京都大学
福井謙一記念研究センター

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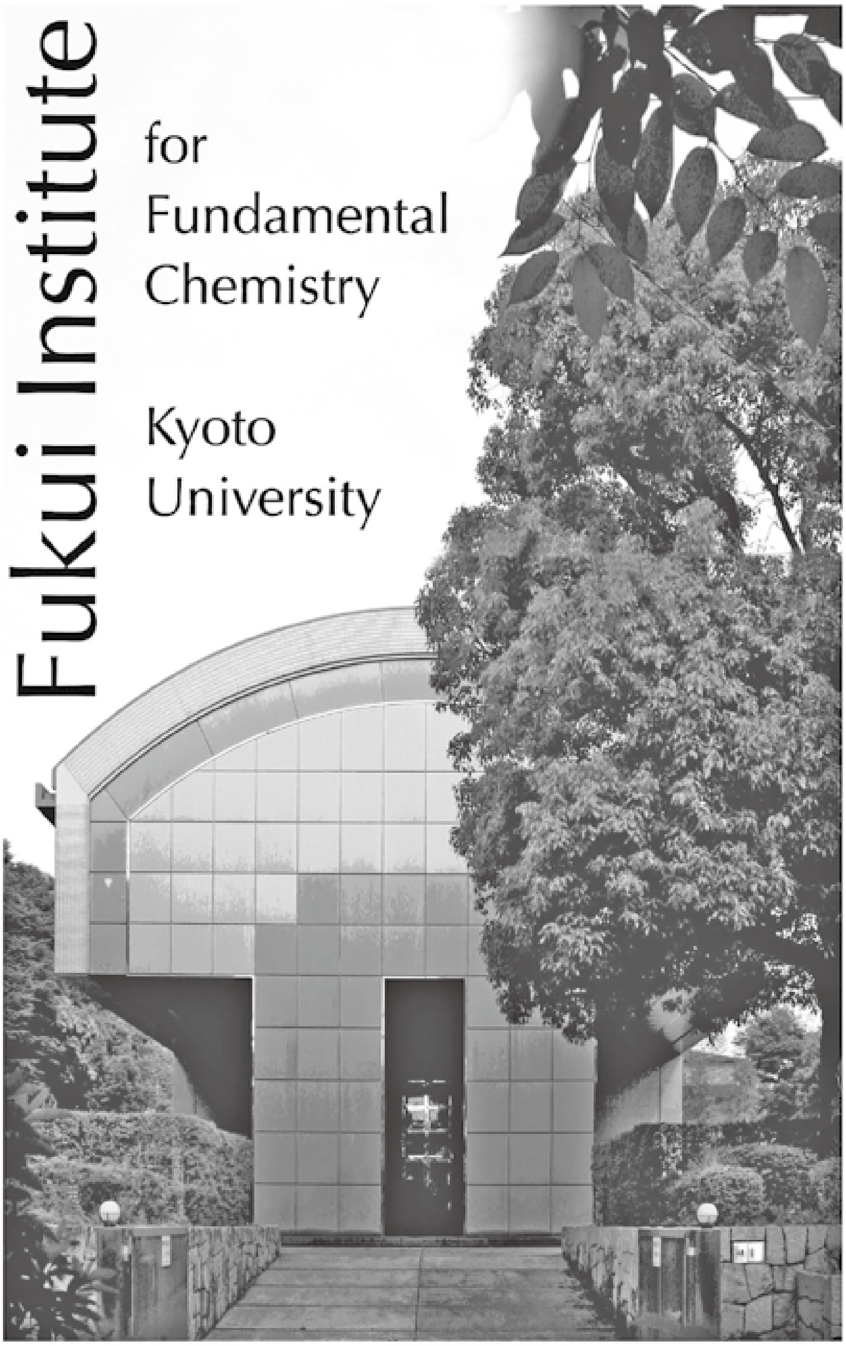
2016



京都大学
福井謙一記念研究センター

は じ め に

2016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1名ずつ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、2012年にシニアリサーチフェローに就任され、この年の11月には、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、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。諸熊先生には2015年からはFIFCリサーチフェローとして研究ならびに若手人材育成にご尽力いただいております。

2009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d電子複合系の理論化学に関する研究を推進しておられます。

また、2012年にはシニアリサーチフェローとして永瀬茂先生（分子科学研究所名誉教授）を招聘しました。永瀬先生は、望む構造、物性、機能を持つ分子を自在に組み立てて思うように反応させる理論と計算およびコンピューターシミュレーションの開発において顕著な業績を挙げられました。2015年からはFIFCリサーチフェローとして高周期典型元素と遷移金属元素化学種の理論化学に関する研究を進めておられます。同じ年に、シニアリサーチフェローとして田中一義先

生（京都大学名誉教授）を招聘しました。田中一義先生は導電性や磁性を有する有機化合物など量子機能材料に関する物理化学的研究において優れた多くの業績を挙げておられ、現在は元素ブロックを有する分子・高分子の理論化学に関する研究を展開されています。さらに、2016年には、化学反応電子動力学の基礎理論研究において著名な高塚和夫先生（東京大学名誉教授）をリサーチリーダーとして招聘しました。センターでは非断熱電子動力学理論による化学反応の解析に関する研究を推進しておられます。

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。2016年には、化学の将来の発展のために若手研究者の育成の大切さを説いておられた福井博士の遺志を汲み、基礎化学・理論化学の分野で顕著な研究業績を挙げた若手研究者を顕彰する「福井謙一奨励賞」を創設しました。第1回の福井謙一奨励賞は、「理論化学研究に立脚した量子干渉現象の分子エレクトロニクスへの展開」に関する成果が評価された九州大学の辻雄太博士に授与されました。

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、東京大学、名古屋大学、分子科学研究所の教授になるなど、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年の福井先生のご逝去の後、2002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、赤木和夫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2月に国際学術連携研究室（2016年12月に国際連携インターディシプリナリー研究推進室と改組）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。2016年は、毎年実施している福井センターシンポジウムに加え、複雑・複合系の理論計算科学に関する日・仏・スペイン合同シンポジウムを開催しました。化学、物理学、生命科学にまたがる複雑・複合系の理論計算科学に関する研究成果を三カ国の若手、中堅研究者が互いに紹介し合い、当研究分野の更なる展開を議論する場となりました。

さらに社会貢献活動の一環として、2011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。

加えて、来る2018年は福井謙一先生の生誕百年にあたります。この記念すべき年に福井先生の業績を改めて振り返る機会を設ける意味で、生誕百年記念行事を企画しております。具体的には、福井先生の誕生日である10月4日に合わせて、シンポジウム、記念式典、京大総合博物館における記念展などを開催する予定で、センター内に福井謙一生誕百年記念事業実施委員会を立ち上げ、行事の実施に向けた準備を進めているところです。

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。

2017年10月

京都大学福井謙一記念研究センター長

田中勝久

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http://www.fukui.kyoto-u.ac.jp/wp-content/themes/fifc/pdf/AnnualReport2016.pdf）

Ⅰ　専任教員・スーパーバイザー

１．教員組織

平成２８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		田中 勝久	工学研究科材料化学専攻
副センター長		谷村 吉隆	理学研究科化学専攻
副センター長		(欠員中)	
協議員	工学研究科長	北村 隆行	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	山本 潤	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	山本 量一	工学研究科化学工学専攻
	教授	高田 彰二	理学研究科生物科学専攻
	教授	林 重彦	理学研究科化学専攻

総合研究部門	准教授	(欠員中)	
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
国際連携インターディシプリナリー研究推進室	特定助教	西本 佳央	専任
諸熊グループ	FIFC リサーチフェロー	諸熊 奎治	研究員
永瀬グループ	FIFC リサーチフェロー	永瀬 茂	研究員
榊グループ	シニアリサーチフェロー	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
高塚グループ	リサーチリーダー	高塚 和夫	研究員
榊グループ	研究員	北浦 和夫	研究員

2．教員プロフィール

(1) センター長

【氏名（ふりがな）】	赤木　和夫　（あかぎ　かずお）
【職名】	教授
【所属】	工学研究科高分子化学専攻
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【ホームページ】	http://www.fps.polym.kyoto-u.ac.jp
【研究分野】	高分子化学、液晶化学、物質化学
【現在の研究課題】	導電性、液晶性、発光性、階層らせん性の共役系高分子の合成と性質
【研究内容キーワード】	導電性高分子、液晶性共役高分子、不斉液晶反応場、階層構造制御
【最終学歴】	京都大工学研究科博士後期課程
【学位】	工学博士
【略歴】	福井大工助手、筑波大物質工講師、助教授、教授、同大学院数理物質科学研究科教授、学際物質科学研究センター長
【在外研究歴】	カリフォルニア大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).
【学術関係の受賞など】	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）、日本化学会賞（2016 年度）

⑵ 副センター長

【氏名（ふりがな）】	田中　勝久　（たなか　かつひさ）
【職名】	教授
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【研究分野】	無機固体化学
【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
【学歴】	1984 年 3 月 京都大学工学部工業化学科卒業 1986 年 3 月 京都大学大学院工学研究科工業化学専攻修士課程修了
【学位】	1991 年 3 月 京都大学工学博士
【略歴】	1986 年 4 月 三重大学工学部助手 1989 年 4 月 京都大学工学部助手 1999 年 7 月 京都工芸繊維大学工芸学部助教授 2004 年 4 月 京都大学大学院工学研究科教授
【所属学会】	日本セラミックス協会、日本化学会、応用物理学会、日本物理学会、粉体粉末冶金協会、日本材料学会、日本金属学会、Materials Research Society、Optical Society of America
【学会活動】	日本セラミックス協会理事、粉体粉末冶金協会理事
【主な著書、学術論文】 （過去 5 年以内）	1. 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. 2. 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. 3. 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. 4. 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. 5. 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. 6. 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. 7. K. Fujita, T. Kawamoto, I. Yamada, O. Hernandez, N. Hayashi, H. Akamatsu, W. Lafargue-Dit-Hauret, X. Rocquefelte, M. Fukuzumi, P. Manuel, A. J. Studer, C. Knee, and K. Tanaka, “$LiNbO_3$-type $InFeO_3$: Room-temperature polar magnet without second-order Jahn-Teller active ions”, *Chemistry of Materials* **28** (2016) 6644-6655.
【学術関係の受賞など】	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. “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.
【学術関係の受賞など】	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 11. 2016年 2016 Thomson Reuters Highly Cited Researcher 12. 2016年 2016 Fred Basolo Medal for Outstanding Research in Inorganic Chemistry 13. 2016年 1st Air Liquide Awards on Essential Small Molecules 2016 14. 2017年 第58回藤原賞

