1) Yoshio Nishimoto
“Method Developments for the Time-Dependent Density-Functional Tight-Binding (TD-DFTB) Method” The 13th symposium of Fukui Institute for Fundamental Chemistry, Kyoto, Feb. 5, 2016.

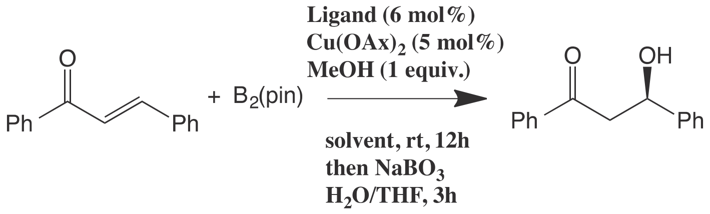
Miho Isegawa

FIFC Fellow

(1) Mechanistic difference of copper(I) and copper(II) catalysis in boron conjugation addition

The sysnthesis of optically active boron compounds are crucial in pharmaceutical applications, because the carbon-boron bond can be replaced by such as carbon-carbon, carbon-nitrogen, and carbon-oxygen bonds. For the carbon-boron bond formation, the catalytic function of the cooper(I) has been well examined, however, the catalytic function of copper(II) has not been addressed.

Recently, Zhu et al. [6] have reported copper(II)-based strategy for the catalytic asymmetric β -borylation. The enantiomeric excess of the reaction in scheme 1 shows high enantioselectivity (ee = 94%) using copper(II) catalysis with chiral ligand and diethylether as a solvent. In contrast, the copper(I) catalysis with the same ligand and THF solvents shows no selectivity. Here the dielectric constant of THF is close to the diethylether, and it is expected that the both solvents of diethylether and THF do not coordinate to the copper site. These facts imply that copper(I) and copper(II) gives different reaction mechanism in the process of carbon-boron bond formation.



Scheme 1. Enatioselevtive reaction for the formation of alcohol.

The reaction given in scheme 1 can be divided into three processes. The first is formation of LCu-B(pin) catalysis. This reaction is described as metathesis process in which copper-boron bond formation and boron-boron bond cleavage simultaneously takes place. The second step is enantioselective process with the carbon-boron bond formation and the process which is the most focused on in this study. The third step is hydroxylation process which takes place stereoselectively.

Our purpose in this study is to elucidate the mechanistic difference of copper(I) and cooper(II) catalysis in the boron conjugation addition. In order to reveal the reaction mechanism, it is crucial to locate the transition and global/local minima. The transition state is estimated using artificial force induced reaction (AFIR) simulation which are one of powerful methods to detect the approximate geometry of transition state. Thus, obtained approximate transition state is refined by full QM calculation with conjunction of implicit solvation model (SMD). To predict the dominant product in the enantioselective process, one needs to know the relative stability of the most stable transition state for each *R*- and *S*- form. To detect the most stable transition state, we applied multi-component AFIR method.

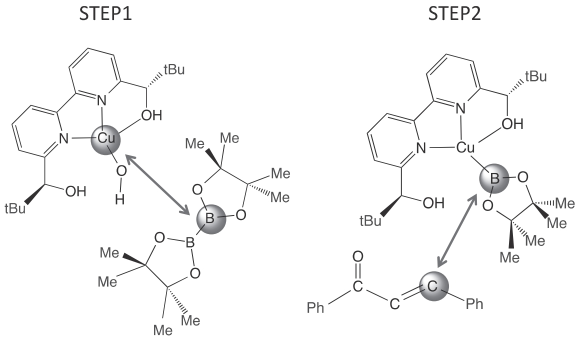


Figure 1. Functional groups given by blue are treated by ONIOM low level (PM6) and the rest of parts are treated by high-levels (M06-L). The attractive artificial force was applied into atoms circled by red.

(2) Reaction mechanism of H_2 and O_2 activation of [NiFe] core

Hydrogen molecule is promising energy resource in our near future as alternative fuel of fossil fuel. Therefore, the construction of the catalytic system which can efficiently produce hydrogen is crucial to attack to the energy problem.

Recently, Ogo et al. succeeded to synthesize organometallic compound which is able to catalyze the activation of hydrogen molecule (Figure 2). This catalysis is made by nickel and iron both of which are earth abundant metal, therefore the derivative of this catalysis can be a candidate for the realistic application. As more details, this catalysis works in the polar organic solvent and the hydrogen bonding cleavage is achieved by added strong base (MeONa). In addition, the notable point is that both hydride transfer and electron transfer is possible in the hydride binding complex as same as [NiFe]H_2ase. On the other hands, the difference from [NiFe]H_2ase is that the hydride binding site is Fe center rather than Ni center.

The main purpose of this study is to characterize the electronic structure of all of intermediates and reveal the reaction mechanism of hydrogen molecule activation based on density functional theory. For the location of the transition state, we employed artificial force induced reaction (AFIR) approach.

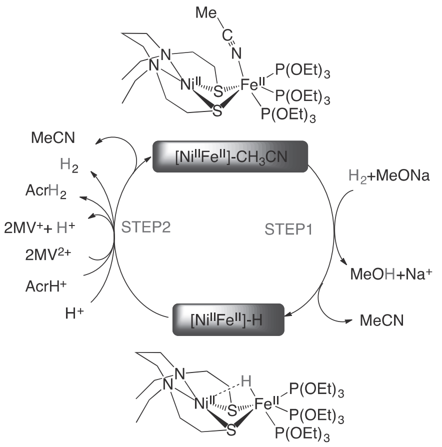


Figure 2. Experimentally proposed reaction mechanism for H_2 activation by [NiFe] core.

(3) O_2 activation of [NiFe] core

The O_2 activation is possible using analogous catalysis to that used in H_2 activation. Figure 2 shows the catalytic cycle experimentally suggested by Kishima et al. The only difference between catalysis which activates hydrogen molecule and oxygen molecule is the ligands which directly bind to the iron center. The ligands used in the O_2 activation has the character of strong electron donation to iron site, which allows the electron moving to the electron of *d*-orbital to the π* molecular orbital of oxygen molecule orbital. In contrast, the ligand which can activate H_2 shows the character of electron withdrawing, therefore the more electron poor condition is realized in iron site for H_2 activation. In the catalysis for O_2 activation, the O_2 binds Fe site with η^2 fashion according to the X-ray structure. The preference of the iron site is consistent with the catalysis in the H_2 activation. This is worthwhile to examine carefully.

In this study, catalytic process is examined dividing into two process, (1) O_2 binding process (2) O_2 bond cleavage process. The starting compounds for both of processes are well characterized with spectroscopic measurement. We explore all of possible binding patterns including different spin multiplicity including experimentally undetected species.

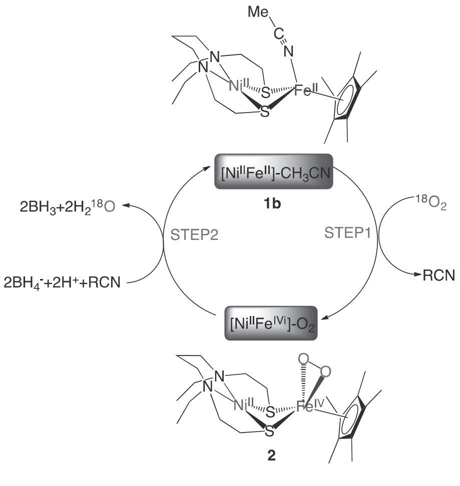


Figure 3. Experimentally proposed reaction mechanism for O_2 activation by [NiFe] core.

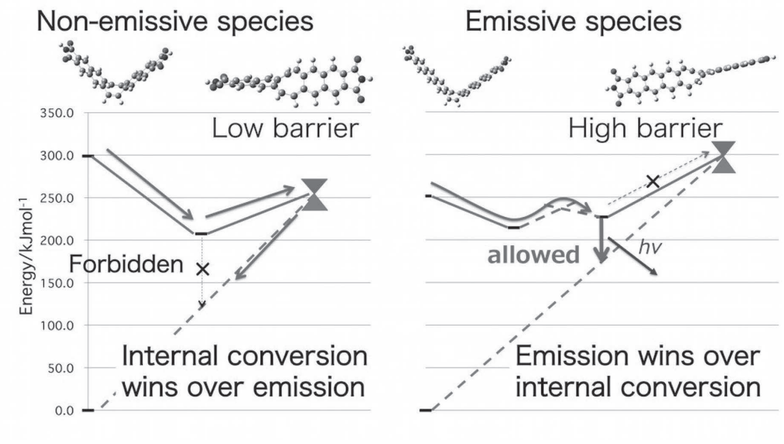
Satoshi Suzuki

Research Fellow

1. Summary of the research of the year

1.1 Exploration of Quenching Pathways of Multiluminescent Acenes Using the GRRM Method with the SF-TDDFT Method

The quenching pathways were investigated for three types of multiluminescent acene derivatives, which show environment-dependent fluorescence. Spin–flip time dependent density functional theory (SF-TDDFT) combined with the Global Reaction Route mapping (GRRM) strategy is employed to locate minimum-energy conical intersections (MECIs). The energies and geometries of the MECIs relative to the Franck–Condon (FC) state control the difference in fluorescence behavior among the three derivatives. For the molecule with a phenyamide moiety, a MECI with energy lower than the FC state with large geometrical change from V-type to flat structure provides an efficient internal conversion (quenching) pathway in solution. For the same molecule, in a solid, this large geometrical change is inhibited, and the second MECI, with an energy lower than FC but higher than the first MECI requiring only a small geometry change of CH out-of-plane bending, contributes to the quenching. The molecule with the napthaleneimide moiety has only one low-energy MECI that requires large geometrical change from the V-type to flat structure. Although this MECI provides the quenching pathway in solution, in the solid, this large motion is inhibited, and the molecule will stay in the excited state and emit. The molecule with an anthraceneimide moiety has no conical intersection lower than the FC state, and no quenching pathway is available in solution or solid. In addition, in this molecule, at the local minimum of the excited state, the dipole transition to the ground state is allowed, and this molecule prefers emission rather than internal conversion.



1.2 ビスジアルキルアミノアントラセン類における凝集誘起発光(AIE)の起源

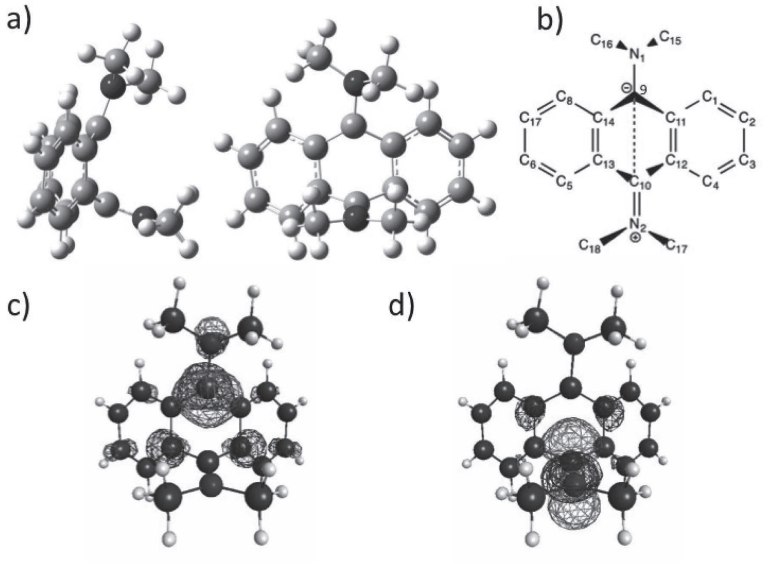
9,10-bis(N,N-dialkylamino)anthracene(BDAA) はアルキルアミノ基で置換されたアントラセンであり、そのシンプルな分子構造にもかかわらず凝集誘起発光(aggregation-induced emission:AIE) を起こす。多くの蛍光分子では凝集により発光性は低下する。AIE は非蛍光性の分子が凝集により蛍光性を持つようになる。一連の BDAA において、大きなストークスシフトが観測され、自己吸収が起こりにくいことが AIE の一因であると実験的に示唆された。
まず、大きなストークスシフトがどのような構造変化によって起こるのかを計算によって確認した。また、BDAA が溶液中で光りにくい原因は溶液中では内部転換による失活が起こりやすいのではないかという過程のもと、（気相中での）円錐交差を計算した。内部転換は円錐交差周辺で起こりやすく、もし円錐交差がエネルギー的に到達不可能であれば内部転換が起こりにくく、溶液中でも光りやすいと考えられる。さらに、液相と固相での発光性の差を議論するために ONIOM 法を用いた円錐交差探索を行った。

A)ストークスシフトの原因

9,10-bis(N,N-dimethylamino)anthracene(BDAA-methyl)の基底状態での安定構造と励起状態での安定構造を計算した。基底状態ではアミノ基がアントラセンに直交する構造が安定であり、syn 体と anti 体が存在する。励起状態では syn 体 anti 体どちらから構造最適化をスタートしても、一つのアミノ基が平面になる共通の Local Minimum に落ち込むことが示唆された。この構造ではアミノ基はアントラセンに直交している。また、二つのアミノ基が平面になるが、アントラセン部分に対して直交していない構造も励起状態の Local Minimum として存在することがわかった。この二種類の Local Minimum はエネルギー的にはほぼ同程度で、間にあるバリアーも低いため、共存しうる。いずれの Local Minimum からの発光だとしても蛍光波長は実験値を再現するため、これらの構造のいずれかからの起こると考えられる。

B)気相中での円錐交差

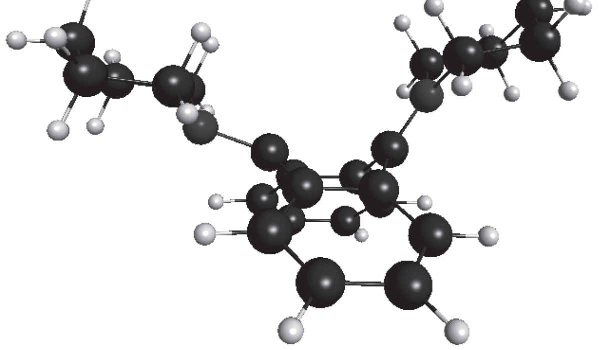
BDAA-methyl の円錐交差を CASSCF/6-31G(d)レベルで計算した。この系では芳香環の大きな歪みを含む円錐交差が存在し、そのエネルギーはフランクコンドン状態に比べて 50kJ/mol 程度安定である。つまり、フランクコンドン状態からエネルギー的には MECI へは到達であり、それがこの分子が内部転換しやすいことを示唆している。一方で、芳香環の折れ曲がりがあることからこのような構造は凝集時には周辺からの立体制約を強く受けると予想される。円錐交差が立体制約を受けることで凝集時に内部転換しづらくなり結果的に発光しやすくなるものと考えられる。



C)固相中での円錐交差

固相中での立体的な制約を見積もるために固体中でも MECI の構造最適化を行い比較した。固相のモデリングには ONIOM 法を採用した。励起状態の分子が基底状態の分子に囲まれているモデルの円錐交差を ONIOM(CASSCF/6-31G:PM6)レベルで計算する。立体的制約が主たる AIE の原因であることを前提としているので、いわゆる Mechanical Embedding で励起状態の分子と環境との相互作用は記述できると考えて良い。CASSCF の電子状態を GAMESS で PM6 計算を Gaussian09 で行い、構造最適化は GRRM プログラムを呼ぶようなインターフェースを作成した。これを用いて固相中の 9,10-bispiperidylanthracene(BDAA-piperidyl)の円錐交差を計算した。参照として気相での円錐交差も計算した。

BDAA-piperidyl についても BDAA-methyl 類似の円錐交差が低エネルギー領域に存在する。この円錐交差も BDAA-methyl の場合同様、フランクコンドン状態に比べてかなり安定である。一方、この構造に対応する固相中での円錐交差を計算するとエネルギーは遥かに不安定化し、フランクコンドン状態よりも 100kJ/mol 以上も高エネルギーとなる。



BDAA-piperidyl の気相中での円錐交差構造

一方、変位の比較的小さい、アントラセン部分の面外変角による円錐交差も存在するが、こちらは気相中でも固相中でもエネルギーが高く内部転換には関わらないと考えられる。以上のことからこの分子における固相での発光しやすさについて、定性的には説明ができた。

2. Original papers

(1) S.Suzuki, S. Maeda, K. Morokuma
Exploration of Quenching Pathways of Multiluminescent Acenes Using the GRRM Method with the SF-TDDFT Method
J. Phys. Chem. A, **119** pp 11479–11487 (2015)

(2) S.Sasaki, S.Suzuki, W.M.C. Sameera, K. Igawa, K. Morokuma, G. Konishi,
Highly twisted N,N-dialkylamines as a design strategy to tune simple aromatic hydrocarbons as steric environment-sensitive fluorophores
J. Am. Chem. Soc., accepted

3. Presentation at academic conferences

(1) 環境依存発光を示すアセンの消光経路探索　○鈴木聡　諸熊奎治　理論化学討論会 2015 大阪

4. Others

Akhilesh Kumar Sharma

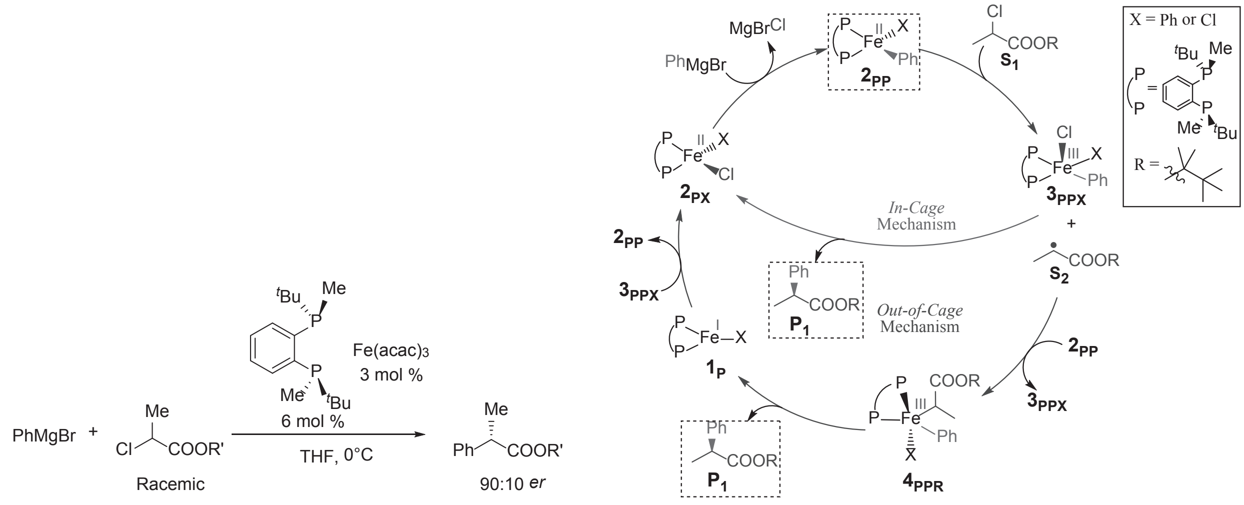
Research Fellow

1. Summary of the research of the year

Computational Insights on the Mechanism and the Origin of Enantioselectivity in Fe-Catalyzed Cross-Coupling Reaction

Transition metals are being used in homogenous catalysis for a long time for variety of transformations, including cross-coupling reactions and formation of asymmetric compounds. Cross-coupling reactions are important and versatile tool to synthesize variety of compounds of industrial and pharmaceutical importance. The most popular coupling reactions are Pd-catalyzed, as evident from the 2010 noble prize in Chemistry for developing these reactions. The efforts for development of new methods involving non-toxic and readily available metals for coupling reactions are increasing nowadays. The Fe can be very important in this regard, as it is non-toxic, readily available and is known to catalyze many enzymatic processes. The research interest for the development of Fe catalyzed reactions is increasing. The mechanistic understanding of Fe–catalyzed reactions is important for further development in this field.

Recently, M. Nakamura and coworkers have reported first Fe-catalyzed enantioselective cross-coupling reaction between aryl Grignard reagent (ArMgBr) and organic halide (R-Cl) (Scheme 1a). They proposed that the reaction proceed through *out-of-cage* mechanism (Scheme 1b). On the basis of radical probe studies radical pathway was proposed. The mechanism of the reaction is not established and there is no clear understanding on the origin of enantioselectivity. We have studied the mechanism of reaction using DFT methods. The AFIR method as implemented in GRRM program is used to explore potential energy surface of the reaction.



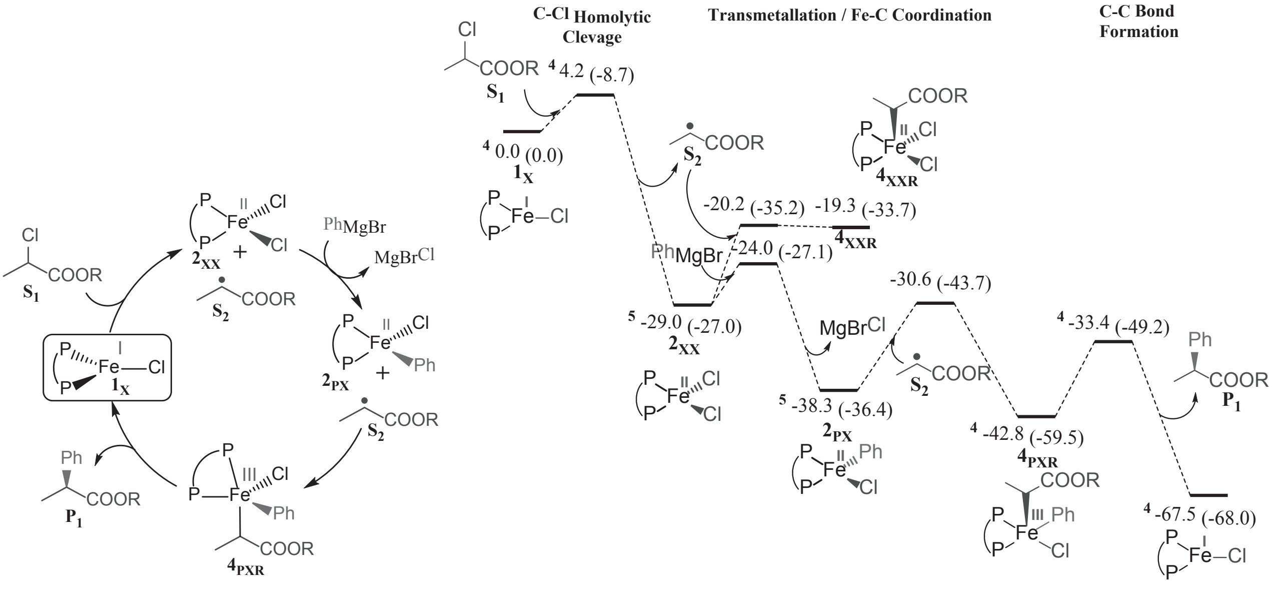
(a) (b)

Scheme 1. (a) Fe-catalyzed enantioselective cross-coupling reaction. (b) The proposed *in-cage* and *out-of-cage* mechanism.

The different Fe-catalyzed coupling reactions involving phosphine ligands are proposed to go through Fe(II) species. We studied the thermodynamics of generation of Fe(II) species from reagents. We found that the energy of Fe(I) and Fe(II) differs only by a small amount (2.7 kcal/mol). The possibility of coordination of solvent (THF) molecules to Fe and Mg are also explored. MC-AFIR method is used for exploring different conformational transition states and intermediates in different steps. The different spin states of the intermediates involved in the reaction are also considered. It is found that for Fe(I) ($\mathbf{1_P}$, $\mathbf{1_X}$), Fe(II) ($\mathbf{2_{PP}}$, $\mathbf{2_{PX}}$) and Fe(III) ($\mathbf{3_{PPX}}$, $\mathbf{3_{PPR}}$, $\mathbf{4_{PXR}}$) the lowest energy spin states are quartet, quintet, and quartet respectively.

The reaction involves three important steps, viz., Fe-catalyzed atom transfer reaction leading to generation of alkyl radical, C-C bond formation and transmetalation. Among the different possible Fe(II) species, [Fe(PP*)Ph$_2$] ($\mathbf{2_{PP}}$) is found to be of lowest energy. However, the reaction starting from [Fe(PP*)Ph$_2$] is less likely, as the activation barrier for biphenyl formation is less from the Fe(III) species ($\mathbf{3_{PPX}}$ and $\mathbf{4_{PPR}}$) in comparison to forward reaction through the proposed *in-cage* or *out-of-cage* reaction mechanism (Scheme 1b). It is in agreement with experimental method which requires slow addition of Grignard reagent. The C-C coupling from $\mathbf{3_{PPX}}$ is found to have higher activation barrier than coupling from $\mathbf{2_{PP}}$ (Scheme 1b). Hence, the reaction through *in-cage* mechanism is less likely in comparison to *out-of-cage* mechanism.

The activation barrier for C-Cl activation through other lower energy Fe(II) species, [Fe(PP*)PhCl] is high (24.0 kcal/mol). Hence, the reaction through Fe(II) species is less probable. As the reaction involves Fe(I), Fe(II) and Fe(III) species, we also considered C-Cl activation from Fe(I) and Fe(III) species. Interestingly the activation barrier for the C-Cl activation by Fe(I) is found to be very low.



(a) (b)

Figure 1. (a) The catalytic cycle based on computational results. (b) Free energy profile at B3LYP-D3BJ for the preferable mechanism in Fe-catalyzed coupling reaction.

The most probable mechanism according to our calculation is given in Figure 1. In the first step C-Cl activation occurs through atom transfer mechanism leading to generation of $\mathbf{2_{XX}}$ and $\mathbf{S_2}$. The active species for C-Cl activation is Fe(I), not Fe(II) as proposed in literature (Figure 1). As the activation barrier for this step is very small, the kinetic resolution of substrate could not be observed. The next step can be transmetalation or Fe-C coordination. The Fe-C coordination from $\mathbf{2}_{\mathbf{XX}}$ is found to be thermodynamically unfavorable. Activation barrier for transmetalation is low and it converts $\mathbf{2}_{\mathbf{XX}}$ to lower energy intermediate $\mathbf{2}_{\mathbf{PX}}$. Lower concentration of Grignard reagent diminishes the possibility of further conversion of $\mathbf{2}_{\mathbf{PX}}$ to $\mathbf{2}_{\mathbf{PP}}$ by transmetalation. The C-C coupling occurs through Fe(II) intermediate ($\mathbf{2}_{\mathbf{PX}}$) as proposed by M. Nakamura and coworkers. It occurs by inner sphere mechanism. It involves first coordination of radical species $\mathbf{S}_{\mathbf{2}}$ to $\mathbf{2}_{\mathbf{PX}}$ (Fe(II) species) leading to formation of Fe(III) intermediate $\mathbf{4}_{\mathbf{PXR}}$, followed by reductive elimination. The calculations for delineating factors responsible for origin of stereoselectivity are in progress. Both Fe-C bond formation and C-C bond formation step could be enantioselectivity determining.