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【主な著書、学術論文】（過去 5 年以内）	1. Yusuke Matsumi, Hiroshi Nakano, Hirofumi Sato, “Constant-potential molecular dynamics simulations on an electrode-electrolyte system: calculation of static quantities and comparison of two polarizable metal electrode models” *Chem. Phys. Lett.* **681**, 80-85 (2017). 2. Yuichiro Yoshida, Hirofumi Sato, John W. R. Morgan, David J. Wales, “Potential energy landscapes of tetragonal pyramid molecules” *Chem. Phys. Lett.* **664**, 5-9 (2016). 3. 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). 4. Kento Kasahara and Hirofumi Sato, “A theory of diffusion controlled reactions in polyatomic molecule system” *J. Chem. Phys.* **145**(19), 194502 (2016). 5. Hirofumi Sato, “A modern solvation theory: quantum chemistry and statistical chemistry” *Phys. Chem. Chem. Phys.* **15**(20), 7450-7465 (2013).
【学術関係の受賞など】	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. S. Bono, Y. Takanishi and J. Yamamoto, Effects of layer order on the mobility of mesogenic molecules in SmA liquid-crystalline emulsions, *Europhys. Lett.,* **113**, 56004 (5P) (2016). 2. E. Gorecka, N. Vaupotič, A. Zep, D. Pociecha, J. Yoshioka, J. Yamamoto, and H. Takezoe, A Twist-Bend Nematic (NTB)Phase of Chiral Materials, *Angew. Chem.* **127**, (2015) 10293-10297. 3. Y. Kimoto, A. Nishizawa, Y. Takanishi, A. Yoshizawa and J. Yamamoto, Layer modulated smectic-C phase in liquid crystals with a terminal hydroxyl group, *Phys. Rev. E,* **89**, 042503 (2014). 4. Y. Uchida, Y. Takanishi and J. Yamamoto, Controlled Fabrication and Photonic Structure of Cholesteric Liquid Crystalline Shells, *Adv. Mat.,* **25** (2013) 3234-3237. 5. J. Yoshioka, Y. Takanishi and J. Yamamoto, Dispersion relations of director fluctuations along the direction perpendicular to the helical axis in cholesteric liquid crystals, *Europhys. Lett.,* **98** (2012) 16006(5P).
【学術関係の受賞など】	2015 年日本液晶学会業績賞

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【主な著書、学術論文】（過去 5 年以内）	1. Y. Doi, A. Matsumoto, T. Inoue, T. Iwamoto, A. Takano, Y. Matsushita, Y. Takahashi, and H. Watanabe, "Re-examination of terminal relaxation behavior of high-molecular-weight ring polystyrene melts", *Rheol. Acta,* **56**:567-581 (2017). 2. O. M. Kwon, H. Watanabe, K. H. Ahn, and S. J. Lee, "Interplay between structure and property of graphene nanoplatelet networks formed by an electric field in a poly(lactic acid) matrix", *J. Rheol.,* **61**, 291-303 (2017) 3. Y. Matsumiya, H. Watanabe, O. Urakawa, and T. Inoue, "Experimental Test for Viscoelastic Relaxation of Polyisoprene Undergoing Monofunctional Head-to-Head Association and Dissociation", *Macromolecules,* **49**, 7088-7095 (2016). 4. S. Ankiewicz, H. Orbey, H. Watanabe, H. Lentzakis, and J. Dealy, On the use of continuous relaxation spectra to characterize model polymers", *J. Rheol.,* **60**, 1115-1120 (2016) 5. 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).

	6. 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). 7. 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). 8. 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). 9. 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). 10. 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 11. 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). 12. 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). 13. 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). 14. 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). 15. 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). 16. 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). 17. 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). 18. 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). 19. 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). 20. 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).
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【学術関係の受賞など】	ドイツ政府　ﾌｨﾘｯﾌﾟ・ﾌﾗﾝﾂ・ﾌｫﾝ・ｼﾞｰﾎﾞﾙﾄ賞（2008年） ﾙｰﾏﾆｱ科学ｱｶﾃﾞﾐｰ　ﾄﾞﾗｺﾞﾐｰﾙ・ﾌﾙﾑｾﾞｽｺ賞（2006年） 米国ｾﾗﾐｯｸｽ学会　ﾘﾁｬｰﾄﾞ・ﾌﾙﾗｰｽ賞（2004年）

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【主な著書、学術論文】 （過去 5 年以内）	1. Simon K. Schnyder, Yuki Tanaka, John J. Molina, and Ryoichi Yamamoto, Collective motion of cells crawling on a substrate: roles of cell shape and contact inhibition, *Scientific Reports,* in print. 2. N. Oyama, J. J. Molina, R. Yamamoto, Purely hydrodynamic origin for swarming of swimming particles, *Phys. Rev. E* **93**, 043114 (2016). 3. J. J. Molina, K. Otomura, H. Shiba, H. Kobayashi, M. Sano, and R. Yamamoto, Rheological evaluation of colloidal dispersions using the smooth profile method: formulation and applications, *J. Fluid Mech.* **792**, 590-619 (2016). 4. A. J. Dunleavy, K. Wiesner, R. Yamamoto, and C. P. Royall, Mutual information reveals multiple structural relaxation mechanisms in a model glassformer, *Nature Communications* **6**, 6089 (2015). 5. S. Yasuda and R. Yamamoto, Synchronized molecular dynamics simulation via macroscopic heat and momentum transfer: an application to polymer lubrication, *Phys. Rev. X* **4**, 041011 (2014). 6. J. J. Molina and R. Yamamoto, Direct numerical simulations of rigid body dispersions. I. Mobility/Friction tensors of assemblies of spheres, *J. Chem. Phys.* **139**, 234105 (2013). 7. H. Mizuno and R. Yamamoto, General constitutive model for supercooled liquids: Anomalous transverse wave propagation, *Phys. Rev. Lett.* **110**, 095901 (2013).
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【所属学会】	日本物理学会、分子シミュレーション研究会
【主な著書、学術論文】 （過去5年以内）	1. 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. 5. H. Mizuno, L.E. Silbert, and M. Sperl, “Spatial Distributions of Local Elastic Moduli Near the Jamming Transition”, *Physical Review Letters,* Vol.**116**, p.068302 (5pages), 2016.
【学術関係の受賞など】	日本物理学会第11回若手奨励賞（2017年3月）

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【研究内容キーワード】	密度汎関数強束縛法・フラグメント分子軌道法・エネルギー微分
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【主な著書、学術論文】（過去 5 年以内）	1. Nishimoto, Y. “Analytic Hyperpolarizability and Polarizability Derivative with Fractional Occupation Numbers for Large Extended Systems”, *J. Chem. Phys.* 2017, **146**. 084101. 2. Nishimoto, Y.; Fedorov, D. G. “Three-body expansion of the fragment molecular orbital method combined with density-functional tight-binding”, *J. Comput. Chem.* 2017, **38**, 406-418. 3. Nishimoto, Y.; Irle, S. “Quantum Chemical Prediction of Vibrational Spectra of Large Molecular Systems with Radial or Metallic Electronic Structure”, *Chem. Phys. Lett.* 2017, **667**, 317-321. 4. Nakata, H.; Nishimoto, Y.; Fedorov, D. G. “Analytic second derivative of the energy for density-functional tight-binding combined with the fragment molecular orbital method”, *J. Chem. Phys.* 2016, **145**, 044113. 5. Nishimoto, Y.; Fedorov, D. G. “The fragment molecular orbital method combined with density-functional tight-binding and the polarizable continuum model”, *Phys. Chem. Chem. Phys.* 2016, **18**, 22047-22061. Selected as a front cover picture.
【学術関係の受賞など】	日本学術振興会特別研究員（DC1）　2012.4-2015.3

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【主な著書、学術論文】 （過去 5 年以内）	過去 5 年間に約 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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【主な著書、学術論文】 （過去 5 年以内）	1. X. Lu, L. Feng, T. Akasaka, and S. Nagase, Current Statues and Future Developments of Endohedral Metallofullerenes, *Chem. Soc. Rev.,* **41**, 7723-7760 (2012). 2. S. Nagase, Multiple Bonds between Lead Atoms and Short Bonds between Transition Metals, *Pure Appl. Chem.,* **85**, 649-659 (2013). 3. X. Lu, T. Akasaka, and S. Nagase, Carbide Cluster Metallofullerenes: Structure, Properties, and Possible Origin, *Acc. Chem. Res.,* **46**, 1627-1635 (2013). 4. M. Yamada, T. Akasaka, and S. Nagase, Carbene Additions to Fullerenes, *Chem. Rev.,* **113**, 7209-7264 (2013). 5. 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). 6. 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). 7. 赤阪健，山田道夫，前田優，永瀬茂，化学の要点シリーズ 17「フラーレンの化学」（日本化学会編），共立出版 (2016).
【学術関係の受賞など】	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】	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）
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【所属学会】	日本化学会、触媒学会、近畿化学協会、ケイ素化学協会、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 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). 3. 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, W. Guan, S. Sakaki, T. Kurahashi, S. Matsubara, *ACS Catalysis,* **5**, 1-10 (2015). 4. 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). 5. 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). 6. 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). 7. Theoretical Study of Hydrogenation Catalysis of Phosphorus Compound and Prediction of Catalyst with High Activity and Wide Application Scope, G. Zeng, S. Maeda, T. Taketsugu, S. Sakaki, *ACS Cat.,* **6**, 4859-4870 (2016). 8. Hetero-dinuclear complexes of 3d metals with a bridging dinitrogen ligand: theoretical prediction of the characteristic features of geometry and spin multiplicity, M. Nakagaki, S. Sakaki, *Phys. Chem. Chem. Phys.,* **18**, 26365-26375 (2016). 9. Catalytic Hydrogenation of Carbon Dioxide with Ammonia-Borane by Pincer-Type Phosphorus Compounds: Theoretical Prediction, GX. Zeng, S. Maeda, T. Taketsugu, S. Sakaki, *J. Am. Chem. Soc.,* **138**, 13481-13484 (2016)
【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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1. 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).
2. 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).
3. 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).
4. 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).
5. 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).
6. 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).
7. Vibronic Couplings in C60 Derivatives for Organic Photovoltaics (N. Iwahara, T. Sato, K. Tanaka, and H. Kaji) *Chem. Phys. Lett.,* **590**, 169-174 (2013).
8. 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).
9. Enhancement of Fluorescence in Anthracene by Chlorination: Vibronic Coupling and Transition Dipole Moment Density Analysis (M. Uejima, T. Sato, K. Tanaka, and H. Kaji) *Chem. Phys*., **430**, 47-55 (2014).
10. 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).
11. 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).
12. 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).
13. 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).
14. 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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19. 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).
20. 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).
21. Enhanced Electroluminescence from a Thermally Activated Delayed-Fluorescence Emitter by Suppressing Nonradiative Decay (K. Shizu, M. Uejima, H. Nomura, T. Sato, K. Tanaka, H. Kaji, and C. Adachi) *Phys. Rev. Appl.,* **3**, 014001 1-7 (2015).
22. Strategy for Designing Electron Donors for Thermally Activated Delayed Fluorescence Emitters (K. Shizu, H. Tanaka, M. Uejima, T. Sato, K. Tanaka, H. Kaji, and C. Adachi) *J. Phys. Chem., C,* **119**, 1291-1297 (2015).
23. Reactivity Index for Diels-Alder Cycloadditions to Large Polycyclic Aromatic Hydrocarbons Using Vibronic Coupling Density (N. Haruta, T. Sato, and K. Tanaka) *Tetrahedron Lett.,* **56**, 590-594 (2015).
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26. 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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29. 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).

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31. 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).
32. 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).
33. 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).
34. (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).
35. 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).
36. 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).
37. Synthesis and Magnetic Properties of Linear Two-coordinate Monomeric Diaryliron(II) Complexes Bearing Fused-ring Bulky “Rind” Groups (S. Goda, M. Nikai, M. Ito, D. Hashizume, K. Tamao, A. Okazawa, N. Kojima, H. Fueno, K. Tanaka, Y. Kobayahsi, and T. Matsuo) *Chem. Lett.,* **45**, 634-636 (2016).
38. Thermodynamical Vibronic Coupling Constant and Density: Chemical Potential and Vibronic Coupling in Reactions (T. Sato, N. Haruta, and K. Tanaka) *Chem. Phys. Lett.,* **652**, 157-161 (2016).
39. Color Tuning of Alternating Conjugated Polymers Composed of Pentaazaphenanthrene by Modulating Their Unique Electronic Structures Involving Isolated-LUMOs (H. Watanabe, M. Hirose, K. Tanaka, K. Tanaka, and Y. Chujo) *Polym. Chem.,* **7**, 3674-3680 (2016).
40. Arsole-Containing π-Conjugated Polymer by the Post-Element-Transformation Technique (Y. Matsumura, M. Ishidoshiro, Y. Irie, H. Imoto, K. Naka, K. Tanaka, S. Inagi, and I. Tomita) *Angew. Chem. Int. Ed.,* **55**, 15040-15043 (2016).
41. Radical Cation of an Oligoarylamine Having a Nitroxide Radical Substituent: A Coexistent Molecular System of Localized and Delocalized Spins (A. Ito, R. Kurata, Y. Noma, Y. Hirao, and K. Tanaka) *J. Org. Chem.,* **81**, 11416-11420 (2016).
42. Borophosphonate Cages as Element-blocks: Ab Initio Calculation of the Electronic Structure of a Simple Borophosphonate, $[HPO_3BH]_4$, and Synthesis of Two Novel Borophosphonate Cages with Polymerizable Groups (J. Zapico, M. Shirai, R. Sugiura, N. Idota, H. Fueno, K. Tanaka, and Y. Sugahara) *Chem. Lett.,* **46**, 181-184 (2017).