2. Original papers

(1) W. M. C. Sameera, Akhilesh Kumar Sharma, Satoshi Maeda, Keiji Morokuma,
“Artificial Force Induced Reaction Method for Systematic Determination of Complex Reaction Mechanisms”
Chem. Rec. 2016, (Accepted).

3. Others (Presentation at symposium)

(1) A. K. Sharma, W. M. C. Sameera, M. Nakamura and K. Morokuma
“Computational Insights on the Mechanism and the Origin of Enantioselectivity in Fe-Catalyzed Cross-Coupling Reaction” The 13th symposium of Fukui Institute for Fundamental Chemistry, Kyoto, Feb. 5, 2016.

Pedro J. Castro

Postdoctoral Fellow

1. Research activities during FY2015 (October 2015 – March 2016)

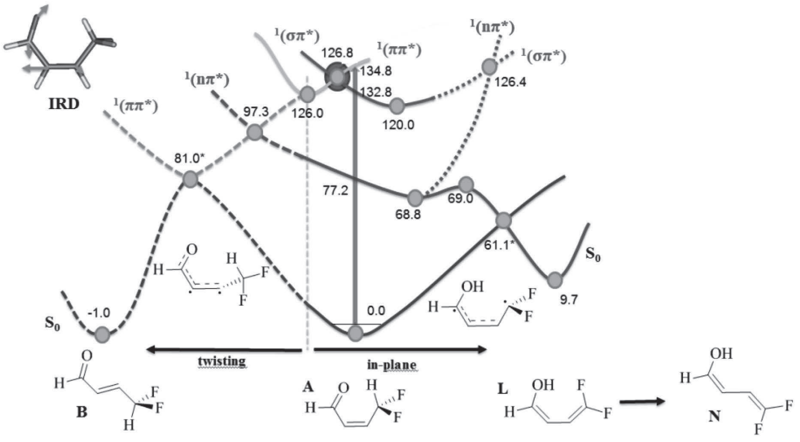
Once the matter is excited with electromagnetic radiation a large number of deactivation pathways compete with each other to decay to the ground state. These deactivation routes can take place through radiative or radiationless processes. As a consequence, some compounds exhibit phenomena such as fluorescence, phosphorescence and photochromism. These photochemical properties have a large amount of applications in different fields, from electronic devices devolvement to health care. Therefore, the understanding of the mechanisms leading to these phenomena guides to the rational design of photofunctional compounds. We have attempted to study these compounds from a static and dynamic point of view by combining methods based on TD-DFT and Trajectory Surface Hopping (TSH) approach. We have used TD-DFT and spin-flip (SF)TD-TDFT in order to describe energy and the electronic structure of the excited states. We have automatically explored the potential energy surfaces using the global route reaction mapping (GRRM) method via artificial force induced reactions (AFIR). The minimum energy conical intersections (MECI) were optimized using GRRM-MSX algorithm. The S_1/S_0-MECI were calculated using either MCSCF or using the lowest triplet (T_1) as reference via (SF)TD-DFT in order to describe the wavefunction for S_1 and S_0 in a balanced way.

2. Resume

A. Non-adiabatic dynamic on the Photochemistry of 4,4-difluorobut-2-enal using TD-DFT and TSH approaches.

The photochemical reactions of small molecules occur upon irradiation by ultraviolet or visible light, and they are a very important chemical process in Earth’s atmosphere, in the atmospheres of other planets, and in interstellar media. Small unsaturated carbonyl compounds play an important role in the chemistry of the polluted troposphere. The fluorinated aldehydes are very reactive under the sunlight driving to species which trigger more atmospheric reactions. This work is concerned a theoretical study of the photochemistry of difluoro-crotonaldehyde. We report the photochemical reaction paths starting from the *cis-keto* isomer. The initial excitation populates the $S_3(\pi\pi^*)$, the main deactivation channels follow non-adiabatic pathways via

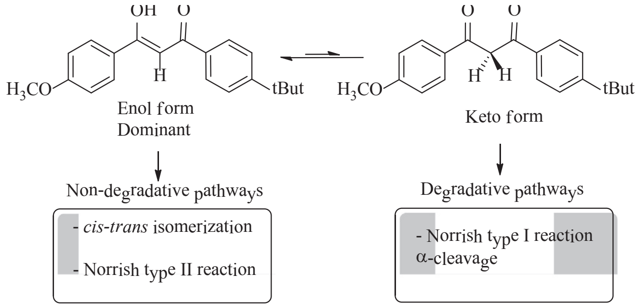
S_1/S_0 conical intersections. The S_1 can own different natures before the crossing with the S_0, so, three main reactions pathways can take place: *cis-trans* isomerization, Norrish type II reaction (γ-hydrogen abstraction) and fluorine photodissociation, when S_1 has a $\pi\pi^*$, $n\pi^*$ and $\sigma_F\pi^*$ nature, respectively. The minimum energy point on S_0 for *cis-keto* (**A**) belongs to C_s symmetry point group. Therefore, $S_3(\pi\pi^*)$ is populated in geometries near to planarity.

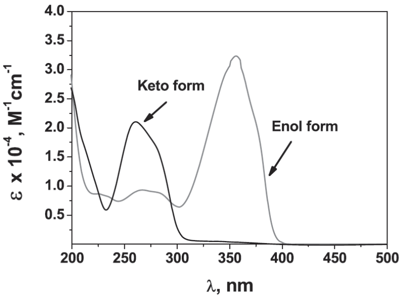


The initial relaxation takes place close to C_s point group until one point of the seam-$S_3(\pi\pi^*)/S_2(\sigma\pi^*)$, wherein a fraction of the population can be transferred to $\sigma\pi^*$ state which is relaxed toward a local minimum on $S_2(\sigma\pi^*)$. However, due to the inertia of the nuclei acquired during the relaxation along $\pi\pi^*$ state, the most of population follow $S_2(\pi\pi^*)$ until an in-place local minimum belonging to C_s characterized by large C-C central distance. Nevertheless, this stationary point corresponds to a saddle point when the all 3N-6 degrees of freedom are taken into account. Therefore, once populated this TS-$S_2(\pi\pi^*)$, the C-C central distance is around 1.45 Å, so the twisting coordinate becomes easier to be accessed. Following this coordinate, a point of the seam-$S_2(\pi\pi^*)/S_1(n\pi^*)$ is reached, whereas MECI belonging to this seam is 96º twisted and keeps C-C central distance equal to 1.45 Å. At this moment, the system could follow $S_1(\pi\pi^*)$ until an point of the seam-$S_1(\pi\pi^*)/S_0$, whose the MECI is 92º twisted and the C-C central distance is 1.48 Å, or follow $S_1(n\pi^*)$ to come back to C_s symmetry in order to reach MECI-$S_1(\pi\pi^*)/S_0$, or what is more reasonable, to reach the seam-$S_1(n\pi^*)/S_0$ from partially twisted geometries which could leads even directly to a *trans-enol* compound (**N**). The preferred deactivation channel is the *cis-trans* isomerization (56.3% of trajectories and 127 *fs* in average), followed for the fluorine photodissociation reaction which is the fastest deactivation channel (23.8% and around 77 *fs*), while the γ-hydrogen abstraction was the less probable (17.5% and 123 *fs* in average). A very small amount of trajectories (around 0.4%) were non-reactive during 300 *fs* or they followed other reaction pathways as Norrish type I reaction (α-cleavage) in 189 *fs* (in average).

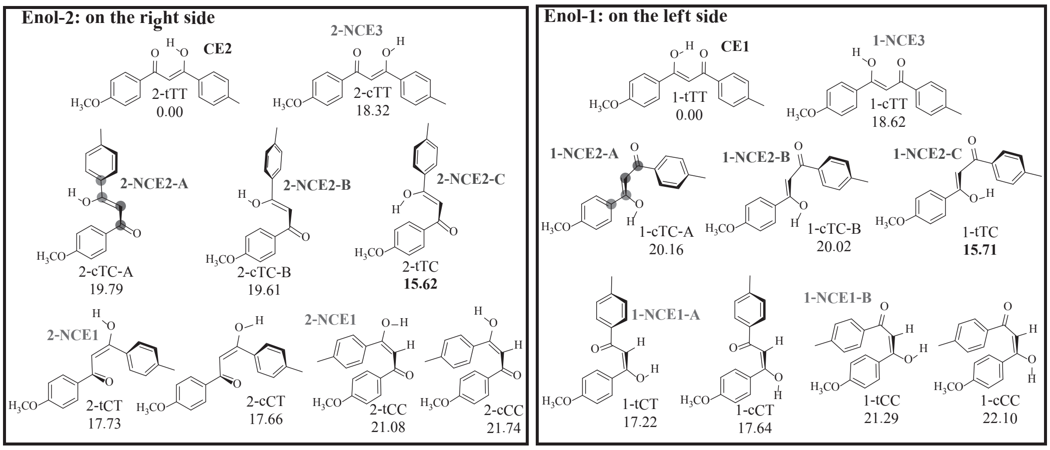
B. Computational study of the non-adiabatic decay of avobenzone

The raising level of awareness regarding the harmful effects of solar radiation has resulted in an increase in the production and consumption of sunscreens. These commercial products contain ultraviolet (UV) filters that absorb, reflect, or scatter UV radiation preventing sunburn, photoaging, even skin diseases such as skin cancer. These compounds are incorporated into not only sunscreens but also a number of personal care products and even in plastics, varnishes, and clothes to enhance their light stability. Avobenzone belongs to the family of dibenzoilmethane (DBM), it is the most commonly used organic UVA filter. It exists in sunscreens in the *enol* form which absorbs strongly in the UVA range. However, under sunlight irradiation tautomerization occurs to the *keto* form, resulting in the loss of UV protection. The loss of UVA protection is attributed to the *enol* → *keto* phototautomerism because *keto* form absorbs in the UVC range.

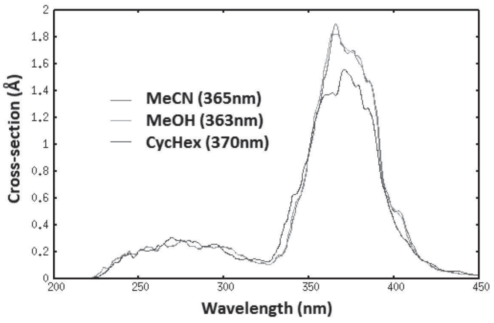


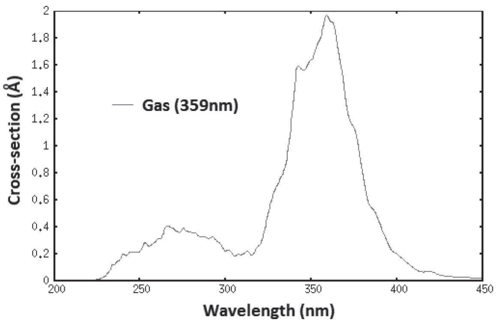


The ground state was explored by using AFIR (γ = 400 kJ) in GRRM package. Around 120 equilibrium geometries were located and classified according the dihedral angles. After removing mirror images and isomers respect to the substituents on the benzene rings, the geometries found are shown in the next picture:

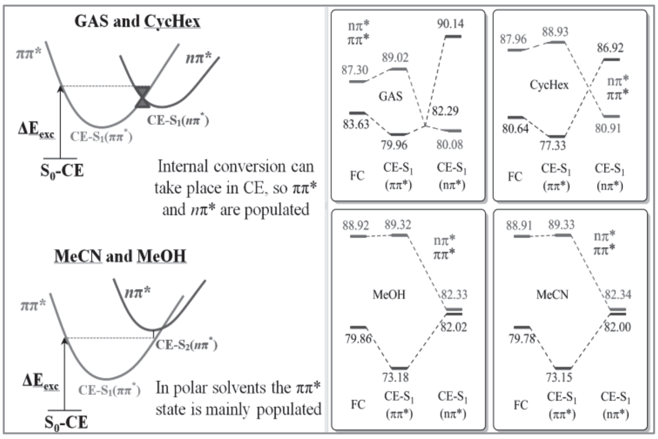


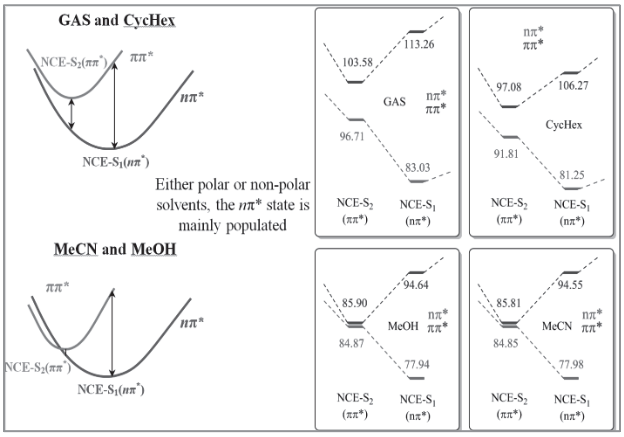
The absorption spectrum was simulated in gas, cyclohexane, methanol and acetonitrile. The cross-sections were based on TD-B3LYP/cc-pVDZ energies. To include the solvent effect was used cLR-PCM with the slow component equilibrated for the ground state. Each absorption spectrum was generated using an ensemble of 300 geometries generated using Wigner distribution of non-coupled harmonic oscillator along normal coordinates around the global minimum for CE1 (chelated enol) isomer at the ground state.





Then, two CE and two NCE (non-chelated enol) minima on S_1 were located; the solvent effect plays an important roll in the relative energies of those stationary points as shown below:





Two MECIs (CE-MECI and NCE-MECI) were located along the seam-$S_1(\pi\pi^*)/S_0$. The CE-MECI and NCE-MECI are located 8.75 and 5.97 kcal·mol^{-1} lower than the excitation energy in gas phase, so they are accessible. One transition state connects the CE-S1(ππ*) with the CE-MECI-$S_1(\pi\pi^*)/S_0$ imposing one barrier of 2.27 kcal·mol^{-1}. At March-2016, this research project is not finished, so the future work implies to study the different pathways to decay to S_0, and the *keto-enolization* reaction.

3. List of publications

Pedro J. Castro and Keiji Morokuma. *"Non-adiabatic dynamic on the Photochemistry of 4,4-difluorobut-2-enal using TD-DFT and TSH approaches"*. In preparation.

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】　金属錯体の化学的性質や反応を知る上で中心金属の電子状態を知る事は極めて重要である。特に d^8 平面４配位型金属錯体に関して、配位子の作る平面上の $d_{x^2-y^2}$ 軌道エネルギーが配位子との電子反発によって高くなり、８つの電子は残る４つの d 軌道を占有する事が一般に知られている。古くから、この配位子平面に直交する d_{z^2} 軌道の方向での中心金属と他分子との相互作用について理論研究が行われており、水分子との相互作用は最も重要なものの１つと考えられてきた。

d^8 平面４配位型金属錯体が全体として正電荷を持つ場合、z 軸上の水分子は O 原子を中心金属へ向けた構造（O 配向）をとる事が実験、理論研究から示唆されている[1]。例として$[\mathrm{Pt(pyridine)_4}]\mathrm{Cl_2}$・$3\mathrm{H_2O}$ 結晶などが挙げられるが、これは水素結合が電子的に富んだ領域と正に誘起された部位の静電相互作用に由来するという一般的理解に反しない。一方、全体で中性電荷となる金属錯体の場合、過去の MP2 計算によれば、水分子の H 原子が電子不足の d^8 中心金属へ向いた構造（H 配向）がエネルギー的に優位であると予測されており、これは一般的理解とは逆方向の水素結合を意味する。この存在は近年、trans-$\mathrm{PtCl_2(NH_3)}$(N-glycine)・$\mathrm{H_2O}$ 結晶における中性子散乱実験で立証された[2]。

これらの実験、理論研究を踏まえて、中性および電荷を持った d^8 平面４配位型金属錯体のモデル系として、Pt^{2+}を中心金属とした trans-$\mathrm{PtCl_2(NH_3)}$(N-glycine) **1a**、$[\mathrm{Pt(NH_3)_4}]^{2+}$ **1b**、$[\mathrm{Pt(CN)_4}]^{2-}$ **1c** 錯体に対し、その z 軸上の水分子との相互作用について気相中での２つの配向の違いを明らかにした。更に d_{z^2} 軌道の影響を調べるため、電子分布の広がりの小さい Pd2+を中心金属とした類似化合物 **2a**、**2b**、**2c** に対しても同様に、水分子の２つの配向における相互作用の違いを比較、検討した。また周囲の環境が与える影響に関しても焦点を置き、３D-RISM-MP2 法によって水溶媒中での振る舞いの違いを検討した。

【方法】　金属錯体と z 軸上の水１分子を QM 領域として扱い、水分子（QM）の２種類の配向に対して次のようにモデル構造を決めた。O 配向では水の O 原子が z 軸上に存在するように、また H 配向では H 原子と O 原子が z 軸上に位置するように束縛条件を加えた上で、3D-RISM-MP2 計算を行い、構造を最適化した。Pt は６０個の内殻電子を、Pd は２８個の内殻電子を Hay-Wadt ECP に置き換えた LANL2TZ(f)を基底関数に選び、残る原子は 6-31++G**基底を用いた。これによって得た金属錯体と水分子の内部座標は固定し、中心金属と水の O 間の距離を変化させる事で気相中のエネルギーおよび水溶媒中の自由エネルギーの振る舞いを調べた。その際により大きな基底関数として水の O と配位子の Cl に aug-cc-pTVZ を、残る配位子に cc-pTVZ を用いて 3D-RISM-MP2 計算を再度行って、BSSE を補正した。

３D-RISM-SCF 計算については、溶質の電子密度から溶媒平衡分布を定める際に、溶質周囲の静電ポテンシャルを求める必要があるが、本研究では（１）式のように溶質周囲の領域では波動

関数から直接計算を、溶質から遠く離れた領域では点電荷近似計算を行い、swithing 関数 Sw(**x**)の導入によって２つを滑らかに繋げる事で、対応する Fock 行列を計算している。

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

この three-regions 3D-RISM-SCF 法に対して MP2 レベルでの自由エネルギーおよび勾配ベクトルの計算を行えるように式の導出と GAMESS におけるプログラム化を行った。3

【結果】 Pt 錯体と水分子の相互作用系に対して得られた H 配向と O 配向のモデル構造を図１に示す。但し、一部の錯体での全自由度に対する構造最適化は目的の H 配向または O 配向の構造とは異なる構造に辿り着くため、H 配向に関しては水の H と O 原子が z 軸上に、O 配向に関しては水の O 原子が z 軸上に存在するように拘束条件を加え、更に cyano 錯体の O 配位に関しては金属-O 原子間の距離を glycine 錯体で得られた値になるように制限を加えてモデル構造を得た。

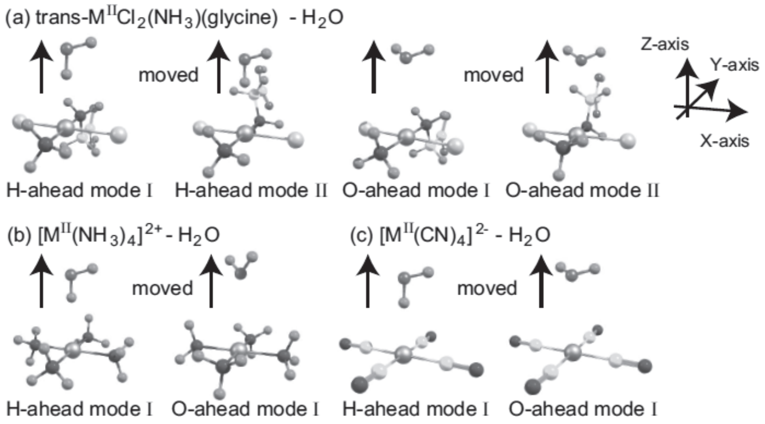


図１：H 配向、O 配向に対する glycine 錯体、ammine 錯体、cyano 錯体のモデル構造

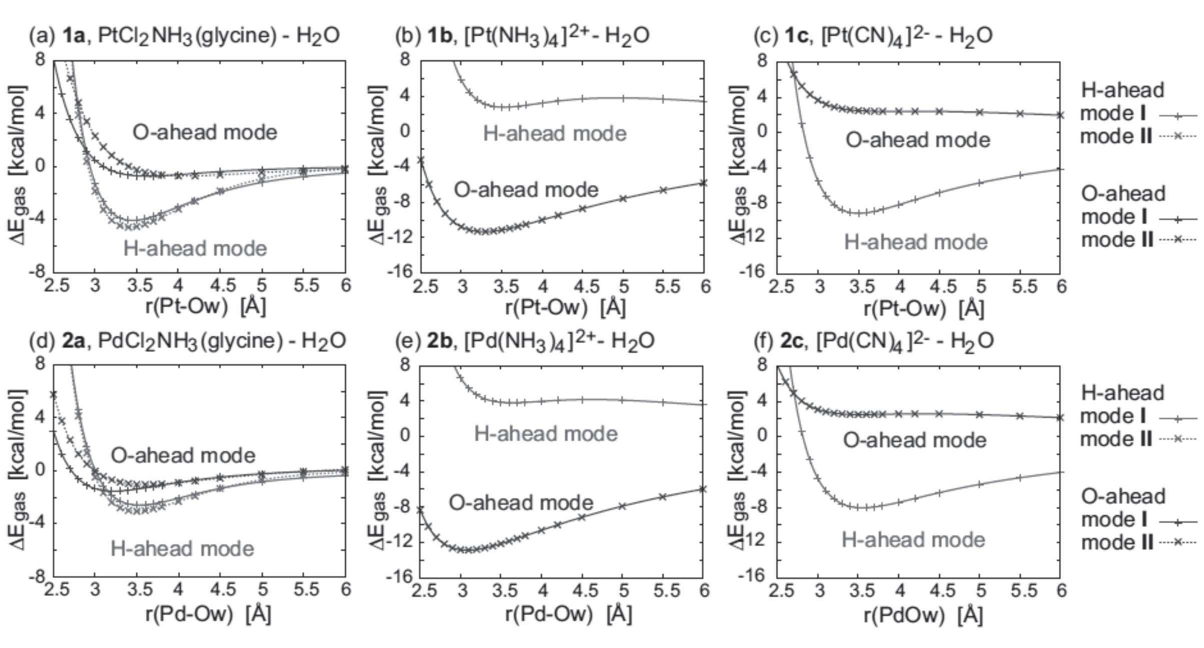


図２：H 配向、O 配向に対するモデル構造からの金属-O 原子距離に沿った気相中エネルギー曲線

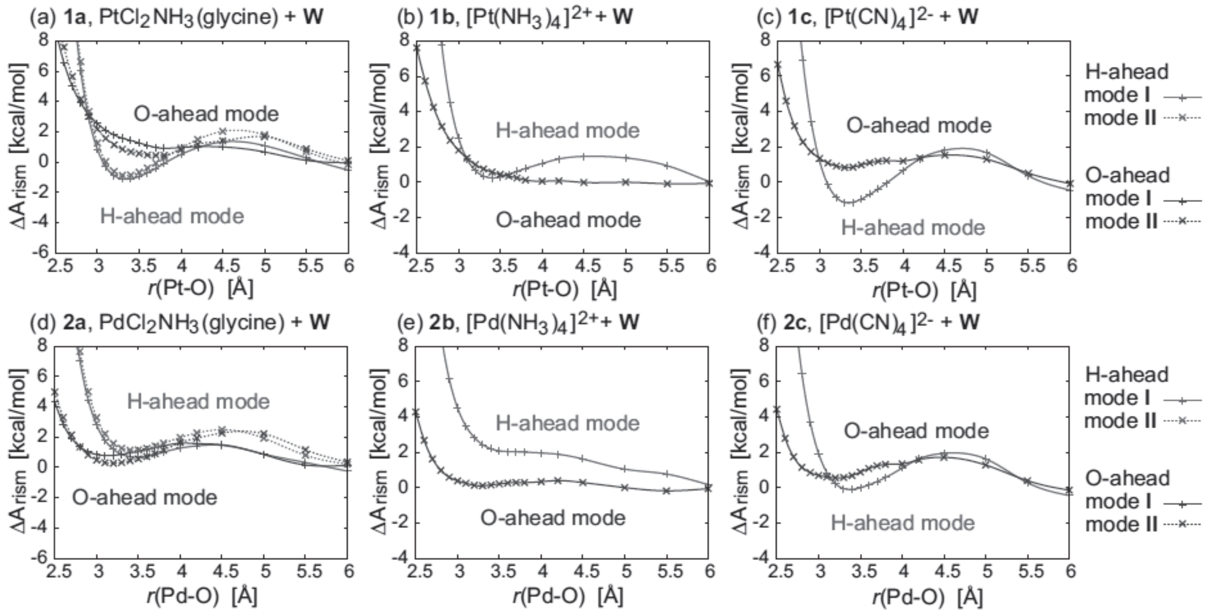


図３：H配向、O配向に対するモデル構造からの金属-O原子距離に沿った水中自由エネルギー曲線

H配向とO配向の相対安定性について、glycine錯体の場合は気相中と水中で定性的な変化はないが、ammine錯体とcyano錯体の場合は大きく異なる事が図２と３の比較から分かる。ammine錯体では気相中でO配向がH配向よりも大きな安定性を示すものの、水中ではその差がなくなり、特にPtではH配向の方が若干ながら安定となる。一方、cyano錯体の場合は気相中でも水中でもO配向がH配向よりも安定であるものの、O配向の相対安定性は気相中に比べて水中では大きく減少している。またPtとPdの違いについて、H配向はPdよりもPtの方が相対安定性は増加し、O配向はPdよりもPtの方が相対安定性は減少している事が計算結果から示されている。