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【所属学会】	日本化学会、日本薬学会
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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).
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【研究分野】	ソフトマター物理
【現在の研究課題】	選択的溶媒和効果を取り入れた電気二重層のダイナミクスの研究、アクティブ流体力学
【研究内容キーワード】	選択的溶媒和効果、電気二重層、アクティブマター
【学歴】	2014年3月　京都大学大学院理学研究科物理学宇宙物理学専攻博士後期課程修了
【学位】	2014年3月　理学博士（京都大学）
【略歴】	2012年4月　JSPS Research Fellow (DC) 2014年4月　JSPS Research Fellow (PD) 2016年12月　京都大学福井謙一記念研究センターフェロー
【所属学会】	日本物理学会
【主な著書、学術論文】（過去5年以内）	1. “Collision between chemically-driven self-propelled drops”, Shunsuke Yabunaka and Natsuhiko Yoshinaga, *Journal of Fluid Mechanics,* November 2016, Pages 205-233 2. “Structure formation due to antagonistic salts”, Akira Onuki, Shunsuke Yabunaka, Takeaki Araki and Ryuichi Okamoto *Current Opinion in Colloid & Interface Science* Volume 22, April 2016, Pages 59-64 3. “Functional renormalization group approach to noncollinear magnets”, B. Delamotte, M. Dudka, D. Mouhanna, and S. Yabunaka, *Phys. Rev. B* **93**, 064405 4. “Hydrodynamics in bridging and aggregation of two colloidal particles in a near-critical binary mixture”, Shunsuke Yabunaka, Ryuichi Okamoto and Akira Onuki, *Soft Matter,* 2015, **11**, 5738 5. “Geometric pumping induced by shear flow in dilute liquid crystalline polymer solutions”, Shunsuke Yabunaka and Hisao Hayakawa, *J. Chem. Phys.* **142**, 054903 (2015)
【学術関係の受賞など】	JSPS Research Fellowships for Young Scientists(DC) 2012-2014 JSPS Research Fellowships for Young Scientists(PD) 2014-2017 Journal of Chemical Physics Editors’ choice 2015

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【研究分野】	Soft matter physics, Biophysics, Computational physics
【現在の研究課題】	Structure and dynamics of cellular tissues, anomalous transport in heterogeneous media
【研究内容キーワード】	Cell migration, epithelial tissues, Lorentz model, percolation, anomalous diffusion
【学歴】	January 2010, Diploma in Physics, University of Konstanz, Konstanz, Germany May 2014, Doctor of Science , University of Düsseldorf, Düsseldorf, Germany
【学位】	Doctor of Science from University of Düsseldorf
【略歴】	June 2014 - November 2014, Postdoctoral Fellow, University of Düsseldorf December 2014 - December 2016, Postdoctoral Fellow, Department of Chemical Engineering, Kyoto University
【所属学会】	German Physical Society (DPG)
【主な著書、学術論文】 （過去 5 年以内）	1. S. K. Schnyder, T. O. E. Skinner, A. Thorneywork, D. G. A. L. Aarts, J. Horbach, R. P. A. Dullens, “Dynamic heterogeneities and non-Gaussian behaviour in 2D randomly confined colloidal fluids”, *Physical Review E* (2017). 2. M. Heinen, S. K. Schnyder, J. F. Brady, H. Löwen, “Classical liquids in fractal dimension”, *Physical Review Letters* **115**, 097801 (2015). 3. S. K. Schnyder, M. Spanner, F. Höfling, T. Franosch, J. Horbach, “Rounding of the localization transition in model porous media”, *Soft Matter* **11**, 701 (2015). 4. T. O. E. Skinner, S. K. Schnyder, D. G. A. L. Aarts, J. Horbach, R. P. A. Dullens, “Localization Dynamics of Fluids in Random Confinement”, *Physical Review Letters* **111**, 128301 (2013). 5. M. Spanner, S. K. Schnyder, F. Höfling, Th. Voigtmann, T. Franosch, “Dynamic arrest in model porous media–intermediate scattering functions”, *Soft Matter* **9**, 1604-1611 (2013).

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【研究分野】	計算化学
【現在の研究課題】	Reaction process for electrochemical and photochemical conversion of carbon dioxide
【研究内容キーワード】	触媒、分子変換機構、スペクトロスコピー、化学エネルギー変換
【学歴】	2009年9月 京都大学大学院理学研究科化学専攻博士課程修了
【学位】	2009年9月 京都大学理学博士
【略歴】	2010年1月　米国ミネソタ大学博士研究員 2013年3月　京都大学福井謙一記念研究センター研究員 2014年6月　ドイツ マックスプランク研究所化学エネルギー変換博士研究員 2016年1月　京都大学福井謙一記念研究センター研究員
【主な著書、学術論文】 （過去5年以内）	1. Copper-catalyzed Enantioselective Boron Conjugate Addition: DFT and AFIR Study on Different Selectivities of Cu(I) and Cu(II) Catalysts, M. Isegawa, W. M. C. Sameera, A. K. Sharma, T. Kitanosono, Masako Kato, S. Kobayashi, K. Morokuma, *ACS Catalysis,* (2017). 2. Ionization Energies and Aqueous Redox Potentials of Organic Molecules: Comparison of DFT, Correlated ab Initio Theory and Pair Natural Orbital Approaches, M. Isegawa, F. Neese, D. A. Pantazis, *J. Chem. Theory Comput.* **12**, 2272 (2016). 3. 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). 4. 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). 5. 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). 6. Electrostatically Embedded Molecular Tailoring Approach and Validation for Peptides, M. Isegawa, B. Wang, D. G. Truhlar, *J. Chem. Theory Comput.* **9**, 1381 (2013).

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【現在の研究課題】	蛍光分子の円錐交差探索
【研究内容キーワード】	励起状態、項間交差
【学歴】	2014 年 3 月　九州大学理学府　化学専攻修了
【学位】	2014 年 3 月　博士（理学）　九州大学
【略歴】	2014 年 4 月　福井謙一記念研究センター
【所属学会】	分子科学会、理論化学研究会
【主な著書、学術論文】 （過去 5 年以内）	1. T. Tsuneda, J.-W. Song,S. Suzuki, and K. Hirao ”On Koopmans'theorem in density functional theory” *J. Chem. Phys.* **133**, 174101 (2010). 2. S.Suzuki, 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.,* **138**, 8194-8206 (2016)
【学術関係の受賞など】	2012 年 9 月　Best Poster Awardsat the Annual Meeting of the Japan Society for Molecular Science

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【現在の研究課題】	Mechanistic study of organic and organometalic reactions
【研究内容キーワード】	DFT, AFIR, Reaction Mechanism, Stereoselectivity
【学歴】	Master of Science, Himachal Pradesh University, Shimla, India (2006)
【学位】	Ph.D., Indian Institute of Technology (IIT), Bombay, Mumbai, India (2014)
【略歴】	Research Associate, Indian Institute of Technology (IIT), Bombay, Mumbai, India (2014-2015)
【主な著書、学術論文】 （過去5年以内）	1. Akhilesh K. Sharma, Raghavan B. Sunoj, "Refined Transition-State Models for Proline-Catalyzed Asymmetric Michael Reactions under Basic and Base-Free Conditions" *J. Org. Chem.* **77** (23), 10516-10524 (2012). 2. Dmitry Katayev, Yi-Xia Jia, Akhilesh K. Sharma, Dipshikha Banerjee, Celine Besnard, Raghavan B. Sunoj, and E. Peter Kundig, "Synthesis of 3,3-Disubstituted Oxindoles by Palladium-Catalyzed Asymmetric Intramolecular α-Arylation of Amides: Reaction Development and Mechanistic Studies" *Chem. Eur. J.* **19**, 11916-11927 (2013). 3. Akhilesh K. Sharma, Dipankar Roy and Raghavan B. Sunoj, "Mechanism of Catalytic Methylation of 2-Phenylpyridine Using di-tert-Butyl Peroxide" *Dalton Trans.* **43**, 10183-10201 (2014). 4. W. M. C. Sameera, Akhilesh K. Sharma, Satoshi Maeda, Keiji Morokuma, "Artificial Force Induced Reaction Method for Systematic Determination of Complex Reaction Mechanisms" *Chemical Record,* **16** (5), 2349-2363 (2016). 5. Ming-Chung Yang, Akhilesh K. Sharma, W. M. C. Sameera, Keiji Morokuma, and Ming-Der Su, "Theoretical Study of Addition Reactions of L4M(M = Rh, Ir) and L2M(M = Pd, Pt) to Li+@C60" *J. Phys. Chem. A* **121**(13), 2665-2673 (2017). 6. Miho Isegawa, W. M. C. Sameera, Akhilesh K. Sharma, Taku Kitanosono, Masako Kato, Shu Kobayashi, and Keiji Morokuma, "Copper-catalyzed Enantioselective Boron Conjugate Addition: DFT and AFIR Study on Different Selectivities of Cu(I) and Cu(II) Catalysts" *ACS Catal.* DOI: 10.1021/acscatal.7b01152.
【学術関係の受賞など】	"2014 Eli Lilly and Company Asia Outstanding Thesis Award" for Best Thesis Fellowship from council for Scientific and Industrial Research (CSIR), India to Pursue PhD.

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【現在の研究課題】	Theoretical/Computational Chemistry for Complex Molecular Systems
【研究内容キーワード】	Transition state, Catalysis, Catalytic reaction, Reaction mechanism
【学歴】	Ph.D. (Nanoscience Technology), Chulalongkorn University, Thailand (2016) B.Sc. (Physics, 2nd class Hon.), Chulalongkorn University, Thailand (2011)
【学位】	Doctor of Philosophy from Chulalongkorn University, Thailand
【主な著書、学術論文】（過去5年以内）	1. Maneeporn Puripat, Romain Ramozzi, Miho Hatanaka, Waraporn Parasuk, Vudhichai Parasuk, and Keiji Morokuma, "The Biginelli reaction is a urea-catalyzed organocatalytic multicomponent reaction" *J. Org. Chem.* **80** (14), 6959-6967 (2015). 2. Arifin, Maneeporn Puripat, Daisuke Yokogawa, Vudhichai Parasuk, and Stephan Irle, "Glucose transformation to 5-hydroxymethylfurfural in acidic ionic liquid: A quantum mechanical study" *J. Comput. Chem.* **37** (3), 327-335 (2016).
【学術関係の受賞など】	The Development and Promotion of Science and Technology Talents Project (DPST) (Royal Government of Thailand scholarship) of Thailand (2004-2016)

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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、周期的分子結晶解析
【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】	分子科学会、理論化学会、錯体化学会
【主な著書、学術論文】（過去 5 年以内）	1. Aono S, Nakagaki M., and Sakaki S. “Theoretical Study of One-Electron Oxidized Salen Complexes of Group 7 (Mn(III), Tc(III), and Re(III)) and Group 10 Metals (Ni(II), Pd(II), and Pt(II)) with 3D-RISM-GMC-QDPT Method: Localized vs. Delocalized Ground and Excited States in Solution” *Phys. Chem. Chem. Phys.* **19**, 16831-16849, (2017). 2. 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). 3. 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). 4. 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) 5. 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) 6. 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).