このH配向とO配向の相対安定性の違いについて調べるため、錯体-水分子間相互作用についてエネルギー分解解析を行った（表１）。解析の結果、glycine錯体のH配向の安定化には電子相関（分散）エネルギーが大きく寄与している事、ammine錯体のO配向の安定化には静電エネルギーが大きく寄与している一方でH配向の安定化には分散エネルギーが寄与する事、cyano錯体のH配向の安定化には静電エネルギーと分散エネルギーの両者が寄与している事が分かった。またPtとPdの相違として、分散エネルギーはあまり異ならないが、静電エネルギーにおいてPtの方がPdよりもH配向を安定化する一方でO配向を不安定化する事が分かった。これはPtの方がPdよりもd_{z^2}軌道の広がりが大きい点を考慮すれば妥当な結果である。また電子移動エネルギーについて、期待していた程にはO配向の安定化に大きく寄与していない事も分かった。しかしながら、H配向とO配向では錯体-配位子間の電子移動に対して逆の効果を与える事が電荷分布解析の結果から判明し、H配向では静電的効果からd軌道エネルギーが下がるので配位子→金属への電荷移動が増大し、更に一部の電子が錯体→水へ移動する傾向がある点と、O配向では静電的効果からd軌道エネルギーが上げるので配位子→金属への電荷移動が減少し、更に微量ながら水→錯体へ電荷移動する傾向がある点も判明した。

また気相中と水中のエネルギー曲線の違いは主に溶媒和自由エネルギーが原因となっている事も分かった。その大きさはPtとPdであまり変わらないが、ammine錯体とcyano錯体の場合、H配向とO配向の間で顕著な差がある。ammine錯体の場合はO配向よりもH配向の方が溶媒和自由エネルギーによる安定化が大きく、cyano錯体の場合はH配向よりもO配向の方が大きい。

表１：水中における錯体-水分子間のエネルギー分解解析

	Pt complex							
	1a, $PtCl_2(NH_3)$(glycine)				**1b**, $[Pt(NH_3)_4]^{2+}$		**1c**, $[Pt(CN)_4]^{2-}$	
Geom.	H-I	H-II	O-I	O-II	H-I	O-I	H-I	O-I
$E_{\mathrm{int}}^{\mathrm{MP2}}$	-4.0	-4.8	-0.6	0.3	3.0	-11.2	-8.2	3.2
components of $E_{\mathrm{int}}^{\mathrm{MP2}}$								
E_{DISP}	-5.7	-6.4	-0.8	-1.4	-4.0	-0.1	-6.1	-1.0
$E_{\mathrm{int}}^{\mathrm{RHF}}$	1.7	1.6	0.2	1.7	6.9	-11.0	-2.1	4.2
components of $E_{\mathrm{int}}^{\mathrm{RHF}}$								
E_{ES}	-4.9	-5.9	-2.2	-1.6	6.9	-10.9	-7.1	3.1
$E_{\mathrm{EX}}+E_{\mathrm{REP}}$	10.1	11.3	2.8	4.3	5.5	2.5	10.9	2.7
$E_{\mathrm{POL}}+E_{\mathrm{CT}}+E_{\mathrm{MIX}}$	-3.5	-3.8	-0.4	-1.0	-5.4	-2.6	-5.9	-1.6
(E_{POL})	(-5.3)	(-5.9)	(-0.4)	(-1.3)	(-5.3)	(-2.1)	(-11.4)	(-2.0)
(E_{CT})	(-3.4)	(-3.6)	(-0.6)	(-0.9)	(-3.0)	(-1.5)	(-3.8)	(-0.9)
(E_{MIX})	(5.2)	(5.7)	(0.6)	(1.2)	(3.0)	(1.0)	(9.3)	(1.3)
	Pd complex							
	2a, $PdCl_2(NH_3)$(glycine)				**2b**, $[Pd(NH_3)_4]^{2+}$		**2c**, $[Pd(CN)_4]^{2-}$	
Geom.	H-I	H-II	O-I	O-II	H-I	O-I	H-I	O-I
$E_{\mathrm{int}}^{\mathrm{MP2}}$	-2.6	-3.2	-1.4	-0.6	3.9	-12.5	-7.2	3.9
components of $E_{\mathrm{int}}^{\mathrm{MP2}}$								
E_{DISP}	-4.7	-5.3	-0.8	-1.2	-3.3	0.1	-5.5	-1.3
$E_{\mathrm{int}}^{\mathrm{RHF}}$	2.1	2.1	-0.6	0.6	7.2	-12.6	-1.7	5.2
components of $E_{\mathrm{int}}^{\mathrm{RHF}}$								
E_{ES}	-0.6	-1.6	-6.2	-4.7	10.1	-13.7	-4.3	-0.1
$E_{\mathrm{EX}}+E_{\mathrm{REP}}$	5.0	6.1	5.9	5.9	2.7	5.1	6.8	6.7
$E_{\mathrm{POL}}+E_{\mathrm{CT}}+E_{\mathrm{MIX}}$	-2.3	-2.4	-0.3	-0.6	-5.6	-4.0	-4.2	-1.4
(E_{POL})	(-2.9)	(-3.2)	(-1.2)	(-1.2)	(-5.5)	(-4.1)	(-7.5)	(-3.9)
(E_{CT})	(-1.7)	(-1.7)	(-1.0)	(-1.0)	(-2.2)	(-2.0)	(-2.1)	(-1.5)
(E_{MIX})	(2.3)	(2.5)	(1.9)	(1.6)	(2.1)	(2.1)	(5.6)	(4.0)

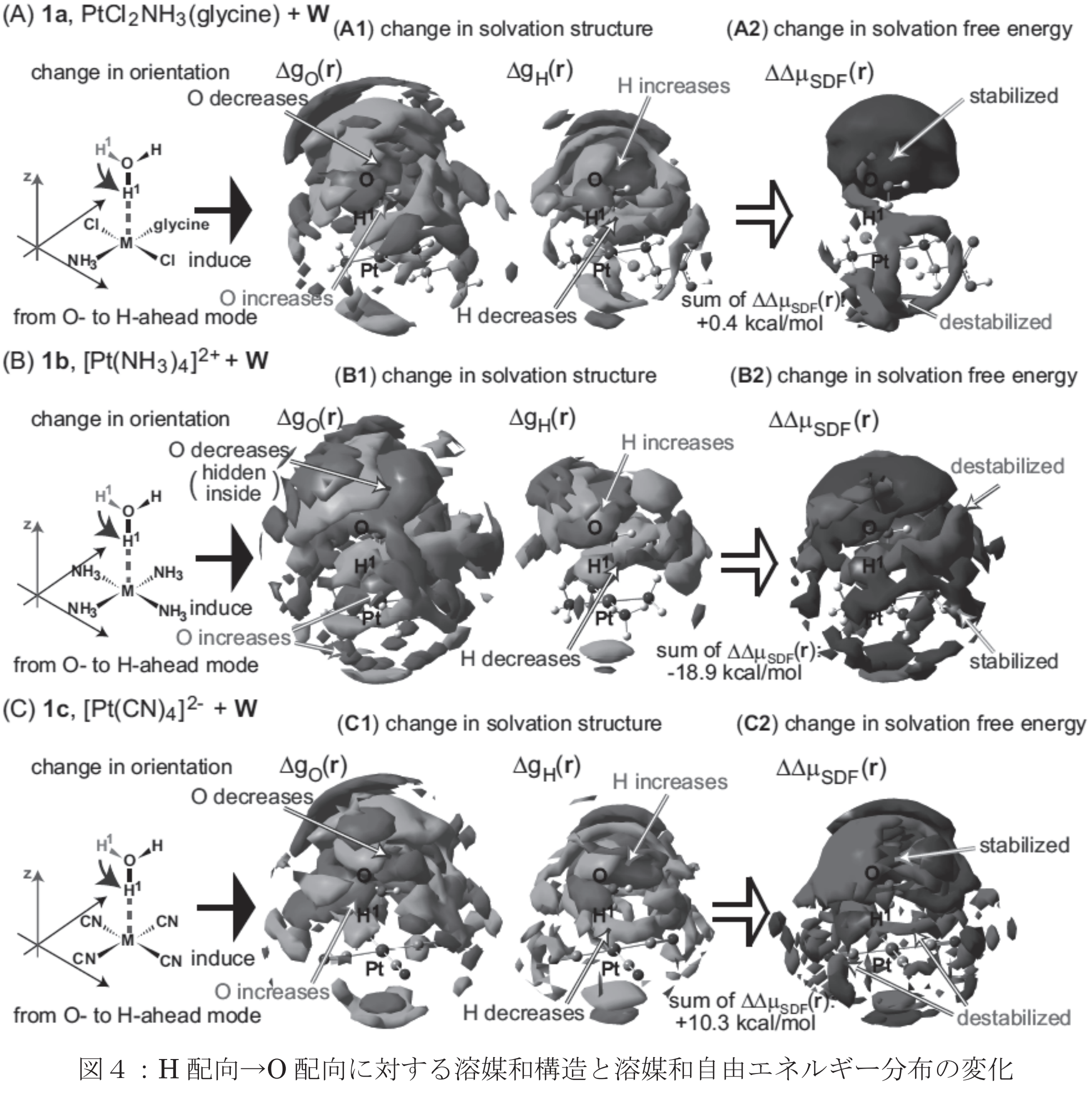


図４：H 配向→O 配向に対する溶媒和構造と溶媒和自由エネルギー分布の変化

これはammine錯体とcyano錯体の間で全電荷の符号が異なる事から生じており、ammine錯体では配位子周囲の水はO原子を向ける傾向があるのに対し、cyano錯体ではH原子を向ける傾向がある事が水分子の分布関数から理解できる（図４）。この配位子周囲の水の向きと大きな静電安定化を稼ぐ事が出来る位置にH原子を持ち、更に錯体電荷移動を誘起するのは、ammine錯体の場合はH配位であり、cyano錯体の場合はO配位である事が分かった。

このように気相中ではH配向とO配向で大きな静電エネルギーの違いがあるような電荷系であっても、水中では配位子周囲の溶媒効果によって、その静電エネルギーの優位性は大きく相殺される傾向があり、特にPt錯体になるとammine錯体のように正電荷を持つ系であってもH配向が生じ得る事が分かった。

[1] : J. Kozelka, J. Berges, R. Attias, J. Fraitag, Angew. Chem. **2000**, 112, 204.

[2] : S. Rizzato, J. Berges, S. A. Mason, A. Albinati, J Kozelka, Angew. Chem. **2010**, 49, 7443.

[3] : S. Aono, T. Mori, S. Sakaki, J. Chem. Theory Comput. **2016**, 12, 1189.

2. 論文

(1) Shinji Aono, Toshifumi Mori, and Shigeyoshi Sakaki,
“3D-RISM-MP2 Approach to Hydration Structure of Pt(II) and Pd(II) Complexes: Unusual H-Ahead Mode vs Usual O-Ahead One”
J. Chem. Theory Comput. 12 (3), 1189-1206 (2016).

3. 学会発表

(1) 青野信治、榊茂好
「QM/MM法によるRu(II)-SO2錯体の結晶内異性化反応の理論的研究」
第9回分子科学討論会　東京　2015/9/19　4E03

(2) Shinji Aono, Shigeyoshi Sakaki
「Unusual H2O interaction with Pd(II) and Pt(II) complexes through H atom; 3D-RISM-SCF/MP2 Study」
The 15th International Congress of Quantum Chemistry　2015/6/10　poster III.16

(3) Shinji Aono, Shigeyoshi Sakaki
「Isomerization of ruthenium(II) sulfur dioxide complex in crystal; Theoretical study with QM/MM approach」
The 7th Asia-Pasific Conference of Theoretical and Computational Chemistry
2016/1/27　O17D

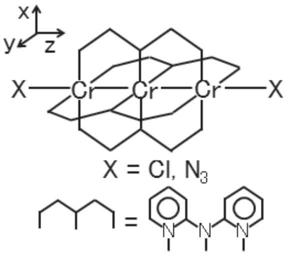
4. その他

(1) 「QM/MM法によるRu(II)-SO2錯体の結晶内異性化反応の理論的研究」
京都大学第13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
2016/2/5　P30

中垣　雅之

FIFC フェロー

1. 今年度の研究の要約



スキーム 1

【緒言】ジピリジルアミン(dpa)を配位子とする錯体は、金属-金属結合を有する二核及び三核錯体として広く研究されている(スキーム 1)。Cr(II)の三核錯体は axial 位の配位子の違いにより、Cl 錯体では 2 つの Cr-Cr 結合が等価な対称構造が [1]、N_3 錯体では一方が長くもう一方が短い非対称構造が [2] 報告されている。このことから三核錯体における金属結合は多中心結合であり、その結合性や電子・スピン状態は二核錯体とは大きく異なると考えられる。また過去の多くの二核錯体の研究で多重金属結合における多参照性の重要性が報告されてきたが、三核錯体の研究例は密度汎関数法によるものが主であり、多参照性計算による理論研究は行われておらず、電子状態の理解が十分でない。

本研究では、多参照理論に基づいた高精度計算法である DMRG-CASSCF/CASPT2 法を用いて多中心多重金属結合を有する錯体の電子状態の解明を試みた。

【計算方法】構造最適化には DFT(B3PW91)法と CASPT2 法を用い、分子軌道の生成には通常の CASSCF 法を、エネルギー計算には DMRG-CASSCF/CASPT2 法を用いた。また局在化軌道(LMO)を用いた CASCI 法によりスピン分布に関する解析及び 2 つの金属結合の結合次数を求めた。CASSCF の active space には空軌道である d_{x2-y2} 軌道を除く d 軌道(12 電子 12 軌道)を用いた。遷移金属の内殻電子は Stuttgart-Dresden-Bonn の ECP で置き換え、原子価軌道には triple zeta 基底関数を用いた。その他の原子には DFT 法では cc-pVDZ を DMRG-CASPT2 法では C,H 原子には DZ 基底を N,Cl 原子には DZP 基底を用いた。

【結果及び考察】DFT 法を用いた構造最適化を行った結果、Cl 錯体、N_3 錯体の双方で 2 つの Cr-Cr 結合長の長さが等しい対称な安定構造が得られた。その Cr-Cr 結合長はそれぞれ 2.464Å 及び 2.461Å であり、対称構造を持つ Cl 錯体の実験値 2.365Å よりも約 0.1Å 長い。Cl 錯体において Cr-Cr 結合長を変化させたポテンシャル曲線を図 1 に示す。

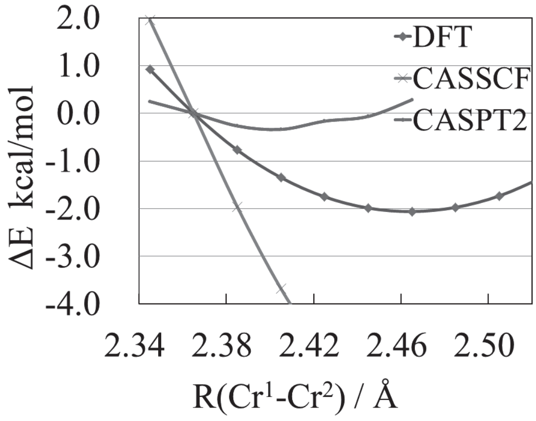


図 1.Cr-Cr 結合長に対するポテンシャル曲線。

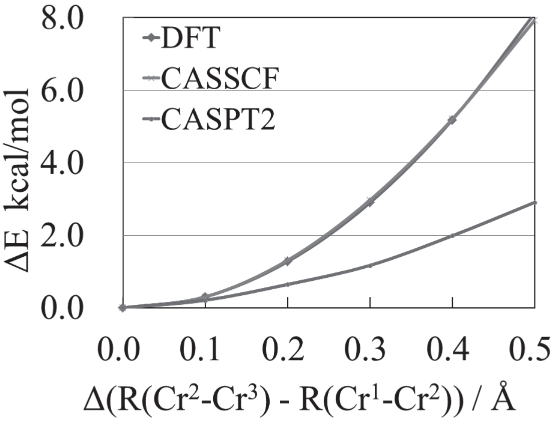


図 2.Cr-Cr 結合長の非対称ポテンシャル曲線。

DMRG-CASSCF 法では DFT 法よりも結合長が過大評価されたが、DMRG-CASPT2 法では 2.40Å 付近で極小になり、実験値に近い結果が得られた。2 つの Cr-Cr 結合長の差を変数としたポテンシャル曲線を図 2 に示す。いずれの計算方法においても２つの金属結合間距離の相違が大きくなるに従いエネルギーの単調な不安定化が見られたが、DMRG-CASPT2 法では他の計算法に比べエネルギーの不安定化が半分以下である。

N_3 錯体においても Cl 錯体同様に、DMRG-CASPT2 法で対称構造では Cr-Cr 結合長 2.38Å で極小となった。実験値を起点にした非対称構造のポテンシャル曲線を図 3 に示す。先に長い Cr-Cr 結合を最適化した結果 2.51Å と実験値に近い値が得られた。その後、短い Cr-Cr 結合の最適化を行うと、DFT 法及び CASSCF 法では非対称構造が大きく不安定で対称構造へと収束するのに対し(図 3a)、DMRG-CASPT2 法では 2.27Å で極小になり、2 本の結合長が 0.24 Å 異なる非対称構造が得られた。この構造は非対称構造よりも不安定であるが、そのエネルギー差は 1kcal/mol と小さい。

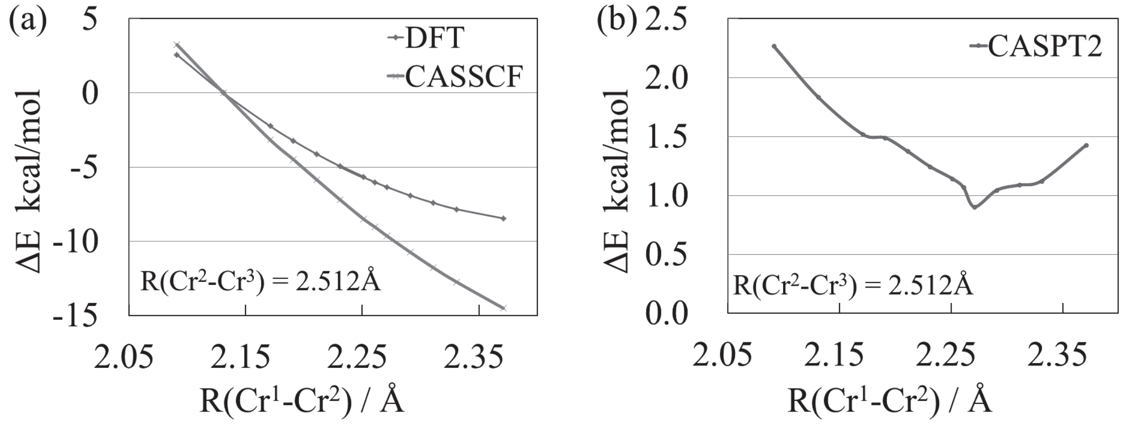


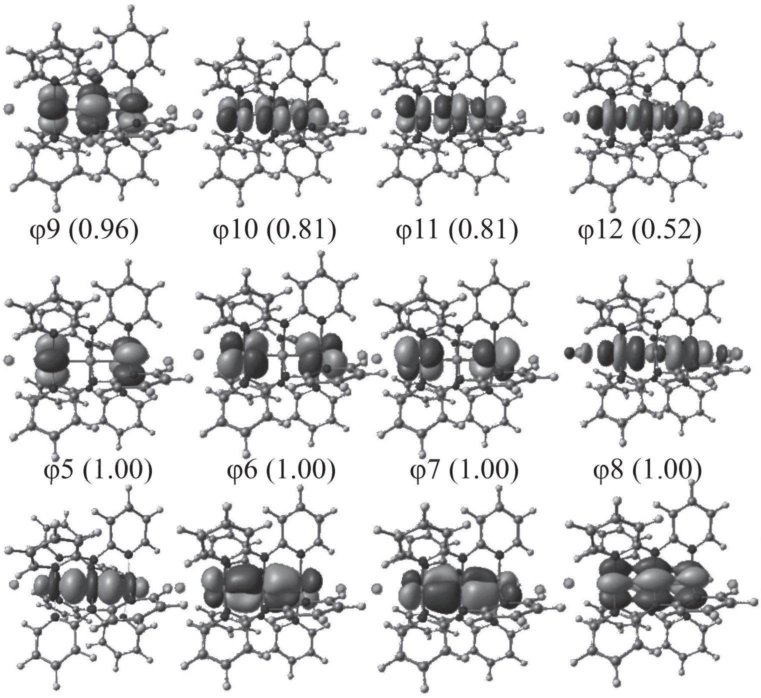
図 3.N_3 錯体の非対称構造の Cr-Cr 結合長のポテンシャル曲線。

Cl 錯体の基底状態である５重項状態の CASSCF 自然軌道を図 4 に示す。三核錯体においても二核錯体と同様に、σ 型と δ 型が１つ π 型が２つの計４つの結合性軌道を有する。結合性軌道の占有数は σ 軌道が 1.45, ２つの π 軌道が 1.19, δ 軌道が 1.04 であり多配置性が非常に大きいことが示唆される。同じ配位子をもつ二核錯体 $Cr_2(dpa)_4$ の占有数はそれぞれ、σ が 1.65, π が 1.55, δ が 1.16 であることから、二核錯体と三核錯体との相違は π 結合で最も大きい。また三核錯体では二核錯体とは異なり、中心の Cr 原子の軌道を含まない非結合性軌道が４つ存在する。非対称構造ではこれらの非結合性軌道の代わりに、結合長の長い側の末端の Cr 原子に局在化した d 軌道が自然軌道として得られる。スピン状態間のエネルギー差を表１に示す。

非結合性軌道 φ5-φ8 だけでなく φ4 及び φ9 軌道の占有数も１に近いにもかかわらず７重項状態は５重項状態に比べて非常に不安定である。これは後述するスピン密度の分布と深く関係している。

表１ スピン状態の相対エネルギー

スピン多重度	ΔE (kcal/mol)
11	31.9
9	18.7
7	9.3
5	0.0
3	8.3
1	14.1



φ9 (0.96)　φ10 (0.81)　φ11 (0.81)　φ12 (0.52)

φ5 (1.00)　φ6 (1.00)　φ7 (1.00)　φ8 (1.00)

φ1 (1.48)　φ2 (1.19)　φ3 (1.19)　φ4 (1.04)

図 4. 対称構造の $Cr_3(dpa)_4Cl_2$ の CASSCF 自然軌道。括弧内は占有数を表す。

表 2 Cr 原子 d 軌道の電子及びスピン分布

		Cr^1	Cr^2	Cr^3
X=Cl (sym)	electron	3.99	4.00	3.99
	spin	3.27	−2.55	3.27
$X=N_3$ (sym)	electron	3.99	4.01	3.99
	spin	3.27	−2.54	3.27
$X=N_3$ (asym)	electron	3.99	4.01	3.99
	spin	2.74	−2.36	3.61

表 3 2 つの Cr-Cr 結合の結合次数

	Cr^1-Cr^2	Cr^2-Cr^3
X=Cl (sym)	0.634	0.634
$X=N_3$ (sym)	0.706	0.706
$X=N_3$ (asym)	0.948	0.465

局在化軌道を用いた CASCI 法を行い、各構造における金属原子のスピン密度を求めた値を表 2 に示す。対称構造では末端の Cr 原子は 3.27 のスピンを、中央 Cr 原子は末端 Cr とは逆向きスピン 2.54 をもち、系全体として５重項をとる。これらの値は二核錯体の反結合性軌道の占有数から見積もられるラジカル性(2.09)よりも相当程度大きい。また非対称構造になると、結合長の長い離れた Cr 原子はスピンが増加、より短い結合長をもつ２つの Cr 原子はスピンが減少するが依然として３つの Cr 原子すべてが大きなスピンをもっていることがわかる。

自然軌道の占有数からは 3 つの金属原子に非局在化した結合次数しか得られないため、局在化軌道の密度行列を基に２原子間の金属結合に分割した結合次数を表３に示す。自然軌道を用いた Cl 錯体の金属結合の全体の結合次数は 0.90 であるが実際の２原子間の結合は 0.63 とさらに小さいことがわかる。また、N_3 錯体の対称構造と非対称構造における結合次数を比較すると、片側の結合次数の増加ともう一方の減少は同程度であり、弱い結合は強い結合のおよそ半分の結合次数である。

本研究において、密度汎関数法では定性的にも不十分であった三核錯体の金属結合に関して、DMRG-CASPT2 法を用いて、金属結合長変化に対して非常になだらかなポテンシャル曲面を明らかにし、局在化軌道を用いた解析によって、その電子構造について特徴的なスピン分布や金属結合の結合次数を明らかにした。

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2. 論文

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Theoretical Prediction of Characteristic Features of Geometry and Spin Multiplicity"
Submitting to *Phys. Chem. Chem. Phys.*

3. 学会発表

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I.144 poster

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(3) 中垣雅之，中谷直輝，長谷川淳也，榊茂好
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第9回分子科学討論会2015東京　東京　2013/9/16-19 2P107 ポスター

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モリブデン及びタングステン-シリレン錯体の反応機構:
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第13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 2016/2/5

(2) 中垣 雅之，榊 茂好
逆サンドイッチ型錯体の電子構造:
スピン状態の支配要因と異核錯体の特異な電子状態
特別シンポジウム「未来への架け橋：分子科学の最前線と将来展望」福岡 2016/3/5

Shuwei Tang

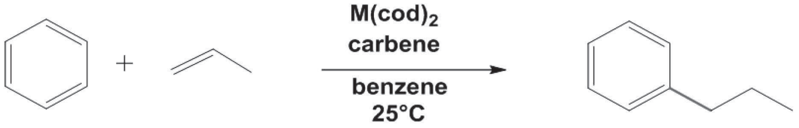
SPR Fellow

1. Summary of the research of the year

Theoretical Study of Aromatic C-H σ-Bond Activation by Ni(0), Pd(0), and Pt(0) Alkene Complexes: Concerted Oxidative Addition to Metal Center vs. Oxidative Addition Across to M-Alkene Moiety

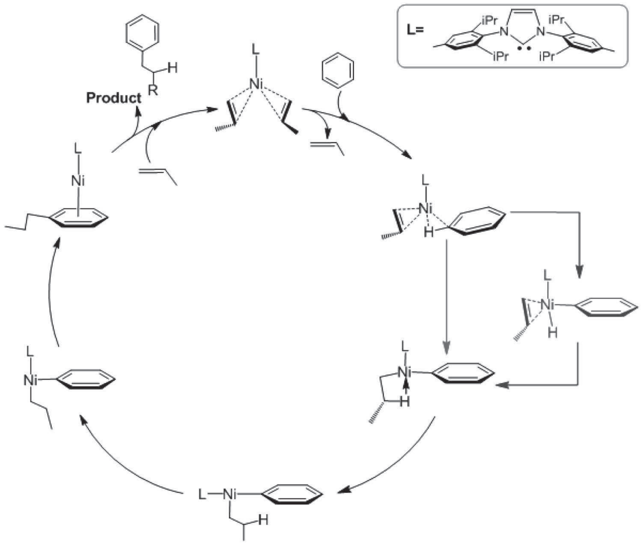
The hydroarylation of un-activated alkenes and alkynes through direct C-H activation of aromatics by transition metal is one of attractive reactions for preparing alkylarenes and alkenylarenes. Recently, remarkable improvements have been succeeded in this catalytic hydroarylation of un-activated alkenes. For instance, Nakao and coworkers reported that nickel(0) complex of monophosphine was capable of performing hydroarylation of un-activated alkenes with high selectivity, as shown in Scheme 1. Hartwig, Einsenstein, and coworkers made exciting progress on this topic. They successfully applied a nickel(0) complex with N-heterocyclic carbene ligand, IPr {IPr = (1,3-Bis2,6-diisopropylphenyl)-1,3-dihydro-2H-imidazol-2-ylidene}, to hydroarylation of an un-activated alkene under mild conditions to afford a mixture of linear and branched alkylarenes. Very recently, Nakao and coworkers reported that a combination of a nickel(0) carbene complex and the Lewis acid directly activates the aromatic C-H bond of *N, N*-dimethylbenzamide to introduce the alkyl group to the phenyl group with good to excellent yields and selectivity.

Scheme 1



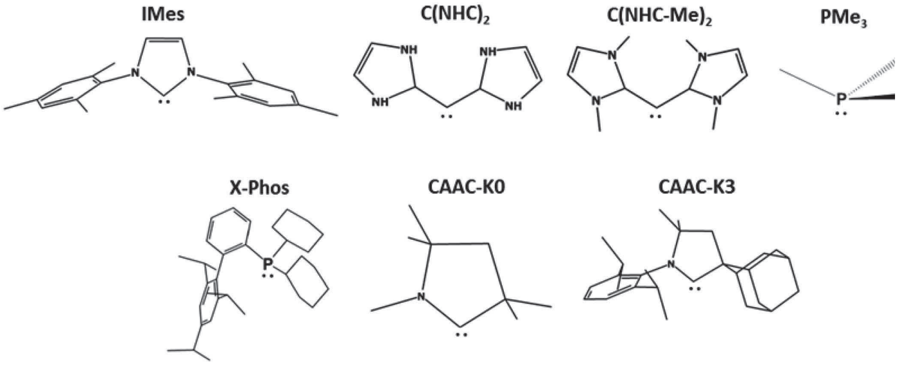
The reaction mechanism of the C-H activation/functionalization of aromatics has been firstly investigated by Eisenstein and coworkers, in which the H transfer from aromatics to alkene followed by reductive elimination was proposed based on DFT computation, as shown in Scheme 2. This C-H activation reaction is completely different from the usual concerted oxidative addition to low-valent metal center.

Scheme 2



In this work, we theoretically investigated the C-H activation reaction of benzene with nickel(0), palladium(0), and platinum(0) complexes, using density functional theory (DFT), where benzene, propene, and IMes (1,3-dimesitiylinidazol-2-ylidene) were employed as models of aromatic compound, alkene, and carbene ligand, respectively, to simplify the system. Our purposes here are to provide theoretical answers to above mentioned questions; for instance, to elucidate the reaction mechanism, to make comparison of reactivity in the C-H activation reaction among nickel(0), palladium(0), and platinum(0) complexes, to disclose the reason why the bulky carbene ligand is used in the catalytic system by comparing the reactivity among IMes, carbodicarbenes such as $C(NHC)_2$ and $C(NHC-Me)_2$, trimethylphosphine (PMe_3), dicyclohexyl{2',4',6'-triisopropyl-(1,1'-biphenyl)-2-yl}phosphane (X-Phos), and cyclic alkyl amino carbine such as CAAC and CAAC-K3 (Scheme 3).

Scheme 3



Because $Ni^0(IMes)(propene)_2$ **1-Ni** is more stable than other possible reactant complexes such as Ni^0(IMes)(propene)(benzene) **2-Ni** and $Ni^0(IMes)(benzene)_2$, **1-Ni** was taken as an energy reference in this study. **1-Ni** has a Y-shaped structure in which two propenes coordinate with the nickel center through a C=C bond, as shown in Figure 1. This is a typical three-coordinated d^{10} complex. The C=C double bond is considerably elongated (1.399 Å) compared to that (1.330 Å) of free propene, indicating the strong π-back donation is formed between nickel and propene. The substitution of benzene for one of propenes occurs to afford **2-Ni**, which is 14.5 kcal/mol above **1-Ni**. In **2-Ni**, the C=C bond of benzene is somewhat elongated to 1.420 Å compared to that (1.392 Å) of free benzene due to the π-back-donation from the nickel center to the benzene. The $Ni\text{-}C_{(IMes)}$ bond (1.948 Å) is also moderately longer than in **1-Ni** (1.933 Å).

To undergo the subsequent C-H activation reaction, **2-Ni** must be converted to an intermediate **3-Ni**, in which the C-H bond of benzene interacts with the nickel center. In **3-Ni**, the C-H bond (1.106 Å) is elongated relative to that (1.089 Å) of free benzene, suggesting that some bonding interaction is formed between the nickel and the C-H bond. As going from **2-Ni** to **3-Ni,** a transition state **$TS_{2/3}$-Ni** is located at 1.2 kcal/mol above **2-Ni**. In **$TS_{2/3}$-Ni**, the benzene coordinates with the nickel center in an η^3-manner, in which the ipso-carbon is 2.677 Å distant from the nickel center but another adjacent carbon and hydrogen atoms are close to the nickel center (2.237 and 2.596Å, respectively). Careful geometry optimization starting from **$TS_{2/3}$-Ni** confirms that it indeed connects two intermediates through anticlockwise and clockwise rotations of the benzene ring. Starting from **3-Ni,** the C-H bond of benzene is cleaved by direct transfer of a hydrogen atom from the benzene to the propene, to afford a nickel(II) propyl phenyl intermediate Ni(IMes)(propyl)Phyenyl) **4-Ni** through a transition state **$TS_{3/4\text{-}Ni}$**. The Gibbs activation energy is 30.8 kcal/mol relative to **1-Ni**. In **$TS_{3/4}$-Ni**, nickel, propene, migrating H (H^1, hereafter) and ipso-carbon (C^{ipso}) are almost on one plane. The H^1 atom is 1.767 Å distant from the ipso carbon, 1.488 Å from the Ni atom, and 1.675Å from the carbon of the C=C double bond of propene, suggesting that the hydrogen atom is moving from benzene to propene, keeping a bonding interaction with the Ni atom. The rather short $Ni\text{-}C^{ipso}$ distance of 1.951 Å indicates that the Ni-phenyl bond is almost formed in **$TS_{3/4}$-Ni**. This **$TS_{3/4}$-Ni** is essentially the same as the transition state of H-transfer from benzene to ethylene reported recently by Eisenstein and coworkers. **4-Ni** has a typical T-shape structure, which is reasonable because this is three-coordinate d^8 Ni(II) complex with NHC, propyl, and phenyl ligands. **4-Ni** is 4.8 kcal/mol more stable than **$TS_{3/4}$-Ni** but much less stable than **1-Ni** by 24.5 kcal/mol. The C-H bond of the propyl group approaches the nickel center to form an agostic C-H interaction, where the Ni-H distance is 1.935 Å and the C-H distance is 1.185 Å. This interaction is formed in this complex because Ni(II) has a d^8 electron configuration and the empty d_σ orbital expands toward the C-H bond. The Ni-C^{ipso} distance is 1.947 Å, which is similar to that in **$TS_{3/4}$-Ni**. This agostic interaction stabilizes **4-Ni** by charge-transfer (CT) interaction from the C-H bond to the nickel center. Considering that the oxidative additions of phenyl chloride, benzyl chloride, and benzonitrile to a nickel(0) complex have been experimentally reported and theoretically analyzed, we tried to locate such a stable nickel(II) hydride phenyl propene complex but failed to optimize it despite a lot of efforts. It is concluded that the usual concerted oxidative addition is difficult in this reaction system.

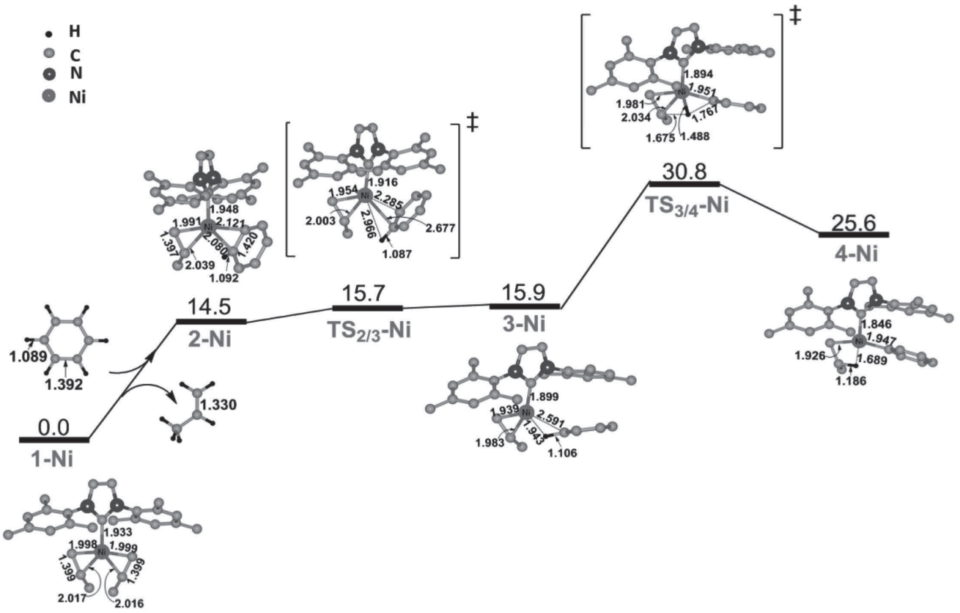


Figure 1. Changes in Gibbs energy (in kcal/mol) at 298.15K and geometries in the Ni(NHC)-promoted C-H σ-bond activation of benzene. Several hydrogen atoms are omitted for clarity. The bond lengths are given in Å.

C-H σ-Bond Activation by Pd(0) and Pt(0) Analouges

To get better understanding of the C-H σ-bond activation by metal(0)-alkene complex, we investigated the C-H activation of benzene by similar palladium(0) and platinum(0) complexes. The geometrical features of the platinum(0) and palladium(0) NHC propene complexes seem essentially the same as those of the Ni(0) analogue, despite several differences are observed between them. However, the most significant difference for the C-H activations activated by Pd or Pt in comparison with Ni is that the C-H σ-bond activation occurs through transition state **$TS_{3/4}$-Pd** or **$TS_{3/4}$-Pt** to afford an intermediate

Pt(IMS)(H^1)(ohenyl)(propene) **4-Pd** or **4-Pt**. In **$TS_{3/4}$-Pt**, the Pt-H^1 and Pt-Ph distances are 1.663 Å and 2.159 Å, respectively, which are longer than those of **$TS_{3/4}$-Ni**. Important geometrical changes are found in the position of the H^1 atom; the C-H^1 distance of the benzene moiety is less elongated and the C-H^1 distance between propene and benzene is considerably longer than in **$TS_{3/4}$-Ni**, indicating that the H^1 atom does not approach the C atom of propene in the Pt reaction system. In **4-Pt**, the H^1 and Ph groups are bound with the Pt atom. It is concluded the concerted oxidative addition occurs in the Pt reaction system. The similar geometry changes are found in the Pd reaction system. It is worthy of note that only the C-H activation by the nickel(0) complex occurs in the different mechanism from the concerted oxidative addition. The Gibbs activation energy ($\Delta G^{o\ddagger}$) is 30.4 kcal/mol in the Pt reaction system and 33.6 kcal/mol in the Pd reaction system relative to **1-Pt** and **1-Pd**. The higher activation energy of the Pd system than that of the Pt system is reasonable because the Pd d orbital exists at lower energy than the Pt d orbital. After the C-H activation, the alkene insertion into the Pt-H bond occurs through a transition state **$TS_{4/5}$-Pt** to afford a platinum(II) propyl phenyl complex **5-Pt**. The $\Delta G^{o\ddagger}$ value is very small (3.7 kacal/mol for the **$TS_{4/5}$-Pt** and 3.9 kcal/mol for **$TS_{4/5}$-Pd** relative to the intermediates **4-Pt** and **4-Pd**), indicating that propene is easily inserted into the Pt-H and Pd-H bonds. In **$TS_{4/5}$-Pt**, the C-H distance between the propene and the H^1 is 1.571 Å and the Pt-H distance is moderately elongated to 1.697 Å, suggesting that this transition state is similar to **4-Pt**. In **5-Pt**, the C-H bond distance of the propyl group is 1.185 Å and the Pt-H distance is 1.935 Å, indicating the presence of the agostic interaction between the C-H of the propyl group and the Pt(II) center like in Ni. **5-Pt** is slightly less stable than **4-Pt** and much less stable than **1-Pt**. The similar geometrical features are found in the Pd reaction system.

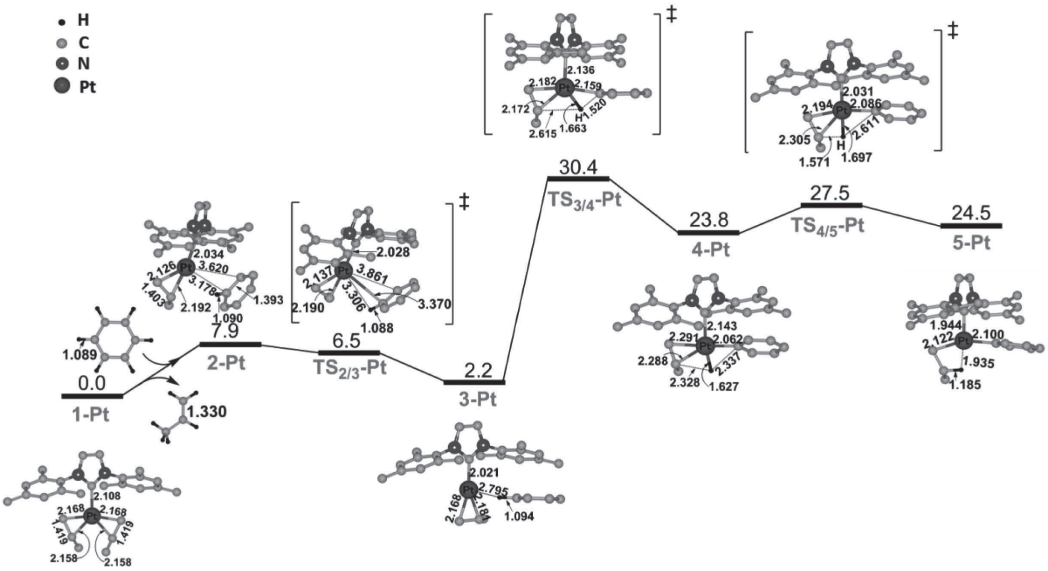


Figure 2. Changes in Gibbs energy (in kcal/mol) at 298K and geometries in the Pt(NHC)-promoted C-H σ-bond activation of benzene. Several hydrogen atoms are omitted for clarity. The bond lengths are given in Å.

Important orbital interaction in the aromatic C-H bond activation by Ni(NHC)(propene) complex

To understand the reaction mechanism, the knowledge of orbital interaction in the reaction is indispensable. We evaluated electron populations of several important MOs of Ni(NHC), propene, and benzene moieties in the reaction. Figure 3 shows these MOs and their population changes (in |*e*| unit) against the C(aryl)-H(active) distance. Apparently, the electron populations of the Ni 3d orbitals considerably decrease, which contributes to the Ni oxidation state change from 0 to +II. The H atomic population decreases around **TS$_{2/3}$-Ni**, which is consistent with the proposal that this C-H activation is understood as the proton-transfer. The electron population of the HOMO (π MO) of the propene moiety monotonously decreases but that of the LUMO (π* MO) increases, indicating that the propene participates in the C-H π-bond cleavage. The population of the π* (LUMO) of benzene moiety increases, while that of the HOMO of benzene changes little around the transition state but starts to decrease as going from the transition state to the product. These results suggest that the HOMO of benzene participates little in the C-H π-bond cleavage but it contributes to the CT from benzene to the Ni(II) center which is formed in the late stage of the reaction. In the Pt reaction system, the electron population of the Pt 5d orbitals also decreases with the elongation of the C-H distance. It is notable that the H atomic population increases in **TS$_{2/3}$-Pt** unlike in **TS$_{2/3}$-Ni**. The electron population of the HOMO of propene does not change very much and that of the LUMO considerably decreases unlike in the Ni case, representing that the propene participates in the C-H σ-bond cleavage in a completely different manner from that in the Ni reaction system. The electron population of the LUMO of benzene increases in the reaction, indicating that the CT occurs from the Pt 5d orbital to the LUMO. A similar finding is observed in the Pd reaction system.

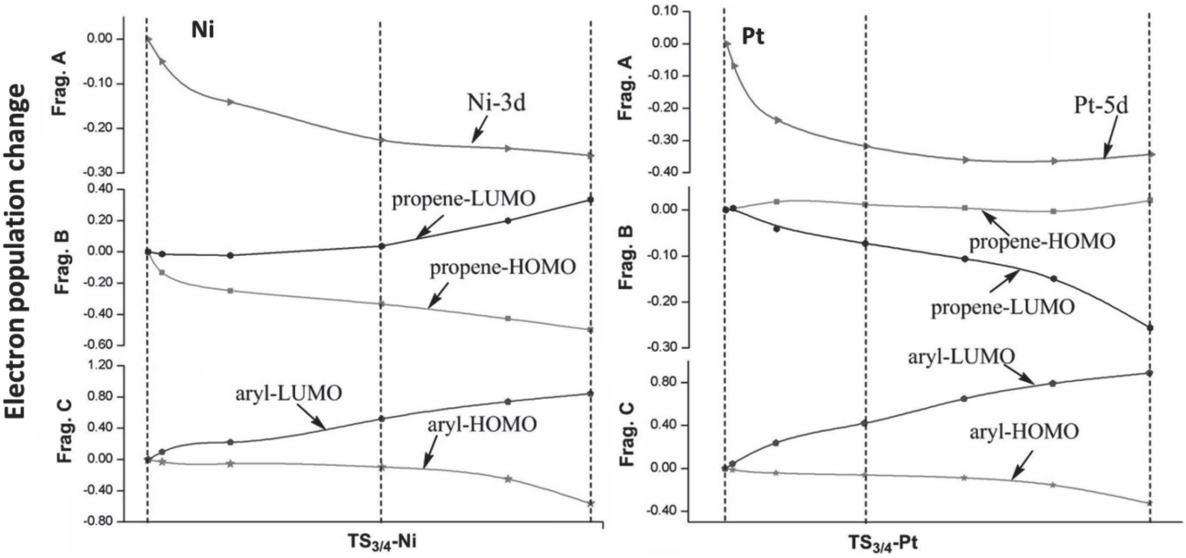
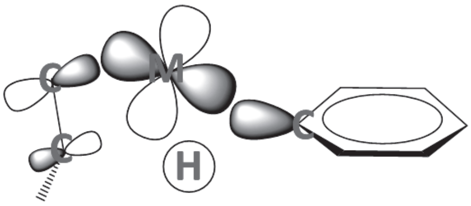


Figure 3. The dependence of electron contributions (in |e|) on the C(aryl)-H(active) distance in the C-H activation process of M/NHC complex (M=Ni, Pt).

The above differences in population changes relate to the difference in reaction mechanism between the Ni and Pt reaction systems. In the oxidative addition to metal center only, the CT mainly occurs from the metal d orbital to the C-H σ*-MO as crucial interaction. Hence, the Pt d orbital population considerably decreases and that of the LUMO of benzene considerably increases. Though propene does not participate directly in this reaction, the CT from the Pt d orbital to the propene π* MO becomes weaker, which leads to the decreasing of the electron population of the LUMO of propene. The HOMO of propene does not participate in the coordinate bond with the Pt(0) atom and its contribution to the reaction is not large, which will be discussed below. In the oxidative addition of the C-H bond to the Ni(0)-propene moiety, the CT occurs from the Ni d orbital to the LUMO of benzene to induce the C-H σ-bond cleavage. This feature is common between the Pt and Ni reaction systems. At the same time, the HOMO of benzene containing the H 1s orbital starts to overlap with the propene HOMO (π MO) in an anti-bonding way because both are doubly occupied, while it interacts with the LUMO of propene in a bonding way because the propene LUMO is at higher energy than the HOMO of benzene, as shown in Scheme 4.

Scheme 4



The antibonding overlap between the propene HOMO and the benzene HOMO corresponds to exchange repulsion, which induces the decrease in the electron populations of both HOMOs, which is certainly seen in Figure 4. This is the origin of the difference between the Pt and Ni reaction system.

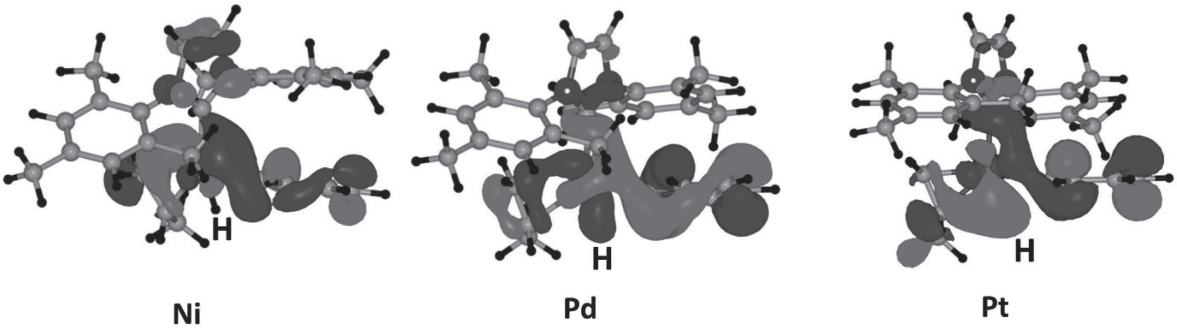


Figure 4. Important orbital overlap in TSs catalyzed by M/NHC (M=Ni, Pd, Pt).

Effects of Various Ligands on the Aromatic C-H Bond Activation by Ni(0) Complex

Unveiling the ligand effects on the C-H activation reaction can provide valuable information about what ligand should be used in this type of C-H activation of aromatics. As summarized in Figure 5, the activation barrier against the nickel(0) benzene propene complex does not relate with the tendency of lone pair MO energy, suggesting that the electronic nature is not primarily important in this C-H cleavage process. However, it should be noted that the bulky ligand decreases the activation barrier; for instance, the activation barrier is smaller in the more bulky CAAC-K3 ligand than in the less bulky CAAC-k0. Also, the activation barrier by X-Phos is smaller than that by PMe_3 and that of $C(NHC\text{-}Me)_2$ is smaller than that of $C(NHC)_2$, as shown in Figure 9. This is interesting because the result is against our expectation that the bulky ligand suppresses the reaction in general.

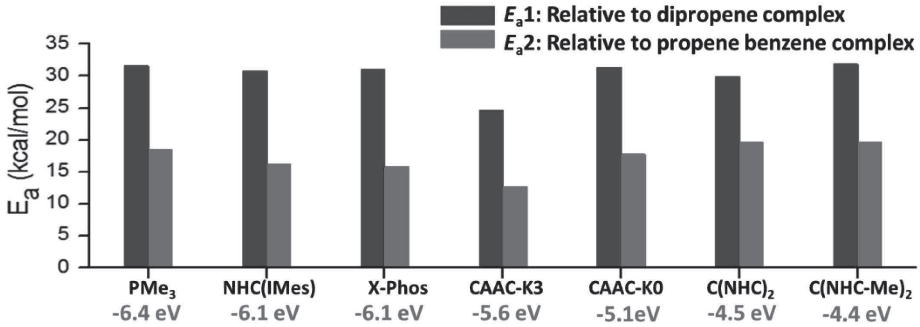


Figure 5. The dependence of activation barriers in TSs on the orbital energy of lone-pair electron in different ligands.

To clarify the reason why bulky ligands decrease the activation barriers, we made comparisons of TS structure among various ligands, as shown in Figure 6. The C-C distance between propene and benzene is much shorter in the case of CAAC-k3 than in the CAAC-k0. The similar trend can be found in other comparisons. These results indicate that the bulky ligand pushes benzene and propene away and thereby the distance between benzene and propene becomes short in the nickel(0) propene benzene complex. Such geometry is favorable for the H transfer from benzene to propene.

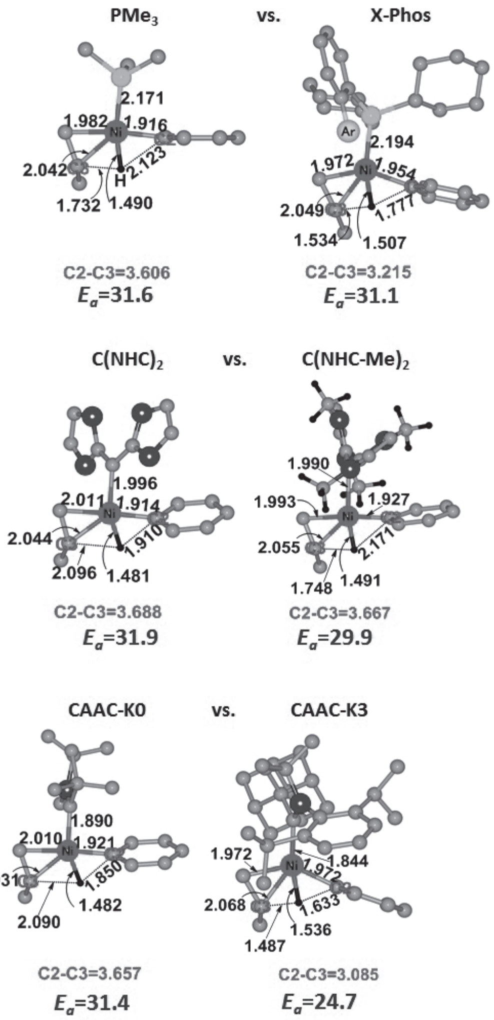


Figure 6. Comparison of activation energy and structures of TSs for the C-H activation process of in different Ni-Ligand moiety. Several hydrogen atoms are omitted for clarity. The bond lengths are given in Å.

2. Original papers

Shuwei Tang, Yoshiaki Nakao, and Shigeyoshi Sakaki, “Theoretical Study of Aromatic C-H σ-Bond Activation by Ni(0), Pd(0), and Pt(0) Alkene Complexes: Concerted Oxidative Addition to Metal Center vs. Oxidative Addition Across to M-Alkene Moiety”, *in preparation*.