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【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 ““Hetero-dinuclear complexes of 3d metals with a bridging dinitrogen ligand: theoretical prediction of the characteristic features of geometry and spin multiplicity” *Phys. Chem. Chem. Phys.,* **18**, 26365-26375 (2016). 2. Takako Muraoka, Haruhiko Kimura, Gama Trigagema, Masayuki Nakagaki, Shigeyoshi Sakaki, and Keiji Ueno “Reactions of Silanone(silyl)tungsten and -molybdenum Complexes with MesCNO, $(Me_2SiO)_3$, MeOH, and H2O: Experimental and Theoretical Studies” *Organometallics,* **36**, 1009-1018(2017). 3. 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) 4. 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) 5. Shinji Aono, Masayuki Nakagaki, Takuya Kurahashi, Hiroshi Fujii, and Shigeyoshi Sakaki “Theoretical Study of One-Electron Oxidized Mn(III)– and Ni(II)–Salen Complexes: Localized vs Delocalized Ground and Excited States in Solution” *J. Chem. Theory Comput.,* **10** 1062-1073 (2014)

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【現在の研究課題】	Theoretical Study of C-O activation by Rh-(PAlP) complex
【研究内容キーワード】	Transition state and electronic property of C-O activation
【学歴】	December 2012, School of Science, Xi’an Jiaotong University
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【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. K. Semba, K. Ariyama, H. Zheng, R. Kameyama, S. Sakaki, Y. Nakao, “Reductive Cross-Coupling of Conjugated Arylalkenes and Aryl Bromides with Hydrosilanes by Cooperative Palladium/Copper Catalysis”, *Angew. Chem. Int. Ed.* **55**, 6275 -6279 (2016) 8. H. Zheng, X. Zhao, S. Sakaki, “[2 + 2]-type Reaction of Metal–Metal σ-Bond with Fullerene Forming an η^1-C_{60} Metal Complex: Mechanistic Details of Formation Reaction and Prediction of a New η^1-C_{60} Metal Complex”, *Inorg. Chem.* **56**, 6746-6754 (2017)

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【現在の研究課題】	Theoretical study of bimetallic alloyed nanoclusters/particles
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【学歴】	June 2016, Doctor of Sci., Polymer chemistry and physics, Northeast Normal University, P.R. China
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【主な著書、学術論文】 （過去5年以内）	1. J. Lu, Y. Zheng, J., Zhang, Tuning the color of thermally activated delayed fluorescent properties for spiro-acridine derivatives by structural modification of the acceptor fragment: a DFT study, *RSC Adv.,* **5**, 18588-18592 (2015). 2. J. Lu, Y. Yao, P. M. Shenai, L. Chen, Y. Zhao, Elucidating the enhancement in optical properties of low band gap polymers by tuning the structure of alkyl side chains, *Phys. Chem. Chem. Phys.,* **17**, 9541-9551 (2015). 3. J. Lu, Y. Zheng, J., Zhang, Rational design of phenoxazine-based donor-acceptor-donor thermally activated delayed fluorescent molecules with high performance. *Phys. Chem. Chem. Phys.,* **17**, 20014-20020 (2015). 4. J. Lu, Y. Zheng, J., Zhang, Computational design of benzo [1,2-b:4,5-b'] dithiophene based thermally activated delayed fluorescent materials, *Dyes and pigments,* **127**, 189-196 (2016).

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【現在の研究課題】	Theoretical Study of Complex Systems Including d-electrons
【研究内容キーワード】	Palladium catalysis, oxidative addition, reaction mechanism
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【学位】	Doctor of Physical Chemistry from Northeast Normal University
【略歴】	Otc. 2016, Lecturer, Jilin University
【主な著書、学術論文】 （過去 5 年以内）	1. Rong-Lin Zhong, Hong-Liang Xu,* Zhi-Ru Li* and Zhong-Min Su*. Role of Excess Electrons in Nonlinear Optical Response. *J. Phys. Chem. Lett.* 2015, **6**, 612-619 2. Rong-Lin Zhong, Hong-Liang Xu,* Shi-Ling Sun, Yong-Qing Qiu, and Zhong-Min Su*. The Excess Electron in a Boron Nitride Nanotube: Pyramidal NBO Charge Distribution and Remarkable First Hyperpolarizability. *Chem. Eur. J.* 2012, **18**, 11350-11355. 3. Rong-Lin Zhong, Ji Zhang, Shabbir Muhammad, Yang-Yang Hu, Hong-Liang Xu,* and Zhong-Min Su*. Boron/Nitrogen Substitution of the Central Carbon Atoms of the Biphenalenyl Diradical pi-Dimer: A Novel 2e–12c Bond and Large NLO Responses. *Chem. Eur. J.* 2011, **17**, 11773-11779 4. Rong-Lin Zhong, Hong-Liang Xu,* Shabbir Muhammad, Ji Zhang and Zhong-Min Su*. The stability and nonlinear optical properties: Encapsulation of an excess electron compound LiCN/Li within boron nitride nanotubes. *J. Mater. Chem.,* 2012, **22**, 2196-2202. 5. Rong-Lin Zhong, Shi-Ling Sun, Hong-Liang Xu,* Yong-Qing Qiu, and Zhong-Min Su*. BN Segment Doped Effect on the First Hyperpolarizibility of Heteronanotubes: Focused on an Effective Connecting Pattern. *J. Phys. Chem. C* 2013, **117**, 10039-10044.

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【現在の研究課題】	非断熱電子動力学理論による化学反応
【研究内容キーワード】	電子動力学，非断熱相互作用，高強度レーザー
【学歴】	2011 年 3 月　慶應義塾大学大学院理工学研究科前期博士課程修了 2014 年 3 月　慶應義塾大学大学院理工学研究科後期博士課程修了
【学位】	2014 年 3 月　博士（理学）（慶應義塾大学）
【略歴】	2014 年 4 月　慶應義塾大学准訪問研究員、2015 年 7 月 東京大学特定研究員
【所属学会】	日本化学会，分子科学会，理論化学研究会
【主な著書、学術論文】（過去 5 年以内）	1. Takahide Matsuoka, Sayo Oonishi, Satoshi Yabushita, “Theoretical study on angular momentum polarization parameters, branching ratios, and anisotropy parameters of chlorine atoms from Photodissociation of Iodine Monochloride”, *Int. J. Quantum Chem.* **113**(3), 375-381 (2013). 2. Takahide Matsuoka, Satoshi Yabushita, “Theoretical study on the photofragment branching ratios and anisotropy parameters of ICl in the second absorption band”, *Chem. Phys. Lett.* **592**, 75-79 (2014). 3. Takahide Matsuoka, Satoshi Yabushita, “Quantum Interference Effects Theoretically Found in the Photodissociation Processes of the Second Absorption Bands of ICl and IBr Molecules”, *J. Phys. Chem.* A **119**(37), 9609-9620 (2015). 4. Takahide Matsuoka, Kazuo Takatsuka, “Dynamics of photoionization from molecular electronic wavepacket states in intense pulse laser fields: A nonadiabatic electron wavepacket study”, *J. Chem. Phys.* **146**(13), 134114 (2017).

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【現在の研究課題】	非断熱電子動力学理論による化学反応の研究
【研究内容キーワード】	非断熱遷移，電荷分離
【学歴】	2015 年 3 月　東京大学大学院理学系研究科化学専攻博士過程修了
【学位】	2015 年 3 月　理学博士（東京大学）
【略歴】	2014 年　東京大学技術補佐員，2015 年　東京大学特任研究員
【所属学会】	分子科学会，理論化学研究会
【主な著書、学術論文】 （過去 5 年以内）	1. J. Manz and K. Yamamoto, *Mol. Phys.* **110**, 517 (2012). 2. K. Yamamoto and K. Takatsuka, *J. Chem. Phys.* **140**, 124111 (2014). 3. K. Yamamoto and K. Takatsuka, *ChemPhysChem* **16**, 2534 (2015). 4. K. Yamamoto and K. Takatsuka, *Chem. Phys.* **475**, 39 (2016). 5. K. Yamamoto and K. Takatsuka, *ChemPhysChem* **18**, 537 (2017)

５．共同研究員プロフィール

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【現在の研究課題】	Reaction of photo-functional molecules, metal catalysis reaction
【研究内容キーワード】	Transition metal catalyzed synthetic reaction 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. Pang, Sumei, Zhao Yanying*, Xue Jiadan, Zheng Xuming. "Solvent-dependent dynamics of hydrogen bonding structure 5-(methylthio)-1, 3, 4-thiadiazole-2 (3H)-thione as determined by Raman spectroscopy and theoretical calculation." *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **171** (2017): 470-477. 2. Liu, Xin, and Yanying Zhao*. "Adsorption Kinetics of Methylene Blue on Synthesized DMF-MIL-101 (Cr), a DMF-functionalized Metal-organic Framework." *Key Engineering Materials* **671** (2016). 3. 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) 4. 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. 5. 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). 6. Zhao Yanying*, Zhang Yuchen, Liu Xin, Zheng Xuming Formation, characterization, structure and bonding analysis of the metal-carbon bond OM-(ŋ^6-C_6H_6) (M = Sc, Ti) complexes in solid matrix: Infrared spectroscopic and theoretical study. *J. Orgmet. Chem.* **777**, 25-30 (2015) 7. 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) 8. 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】	Reaction of Transition metal complexes
【研究内容キーワード】	Endohedral metallofullerenes, Triply-bonded molecules
【学歴】	September 2006 - January 2012 National Tsing Hua University, Chemistry Department
【学位】	Doctor of Philosophy
【略歴】	Auguest 2013 – up to date Postdoctoral research fellow
【主な著書、学術論文】 （過去5年以内）	1. Ming-Chung Yang, Akhilesh K. Sharma, W. M. C. Sameera, Keiji Morokuma, and Ming-Der Su* Theoretical Study of Addition Reactions of L4M (M = Rh, Ir) and L$_2$M(M = Pd, Pt) to Li$^+$@C60. *The Journal of Physical Chemistry A,* 2017, **121**, 2665-2673. 2. Jia-Syun Lu, Ming-Chung Yang and Ming-Der Su Triply-bonded indium phosphorus molecules: theoretical designs and characterization. *RSC Advances,* 2017, **7**, 20597-20603. 3. Jia-Syun Lu, Ming-Chung Yang, and Ming-Der Su Indium–Arsenic Molecules with an In≡As Triple Bond: A Theoretical Approach. *ACS Omega,* 2017, 2, 1172-1179. 4. Jia-Syun Lu, Ming-Chung Yang and Ming-Der Su. The effect of substituents on triply bonded boron≡antimony molecules: a theoretical approach. *Phys. Chem. Chem. Phys.,* 2017, **19**, 8026-8033. 5. Jia-Syun Lu, Ming-Chung Yang and Ming-Der Su. The Effect of Substituents on the Stability of Triply Bonded Gallium≡Antimony Molecules: A New Target for Synthesis. *Dalton Transactions,* 2017, **46**,1848-1856.

６．日本学術振興会外国人特別研究員プロフィール

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【現在の研究課題】	excited state emission decay
【研究内容キーワード】	DFT, AFIR, PES
【学歴】	Ph.D. Physical Chemistry, Jilin University, Changchun
【学位】	Ph.D. Physical Chemistry, Jilin University, Changchun
【略歴】	Nanjing University, 2010-2012, Ph.D fellow China University of Mining and Technology, Xuzhou, associate professor
【主な著書、学術論文】（過去５年以内）	1. Xue-Feng Ren, Guo-Jun Kang, Qiong-Qiong He, and et. al, *Theor Chem Acc* 2016, **135**, 24 2. Xue Feng Ren, Guo Jun Kang, Shou Feng Zhang, and et. Al, *J. Photochem. Photobio. A: Chemistry,* 2015, **311**, 85 3. Guo Jun Kang, Xue Feng Ren,* Si Yu Bai, *J Organomet. Chem.* 2015, **785**, 44
【学術関係の受賞など】	JSPS Research Fellowships

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14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　2017年1月27日（金）　10:00 – 19:00

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　10:15 – 11:15
高塚　和夫　（京都大学 福井謙一記念研究センター リサーチリーダー）
「化学反応における電子動力学 －電子の運動が観える時代の基礎化学－」

11:25 – 12:25
八島　栄次　（名古屋大学 大学院工学研究科）
「らせん構造を基本骨格とする超分子・高分子の創成、構造と機能」

12:35 – 13:35
高田　彰二　（京都大学 大学院理学研究科）
「複雑生体分子系のマルチスケールシミュレーション」

―　休　憩　―

15:00 – 15:30　福井謙一奨励賞表彰式

15:30 – 17:20　ポスターセッション

17:30 – 19:00　懇親会（１Ｆ多目的ルーム）

２．セミナー

(1) 第 14 回 福井センターセミナー

日　　時　2016 年（平成 28 年）4 月 13 日（水）　13:30－17:00

場　　所　京都大学福井謙一記念研究センター（１階 106 室）

13:30－14:20
Takahiro Sasamori (Kyoto Univ.)
"What is the Difference of Multiple Bonds between Carbon and heavier Group 14 Elements?"

14:20－15:10
Atsushi Wakamiya (Kyoto Univ.)
"Materials Design for Highly Efficient Perovskite Solar Cells"

15:25－16:15
Hideki Yorimitsu (Kyoto Univ.)
"Journey from Discovery of New Pummerer Chemistry to Catalytic C-S Bond Cleavage"

16:15－17:00
Shigeyoshi Sakaki (Kyoto Univ.)
"The Present and Future of Molecular Theory and Calculations in Transition Metal Chemistry"

(2) その他のセミナー

Contact	Speaker	Title	Affiliation	Date
Shigeyoshi Sakaki	Gernot Frenking	Dative bonding in main-group compounds	Philipps-Universität Marburg	April 26 (Tue), 2016

Contact	Speaker	Title	Affiliation	Date
Shigeyoshi Sakaki	Hannes Jonsson	Mechanism and rate of hydrocarbon and alcohol formation in CO$_2$ electroreduction obtained from detailed atomic scale modeling	University of Iceland	June 10 (Fri), 2016
Kazuo Takatsuka	Jörn Manz	Intramolecular fluxes: form tunnelling to charge migration, or from kiloseconds to attoseconds	Freie Universität Berlin and Shanxi University	July 14 (Thu), 2016
Shigeyoshi Sakaki	Bun Chan	Double-Hybrid Density Functional Theory: Development and Application to Fullerene Chemistry	Nagasaki University	August 25 (Thu), 2016
Shigeyoshi Sakaki	Naoki Nakatani	Density Matrix Renormalization Group in Practice: A Guide to Large Active-Space Multi-Reference Computations	Tokyo Metropolitan University	February 15 (Wed), 2017
Keiji Morokuma	Rajeev Prabhakar	Computational Modeling of Reaction Mechanisms, Drugs and Biomaterials	University of Miami	February 16 (Thu), 2017
Shigeyoshi Sakaki	Ashutosh Gupta	Role of Noble Gas in Binding Ability of Metal Cyanides, Halides and Oxides (Metal = Cu, Ag, Au): A Computational Investigation	Udai Pratap College	March 3 (Fri), 2017
Shigeyoshi Sakaki	Tsuyoshi Kato	Some interesting perspectives of stable silylenes	Université de Toulouse	March 9 (Thu), 2017
Kazuo Takatsuka	Ingo Barth	Quantum Hydrodynamice Approach for Calculations of Electronic Current Densities	Max Planck Institute	March 9 (Thu), 2017
	Jörn Manz	Electronic fluxes during intramolecular adiabatic attosecond charge migration	Berlin Free University	
	Wolfgang Domcke	Burning water with sunlight: guidelines from computational chemistry	Technical University of Munich	March 10 (Fri), 2017

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

＜研究紹介＞

（１）京都大学アカデミックデイへ参加　2016年（平成28年）9月18日

高塚 和夫 リサーチリーダー他が「ポスターを使っての対話」コーナーへ参加
ポスタータイトル：分子内の電子のダイナミクスを観る・操る

榊 茂好 リサーチリーダー他が「ちゃぶ台で対話」コーナーへ参加
話　題：自動車触媒とコンピュータ計算化学
場　所：京都大学百周年時計台記念館

＜学術講演＞

（２）田中 一義 シニアリサーチフェロー　2016年（平成28年）11月15日

演　題：元素ブロック設計のための計算化学とその実例
行事名：日本化学会秋季事業第６回 CSJ 化学フェスタ 2016 特別企画
場　所：江戸川区タワーホール船堀

（３）田中 一義 シニアリサーチフェロー　2016年（平成28年）12月6日

演　題：企業研究者のための計算化学
行事名：京都グリーンケミカル・ネットワーク人材育成事業
場　所：京都市成長産業創造センター

5．福井謙一奨励賞の創設及び奨励賞の授与

福井謙一博士の生誕百年を控え、日頃から、化学の将来の発展のためには若手研究者の育成の大切さを説いておられた福井博士の意志を汲み、基礎化学、理論化学の分野で顕著

な研究業績を挙げた若手研究者を顕彰する福井謙一奨励賞を創設した。

平成28年秋に公募し､応募のあった中から委員会で選考の結果､次のとおり選考された。表彰式は、平成29年1月27日（金）に開催の福井謙一記念研究センターシンポジウムの中で行い受賞者に表彰状と記念楯が授与され、続いて受賞題目に関した講演が行われた。

受賞者：辻 雄太（九州大学 分子システムデバイス国際リーダー教育センター 助教）
受賞題目：理論化学研究に立脚した量子干渉現象の分子エレクトロニクスへの展開

6. 複雑・複合系の理論計算科学に関する日・仏・スペイン合同シンポジウムを開催

本学は、福井謙一博士の存在により、特に化学および生命科学分野で計算科学研究が歴史的に盛んであり、わが国はもとより世界レベルで先導的な研究を進めてきた。本シンポジウムは、わが国の窓口となり、わが国の若手、中堅研究者に、フランス、スペインからの若手、中堅研究者を加え、複雑・複合系に関する理論計算科学に関する研究成果を互いに紹介しあい、理論計算科学を機軸とする融合研究の更なる展開を目指し、このシンポジウムが開催された。（平成28年10月26日～28日）

7. 日本－ブラジル　理論化学・計算化学交流会を開催

国際シンポジウム“Multi-scale Simulation of Condensed-phase Reacting Systems 2016”へのブラジルからの参加者とセンター関係者との交流会を開催。（平成28年10月13日）

8. 日本化学会賞受賞（赤木和夫センター長）

赤木和夫センター長は、日本化学会賞を受賞した。受賞の対象となった業績は「液晶と共役ポリマーとの融合化学の開拓と展開」であった。（平成29年3月17日の日本化学会第97回春季年会）

Ⅳ　研究業績

１．専任教員

Hideyuki Mizuno

Assistant Professor

1. Summary of the research of the year (2016)

Vibrational properties of amorphous solids in the continuum limit

Why low-ω-vibrational and low-T-thermal properties of amorphous solids are markedly different from the crystalline counterparts is a long-standing mystery in condensed matter physics. Crystals follow the universal laws which are controlled by phonon [1]. Experimental observations of the vibrational density of states $g(\omega) \sim \omega^2$, heat capacity $C \sim T^3$, and the thermal conductivity $\kappa \sim T^3$ are rationalized by the Debye theory and the phonon-gas theory based on the phonon. Amorphous solids are characterized as well by the universal laws that are, however, anomalous with respect to the crystalline counterparts [2]. Much attention has been paid to the boson peak (BP): The heat capacity C is larger than the crystalline value at $T \approx 10$[K], which directly reflects the excess vibrational modes around $\omega_{BP} \approx 1$[THz].

Here, we would remark that even at much lower $T \leq 1$[K], thermal properties are already anomalous, e.g., the thermal conductivity increases as $\kappa \sim T^2$, instead of $\kappa \sim T^3$ [3]. This indicates that the vibrational modes are not rationalized by the phonon even at very low $\omega \approx 0.1$[THz], one order of magnitude lower than ω_{BP}. This behavior is highly counter-intuitive because any solid matter, not only crystalline but also amorphous, is expected to behave as a homogeneous elastic medium in the continuum limit, and its vibrational modes are expected to converge to the phonons in the low-ω regime.

To resolve this issue, we report the first numerical evidence that these anomalous properties of amorphous solids can be described in terms of the coexistence of phonons and “soft localized modes”. In our study [4], we performed extremely large-scale molecular-dynamics simulations on amorphous solids and directly observed very-low-frequency vibrational modes. Here we would emphasize that direct observation of such the low-frequency modes is technically challenging so that it has never been achieved before. We found that phonons and soft localized modes coexist in the low-frequency regime, which should control the low-temperature thermal properties of amorphous solids. Importantly, we discovered that the phonons follow the Debye law, whereas the soft localized modes follow another universal, non-Debye law. These findings provide the first firm theoretical ground to explain the experimentally established anomalous properties of amorphous solids.

References

[1] C. Kittel, Introduction to Solid State Physics, 7th ed. (John Wiley and Sons, New York, 1996).
[2] W. A. Phillips, Amorphous Solids: Low Temperature Properties, 3rd ed. (Springer, Berlin, 1981).
[3] R. C. Zeller and R. O. Pohl, Phys. Rev. B 4, 2029 (1971).
[4] H. Mizuno, H.Shiba, A.Ikeda, arXiv:1703.10004 (2017).

2. Original papers

[1] H. Mizuno, S. Mossa, and J.-L. Barrat, “Relation of vibrational excitations and thermal conductivity to elastic heterogeneities in disordered solids”, Physical Review B, Vol.94, p.144303 (22pages), 2016.

[2] H. Mizuno, K. Saitoh, and L. E. Silbert, “Elastic moduli and vibrational modes in jammed particulate packings”, Physical Review E, Vol.93, p.062905 (21pages), 2016.

[3] H. Mizuno, L. E. Silbert, M. Sperl, S. Mossa, and J.-L. Barrat, “Cutoff nonlinearities in the low-temperature vibrations of glasses and crystals”, Physical Review E, Vol.93, p.043314 (18pages), 2016.

[4] H. Mizuno, L. E. Silbert, and M. Sperl, “Spatial Distributions of Local Elastic Moduli Near the Jamming Transition”, Physical Review Letters, Vol.116, p.068302 (5pages), 2016.

[5] K. Saitoh and H. Mizuno, “Enstrophy cascades in two-dimensional dense granular flows”, Physical Review E, Vol.94, p.022908 (11pages), 2016.

[6] K. Saitoh and H. Mizuno, “Anomalous energy cascades in dense granular materials yielding under simple shear deformations”, Soft Matter, Vol.12, p.1360-1367 (8pages), 2016.

3. Presentation at academic conferences (invited talk)

[1] 水野英如, “ジャミング転移点近傍における粉体の弾性応答”, 粉体工学会「計算粉体力学研究会」, 同志社 大学, 京都, 2016.7.4.

[2] 水野英如, “ガラスとナノ構造化物質の力学・熱物性の理論的研究”, 日本物理学会第 11 回若手奨励賞(領域 12) 受賞記念講演, 大阪大学, 大阪, 2017.3.17.