3. Presentation at academic conferences

Shuwei Tang, Yoshiaki Nakao, and Shigeyoshi Sakaki, "Theoretical Study of Aromatic C-H σ-Bond Activation by Ni(0), Pd(0), and Pt(0) Alkene Complexes: Concerted Oxidative Addition to Metal Center vs. Oxidative Addition Across to M-Alkene Moiety", 第3回中尾T CREST合同研究会について, kyoto, July 25, 2015.

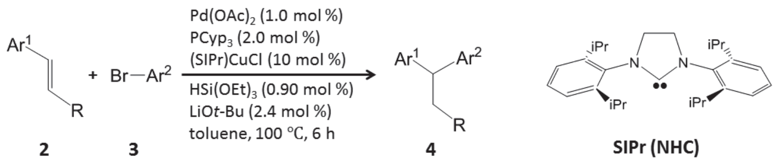
Hong Zheng

SPR Fellow

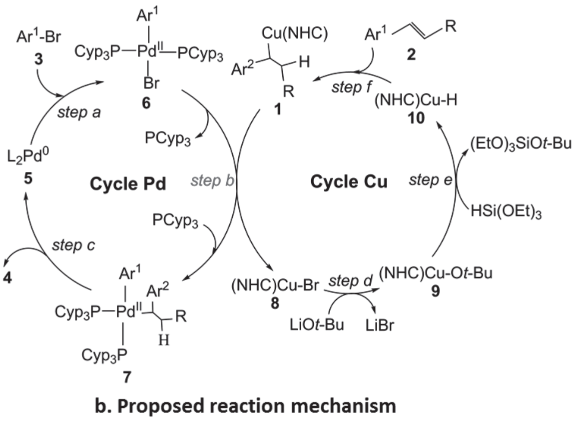
1. Summary of the research of the year

Characteristic Features of Transmetallation of Pd(II)-Ph Complex with Cu(I)-alkyl Complexes: Theoretical Study

Recently a new kind of reductive cross-coupling of arylalkene with aryl bromide by Pd/Cu catalysis has been experimentally succeeded, as shown in Scheme 1. Being different from conventional cross-coupling reaction which requires pre-synthesis of organometallics, this reaction needs only one step and pre-synthesis of organometallics is not needed but it is supplied by insertion of alkene into metal-hydride. The proposed reaction mechanism consists of cycle Pd and cycle Cu (Scheme 1b). Firstly, the Cu hydride **10** reacts with an aryl-alkene complex **2** to afford a Cu(I)-alkyl complex **1**. Then **1** reacts with a three-coordinated Pd bromide through transmetallation reaction (step b). Afterward, reductive elimination occurs in the transmetallation product **7** to give the target molecule **4**. The transmetallation between Pd(II) and Cu(I) complexes is rear and believed to be the most important step in this cross-coupling reaction. However, the reaction mechanism is not clear and thus theoretical investigation is indispensable.



a. Cross-coupling reaction of arylalkene with aryl bromide

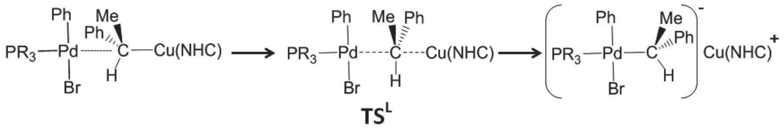


b. Proposed reaction mechanism

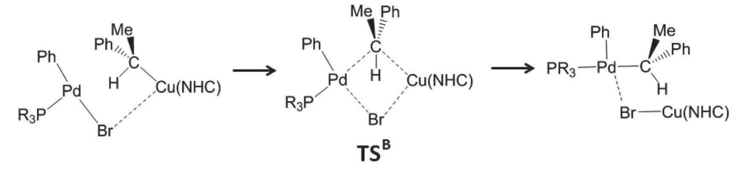
Scheme 1. Reductive cross-coupling of arylalkene with aryl bromide and proposed reaction mechanism.

In this work, detailed investigations on the transmetallation between $PdBrPhPCyp_3$ and Cu(NHC)(CHMePh) complexes were performed. Three types of transmetallation mechanism were investigated and compared with the experimental results. The electronic processes of these three mechanisms were analyzed to understand the important factor of this reaction.

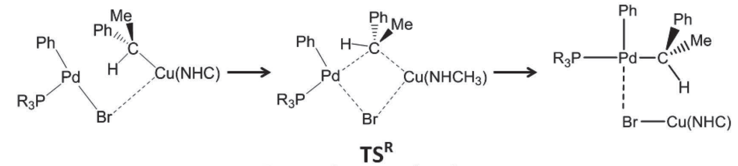
Reaction between $PdBrPhPCyp_3$ and Cu(NHC)(CHMePh). Although four-coordinated Pd complex **6** exists in the reaction cycle, it is the three-coordinated Pd complex participates in the transmetallation according to experimental observation. Complexes **6** and **1** firstly form a weak contact adduct **RAD** (Figure 1). Then one $PCyp_3$ ligand is dissociated and **AD1** is obtained. There are two possible transmetallation mechanisms, inversion and retention mechanisms. The inversion mechanism includes linear and bridging cases (Scheme 2a and b). In inversion mechanism, the aryl-alkyl group CHMePh becomes planar in transition state (TS^L and TS^B) and its conformation changes in product. One Pd-Br-Cu bridge exists in the bridging case but does not in the linear case. In retention mechanism, the CHMePh group changes its orientation in TS^R but the conformation is kept (Scheme 2c).



a. Inversion mechanism with linear case



b. Inversion mechanism with bridging case



c. Retention mechanism

Scheme 2. Inversion and retention mechanisms in transmetallation.

The inversion mechanism with linear case occurs from **AD2** through $\mathbf{TS1^L}$ (Figure 1). **AD2** is obtained from **AD1** with small geometrical change. The crucial geometrical change in $\mathbf{TS1^L}$ is the CHMePh group becomes planar: BA around C in **AD2** is 345° but in $\mathbf{TS1^L}$ is 358°. The Pd-Cu distance dcreases to 2.529 Å in $\mathbf{TS1^L}$ but the Cu-C distance changes little. Then, BA around C decreases to 338° and the Pd-C bond is formed in an intermediate $\mathbf{INT^L}$. Hence, the conformation of CHMePh is changed. However, the Cu atom coordinates with the phenyl group of CHMePh in $\mathbf{INT^L}$ and the Pd center temporally becomes four-coordinated. Then, the Cu atom is moving toward Br atom and the Cu-Br distance becomes shorter in $\mathbf{TS2^L}$ and finally the Cu-Br bond is formed in $\mathbf{P1a^L}$.

The inversion mechanism with bridging case needs only one transition state ($\mathbf{TS^B}$), as shown in Figure 1. The geometry of CHMePh group is more product like in $\mathbf{TS^B}$ than that in $\mathbf{TS1^L}$ since BA around C is 349° and Pd-C distance (2.179 Å) is close to the value in $\mathbf{P1^B}$ (2.117 Å). The Cu-Br is also somehow formed in $\mathbf{TS^B}$. The geometrical difference between $\mathbf{P1^L}$ and $\mathbf{P1^B}$ is the orientation of Pd complex: Pd-C and Cu-Br bonds are almost conplanar in $\mathbf{P1^L}$ but perpendicular in $\mathbf{P1^B}$.

In the retention mechannism, the CHMePh group changes its orientation to contact with Pd in $\mathbf{TS1^R}$. The Pd-C and Cu-Br distances decreases by about 0.4 Å but Cu-C changes little in $\mathbf{TS1^R}$. However, $\mathbf{TS1^R}$ is an isomerization TS connnecting with an intermediate $\mathbf{INT^R}$, in which the Pd-Cu distance and ∠Pd-Br-Cu angle decrease very much and the CHMePh group rotates backward. Then transmetallation occurs through **TS2**$^{\mathbf{R}}$. In **TS2**$^{\mathbf{R}}$, the Cu-C bond is broken and the CHMePh group moves toward Pd, resulting in much smaller Pd-C and Cu-Br distances. Finally the transmetallation product **P1**$^{\mathbf{B}}$ is obtained in which the conformation of CHMePh group does not change.

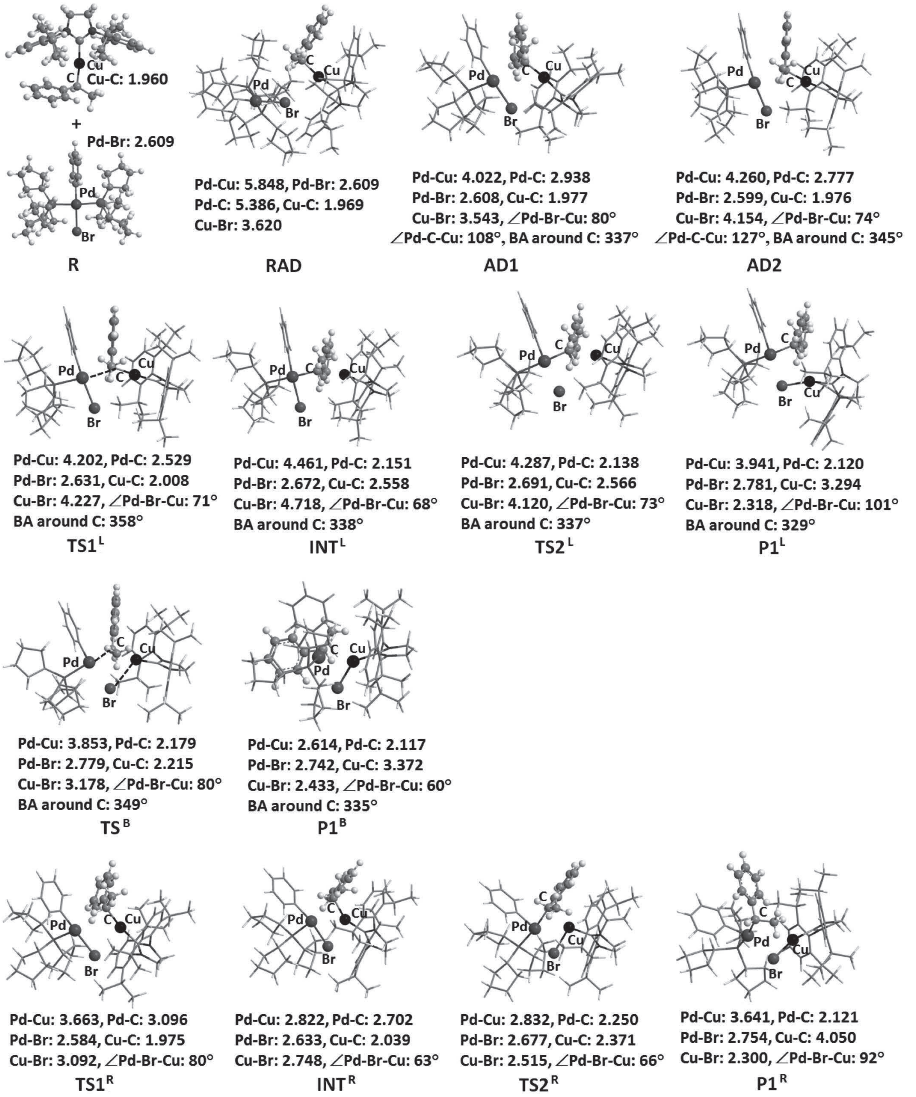


Fig 1. Geometrical parameters of complexes in transmetallation mechanisms between $PdBrPhPCyp_3$ and Cu(I)(CHMePh). The bond distances are represented in Angstrom. BA around C represents the sum of three bond angles around active carbon of CHMePh group.

The energy changes are exhibited in Figure 2. the formation of the weak contact adduct **RAD** is moderately exothermic with a relative Gibbs energy of -4.0 mol/mol, and the dissociation of $PCyp_3$ needs 27.7 kcal/mol. **AD1** is only 0.6 kcal/mol lower than **AD2** since the geometrical difference between **AD1** and **AD2** is very small. In the inversion mechanism with linear case, **TS1**$^{\mathbf{L}}$ is 0.3 kcal/mol lower than **AD2** in Gibbs energy but 0.8 kcal/mol higher in potential energy, meaning the transfer of CHMePh occurs without energy barrier. The intermediate of this pathway is only 3.3 kcal/mol lower than **AD2** since Cu-C bond is very weak but Cu-Br bond is not formed yet. In the inversion mechanism with bridging case, despite of stronger Pd-C and Cu-Br bonds in **TS**$^{\mathbf{B}}$, **TS**$^{\mathbf{B}}$ is not favorable for transmetallation due to a large activation energy of 40.5 kcal/mol. The most important transition state in the retention mechanism is **TS2**$^{\mathbf{R}}$, whose activation energy is 37.3 kcal/mol. Therefore, the inversion mechanism with linear case is the most favorable mechanism among the three mechanisms and further reductive elimination starts from **P1**$^{\mathbf{L}}$. **TS2**$^{\mathbf{L}}$ and the transition state of reductive elimination **TS**$^{\mathbf{E}}$ are lower than **TS1**$^{\mathbf{L}}$ and herein **TS1**$^{\mathbf{L}}$ is the most important transition state in this pathway.

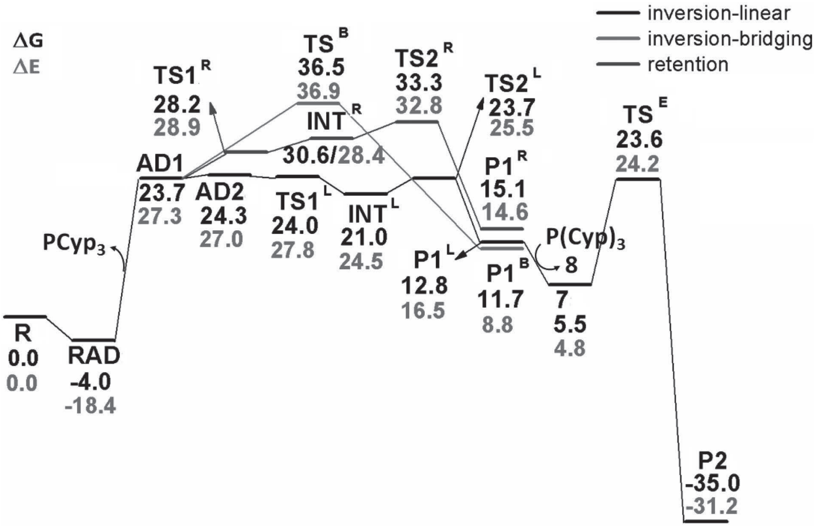
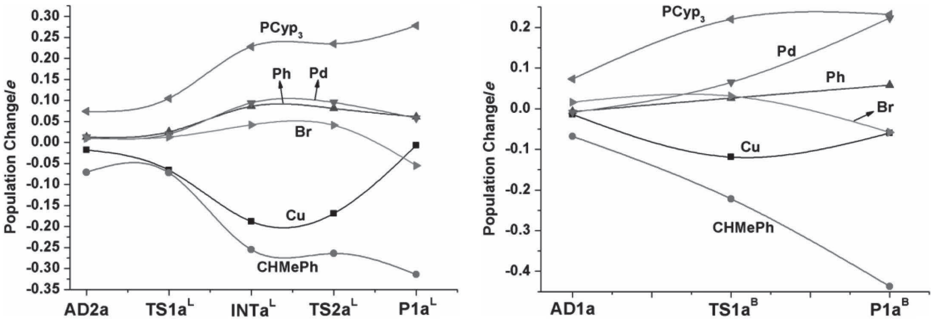


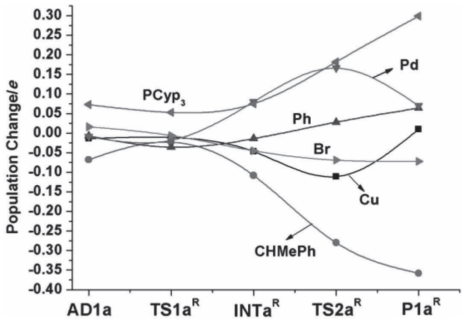
Fig 2. Energy changes (in kcal/mol) of three mechanisms.

Electronic process. In the inversion mechanism with linear case, small charge transfer occurs in the reactant **AD2** (Figure 3a): the populations of Pd and Ph have similar changes as going from **AD2** to **P1**$^{\mathbf{L}}$. The PdPh fragment and PCyp$_3$ increase by 0.100 *e* in total, while that of Cu and CHMePh decrease by 0.018 *e* and 0.071 *e*, respectively. Since the interaction between Pd and CHMePh becomes stronger in **TS1**$^{\mathbf{L}}$, the PdPh fragment and PCyp$_3$ onbtain more populations from Cu atom. Then, the charge transfer from Cu complex to Pd complex further increases to a larger extent in **INT**$^{\mathbf{L}}$, in which both Cu and CHMePh donate electrons to PhPh and PCyp$_3$. The population of Br atom increases little as going from **AD1** to **INT**$^{\mathbf{L}}$ sinse its bonding feature does not change and it is distant from Cu. As the coordination between Cu and the phenyl group of CHMePh disappears and Cu-Br bond is formed from **INT**$^{\mathbf{L}}$ to **TS2**$^{\mathbf{L}}$, the population of PdPh and Br decrease by 0.061 *e* and 0.097 *e*, respectively, while that of Cu increases by 0.181 *e*. The population of PCyp$_3$ increases by 0.050 *e*, which is compensated by the change of CHMePh from **INT**$^{\mathbf{L}}$ to **TS2**$^{\mathbf{L}}$. In the inversion mechanism with bridging case, the population of CHMePh decreases and that of PCyp$_3$ and PdPh increase as going from **AD1** to **P1**$^{\mathbf{B}}$ (Figure 3b). The population of Cu decreases by around 0.1 *e* from **AD1** to **TS1**$^{\mathbf{B}}$, and then this change is compensated by Br atom at **P1**$^{\mathbf{B}}$ since Cu-Br is formed.



a. Inversion mechanism with linear case

b. Inversion mechanism with bridging case



c. Retention mechanism

Fig 3. Important population changes from seperated Pd(II)Ph and Cu(I)-CHMePh complexes to the geometries of inversion/retention mechanisms. Ph is the phenyl group of Pd(II)Ph complex.

Different population changes are found in the retention mechanism. Firstly the population of PdPh fragment decreases and that of CHMePh increases little as going from **AD1** to **TS1^R** (Figure 3c). This is because the orientation of CHMePh changes but the Pd-C distance increases a little in **TS1^R**. The population of Pd and Ph increases and that of CHMePh decreases as going from **TS1^R** to **INT^R**, suggesting stronger interaction between Pd and Cu complexes in **INT^R**. Then, the population of CHMePh decreases by 0.224 *e* from **INT^R** to **TS2^R**, which is mainly compensated by the population increases of Ph and PCyp$_3$. The population of Cu decreases by 0.064 *e* from **INT^R** to **TS2^R** because the Cu-C bond is broken but Cu-Br bond is still weak in **TS2^R**. The population increase of Pd (0.086 *e*) approximately corresponds to the population decreases of Cu and Br from **INT^R** to **TS2^R**. However, in the **P1^R** complex the population of Cu returns to the value in **AD1** because the Cu-Br bond is formed, while that of Pd returns to value in **INT^R** and that of Br also decreases a little.

In conclusion, in the transmetallation reaction between PdBrPhPCyp$_3$ and Cu(NHC)(CHMePh), the inversion mechanism with linear case is more favored than other mechanisms thanks to smaller activation energy. This is in agreement with the experimental results. The most important change in inversion TS is CHMePh becomes planar. The charge transfer is found to be significant in transmetallation. The population of PCyp$_3$ increases during this reaction, implying strong trans-influence of PCyp$_3$. These results provide good understanding of transmetallation between PdBrPhPCyp$_3$ and Cu(NHC)(CHMePh) and are valuable for our future investigations of transmetallations with different PR$_3$ and alkyl groups.

2. Original papers

(1) Hong Zheng, Kazuhiko Semba, Yoshiaki Nakao, Shigeyoshi Sakaki, "Characteristic Features of Transmetallation of Pd(II)-Ph Complex with Cu(I)-alkyl Complexes: Theoretical Study" *In preperation*.

3. Others

(1) Hong Zheng, Kazuhiko Semba, Yoshiaki Nakao, Shigeyoshi Sakaki, "Characteristic Features of Transmetallation of Pd(II)-Ph Complex with Co(I)- and Cu(I)-alkyl Complexes: Theoretical Studies" CREST「新機能創出を目指した分子技術の構築」領域平成 27 年度第 2 回領域会議, Kyoto, December 5, 2015

Nishamol Kuriakose

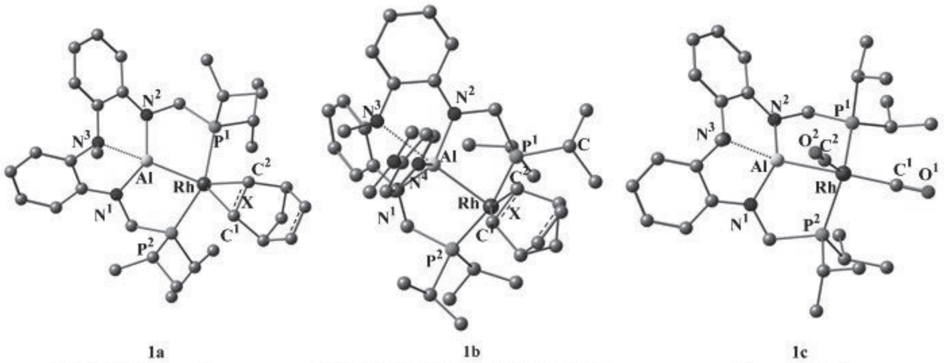
Research Fellow

1. Summary of the research of the year

Rhodium (I) Complex with Anionic Aluminum Ligand: Bonding Nature and reactivity

Isolation and stabilization of highly reactive species and its use in the transformation process are an important area of research. In this regard low valent element heterocycles of group 13 are widely recognized for its potential in important chemical reactions. The characteristic features of these heterocyclic species are the presence of a lone pair and a vacant π-orbitals at the element centre which in turn leads to its bifunctional nature of nuleophicity and electrophilicity. Transition metal complexes with such group 13 element heterocycles lead to interesting complexes due to the strong σ-donating ability of these ligands. In transition metal complexes these ligands can coordinate with the metal centre as reactive ligands or as supporting ligands. One interesting example reported is the transition metal complex with anionic boryl ligands, which are successfully employed in catalytic borylation reaction and other functionalization reactions. Higher analogues of group 13 anionic multidentate pincer ligands and its transition metal complexes are less studied. Many theoretical investigations have been performed to understand the electronic properties of Group 13 element analogue of N-heterocyclic carbene (Arduengo-type carbene) bearing a negative charge. Recently Nakao and co-workers synthesized a rhodium complex with an alanyl pincer-type ligand through the reduction of a rhodium/aluminum heterobimetallic complex. In this complex the aluminum acts as a Z-type ligand. We have performed theoretical calculation to understand the metal ligand bond interaction in Rh-complex with Z-type ligand.

The optimized geometry of the experimentally obtained complexes is shown in Figure 1. We have conducted a series of theoretical calculations with DFT method to understand the bonding nature of these complexes. The complex 1**a** and 1**b** has a similar trigonal pyramidal structure and 1**c** has a five coordinated trigonal bipyramidal structure. In order to obtain the frontier molecular orbitals of the anionic aluminum ligand, we have considered a model aluminum ligand **L1** of PAlP, in which H atoms are substituted for $PiPr_2$ moieties (See Figure 2a). In **L1** the $Al\text{-}N^3$ possesses an elongated bond of 2.337Å and the other Al-N bonds possesses a shorter bond length of 2.015 Å. The Mayer's bond order corresponding to the AlN^1, AlN^2 and AlN^3 bonds are 0.603, 0.603 and 0.283 respectively. These values are consistent with the observed Al-N bond length in the ligand moiety. The HOMO is a lone pair orbital located on the aluminum center and the empty 3p orbitals on the Al are found at LUMO + 9, LUMO+40 and LUMO+41 (Figure 2b). Since the two Al-N bonds are not purely covalent Al can be considered to have only two electrons which suggest a formal +1 charge on the Al atom. The molecular orbitals of the L1 ligands shows the presence of six electrons on each N atoms N^1 and N^2 (see Figure 3), therefore the N^1 and N^2 can considered to have a formal negative charge. Considering these features, **L1** can be represented as a canonical form of diamido–Al+ [Figure 2c, 2d].



1a

Al-N^1 1.865 Rh-C^1 2.198
Al-N^2 1.881 Rh-C^2 2.207
Al-N^3 2.158 C^1-C^2 1.417
Rh-Al 2.393 Rh-Al-N^3 138.2°
Rh-P^1 2.322 P^1-Rh-P^2 141.5°
Rh-P^2 2.323 Al-Rh-X^a 147.6°

1b

Al-N^1 1.918 (1.889) Rh-C^1 2.150 (2.151)
Al-N^2 1.915 (1.874) Rh-C^2 2.126 (2.134)
Al-N^3 2.376 (2.428) C^1-C^2 1.445 (1.451)
Al-N^4 2.033 (1.970) N^3-Al-N^4 80.1° (79.3°)
Rh-Al 2.430 (2.433) Rh-Al-N^3 177.2° (177.2°)
Rh-P^1 2.294 (2.255) P^1-Rh-P^2 111.6° (111.3°)
Rh-P^2 2.319 (2.286) Al-Rh-X^a 103.1°

1c

Al-N^1 1.850 C^1-O^1 1.158
Al-N^2 1.885 C^2-O^2 1.163
Al-N^3 2.091 Rh-Al-N^3 141.6°
Rh-Al 2.423 P^1-Rh-P^2 119.4°
Rh-P^1 2.391 C^1-Rh-C^2 106.7°
Rh-P^2 2.381 Al-Rh-C^1 170.2°
Rh-C^1 1.929 Al-Rh-C^2 83.0°
Rh-C^2 1.900

Figure 1. The optimized geometry of rhodium complexes **1a**, **1b** and **1c** with selected bond lengths (Å) and bond angles (°); the experimental values are given inside the parenthesis; H atoms have been omitted for clarity.

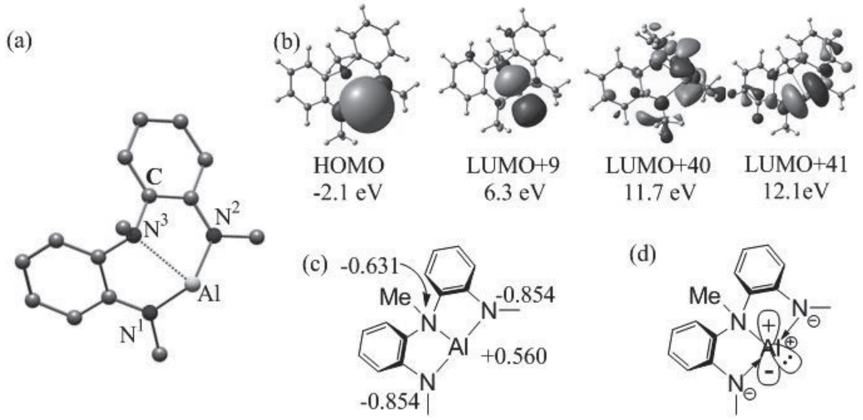


Figure 2. Geometry, electron distribution, and canonical form of a model of anionic aluminum ligand **L1**.