4. Others

[1] 池田昌司, 水野英如, 尾澤岬, 宮崎州正, “ガラス転移とアモルファス固体：最近の理論研究から”, ニューガラス, Vol.31, p.3-6 (4pages), 2016.（依頼解説）

Yoshio Nishimoto

Program-Specific Assistant Professor

1. Summary of the research of the year

Theoretical Developments of FMO-DFTB

I'm developing a large-scale quantum-mechanical method, FMO-DFTB [1], these days. FMO-DFTB is a combined method between the fragment molecular orbital (FMO) approach and the density-functional tight-binding (DFTB) method. A previous study revealed the efficiency of FMO-DFTB, and a geometry optimization of a one-million-atom system could be successfully completed.

The first development is referred to as FMO-DFTB/PCM [2], which is the combination of FMO-DFTB and the polarizable continuum model (PCM). Application of FMO-DFTB to some proteins which usually have a lot of charged residues has been prohibited, because SCF convergence of dimers (and trimers) has been poor without solvent effects. In this study, I developed the energy and its analytic gradient of FMO-DFTB/PCM. The energy and its derivative can be implemented by following previous studies. Since FMO is not a fully variational method, one has to compute the response of molecular orbitals (MOs) in computing the analytic gradient. The response can be efficiently computed by solving the Z-vector equation for each monomer self-consistently with respect to the auxiliary density on each monomer.

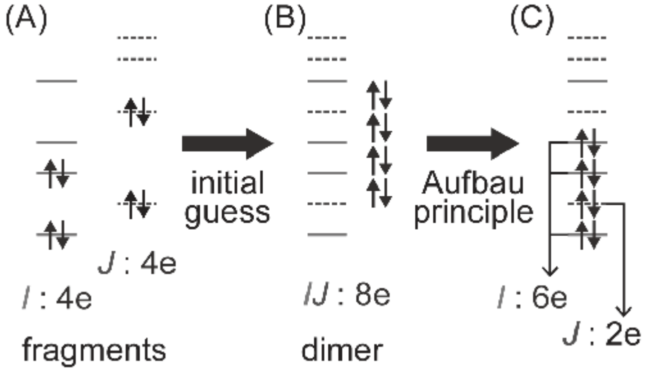

Fig. 1 A possible initial electronic configuration of a dimer without PCM.

By comparing the MO diagrams obtained with and without PCM, I found that there is a large difference between the levels of the HOMO and the LUMO. In the computation in vacuum without PCM, the level of the HOMO of a monomer with a negative charge tends to be high. In this case, the level of the HOMO may be higher than that of the LUMO. If one performs a dimer SCF calculation by combining these monomers (Fig. 1(A)), the HOMO of a fragment is higher than the LUMO of another fragment. Here, *I*th and *J*th fragments roughly corresponds to positively and negatively charged fragments, respectively. In this case, electron transfer may occur between the two fragments, if electrons occupy orbitals according to the building principle, and the electronic state may break down as a consequence. If such a breakdown occurs, the accuracy may be extremely poor or the SCF cycle may not converge. On the other hand, if PCM is employed, the reversal of the energy level does not occur, so there are no such problems in the computation. Eventually, a geometry optimization for the bovine chymotrypsinogen A (PDB ID: 2CGA) consisting of 3578 atoms could be completed.

Another development is the inclusion of the three-body effect, referred to as FMO3-DFTB [3]. The previous developments were limited to the two-body case (FMO2), and the inclusion of the three-body effect should be beneficial in improving the accuracy of FMO-DFTB. I could indeed verify this; for instance, there was an error of 25.88 kcal/mol for the 2CGA protein with the conventional FMO2-DFTB/PCM<1>, while the error was decreased to 7.71 kcal/mol with FMO3-DFTB/PCM<1>. However, the computational cost is approximately four times more expensive.

I also performed molecular dynamics (MD) simulations for $Na^+(H_2O)_{473}$ and predicted the hydration number of the sodium cation. Because the positive charge should delocalize around Na^+, FMO2-DFTB which is not sufficiently take into account many body effects may not describe the coordination structure around Na^+ correctly. FMO2-DFTB predicted a hydration number of 8.6, while FMO3-DFTB which was developed in this study did that of 6.5. The value obtained with 6.5 reasonably agrees with the hydration number predicted with other methodologies (5–6), and in addition, it is also found that FMO2-DFTB highly overestimates the hydration number. Indeed, FMO2-DFTB (the black line in Fig. 2) overestimates the first peek at around a Na^+–O distance of 2.5 Å, compared with FMO3-DFTB (the red line in Fig. 2). In another comparison using a smaller system also revealed that FMO3-DFTB reproduced the radial distribution function predicted by full DFTB (without fragmentation) fairly well.

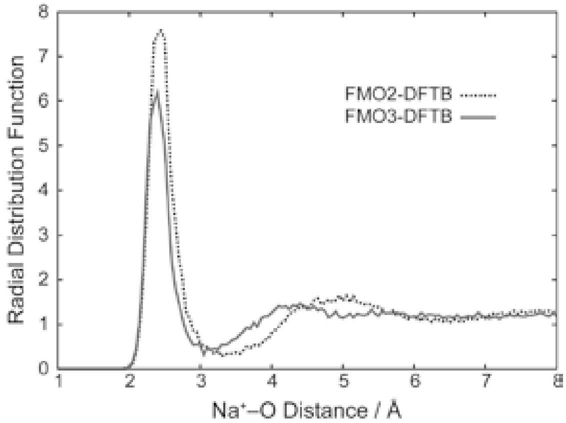

Fig. 2 Radial distribution function between Na^+–O.

A collaboration study made it possible to calculate the second-order geometrical derivative of the total energy within FMO-DFTB approximately [4]. A computation of the second-order geometrical derivative for a system consisting of 1125 atoms ($(H_2O)_{375}$) with FMO-DFTB was 3465 times faster than the corresponding computation without fragmentation. Eventually, it was possible to calculate the derivative for a system consisting of 10,041 atoms. The evaluation itself took only 17.2 minutes using six CPU cores, but the normal mode analysis (diagonalization of Hessian) took 262.4 minutes, and it is the bottleneck. Calculations for even larger systems is somewhat challenging at the moment, because of large memory requirement; the computation for 10,041 atoms required a total memory of 10.2 GB per core.

Development of Analytic Derivatives with Fractional Occupation Number

I also developed analytic derivatives with the fractional occupation number (FON). One problem in the calculation for large extended systems is the steep increase of computational cost, but another problem is the difficulty of SCF convergence because of a small HOMO–LUMO gap. The problem may be attributed to the fact that the orbital occupation number is integer and may be avoided by employing the FON with reasonable computational cost.

In computing second- and higher-order derivatives, coupled-perturbed (CP) equations are usually solved. In the conventional CP equation, an explicit computation of dependent pairs (rotation within the fully occupied or unoccupied region) can be avoided, because the total energy is invariant to a rotation of MOs within the diagonal blocks. It is thus possible to avoid the division by the difference of the orbital energies. The difference between the orbital energy of two MOs in the off-diagonal blocks are usually large, so the existence of degenerated orbitals are not problematic in solving CP equations. However, with FON, one additionally has to consider the response term in partially occupied MOs. Since the denominator of the response term is the difference between two orbital energies, the response term may be extremely large when degenerated orbitals are partially occupied, and the convergence of CP equations may be challenging. In one of the two studies [5], I solved the problem in the first-order CP equation and made it possible to compute second-order geometrical derivatives analytically.

In the other study [6], I derived and implemented analytic third-order derivatives (hyperpolarizability and polarizability derivative) with FON. With integer occupation, it is well know that the analytic third-order derivative can be computed using first-order response terms by exploiting Wigner's $2n+1$ rule. Here, I derived that one with FON. I used the fact that the Lagrangian is stationary with respect to the change of the MO coefficient and the occupation number. The expression obtained here can employ limit values for small difference of orbital energies, so it is possible to compute third-order derivatives even with degenerated orbitals. The derived equations for the density-functional tight-binding (DFTB) method were implemented into GAMESS-US. By modifying the expression for the terms relevant to the two-electron integral and exchange–correlation terms, it can be applicable to Hartree–Fock and DFT.

The developed method was applied to a series of zigzag-type graphene nanoribbon (ZGNR). Non-resonance Raman spectra may be simulated by computing the polarizability derivative semi-numerically, but spectra obtained in this way is very sensitive to the choice of electric field for a system with a small HOMO–LUMO gap such as ZGNR. Moreover, we do not know an optimum electric field beforehand. By computing the derivative analytically, I verified that it is possible to obtain non-resonance Raman spectra that do not include numerical error.

Eventually, by exploiting the efficiency of DFTB, I performed a calculation with a ZGNR consisting of 1012 atoms. By performing a parallel calculation using four E5-1650 v3 calculation node (24 CPU cores in total), a computation of energy, gradient, Hessian, dipole derivative, hyperpolarizability, and

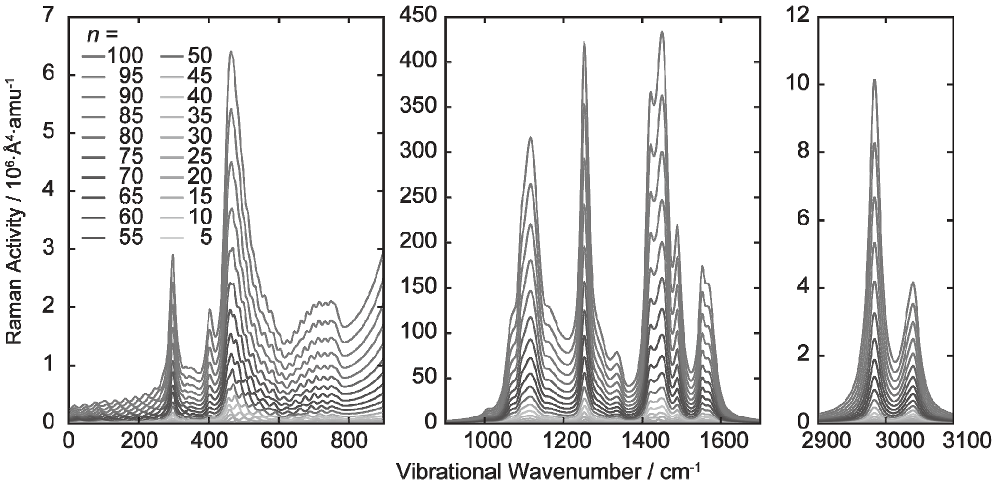

Fig. 3 Non-resonance Raman activity spectra of ZGNRs

polarizability derivative of the ZGNR finished in 7.55 hours. The scaling of the computation was 3.98 with respect to the number of atoms. Eventually, the evolution of the non-resonance Raman activity spectrum for the ZGNRs consisting of less than 1012 atoms can be simulated (Fig. 3). The evolution of the spectrum is systematic. I expect that the developed method is useful in simulating infrared and non-resonance Raman spectra of large extended systems.

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Phys. Chem. Chem. Phys. 18(32), 21997–22734 (2016).

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Chem. Phys. Lett. 667, 317–321 (2017).

(4) Yoshio Nishimoto and Dmitri G. Fedorov
“Three-body expansion of the fragment molecular orbital method combined with density-functional tight-binding”
J. Comput. Chem. 38(7), 406–418 (2017).

(5) Yoshio Nishimoto
“Analytic Hyperpolarizability and Polarizability Derivative with Fractional Occupation Numbers for Large Extended Systems”
J. Chem. Phys. 146(8), 084101 (2017).