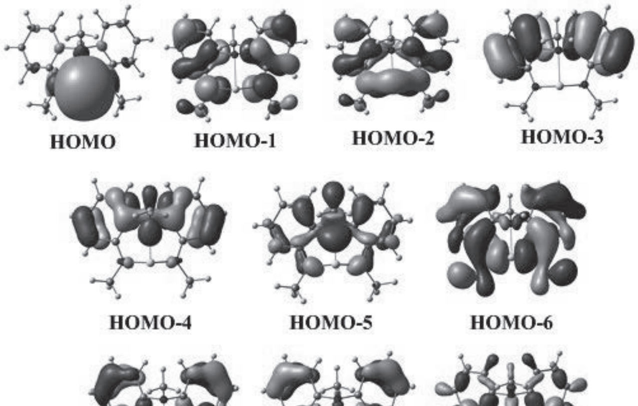


Figure 3. Molecular orbitals of the anionic aluminum ligand **L1**.

The Kohn-Sham orbitals of the Rh-complexes shows significantly large bonding overlap between the Rh d and the Al lone pair orbitals [Figure 4(a-c)]. This suggests that a large covalent bonding interaction is formed between the Rh and Al atoms in these complexes. Because the d orbital (-8.5 eV) of a neutral [Rh(nbd)] is at lower energy than the Al valence orbital (-4.7 eV) of PAIP, the Rh-Al bond is polarized as $Rh^{\delta-}$ and $Al^{\delta+}$.

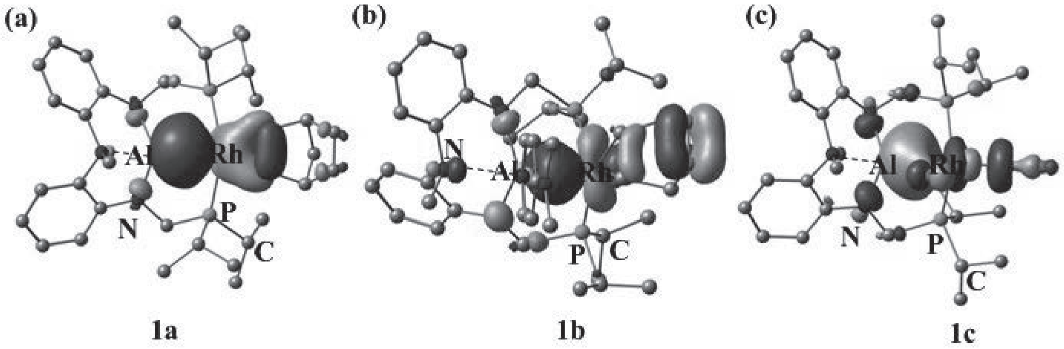


Figure 4. The molecular orbital involving Rh-Al interaction in **1a**, **1b** and **1c**.

In **1a**, the position of the C=C double bond of norbornadiene coordinating is above the molecular plane. Similar arrangement is observed for the case of **1b** also. This can be due to the geometrical constraint by the Al-N(Ph)-CH_2-P chain structure which induces the $PiPr_2$ moieties to take positions below the molecular plane with the PRhP angle of 141.5° and 111.6°, respectively (Figure 1). When the PRhP angle is 140 to 110°, the two phosphines destabilizes d orbital which expands to the opposite direction from the phosphines. Because of the strong π-back donation, the C=C double bond takes the position trans to these two phosphines which in turn lead to the strong overlap with the d orbital. The presence of the empty Al 3p orbitals allow the Rh-complexes to coordinates with DMAP very easily. This coordination increases the constraint on the Al-N(Ph)-CH_2-P chain to decrease the P1-Rh-P_2 angle. As a result, the PiPr moieties move more downward from the molecular plane and thereby the C=C double bond moves more upward. Therefore, in **1c** the C=C double bond occupies almost perpendicular position to the Rh-Al bond. In **1c**, two CO molecules coordinate with the Rh probably because of smaller steric repulsion by CO. This complex has a typical trigonal bipyramidal structure (Figure 1). The Rh-C^1 at the position trans to the PAIP is moderately longer than the Rh-C^2 by 0.03 Å but this does not indicate weak trans-influence of PAIP, because the equatorial CO cannot interact with a good acceptor orbital. The trans-influence of PAlP is estimated in camparison with CH_3 group (see **1d** in Figure 5). In the presence of -CH_3 group the Rh-C^1 distance is moderately longer in **1c** than in **1d**. This indicates that the trans-influence of aluminum ligand is similar or moderately stronger than that of CH_3. (see Figure 5). From these features, it is concluded that this new PAlP ligand has unique natures and its Rh(I) complex **1a** is reactive for the heterolytic σ-bond activation because the empty 3p of Al can interact a nucleophilic moiety of reactant and the doubly occupied 4d of Rh can interact with an electrophilic moiety.

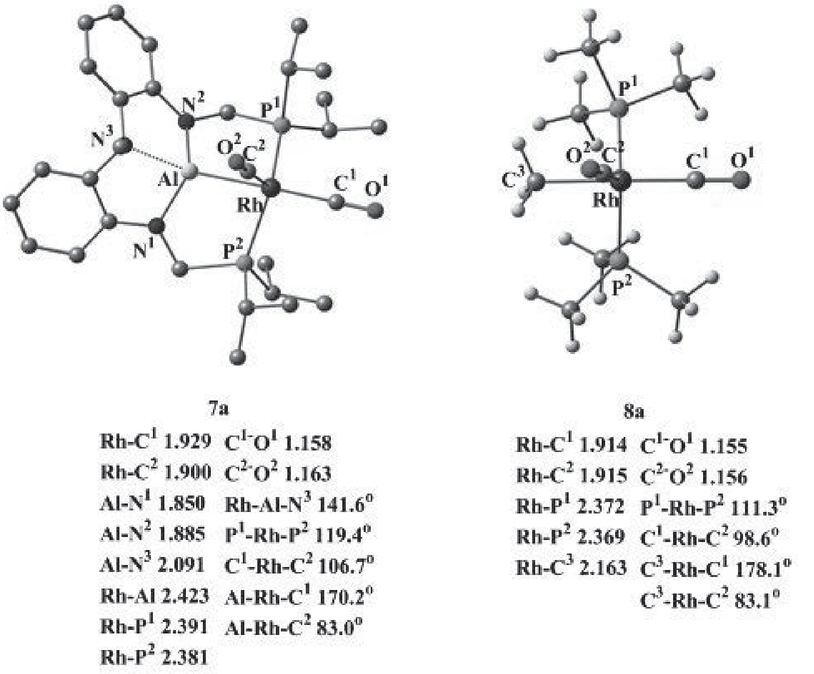


Figure 5. Optimized geometry of **1c** and $Rh(CH_3)(PMe_3)_2(CO)_2$ (**1d**).

2. Original papers

1. Teruhiko Saito, Nishamol Kuriakose, Shigeyoshi Sakaki,* Yoshiaki Nakao* Synthesis of neutral and anionic Aluminum containing Rhodium complexes and their reactivity toward cleavage of srong σ–bonds, (*communicated*).

3. Others (Presentation at symposium)

(1) Nishamol Kuriakose, Teruhiko Saito, Yoshiaki Nakao, Shigeyoshi Sakaki
“Sigma-Bond Activation by New Nickel(0) Complex with Z-type Aluminum Ligand: Theoretical Study” The 13th symposium of Fukui Institute for Fundamental Chemistry, Kyoto, Feb. 5, 2016.

６．共同研究員

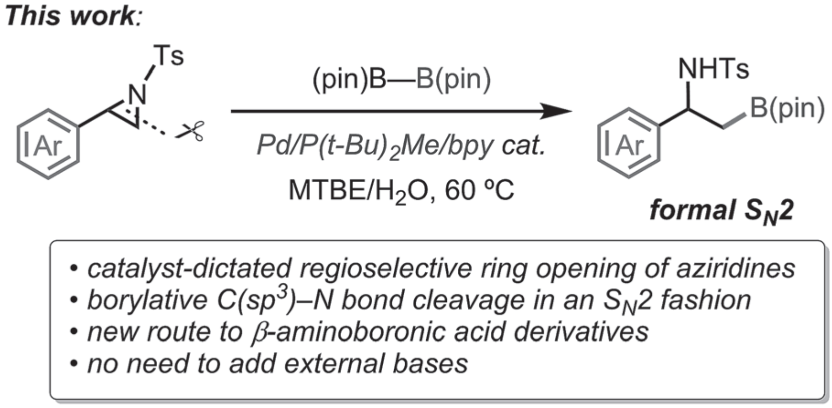
W. M. C. Sameera

JSPS Postdoctoral Fellow, Fukui Kenichi Memorial Research Group 1

1. Summary of the research

Palladium catalyzed regioselective ring opening and borylation of 2-arylaziridines with bis(pinacolato)diboron

Aziridines are versatile building blocks in modern organic synthesis. Regioselective ring opening of an aziridine is a useful strategy for the synthesis of biologically important compounds. We have developed a palladium catalyzed regioselective borylative ring opening reaction of 2-arylaziridines, giving rise to give β-amino-barylethylborates (Figure 1). This is the first example of ring opening borylation of non-vinylic aziridines and direct borylative $C(sp^3)$–N bond cleavage of neutral organic substrates. This work was performed in collaboration with Prof. Takeda (Osaka University).



- *catalyst-dictated regioselective ring opening of aziridines*
- *borylative $C(sp^3)$–N bond cleavage in an S_N2 fashion*
- *new route to β-aminoboronic acid derivatives*
- *no need to add external bases*

Figure 1. Palladium catalyzed regioselective ring opening borylation of 2-arylaziridines with bis(pinacolato)diboron.

Based on our NMR studies and density functional theory (DFT) calculations, we have concluded that the active intermediate for the reaction is a PdL_2 complex [L = $P(t\text{-}Bu)_2Me$]. Then, the multi-component artificial force induced reaction method (MC-AFIR) was used to find transition states for the regioselectivity-determining aziridine ring opening step that proceeds in an S_N2 fashion. Based on a Boltzmann distribution of 20 calculated TSs, the regioselectivity of the reaction was calculated (89:11), and explained the experimental regioselectivity. Figure 2 shows the mechanism of the full catalytic cycle that consists of a selectivity-determining aziridine ring opening (i.e. oxidative addition), a proton transfer process, phosphine ligand dissociation from the catalyst, rate determining boron–boron bond cleavage, phosphine ligand coordination, and reductive elimination. The calculated overall mechanism and selectivity are consistent with the experimental results. This study was published in *Chem. Sci.* DOI: 10.1039/C6SC01120A

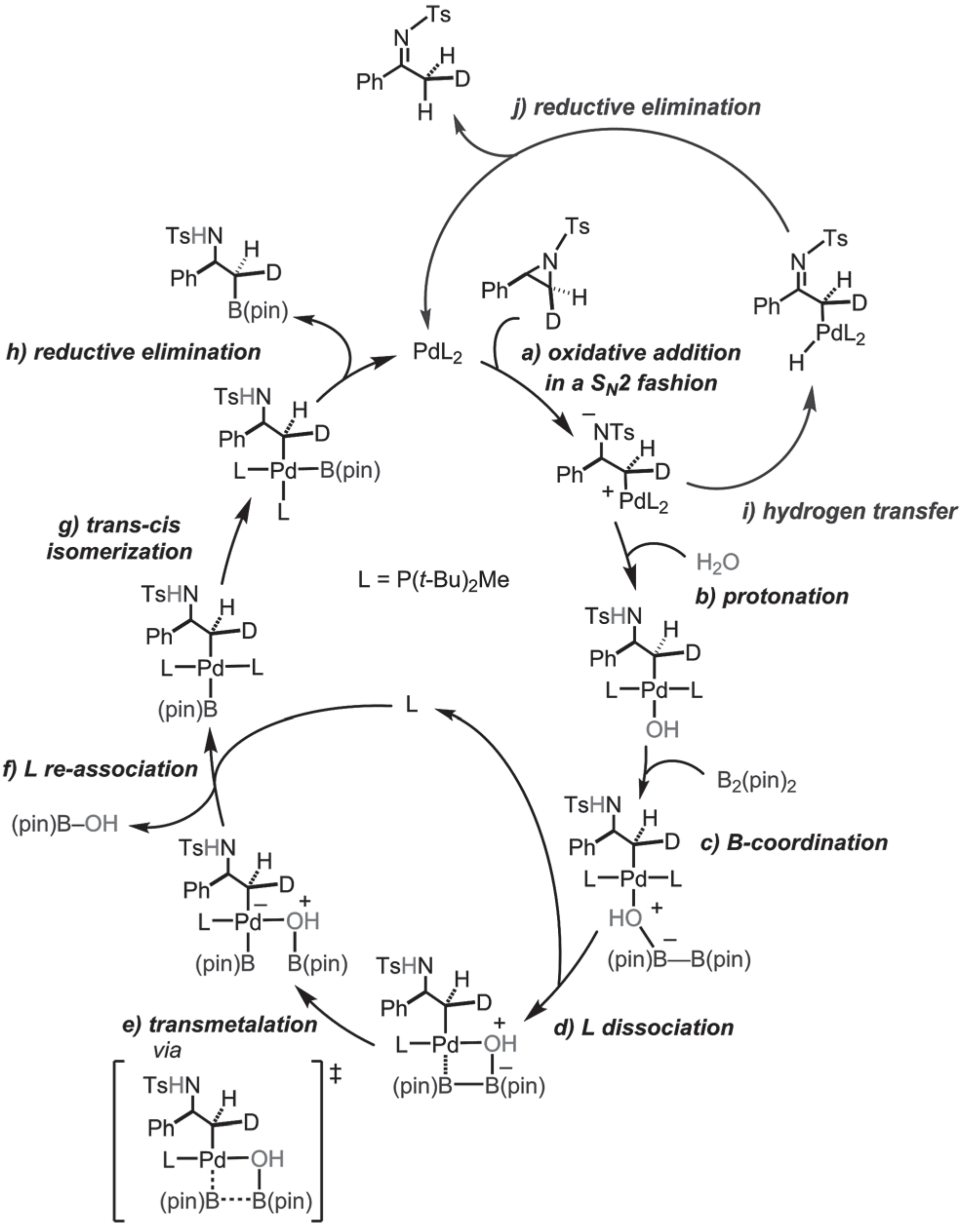
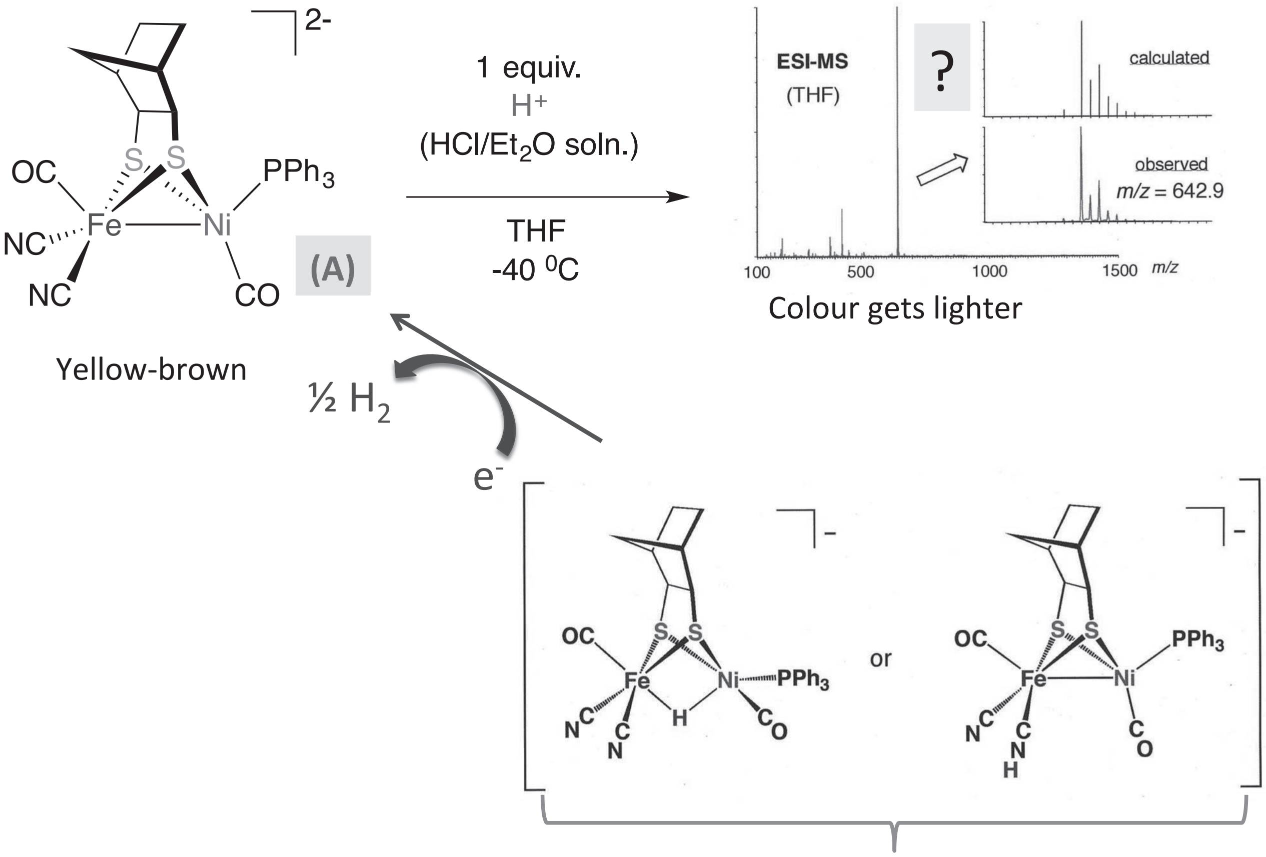


Figure 2. Mechanism of the full catalytic cycle from experimental and computational studies.

A biomimetic [Ni-Fe] cluster

Hydrogenases (H_2ases) catalyzes the reversible oxidation of H_2. Three main families have been identified for H_2ases, and are labeled according to the metal stoichiometry of their active sites; [NiFe]-, [FeFe]-, and [Fe]-H_2ases. Hydrogen is a widely used reagent and a vector for energy storage and a fuel for fuel cells. Because of the many potential uses of H_2, much interest has focused on replicating the catalytic properties of hydrogenase enzymes using molecular models of their active sites. We aim to understand the reaction between a Ni-Fe cluster and its proton reactions. This work was performed in collaboration with Prof. Tatsumi (Nagoya University).



Experimental group proposed these two structures

Figure 3. Protonation of the Ni-Fe cluster.

Among the calculated spin states of the Ni-Fe cluster, closed-shell singlet state is the most stable electronic state. Optimized structure of the singlet state and the X-ray structures are in very good agreement (Figure 4). In the triplet state, spin density of Fe (2.08) indicated that the two unpaired electrons are localized on Fe. Triplet state is 14.7 kcal/mol higher than the closed-shell singlet, and the calculated $<S^2>$ value of the triplet state, 2.05, is similar to the ideal values of 2.00. The quintet state is 13.0 kcal/mol higher than the singlet state, where spin densities are mainly located on Fe (3.57), while some spin densities are delocalised over Ni (0.21) and S (0.16). We have checked the performance of several other density functions, namely BLYP-D3, BHandH, M06, and TPSSTPSS-D3. Among the tested density functionals, B3LYP-D3 functional works well for this system. Therefore, we continue our discussion with the B3LYP-D3 functional. Based on our electronic structure analysis, we concluded that the ground state of the Ni-Fe cluster is a closed-shell singlet, and the oxidation states of the metals are Fe(II) and Ni(0). Then, the protonation would start from the singlet ground state of the cluster.

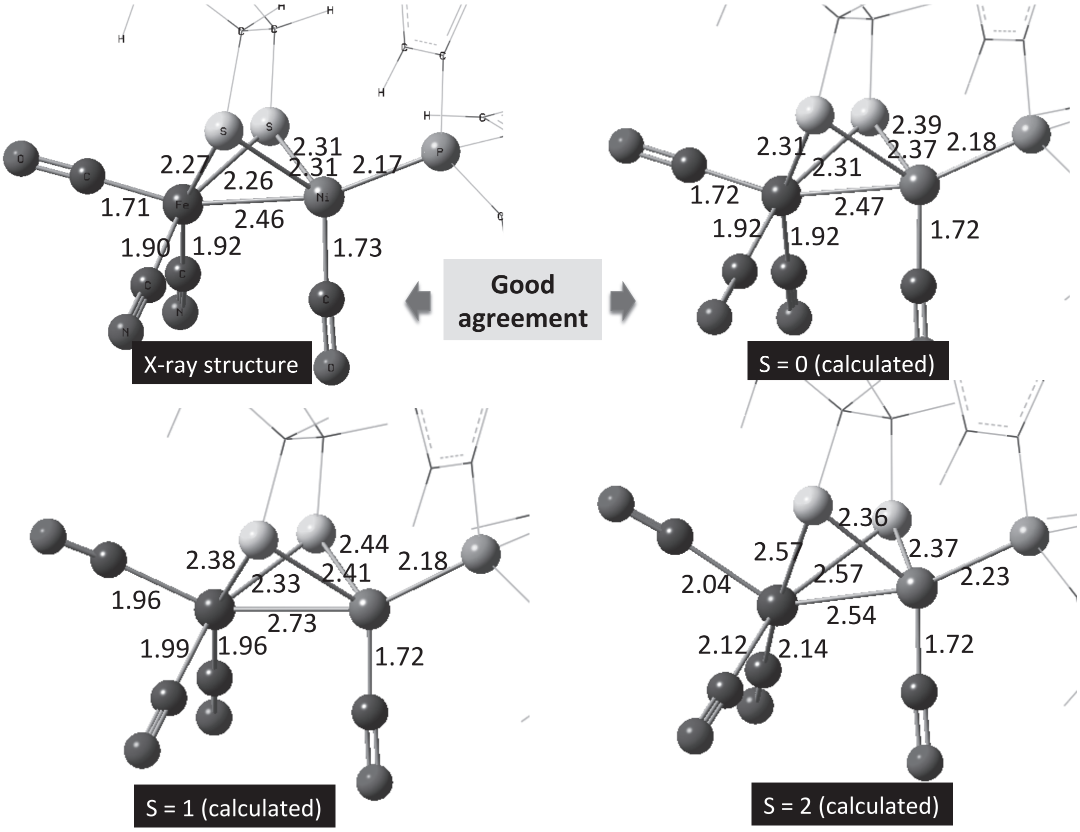


Figure 4. X-ray structure and the optimised structures of the possible electronic states of the Ni-Fe cluster.

We have used MC-AFIR method to search possible reaction paths for the protonation process. 38 reaction paths were determined by a fully-automatic MC-AFIR search. Depending on the protonation position, we have categorized the products in to 5 groups (Figure 5). Among them, most of the reaction paths showed protonation of the S (19 paths) and CN (12 paths). Relatively small number of paths was found for the protonation of Ni (5 paths), and only one path showed the protonation of CO. A bridging H complex was also formed through 1 path.

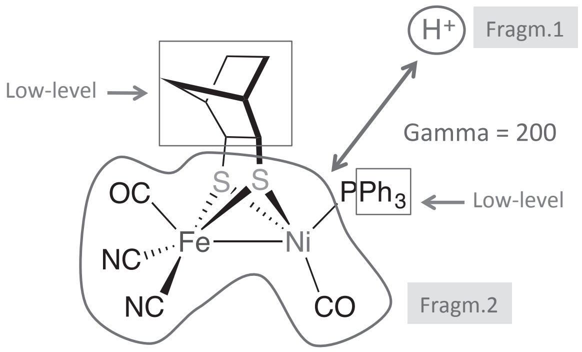


Figure 5. Fermentation of the molecular system for MC-AFIR calculations, and partition of the molecular system for the ONIOM calculations.

Among the protonated products, thermodynamically most stable complex **(i)** showed protonation of a S group. Among the other possible products, **(ii)** (2.2 kcal/mol, protonation of Ni), **(iii)** (3.2, protonation of CN), and **(iv)** (2.3 kcal/mol) are only few kcal/mo higher in energy, and therefore they may be formed under the reaction conditions. Work in progress for isolating the product complexes, and manuscript is in preparation.

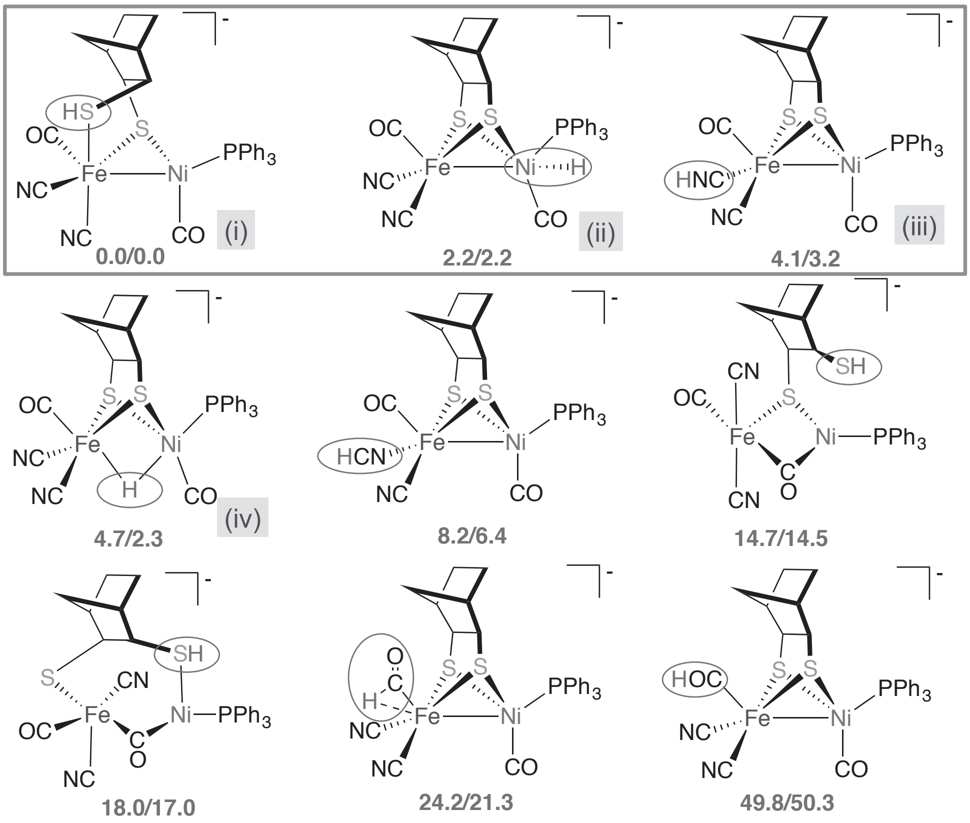


Figure 6. Possible product complexes and their relative energies (ΔE/ΔG).