3. Presentation at academic conferences

(1) 西本　佳央、フェドロフ　ドミトリ
「FMO法とDFTB法とPCM法の組み合わせ（FMO-DFTB/PCM）」
第10回分子科学討論会（3G14）、兵庫県、2016年9月15日

(2) 西本　佳央、イレ　ステファン
「小数軌道占有数を用いた二次微分計算」
日本化学会第97春季年会（1A7-01）、神奈川県、2017年3月16日

4. Others

(1) 西本　佳央
「小数軌道占有数を用いた解析的微分法の開発」
第14回福井謙一記念研究センターシンポジウム、京都府、2017年1月27日

２．FIFC リサーチフェロー

Shigeru Nagase

FIFC Research Fellow

1. Summary of the Research of the Year

(a) Formation Mechanisms of Graphitic-N: Oxygen Reduction and Nitrogen Doping of Graphene Oxides

Deoxygenation and nitrogen-doping mechanisms of graphene oxides with participation of foreign NH_3 molecules were investigated by density functional theory calculations. First, it was proved that reduction on perfect graphene oxide without any structural defect is facilitated at high temperature, but the following doping process is impracticable because of the huge energy requirement for C−C cleavage. To elucidate the formation of hexagonal graphitic-N, we explored oxygen reduction and subsequent nitrogen-doping processes on defective graphene oxides with single vacancies for the first time. All possible reaction pathways were taken into account, and the results demonstrate that the formation of graphitic-N from NH_3 and defective graphene oxides with one carbonyl or two hydroxyl groups is feasible in energy. The dominant reaction route is found to be exothermic with a practical reaction rate of $2.26 \times 106\ s^{-1}$ at 900 °C, which is in good agreement with experimental observations.

(b) $D_{2d}(23)$-C_{84} versus $Sc_2C_2@D_{2d}(23)$-C_{84}: Impact of Endohedral Sc_2C_2 Doping on Chemical Reactivity in the Photolysis of Diazirine

We compared the chemical reactivity of $D_{2d}(23)$-C_{84} and that of $Sc_2C_2@D_{2d}(23)$-C_{84}, both having the same carbon cage geometry, in the photolysis of 2-adamantane-2,3′-[3H]-diazirine, to clarify metal-atom doping effects on the chemical reactivity of the carbon cage. Experimental and computational studies have revealed that the chemical reactivity of the $D_{2d}(23)$-C_{84} carbon cage is altered drastically by endohedral Sc_2C_2 doping. The reaction of empty $D_{2d}(23)$-C_{84} with the diazirine under photoirradiation yields two adamantylidene (Ad) adducts. NMR spectroscopic studies revealed that the major Ad monoadduct (C_{84}(Ad)-A) has a fulleroid structure and that the minor Ad monoadduct (C_{84}(Ad)-B) has a methanofullerene structure. The latter was also characterized using X-ray crystallography. C_{84}(Ad)-A is stable under photoirradiation, but it interconverted to C_{84}(Ad)-B by heating at 80 °C. In contrast, the reaction of endohedral $Sc_2C_2@D_{2d}(23)$-C_{84} with diazirine under photoirradiation affords four Ad monoadducts ($Sc_2C_2@C_{84}$(Ad)-A, $Sc_2C_2@C_{84}$(Ad)-B, $Sc_2C_2@C_{84}$(Ad)-C, and $Sc_2C_2@C_{84}$(Ad)-D). The structure of $Sc_2C_2@C_{84}$(Ad)-C was characterized using X-ray crystallography. Thermal interconversion of $Sc_2C_2@C_{84}$(Ad)-A and $Sc_2C_2@C_{84}$(Ad)-B to $Sc_2C_2@C_{84}$(Ad)-C was also observed. The reaction mechanisms of the Ad addition and thermal interconversion were elucidated from theoretical calculations. Calculation results suggest that C_{84}(Ad)-B and $Sc_2C_2@C_{84}$(Ad)-C are thermodynamically favorable products. Their different chemical reactivities derive from Sc_2C_2 doping, which raises the HOMO and LUMO levels of the $D_{2d}(23)$-C_{84} carbon cage.

(c) Molecular Location Sensing Approach by Anisotropic Magnetism of an Endohedral Metallofullerene

Location recognition at the molecular scale provides valuable information about the nature of functional molecular materials. This study presents a novel location sensing approach based on an endohedral metallofullerene, Ce@C_{82}, using its anisotropic magnetic properties, which lead to temperature-dependent paramagnetic shifts in ^{1}H NMR spectra. Five site-isomers of Ce@$C_{82}CH_2$-3,5-$C_6H_3Me_2$ were synthesized to demonstrate the spatial sensing ability of Ce@C_{82}. Single-crystal structures, absorption spectra, and density functional theory calculations were used to select the plausible addition positions in the radical coupling reaction, which preferentially happens on the carbon atoms with high electron density of the singly occupied molecular orbital (SOMO) and positive charge. Temperature dependent NMR measurements demonstrated unique paramagnetic shifts of the ^{1}H peaks, which were derived from the anisotropic magnetism of the f-electron in the Ce atom of the isomers. It was found that the magnetic anisotropy axes can be easily predicted by theoretical calculations. Further analysis revealed that the temperature-dependent trend in the shifts is clearly predictable from the distance and relative position of the proton from the Ce atom. Hence, the Ce-encapsulated metallofullerene Ce@C_{82} can provide spatial location information about nearby atoms through the temperature-dependent paramagnetic shifts of its NMR signals. It can act as a molecular probe for location sensing by utilizing the anisotropic magnetism of the encapsulated Ce atom. The potentially low toxicity and stability of the endohedral fullerene would make Ce@C_{82} suitable for applications in biology and material science.

(d) Stabilization of a Chlorinated $^{\#4348}C_{66}:C_{2v}$ Cage by Encapsulating Monometal Species: Coordination between Metal and Double Hexagon-Condensed Pentalene

Carbon cages in endohedral and exohedral fullerene derivatives are usually different. A recent report suggested that chlorofullerene $C_{66}Cl_{10}:C_s$ and endohedral metallofullerene (EMF) Sc_2@C_{66} shared the same cage $^{\#4348}C_{66}:C_{2v}$, while it was denied by the definitive characterization of Sc_2@C_{66}, which actually possesses the $^{\#4059}C_{66}:C_{2v}$ isomer. Here, we show that a $^{\#4348}C_{66}:C_{2v}$ cage with a double hexagon-condensed pentalene (DHCP) moiety, which was captured by exohedral chlorination, is also capable of being stabilized by encapsulating tri- or divalent monometal (M) species. On the basis of density functional theory calculations combined with statistical mechanics analyses, it was demonstrated that $^{\#4348}C_{66}:C_{2v}$-based mono-EMFs M@C_{2v}(4348)-C_{66} (M = Tb, La, Y, and Yb) are the most stable and predominant isomers at the fullerene formation temperature region, while another chlorinated cage $^{\#4169}C_{66}:C_s$, featured with triple sequentially fused pentagon (TSFP) moiety, is less favorably obtained in the form of EMFs, although these two cages can be interconverted by a simple Stone−Wales transformation. The superiority of M@C_{2v}(4348)-C_{66} over M@C_s(4169)-C_{66} comes from the stronger interaction of M−DHCP over that of M−TSFP in both ionic and covalent bonding aspects. In addition, size-selective complexation of host [n]cycloparaphenylene ([n]CPP) and Tb@C_{2v}(4348)-C_{66} was simulated, showing that

[10]CPP exhibits the best affinity toward Tb@C_{66}, which provides a new opportunity for isolation and characterization of C_{66}-based mono-EMFs.

(e) Dispersion Forces, Disproportionation, and Stable High-Valent Late Transition Metal Alkyls

The transition metal tetra- and trinorbornyl bromide complexes, M(nor)$_4$, Ni(nor)$_3$Br, and their homolytic fragmentations (M = Fe, Co, Ni and nor = 1-bicyclo[2.2.1]hept-1-yl) were investigated computationally using hybrid density functional theory (DFT) at the B3PW91 and dispersion-corrected B3PW91-D3 levels. Experimental structures were well replicated; the dispersion correction resulted in shortened M-C bond lengths for the stable complexes, and it was found that Fe(nor)$_4$ receives a remarkable 45.9 kcal/mol stabilization from the dispersion effects whereas the tetragonalized Co(nor)$_4$ shows stabilization of 38.3 kcal/mol. Ni(nor)$_4$ was calculated to be highly tetragonalized with long Ni-C bonds, providing a rationale for its current synthetic inaccessibility. Isodesmic exchange evaluation for Fe(nor)$_4$ confirmed that dispersion force attraction between norbornyl substituents is fundamental to the stability of these species.

(f) A Dianionic Species with a Bond between pentacoordinated Sn Atoms: Bonding Properties of the Sn-Sn bond

The first dianionic compound bearing a bond between two pentacoordinated tin atoms, a distannate, was synthesized in a stable form by using two sets of an electron-withdrawing C,O-bidentate ligand on each tin atom. The structure of the distannate was determined by NMR spectroscopy and X-ray crystallographic analysis. The Sn–Sn bond of the distannate was shown to be a single bond featuring high s-character. The ^1J(Sn–Sn) coupling constant was larger than that of Sn(sp^3)–Sn(sp^3) bonds found in most hexaorganodistannanes. This bond feature was also supported by computational studies. The Sn–Sn bond was cleaved by treatment with hydrochloric acid, which shows a different reactivity to the homonuclear bonds of pentacoordinated disilicates and digermanates.

(g) Other Research Subjects

(1) "Computed Relative Populations of D_2(22)-C_{84} Endohedrals with Encapsulated Monomeric and Dimeric Water", (2) "Regioselective Multistep Reconstruction of Half-Saturated Zigzag Carbon Nanotubes", (3) "Strong Electronic Coupling and Electron Transfer in a Ce_2@I_h-C_{80}-H_2P Electron Donor Acceptor Conjugate", (4) "Sc_3N@C_s(39715)-C_{82}: A Missing Isomer Linked to Sc_3N@C_{2v}(39718)-C_{82} by a Single Step Stone-Wales Transformation", (5) "Unconventional Electronic Structure and Chlorination/Dechlorination Mechanisms of $^{\#1911}C_{64}$ Fullerene", (6) "Dispersion-Force-Assisted Disproportionation: A Stable Two-Coordinate Copper (II) Complex", (7) "(η^4-Butadiene)Sn(0) Complexes: A New Approach for Zero-Valent p-Block Elements Utilizing a Butadiene as a 4π-Electron Donor ", (8) "Isolation and Ambident Reactivity of a Chlorogermylenoid", (9) "Synthesis of a 1-Aryl-2,2-chlorosily(phospha)silene Coordinated by an N-Heterocyclic Carbene", (10) "Tuning of the Photoluminescence and Up-Conversion Photoluminescence Properties of Single-Walled Carbon Nanotubes

by Chemical Functionalization", (11) "Thermal Stability of Oxidized Single-Walled Carbon Nanotubes: Competitive Elimination and Decomposition Reaction Depending on their Degree of Functionalization" (12) "Reaction of a Stable Digermyne with Acetylenes: Synthesis of a 1,2-Digermabenzene and a 1,4-Digermabarrelene", (13) "The Unanticipated Dimerization of Ce@C_{2v}(9)-C_{82} upon Cocrystallization with Ni(octaethyporphyrin) and Comparison with Monomeric M@C_{2v}(9)-C_{82} (M = La, Sc, and Y)"

2. Original papers

(1) W. –W. Wang, J. –S. Dang, X. Zhao, and S. Nagase,
"Formation Mechanisms of Graphitic-N: Oxygen Reduction and Nitrogen Doping of Graphene Oxides"
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"Molecular Location Sensing by Anisotropic Magnetism of an Endohedral Metallofullerene"
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(7) Q. –Z. Li, J. –J. Zheng, L. He, S. Nagase, and X. Zhao,
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"D_{2d}(23)-C_{84} versus Sc_2C_2@D_{2d}(23)-C_{84}: Impact of Endohedral Sc_2C_2 Doping on Chemical Reactivity in the Photolysis of Diazirine"
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3. Books

赤阪　健，山田道夫，前田　優，
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日本化学会編，共立出版，2016.