2. List of original papers

1. BOOK CHAPTER: R. Ramozzi, W. M. C. Sameera, K. Morokuma, "Predicting reaction pathways from reactants", Applied Theoretical Chemistry, World scientific publishing. (Submitted)
2. REVIEW: W. M. C. Sameera, A. K. Sharma, S. Maeda, K. Morokuma, "Artificial force induced reaction method for systematic determination of complex reaction mechanisms", *Chem. Rec.* (Accepted)
3. S. Sasaki, S. Suzuki, W. M. C. Sameera, K. Igawa, K. Morokuma, G. Konishi, "Highly twisted N,N-dialkylamines as a design strategy to tune simple aromatic hydrocarbons as steric environment-sensitive fluorophores". *J. Am. Chem. Soc.* (In press) DOI: http://dx.doi.org/10.1021/jacs.6b03749
4. Y. Takeda, A. Kuroda, W. M. C. Sameera, K. Morokuma, S. Minakata, "Palladium -catalyzed regioselective ring-opening borylation of 2-arylaziridines with bis(pinacolato)diboron: experimental and computational studies", *Chem. Sci.* (In press) DOI: 10.1039/C6SC01120A
5. REVIEW: W. M. C. Sameera, S. Maeda, K. Morokuma, "Computational catalysis using the artificial force induced reaction (AFIR) method", *Acc. Chem. Res.* 2016, 49, 763-773.

6. I. Funes-Ardoiz, W. M. C. Sameera, R. M. Romero, C. Martínez, J. A. Souto, D. Sampedro, K. Muñiz, F. Maseras, "DFT rationalization of the diverse outcomes of the iodine(III)-mediated oxidative amination of alkenes", *Chem. Eur. J.* 2016, 22, 1-10.
7. 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.* 2015, 137, 11085-11094.
8. REVIEW: 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.
9. REVIEW: M. Besora, A. A. C. Braga, W. M. C. Sameera, J. Urbano, M. R. Fructos, P. J. Perez, F. Maseras, "A computational view on the reactions of hydrocarbons with coinage metal complexes", *J. Organomet. Chem.* 2015, 784, 2-12.

3. List of presentations at meetings.

1. W. M. C. Sameera, Keiji Morokuma, "Theoretical studies of control and design of catalytic reactions using stimuli-responsive chemical species, stimuli-responsive chemical species for the creation of functional molecules", Hiroshima University, Japan. (Poster)
2. W. M. C. Sameera, Keiji Morokuma, "International symposium on new development of physical organic chemistry: construction of chemical principles determining structures, reactions, and properties", Fukuoka, Japan. (Poster)
3. W. M. C. Sameera, Yasuhiro Ohki, Kazuyuki Tatsumi, Keiji Morokuma, "Biomimetic model complexes for [NiFe] hydrogenase: density functional theory and artificial force-induced reaction study", The 13th FIFC symposium, Kyoto University, Japan. (Poster)
4. W. M. C. Sameera, Keiji Morokuma, "Artificial force induced reaction method for mechanistic and selectivity studies of transition metal complexes and clusters, the seventh asia-acific conference of theoretical and computational chemistry (APCTCC 7)", Kaohsiung, Taiwan. (Invited talk)
5. W. M. C. Sameera, Keiji Morokuma, "Artificial force induced reaction method for computational studies of transition metal complexes and clusters", Department of Chemistry and Molecular biology, University of Gothenburg, Sweden. (Invited talk)
6. W. M. C. Sameera, "The quantum mechanics of chemical reactions", JSPS science dialogue program, Tokyo, Japan (2015). (Invited talk)
7. W. M. C. Sameera, Keiji Morokuma, "Artificial force induced reaction method for mechanisms involving transition metal complexes and clusters", The 13th Fukui Centre Seminar, Kyoto University, Japan (2015). (Invited talk)
8. W. M. C. Sameera, Keiji Morokuma, "Carbon-carbon bond formation reactions: DFT and AFIR studies"the 15th ICQC meeting, Beijing, China. (Poster)
9. W. M. C. Sameera, Bethmini Senevirathne, Muhsen Al-lbadi, Stefan Andersson, Gunnar Nyman, "Interstellar radical species binding on ices: a hybrid QM/MM approach", Tokyo Institute and Technology, Japan. (Invited talk)

Yanying Zhao

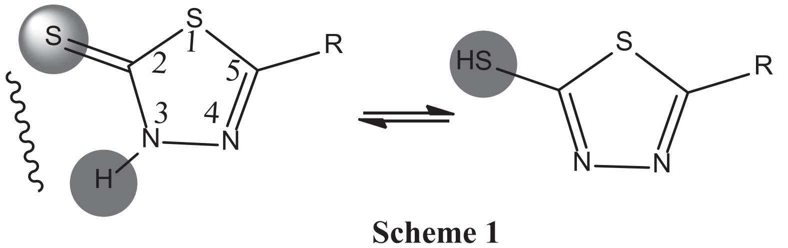
Visiting Scholar

1. Summary of the research of the year

Theoretical Study of Excited State Proton Transfer in 5-substituted-1,3,4-thiodizole-2-thione molecules by GRRM

The photophysics and photochemistry of thiocarbonyls were reviewed by Maciejewski and Steer. Previous studies revealed that the thione forms of small thioamides were much more stable than the thiol tautomers in the ground electronic state. The calculated energy difference between the thione and thiol forms of thioacetamide was 39.1 kJ mol, which precluded thermal population of the thiol form of thioacetamide in the ground electronic state due to a large transition energy barrier. The UV-induced HN–C=S → N=C–SH excited state proton transfer (ESPT) reaction leading to the conversion of thione to thiol was observed for a number of matrix-isolated thioamides. The ESPT reaction is fundamentally different from the classic excited state intramolecular proton transfer (ESIPT) process. ESIPT refers in particular to the proton transfer reaction within an intramolecular hydrogen bond (−C=O···H–NC−). This is fulfilled neither for the heterocyclic compounds nor for thioacetamide.

Here, we theoretically investigated the excited state decay mechanism of 5-substituted-1,3,4-thiadizole-2-thione molecules (Scheme 1) by GRRM method. We carried out geometry optimization using the TD-DFT method. The excited state minima S_1, S_2 and T_1, minimum energy conical intersection and seam crossing points are explored using SC-AFIR method. The results from theoretical calculation are able to interpret our resonance Raman spectroscopic results. The excited state reaction mechanism is tentatively proposed as $S_0 \rightarrow S_2 \rightarrow S_2/S_1$ or $S_2/T_n \rightarrow S_1/S_0$ or $T_1/S_0 \rightarrow S_0'$.



Scheme 1

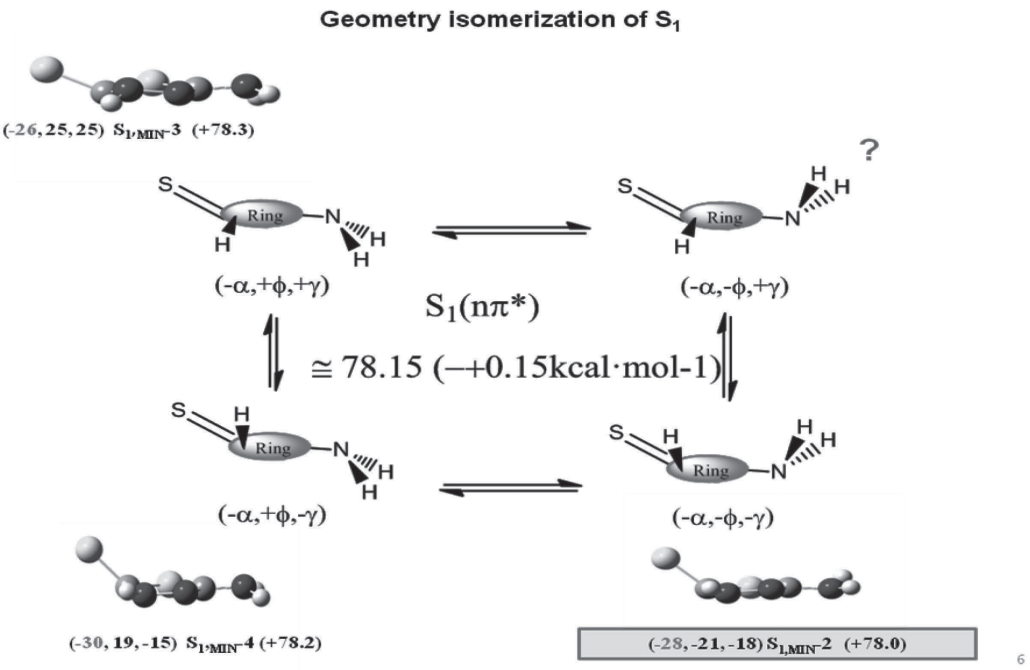


Figure 1. Geometry of local minima S_1 of 5-amino-1,3,4-thiadizole-2-thione at TD/B3LYP/6-311++G level.**

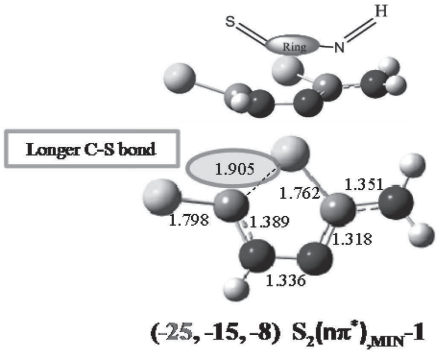


Figure 2. Geometry of local minimum S_2 of 5-amino-1,3,4-thiadizole-2-thione at TD/B3LYP/6-311++G level.**

2. Original papers

(1) Chen Xiao, Zhao Yanying*, Zhang Haibo, Xue jiadan, Zheng Xuming* Excited state proton transfer dynamics of thioacetamide in $S_2(\pi\text{-}\pi^*)$ state: resonance Raman spectroscopic and quantum mechanical calculations study. J. Phys. Chem. A 119, 832-842(2015)

(2) Zhao Yanying, Xu Qiang* Chapter 15, Metal-organic frameworks as platforms for hydrogen generation from chemical hydrides in Organometallics and Related Molecules for Energy Conversion, Green Chemistry and Sustainable Technology. Springer-Verlag Berlin Heidelberg 421-467(2015). W.-Y. Wong (ed.), DOI 10.1007/978-3-662-46054-2_15.

(3) Li Dan, Zhao Yanying*, Xue Jia-Dan, Zheng Xuming Structural dynamics of 4-formaldehyde imidazole and imidazole in light absorbing $S_2(\pi\text{-}\pi^*)$ state Journal of Raman Sepctroscopy 46(3), 293-301(2015).

(4) Zhao Yanying*, Zhang Yuchen, Liu Xin, Zheng Xuming Formation, characterization, structure and bonding analysis of the metal-carbon bond $OM\text{-}(\eta^6\text{-}C_6H_6)$ (M = Sc, Ti) complexes in solid matrix: Infrared spectroscopic and theoretical study. J. Orgmet. Chem. 777, 25-30(2015)

3. Presentation at academic conferences

4. Others

Ming-Chung Yang

Foreign Joint Researcher

1. A DFT Study of Addition Reactions between L_4M(M=Rh, Ir), L_2M(M=Pd, Pt) Fragments and Endohedral Fullerene (Li^+@C60)

Five synthetic routes have been proposed for the addition reactions of metal fragments with C_{60}. Denpending on to the bonding sites, the resulting complexes are denoted as η^1-coordination, $\eta^{2[6,6]}$-coordination ([6,6] indicates the midpoint of two six-membered rings junction), $\eta^{2[6,5]}$-coordination ([6,5] indicates the midpoint of a six and a five-membered ring junction), η^5-coordination, and η^6-coordination. It is known that the reactions of empty C_{60} with electron-rich fragments such as $IrCl(CO)(PPh_3)_2$ and $Pt(PPh_3)_2$ give rise to the iridium fullerene complex $(\eta^2\text{-}C_{60})IrCl(CO)(PPh_3)_2$ and iridium fullerene complex $[(\eta^2\text{-}C_{60})Pt(PPh_3)_2]$. Recently, Tobita *et al.* have reported the structures of iridium and platinum complexes of lithium cation encapsulated fullerene (i.e., $[\{\eta^2\text{-}(Li^+@C_{60})\}IrCl(CO)(PPh_3)_2](PF_6^-)$ and $[\{\eta^2\text{-}(Li^+@C_{60})\}Pt\ (dppf)])(PF_6^-)$, dppf=1,1′-bis(diphenylphosphino)ferrocene). These encapsulated complexes can be identified as $\eta^{2[6,6]}$-coordination, and the most importantly, no other types of coordination was found. It was also observed that the reaction of $[IrCl(CO)(PPh_3)_2]$ with empty C_{60} is reversible, whereas the reaction of $[IrCl(CO)(PPh_3)_2]$ with $Li^+@C_{60}$ is irreversible. In other words, the encapsulated iridium fullerene complex become more stable once the Li^+ is encapsulated into an empty C_{60}. These experimental evidencies raised our interests because it was reported that the encapsulated metal cation can affect the reactivity of the C_{60} in the Diels-Alder reaction. However, to best of our knowledge, no theoretical studies are reported to show the effect of a Li^+ ion on the formation of iridium and platinum complexes, and to study their selectivity.

In this work, we use AFIR method to investigate the addition reaction of L_4M (M=Ir, L_4=Cl(CO)(PPh_3)$_2$) and L_2M (M=Pt, L_2=(PPh_3)$_2$) with $E@C_{60}$ (E=0 and Li^+). AFIR method is useful to obtain approximate reaction paths systematically, and to locate approximate transition state (TSs) and local minima (LMs) on the reaction path. Approximate stationary points can be refined by using the standard computational methods. In the presence of precise reaction mechanism for iridium and platinum complexes in hand, we have extended our stratergy to the elements in the third row, thus, M=Rh and Ir for L_4M fragment and M= Pd and Pt for L_2M fragment. In addition, we would like to understand the role of a Li^+ ion on the on the formation of metal complexes. The following reactions were studied;

$$IrCl(CO)(PPh_3)_2 + C_{60} \rightarrow [\{\eta^2\text{-}C_{60})\}IrCl(CO)(PPh_3)_2] \tag{1a}$$

$$IrCl(CO)(PPh_3)_2 + Li^+@C_{60} \rightarrow [\{\eta^2\text{-}(Li^+@C_{60})\}IrCl(CO)(PPh_3)_2] \tag{1b}$$

$$\mathrm{RhCl(CO)(PPh_3)_2 + C_{60} \rightarrow [\{\eta^2\text{-}C_{60})\}RhCl(CO)(PPh_3)_2]} \quad (2a)$$

$$\mathrm{RhCl(CO)(PPh_3)_2 + Li^+@C_{60} \rightarrow [\{\eta^2\text{-}(Li^+@C_{60})\}RhCl(CO)(PPh_3)_2]} \quad (2b)$$

$$\mathrm{Pt(PPh_3)_2 + C_{60} \rightarrow [\{\eta^2\text{-}C_{60})\}Pt(PPh_3)_2]} \quad (3a)$$

$$\mathrm{Pt(PPh_3)_2 + Li^+@C_{60} \rightarrow [\{\eta^2\text{-}(Li^+@C_{60})\}Pt(PPh_3)_2]} \quad (3b)$$

$$\mathrm{Pd(PPh_3)_2 + C_{60} \rightarrow [\{\eta^2\text{-}C_{60})\}Pt(PPh_3)_2]} \quad (4a)$$

$$\mathrm{Pd(PPh_3)_2 + Li^+@C_{60} \rightarrow [\{\eta^2\text{-}(Li^+@C_{60})\}Pt(PPh_3)_2]} \quad (4b)$$

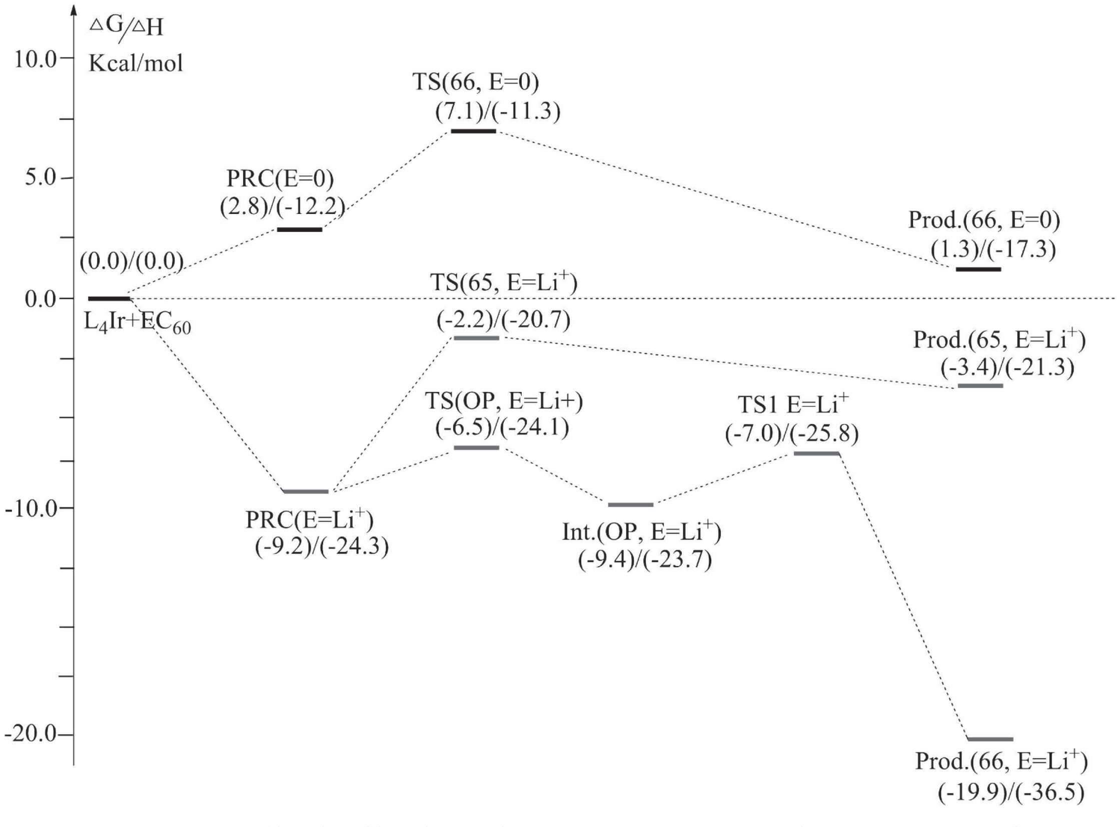


Figure 1. Free energy profile (kcal/mol) of the reactants (L_4Ir + E@C_{60}), L_4Ir----E@C_{60} complex, intermediate, transition states, and final product, based on the M06/SDD/6-31G(d,p) calculations. The red lines indicate the case in the occurrence of Li^+ ion. The abbreviations OP, 66, and 65 stand for one-point attack, [6,6]-attack, and [6,5]-attack, respectively.

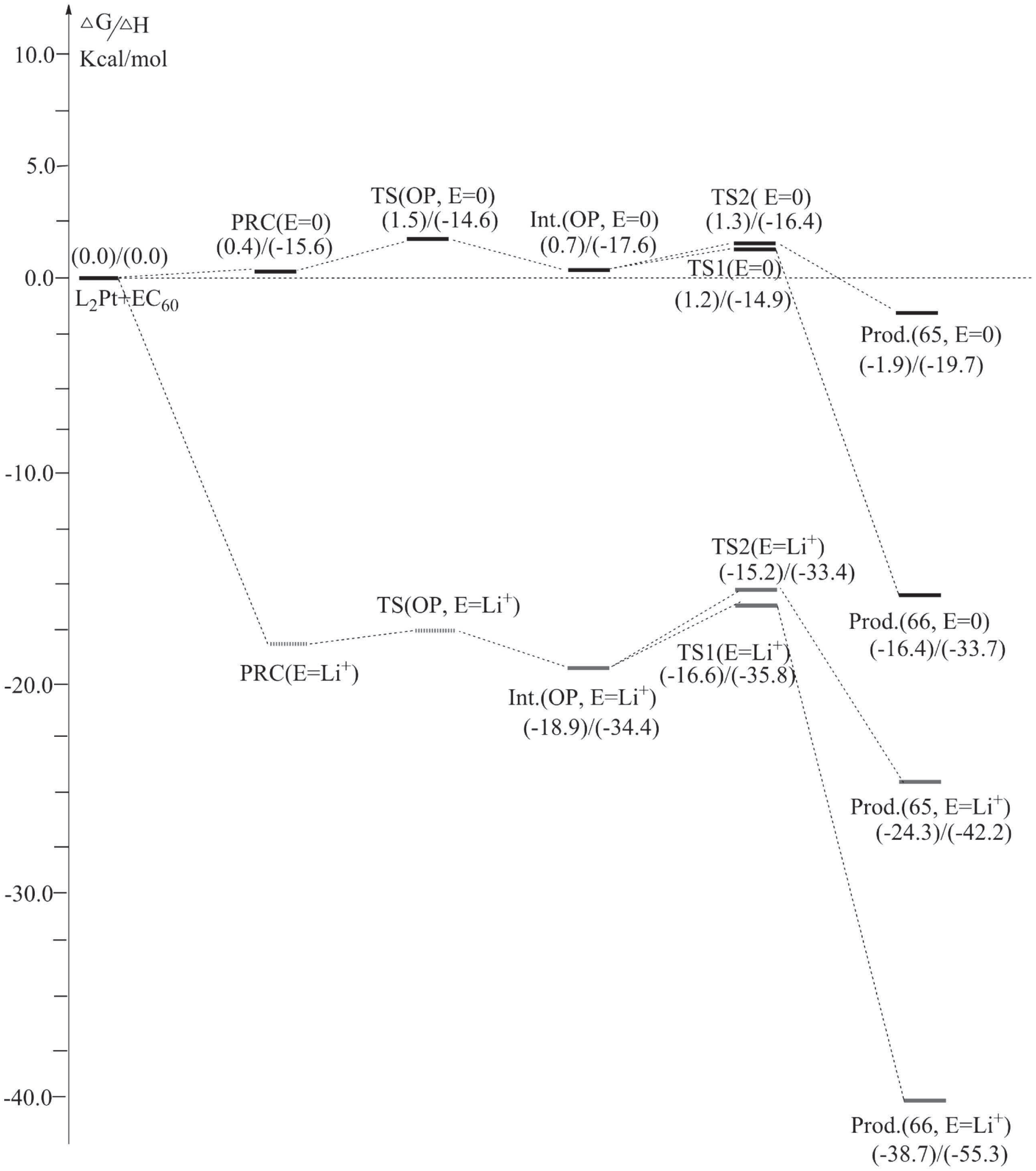


Figure 2. Free energy profile (kcal/mol) of the reactants (L_2Pt + $E@C_{60}$), L_2Pt----$E@C_{60}$ complex, intermediate, transition states, and final product, based on the M06/SDD/6-31G(d,p) calculations. The red lines indicate the case in the occurrence of Li^+ ion. The abbreviations OP, 66, and 65 stand for one-point attack, [6,6]-attack, and [6,5]-attack, respectively.

It is concluded that the multicomponent artificial force-induced reaction (MC-AFIR) search suggested that the [6,6] attacked is the most favorable reaction, which is consistent with the experimental observations.

2. Original papers

(1) Ming-Chung Yang, Akhilesh K. Sharma, W.M.C Sameera, Keiji Morokuma and Ming-Der Su, A DFT Study of Addition Reactions between L_4M(M=Rh, Ir), L_2M(M=Pd, Pt) Fragments and Endohedral Fullerene ($Li^+@C_{60}$)(in preparation)

Ⅴ　資料

1．研究業績一覧（平成 27 年度）

№	Authors	Title	Journal	Volume (Number), first page to last page	year
池田　昌司					
1	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
2	Misaki Ozawa, Walter Kob, Atsushi Ikeda, Kunimasa Miyazaki	Reply to Chakrabarty et al.: Particles move even in ideal glasses	*Proc. Natl. Acad. Sci. USA*	112, E4821	2015
3	Atsushi Ikeda, Ludovic Berthier	Thermal fluctuations, mechanical response, and hyperuniformity in jammed solids	*Phys. Rev. E*	92, 012309	2015
4	Harukuni Ikeda, Atsushi Ikeda	One-dimensional Kac model of dense amorphous hard spheres	*EPL*	111, 40007	2015
水野　英如					
5	A. Nicolas, F. Puosi, H. Mizuno, and J.-L. Barrat	Elastic consequences of a single plastic event: Towards a realistic account of structural disorder and shear wave propagation in models of flowing amorphous solids	*Journal of the Mechanics and Physics of Solids*	78, 333-351	2015
6	H. Mizuno, S. Mossa, and J.-L. Barrat	Beating the amorphous limit in thermal conductivity by superlattices design	*Scientific Reports*	5, 14116 (15pages)	2015
永瀬　茂					
7	J.-D. Guo, S. Nagase, and P. P. Power	Dispersion Force Effects on the Dissociation of “Jack-in-the–Box” Diphosphanes and Diarsanes	*Organometallics*	34, 2028-2033	2015
8	T. Yang, S. Nagase, T. Akasaka, J. M. Poblet, K. N. Houk, M. Ehara, and X. Zhao	(2+2) Cycloaddition of Benzyne to Endohedral Metallofullerenes $M_3N@C_{80}$ (M = Sc, Y): A Rotating-Intermediate Mechanism	*J. Am. Chem. Soc.*	137, 6820-6828	2015
9	T. Sasamori, T. Sugahara, T. Agou, J.-D. Guo, S. Nagase, R. Streubel, and N. Tokitoh	Synthesis and Characterization of a 1,2-Digermabenzene	*Organometallics*	34, 2106-2109	2015
10	T. Agou, T. Wasano, T. Sasamori, J.-D. Guo, S. Nagase, and N. Tokitoh	Ring Expansion to 1-Bromo-1-alumacyclonona-2,4,6,8-tetraene by Insertion of Two Alkyne Molecules into the Al-C Bonds	*Angew. Chem. Int. Ed.*	54, 9568-9571	2015
11	Y.-J. Guo, H. Zheng, T. Yang, S. Nagase, and X. Zhao	Theoretical Insight into the Ambiguous Endohedral Metallofullerene Er_3C_{74}: Covalent Interactions among Three Lanthanide Atoms	*Inorg. Chem.*	54, 8066-8076	2015

№	Authors	Title	Journal	Volume (Number), first page to last page	year
12	T. Sasamori, T. Sugahara, T. Agou, K. Sugamata, J.-D. Guo, S. Nagase, and N. Tokitoh	Reaction of a Diaryldigermyne with Ethylene	*Chem. Sci.*	6, 5526-5530	2015
13	P. Zhao, H. Lei, C. Ni, J.-D. Guo, S. Kamali, J. C. Fettinger, F. Grandjean, G. J. Long, S. Nagase, and P. P. Power	Quasi-Three-Coordinate Iron and Cobalt Terphenoxide Complexes $\{\mathrm{Ar}^{\mathrm{iPr8}}\mathrm{OM}(\text{ì-O})\}_2$ ($\mathrm{Ar}^{\mathrm{iPr8}}$ = $\mathrm{C_6H}$-2,6-($\mathrm{C_6H_2}$-2,4,6-iPr3)2-3,5-$^{\mathrm{i}}\mathrm{Pr}_2$; M = Fe or Co) with $\mathrm{M(III)_2(\text{ì-O})_2}$ Core Structures and the Peroxide Dimer of 2-Oxepinoxyl Relevant to Benzene Oxidation	*Inorg. Chem.*	54, 8914-8922	2015
14	T. Morosaki, W.-W. Wang, S. Nagase, and T. Fujii	Synthesis, Structure, and Reactivities of Iminosulfane- and Phosphane-Stabilized Carbones Exhibiting Four-Electron Donor Ability	*Chem. Eur. J.*	21, 15405-15411	2015
15	J.-D. Guo, D. J. Liptrot, S. Nagase, and P. P. Power	The Multiple Bonding in Heavier Group 14 Element Alkene Analogues is Stabilized Mainly by Dispersion Force Effects	*Chem. Sci.*	6, 6235-6244	2015
16	M. Kako, K. Miyabe, K. Sato, M. Suzuki, N. Mizorogi, W.-W. Wang, M. Yamada, Y. Maeda, M. M. Olmstead, A. L. Balch, S. Nagase, and T. Akasaka	Preparation, Structural Determination, and Characterization of Electronic Properties of Bis-Silylated and Bis-Germylated $\mathrm{Lu_3N@}I_h\mathrm{\text{-}C_{80}}$	*Chem. Eur. J.*	21, 16411-16420	2015
17	T. Kuwabara, M. Nakada, J.-D. Guo, S. Nagase, and M. Saito	Diverse Coordination Modes in Tin Analogues of a Cyclopentadienyl Anion Depending on the Substituents on the Tin Atom	*Dalton Trans.*	44, 16266-16271	2015
18	Y. Maeda, T. Tsuchiya, T. Kikuchi, H. Nikawa, T. Yang, X. Zhao, Z. Slanina, M. Suzuki, M. Yamada, Y. Lian, S. Nagase, X. Lu, and T. Akasaka	Effective Derivatization and Extraction of Insoluble Missing Lanthanum Metallofullerenes $\mathrm{La@C_{2n}}$ (n = 36-38) with Iodobenzene	*Carbon*	98, 67-73	2016
19	Z. Slanina, F. Uhlík, X. Lu, T. Akasaka, K. H. Lemke, T. M. Seward, S. Nagase, and L. Adamowicz	Calculations of the Water-Dimer Encapsulated into $\mathrm{C_{84}}$	*Fullerenes, Nanotubes, Carbon Nanostruct.*	24, 1-7	2016
20	R. Zhao, Y. Guo, P. Zhao, M. Ehara, S. Nagase, and X. Zhao	Warning to Theoretical Structure Elucidation of Endohedral Metallofullerenes	*J. Phys. Chem. C*	120, 1275-1283	2016
21	T. Sasamori, J. M. V. Franco, J.-D. Guo, K. Sugamata, S. Nagase, R. Streubel, and N. Tokitoh	Selenium-Substituted Phosphaalkenes Obtained through 1, 2-Elimination of Chlorosilanes from Selenenylchlorophines	*Eur. J. Inorg. Chem.*	678-684	2016
22	J.-D. Guo, T. Sasamori, Y. Yamamoto, H. Matsubara, S. Nagase, and H. Yorimitsu	Computational Picture of Silyl Transfer from Silylsilatranes to Arylpalladium Chloride	*Bull. Chem. Soc. Jpn.*	89, 192-194	2016

№	Authors	Title	Journal	Volume (Number), first page to last page	year
23	S. Kato, O. Niyomura, K. Tani, M. Ebihara, J.-D. Guo, and S. Nagase	Crystal Structure of 4-methybenzenecarbothioic Acid and Computational Investigations of Benzenecarbochlcogenoic Acids (C_6H_5COEH and C_6H_5CEOH, E = S, Se, Te)	*Bull. Chem. Soc. Jpn.*	89, 361-368	2016
榊　茂好					
24	Wei Guan, Shigeyoshi Sakaki, Takuya Kurahashi, and Seijiro Matsubara	Reasons Two Nonstrained C-C σ-Bonds Can Be Easily Cleaved in Decyanative [4+2] Cycloaddition Catalyzed by Nickel(0)/Lewis Acid Systems. Theoretical Insight	*ACS Catalytsis*	5, 1-10	2015
25	Noriaki Ochi, Tsuyoshi Matsumoto, Takuya Dei, Yoshiaki Nakao, Hirofumi Sato, Kazuyuki Tatsumi, Shigeyoshi Sakaki	Heterolytic Activation of Dihydrogen Molecule by Hydroxo-/Sulfido-Bridged Rutheni um–Germanium Dinuclear Complex. Theoretical Insights	*Inorg. Chem.*	54, 576-585	2015
26	Hisako Hashimoto, Yuto Odagiri, Yasuhiro Yamada, Nozomi Takagi, Shigeyoshi Sakaki, and Hiromi Tobita	Isolation of a Hydrogen-Bridged Bis(silylene) Tungsten Complex: A Snapshot of a Transi-tion State for 1,3-Hydrogen Migration	*J. Am. Chem. Soc.*	137, 158-161	2015
27	Naokazu Yoshikawa, Shinichi Yamabe, Shigeyoshi Sakaki, Nobuko Kanehisa, Tsuyoshi Inoue,and Hiroshi Takashima	Transition States of the 3MLCT to 3MC Conversion in Ru(bpy)2(phen derivative)2+ Complexes	*J. Mol. Struct.*	1094, 98-108	2015
28	Hajime Kameo, Tatsuya Kawamoto, Didier Bourissou, Shigeyoshi Sakaki, and Hiroshi Nakazawa	Evaluation of the sigma-Donation from Group 11 Metals (Cu, Ag, Au) to Silane, Ger-mane, and Stannane Based on the Experimental/Theoretical Systematic Approach	*Organometallics*	34, 1440-1448	2015
29	Guixian Zeng, Satoshi Maeda, Ttetsuya Taketsugu, and Shigeyoshi Sakaki	Catalytic Transfer Hydrogenation by Trivalent Phosphorus Compound: Phosphorus-Ligand Cooperation Pathway or PIII/PV Redox Pathway?	*Angew. Chem. Int. Ed.*	128, 4721-4725	2015
30	Nozomi Takagi, Kazuya Ishimura, Masafuyu Matsui, Ryoichi Fukuda, Toru Matsui, Takahito Nakajima, Masahiro Ehara, and Shigeyoshi Sakaki	How Can We Understand Au8 Cores and Entangled Ligands of Selenolate- and Thio-late-Protected Gold Nanoclusters Au24(ER)20 and Au20(ER)16 (E = Se, S; R = Ph, Me)? A Theoretical Study	*J. Am. Chem. Soc.*	137, 8593-8602	2015
31	K. Kido, K. Kasahara, H. Sato, S. Sakaki	A molecular level study of selective cation capture by a host-guest mechanism for 25, 26, 27, 28-tetramethoxycalix[4]arene in MClO4 solution (M=Na, K)	*Mol. Simu.SI*	41, 881-891	2015
32	Masafuyu Matsui, Masato Machida, Shigeyoshi Sakaki	Characterization of AlPO4(110) Surface in Adsorption of Rh Dimer and Its Comparison with gamma-Al2O3(100) Surface: A Theoretical Study	*J. Phys. Chem. C*	119, 19752-19762	2015
33	Hajime Kameo, Shigeyoshi Sakaki	Activation of Strong Boron-Fluorine and Silicon-Fluorine sigma-Bonds: Theoretical Un-derstanding and Prediction	*Chem. Eur. J.*	21, 13588-13597	2015

№	Authors	Title	Journal	Volume (Number), first page to last page	year
34	Yue Chen, Yusuke Sunada, Hideo Nagashima, Shigeyoshi Sakaki,	Theoretical Study of Pd11Si6 Nanosheet Compounds Including Seven-Coordinated Si Spe-cies and Its Ge Analogues	*Chem. Eur. J.*	22, 1076-1087	2015
35	Masayuki Nakagaki and Shigeyoshi Sakaki	CASPT2 study of inverse sandwich-type dinuclear 3d transition metal complexes of eth-ylene and dinitrogen molecules: similarities and differences in geometry, electronic structure, and spin multiplicity	*Phys. Chem. Chem. Phys.*	17, 16294-16305	2015
36	Hajime Kameo, Tatsuya Kawamoto, Shigeyoshi Sakaki, and Hiroshi Nakazawa	Can One σ*-Antibonding Orbital Interact with Six Electrons of Lewis Bases? Analysis of a Multiply Interacting σ* Orbital	*Organometallics*	33, 5960-5963	2015
37	Shigeyoshi Sakaki	Theoretical and Computational Study of a Complex System Consisting of Transition Metal Element(s): How to Understand and Predict Its Geometry, Bonding Nature, Molec-ular Property, and Reaction Behavior	*Bull. Chem. Soc. Jpn.*	88, 889-938	2015
田中 一義					
38	Naoki Haruta, Tohru Sato, and Kazuyoshi Tanaka	Reactivity Index for Diels-Alder Cycloadditions to Large Polycyclic Aromatic Hydrocarbons Using Vibronic Coupling Density	*Tetrahedron Lett.*	56, 590-594	2015
39	Takuya Matsumoto, Kazuo Tanaka, Kazuyoshi Tanaka, and Yoshiki Chujo	Synthesis and Characterization of Heterofluorenes Containing Four-coordinated Group 13 Elements: Theoretical and Experimental Analyses and Comparison of Structures, Optical Properties and Electronic States	*Dalton Trans.*	44, 8697-8707	2015
40	Yuichi Hirai, Takayuki Nakanishi, Yuichi Kitagawa, Koji Fushimi, Tomohiro Seki, Hajime Ito, Hiroyuki Fueno, Kazuyoshi Tanaka, Toshifumi Satoh, and Yasuchika Hasegawa	Luminescent Coordination Glass: Remarkable Morphological Strategy for Assembled Eu (III) Complexes	*Inorg. Chem.*	54, 4364-4370	2015
41	Furitsu Suzuki, Katsuyuki Shizu, Hisafumi Kawaguchi, Shinya Furukawa, Tohru Sato, Kazuyoshi Tanaka, and Hironori Kaji	Multiscale Simulation of Charge Transport in a Host Material, *N, N'*-Dicarbazole-3,5-benzene (mCP), for Organic Light-Emitting Diodes	*J. Mater. Chem. C*	3, 5549-5555	2015
42	Daisuke Sakamaki, Soichiro Yano, Toshiyuki Kobashi Shu Seki, Takuya Kurahashi, Seijiro Matsubara, Akihiro Ito, and Kazuyoshi Tanaka	A Triphenylamine with Two Phenoxy Radicals Having Unusual Bonding Patters and a Closed-Shell Electronic State	*Angew. Chem. Int. Ed.*	54, 8267-8270	2015
43	Shintaro Iwamoto, Yuu Inatomi, Daisuke Ogi, Satoshi Shibayama, Yukiko Murakami, Minami Kato, Kazuyuki Takahashi, Kazuyoshi Tanaka, Nobuhiko Hojo, and Yohji Misaki	New Tris- and Pentakis-Fused Donors Containing Extended Tetrathiafulvalenes: New Positive Electrode Materials for Reachargeable Batteries	*Beilstein J. Org. Chem.*	11, 1136-1147	2015

№	Authors	Title	Journal	Volume (Number), first page to last page	year
44	Masashi Uebe, Akihiro Ito, Yuichiro Kameoka, Tohru Sato, and Kazuyoshi Tanaka	Fluorescence Enhancement of Non-Fluorescent Triphenylamine: A Recipe to Utilize Carborane Cluster Substituents	*Chem. Phys. Lett.*	633, 190-194	2015
45	Katsuyuki Shizu, Hiroki Noda, Hiroyuki Tanaka, Masatsugu Taneda, Motoyuki Uejima, Tohru Sato, Kazuyoshi Tanaka, Hironori Kaji, and Chihaya Adachi	Highly Efficient Blue Electroluminescence Using Delayed-Fluorescence Emitters with Large Overlap Density between Luminescent and Ground States	*J. Phys. Chem. C*	119, 26283-26289	2015
46	Takayuki Maegawa, Yasuyuki Irie, Hiroaki Imoto, Hiroyuki Fueno, Kazuyoshi Tanaka, and Kensuke Naka	para-Bisvinylhexaisobutyl-Substituted T_8 Caged Monomer: Synthesis and Hydrosilylation Polymerization	*Polym. Chem.*	6, 7500-7504	2015
47	Liangchun Li, Tsukasa Matsuo, Daisuke Hashizume, Hiroyuki Fueno, Kazuyoshi Tanaka, and Kohei Tamao	Coplanar Oligo(*p*-phenylenedisilenylene)s as Si=Si Analogues of Oligo(*p*-phenylenevinylene)s: Evidence for Extended π-Conjugation through the Carbon-Silicon π-Frameworks	*J. Am. Chem. Soc.*	137, 15026-15035	2015
48	Ryohei Kurata, Kazuyoshi Tanaka, and Akihiro Ito	Isolation and Characterization of Persistent Radical Cation and Dication of 2,7-Bis(dianisylamino)pyrene	*J. Org. Chem.*	81, 137-145	2016
49	Megumi Kobayashi, Naoki Hayakawa, Tsukasa Matsuo, Baolin Li, Takeo Fukunaga, Daisuke Hashizume, Hiroyuki Fueno, Kazuyoshi Tanaka, and Kohei Tamao	(Z)-1,2-Di(1-pyrenyl)disilene: Synthesis, Structure, and Intramolecular Charge-Transfer Emission	*J. Am. Chem. Soc.*	138, 758-761	2016
50	Akihiro Ito, Masashi Uebe, Kazuki Takahashi, Hiroshi Ishikawa, Daisuke Sakamaki, Hiroyasu Sato, Takashi Matsumoto, and Kazuyoshi Tanaka	Synthesis and Characterization of 6,13-Diamino-Substituted Pentacenes	*Chem. Eur. J.*	22, 2165-2170	2016
51	Hirotaka Uji, Kazuyoshi Tanaka, and Shunsaku Kimura	O_2-Triggered Directional Switching of Photocurrent in Self-Assembled Monolayer Composed of Porphyrin- and Fullerene-Terminated Helical Peptides on Gold	*J. Phys. Chem. C*	120, 3684-3689	2016
齋藤　拓也					
52	Takuya Saito, and Takahiro Sakaue	Driven anomalous diffusion: An example from polymer stretching	*Phys. Rev. E*	92, 012601	2015
多羅間　充輔					
53	M. Tarama and T. Ohta	Reciprocating motion of active deformable particles	*Europhys. Lett.*	114, 30002	2016
西本　佳央					
54	Yoshio Nishimoto, Dmitri G. Fedorov, and Stephan Irle	Third-order density-functional tight-binding combined with the fragment molecular orbital method	*Chem. Phys. Lett.*	636, 90-96	2015

№	Authors	Title	Journal	Volume (Number), first page to last page	year
55	Yoshio Nishimoto	Time-dependent density-functional tight-binding method with the third-order expansion of electron density	*J. Chem. Phys.*	143(9), 094108	2015
56	Yoshio Nishimoto, Hiroya Nakata, Dmitri G. Fedorov, and Stephan Irle	Large-Scale Quantum-Mechanical Molecular Dynamics Simulations Using Density-Functional Tight-Binding Combined with the Fragment Molecular Orbital Method	*J. Phys. Chem. Lett.*	6(24), 5034-5039	2015
57	Yoshio Nishimoto	DFTB/PCM Applied to Ground and Excited State Potential Energy Surfaces	*J. Phys. Chem. A*	120(5), 771-784	2016
伊勢川　美穂					
58	Miho Isegawa, Satoshi Maeda, Dean J. Tantillo, Keiji Morokuma	Ionization Energies and Aqueous Redox Potentials of Small Organic Molecules: Capabilities and Limitations of Modern Methods	*J. Chem. Theory Comput.*	12, 2272-2284	2016
鈴木　聡					
59	S.Suzuki, S. Maeda, K. Morokuma	Exploration of Quenching Pathways of Multiluminescent Acenes Using the GRRM Method with the SF-TDDFT Method	*J. Phys. Chem. A*	119 (47), 11479-11487	2015
Akhilesh Kumar Sharma					
60	W. M. C. Sameera, Akhilesh Kumar Sharma, Satoshi Maeda, Keiji Morokuma	Artificial Force Induced Reaction Method for Systematic Determination of Complex Reaction Mechanisms	*Chem. Rec.*	DOI: 10.1002/ ter.201600052	2016
青野　信治					
61	Shinji Aono, Toshifumi Mori, and Shigeyoshi Sakaki	3D-RISM-MP2 Approach to Hydration Structure of Pt(II) and Pd(II) Complexes: Unusual H-Ahead Mode vs Usual O-Ahead One	*J. Chem. Theory Comput.*	12 (3), 1189-1206	2016
W. M. C. Sameera					
62	S. Sasaki, S. Suzuki, W. M. C. Sameera, K. Igawa, K. Morokuma, G. Konishi	Highly twisted N,N-dialkylamines as a design strategy to tune simple aromatic hydrocarbons as steric environment-sensitive fluorophores	*J. Am. Chem. Soc*	138, 8194-8206	2016
63	Y. Takeda, A. Kuroda, W. M. C. Sameera, K. Morokuma, S. Minakata	Palladium-catalyzed regioselective ring-opening borylation of 2-arylaziridines with bis(pinacolato)diboron: experimental and computational studies	*Chem. Sci.*	7, 6141-6152	2016
64	W. M. C. Sameera, S. Maeda, K. Morokuma	Computational catalysis using the artificial force induced reaction (AFIR) method	*Acc. Chem. Res.*	49, 763-773.	2016
65	I. Funes-Ardoiz, W. M. C. Sameera, R. M. Romero, C. Martínez, J. A. Souto, D. Sampedro, K. Muñiz, F. Maseras	DFT rationalization of the diverse outcomes of the iodine(III)-mediated oxidative amination of alkenes	*Chem. Eur. J.*	22, 1-10.	2016

№	Authors	Title	Journal	Volume (Number), first page to last page	year
66	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*	137, 11085-11094	2016
67	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.*	115, 5678-5796.	2015
68	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

２．共同研究者受入れ状況（平成27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	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
諸熊 奎治	W.M.C. SAMEERA	外国人共同研究者	平成26年9月16日～ 平成28年7月31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	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
諸熊 奎治	NGUYEN Hoa My	招へい外国人学者	平成27年6月6日～ 平成27年8月28日	ベトナム大学（ベトナム）・講師	メチシリン耐性黄色ブドウ球菌(MRSA)のベータラクタム抗生物質抵抗性の計算化学的方法による研究
諸熊 奎治	YANG Ming-Chung	外国人共同研究者	平成27年8月10日～ 平成28年8月9日	National Chiayi University（台湾）・博士研究員	複雑分子系の計算化学的研究
永瀬　茂	YUAN Kun	外国人共同研究者	平成27年10月10日～ 平成28年1月10日	Xi'an Jiaotong University（中国）・PhD学生	ナノカーボンの分子間相互作用の量子化学計算
諸熊 奎治	EISENSTEIN Odile	招へい外国人学者	平成27年10月23日～ 平成27年11月21日	University of Montpellier 2（フランス）・名誉教授	有機金属化学と均一系触媒反応の理論化学・計算化学的研究
諸熊 奎治	ZHAO Yanying	招へい外国人学者	平成27年12月1日～ 平成28年11月30日	Zhejiang Sci-Tech University（中国）・准教授	複雑分子系の理論と計算研究
榊　茂好	KWAN HUNG, Enrique	外国人共同研究者	平成28年2月1日～ 平成29年1月31日	中央大学（日本）・博士研究員	アルカンの触媒的脱水素化反応の計算化学研究

3．海外渡航一覧（平成27年度）

職　　名	氏　　名	期間（自）	期間（至）	目 的 地
准　教　授	池田　昌司	2015/5/2	2015/5/9	フランス
研　究　員	諸熊　奎治	2015/6/6	2015/6/14	中国
共同研究者	W.M.C. Sameera	2015/6/6	2015/6/14	中国
共同研究者	RAMOZZI, Romain Raurcel, Marcel	2015/6/6	2015/6/14	中国
共同研究者	JAMAL, Adeel Ashraf	2015/6/6	2015/6/14	中国
特定研究員	青野　信治	2015/6/8	2015/6/13	中国
特定研究員	中垣　雅之	2015/6/8	2015/6/13	中国
特定研究員	多羅間　充輔	2015/6/16	2015/7/3	ドイツ
研　究　員	諸熊　奎治	2015/7/12	2015/7/19	アメリカ合衆国
研　究　員	諸熊　奎治	2015/8/23	2015/8/26	中国
研　究　員	諸熊　奎治	2015/8/31	2015/9/7	ノルウェー、スウェーデン
准　教　授	池田　昌司	2015/10/13	2015/10/17	大韓民国
研　究　員	榊　　茂好	2015/11/19	2015/11/30	スペイン
研　究　員	諸熊　奎治	2015/11/21	2015/11/30	スペイン
共同研究者	JAMAL, Adeel Ashraf	2015/12/13	2015/12/20	アメリカ合衆国
研　究　員	諸熊　奎治	2015/12/14	2015/12/21	アメリカ合衆国
研　究　員	榊　　茂好	2015/12/15	2015/12/21	アメリカ合衆国
研　究　員	永瀬　　茂	2015/12/15	2015/12/21	アメリカ合衆国
特定研究員	多羅間　充輔	2015/12/17	2015/12/20	アメリカ合衆国
研　究　員	諸熊　奎治	2016/1/24	2016/1/29	台湾
研　究　員	榊　　茂好	2016/1/24	2016/1/29	台湾
研　究　員	永瀬　　茂	2016/1/24	2016/1/29	台湾
共同研究者	W.M.C. Sameera	2016/1/24	2016/1/29	台湾
特定研究員	青野　信治	2016/1/25	2016/1/28	台湾

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13回

京都大学 福井謙一記念研究センターシンポジウム

開会式 (Opening)

［開会の辞］赤木 和夫（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)

田中 一義（京都大学 福井謙一記念研究センター） 10:15–11:15
「発光性分子材料の理論化学的設計」

西森 秀稔（東京工業大学 大学院理工学研究科） 11:30–12:30
「量子アニーリング理論とD-Waveマシン」

– 昼食 –

八尾 誠（京都大学 大学院理学研究科） 14:00–15:00
「X線自由電子レーザーとの付き合い方」

ポスターセッション (Poster session) 15:30–17:20
懇親会(Banquet) 17:30–19:00

平成28年2月5日㊎

会場：京都大学 福井謙一記念研究センター

2016. 2. 5　Fukui Institute for Fundamental Chemistry, Kyoto University

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第13回京都大学福井謙一記念研究センターシンポジウム
プログラム

日時　平成28(2016)年2月5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 10:00～15:00)

- 開会の辞　**赤木 和夫**（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

- **田中 一義** (京都大学 福井謙一記念研究センター)　司会：永瀬 茂（福井センター）
  「発光性分子材料の理論化学的設計」　・・・10:15-11:15

― 休憩 ―

- **西森 秀稔** (東京工業大学 大学院理工学研究科)　司会：佐々 真一（京大院理）
  「量子アニーリング理論とD-Waveマシン」　・・・11:30-12:30

― 昼休み ―

- **永谷 清信***(京都大学 大学院理学研究科)　司会：池田 昌司（福井センター）
  「X線自由電子レーザーとの付き合い方」　・・・14:00-15:00
  *八尾誠先生のご都合により、永谷清信先生に同内容でご代講いただく事になりました。

― 休憩 ―

ポスターセッション　(3階大会議室 15:30～17:20)

懇親会　(1階多目的ルーム 17:30～19:00)

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. 密度行列繰込み群による鉄―硫黄クラスターの構造および電子状態に関する理論的研究
○中谷 直輝、長谷川 淳也（北大触媒研）

2. Computational Investigation of the Structural Dependence of Switching Efficiency of Exchange Interaction and Hyperpolarizability on Diarylethenes
○西澤 尚平[1]、Arnaud Fihey[2]、Denis Jacquemin[2]、長谷川 淳也[3]、松田 建児[1]（京大院工[1]、ナント大 CEISAM[2]、北大触セ[3]）

3. 有限温度における分子運動エネルギーの同位体効果
○河津 励[1,2]、立川 仁典[2]（分子研[1]、横市大院生命ナノ[2]）

4. 金属－炭素結合の開殻性と三次非線形光学特性についての研究
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５．福井センターセミナー　ポスター・プログラム

第13回
福井センターセミナー
The 13th Fukui Center Seminar

2015年9月29日(火) 15:00-17:20

京都大学福井謙一記念研究センター1F 多目的室 (Room: 1F 106)
http://www.fukui.kyoto-u.ac.jp/
〒606-8103 京都市左京区高野西開町34-4（TEL075-711-7708）
(at FIFC, Kyoto Univ. on September, 29(Tue.), 2015)

15:00～15:40　W. M. C. SAMEERA (FIFC)

“Artificial force induced reaction method for mechanisms involving transition metal complexes and clusters”

15:40～16:20　Takuya SAITO (FIFC)

“Driven Anomalous Diffusion in Polymer Stretching”

Break (10 min.)

16:30～17:20　Masayuki OHZEKI (Kyoto Univ.)

“Accelerated Langevin Dynamics and its application to machine learning”

多数の方のご来場を歓迎いたします
We welcome all of you to join.

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