３．シニアリサーチフェロー

Shigeyoshi Sakaki

Research Leader, Kenichi Fukui Memorial Research Groups II

1. Summary of the research of 2016

The complex systems consisting of transition metal element(s), heavy main-group element(s), organic group(s) are importnat research targets in wide areas of modern chemistry. Such complex systems play important roles as metal enzymes, industrial catalysts, catalysts for fine organic synthesis, 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 new geometry, new bonding nature, rich molecular property, rich reactivity, and various catalyses. 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 multi-nuclear transition metal complexes which need the application of multi-reference wave-function theory in the theoretical calculation. Another example is the significantly large coupling of surrounding atmosphere (such as solvation effects, molecular crystal effects and so on) with electronic structure.

Our group is theoretically investigating the complex systems bearing complicated electronic structure with electronic structure theory. In 2016, we performed various theoretical studies, as follows: (i) CASPT2 study of inverse sandwich-type dinuclear 3d transition metal complexes with two different metal centers, (ii) theoretical study of unusual solvation structure of water with Pt(II) and Pd(II) complexes, (iii) theoretical prediction of new catalysis of three-coordinate phosphorus compound, (iv) theoretical analysis of reaction mechanism of Pd/Cu-cooperative catalysis in reductive cross-coupling of styrene and aryl bromides, (v) theoretical study of para-selective alkylation of benzamides and aromatic ketones by cooperative nickel/aluminum catalysis, and (vi) Activation of Strong Boron–Fluorine and Silicon–Fluorine σ-Bonds: Theoretical Understanding and Prediction. We wish to report some of them, below.

(i) CASPT2 study of inverse sandwich-type dinuclear 3d transition metal complexes with two different metal centers

Spin multiplicities and coordination structures of dinitrogen-bridged hetero-dinuclear complexes of 3d metals, (μ-N2)[M1(AIP)][M2(AIP)] (AIPH = (Z)-1-amino-3-imino-prop-1-ene; M1, M2 = V(I) to Co(I)),

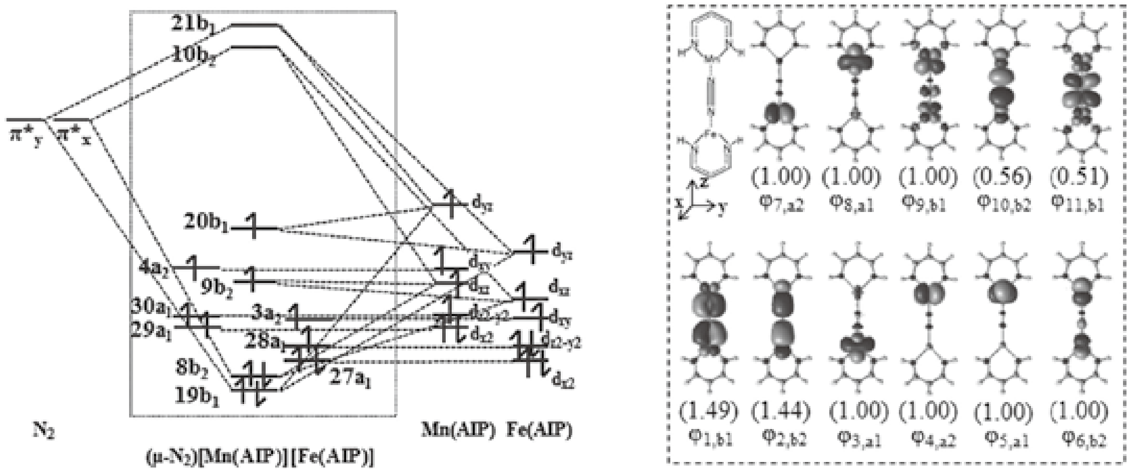
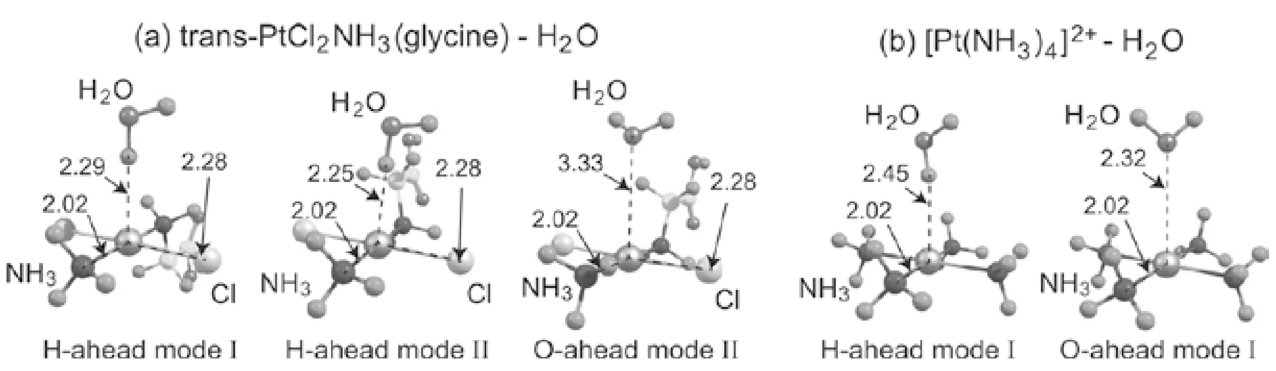


Figure 1. Mn-Cr heterodinucler inverse sandwich complex with the highest spin multiplicity of dectet.

were investigated with CASPT2 method. (μ-N_2)[V(AIP)][Cr(AIP)] has a low spin doublet ($^2B_2$) ground state with an η^2-side-on dinitrogen coordination structure but (μ-N_2)[Mn(AIP)][Fe(AIP)] has a high spin octet ($^8A_2$) ground state with an η^1-end-on coordination structure. These results are similar to those of the homo-dinuclear Cr and Fe analogues, respectively. In (μ-N_2)[Cr(AIP)][M(AIP)] (M = Mn(I), Fe(I), or Co(I)) consisting of the early 3d metal (Cr) and late one (Mn to Co), on the other hand, we found characteristic features in the geometry and the ground state electronic structure which are different from those of homo-dinuclear analougues. The Cr-Mn complex has a high spin decets ($^{10}B_1$) ground state with an η^2-side-on structure. This decets state is the highest spin multiplicity in the dinuclear transition metal complexes, to our knowledge. The A_2 state with a doublet spin multiplicity is moderately less stable than the 10B1 state. The optimized structures and the molecular orbitals indicate that the Cr atom strongly interacts with the N2 moiety in the $^{10}B_1$ state but the Mn atom strongly interacts with the N2 moiety in the $^2A_2$ state. The Cr-Fe complex has a high spin nonet ($^9B_1$) ground state with an η^2-side-on structure like the Cr-Mn complex, but only the Cr-Co complex has a medium spin quartet $^4A_2$ ground state with an η^2-side-on structure. The different ground electronic state of the Cr-Co complex arises from the presence of 3d orbital at low energy. Based on these results, it is concluded that the geometry is determined by the Cr center but the electronic structure and the spin multiplicity are determined by the combination of early and late 3d metals in the dinitrogen-bridged hetero-dinuclear chelates of 3d metals.

(ii) Theoretical Study of unusual solvation structure of water with Pt(II) and Pd(II) complexes

Solvation of transition metal complexes with water has been one of the fundamental topics in physical and coordination chemistry. In particular, Pt(II) complexes have recently attracted considerable interest for their relation to anticancer activity in cisplatin and its analogues, yet the interaction of the water molecule and the metal center has been obscured. The challenge from a theoretical perspective remains that both the microscopic solvation effect and the dynamical electron correlation (DEC) effect have to be treated simultaneously in a reasonable manner. In this work we derive the analytical gradient for the three-dimensional reference interaction site model Møller−Plesset second order (3D-RISM-MP2) free energy.


(a) trans-$PtCl_2NH_3$(glycine) - H_2O

(b) $[Pt(NH_3)_4]^{2+}$ - H_2O

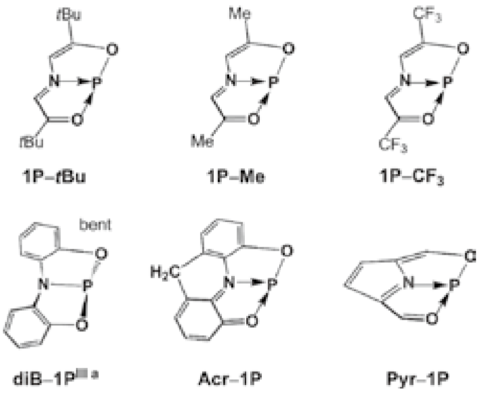
Figure 2. Micro-solvation structure of H_2O with neutral Pt(II) and cationic Pt(II) complexes optimized by the 3D-RISM-SCF-MP2 method.

On the basis of the three-regions 3D-RISM self-consistent field (SCF) method recently proposed by us, we apply a new layer of the Z-vector method to the CP-RISM equation as well as point-charge approximation to the derivatives with respect to the density matrix elements in the RISM-CPHF equation to remarkably reduce the computational cost. This method is applied to study the interaction of H_2O with the d^8 square planar transition metal complexes in aqueous solution, trans-$[Pt^{II}Cl_2(NH_3)(glycine)]$ (1a), $[Pt^{II}(NH_3)_4]^{2+}$ (1b),

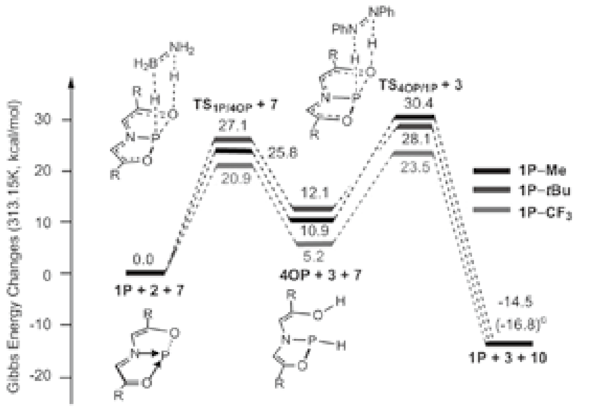
$[Pt^{II}(CN)_4]^{2-}$ (1c), and their Pd(II) analogues 2a, 2b, and 2c, respectively, to elucidate whether the usual H_2O interaction through O atom (O-ahead mode) or unusual one through H atom (H-ahead mode) is stable in these complexes. We find that the interaction energy of the coordinating water and the transition metal complex changes little when switching from gas to aqueous phase, but the solvation free energy differs remarkably between the two interaction modes, thereby affecting the relative stability of the H-ahead and O-ahead modes. Particularly, in contrast to the expectation that the O-ahead mode is preferred due to the presence of positive charges in 1b, the H-ahead mode is also found to be more stable. The O-ahead mode is found to be more stable than the H-ahead one only in 2b. The energy decomposition analysis (EDA) at the 3D-RISM-MP2 level revealed that the O-ahead mode is stabilized by the electrostatic (ES) interaction, whereas the H-ahead one is mainly stabilized by the DEC effect. The ES interaction is also responsible for the difference between the Pd(II) and Pt(II) complexes; because the electrostatic potential is more negative along the z-axis in the Pt(II) complex than in the Pd(II) one, the O-ahead mode prefers the Pd(II) complexes, whereas the H-ahead becomes predominant in the Pt(II) complexes.

(iii) Theoretical prediction of new transfer-hydrogenation catalysis of three-coordinate phosphorus compound: Application to aldehyde and ketone

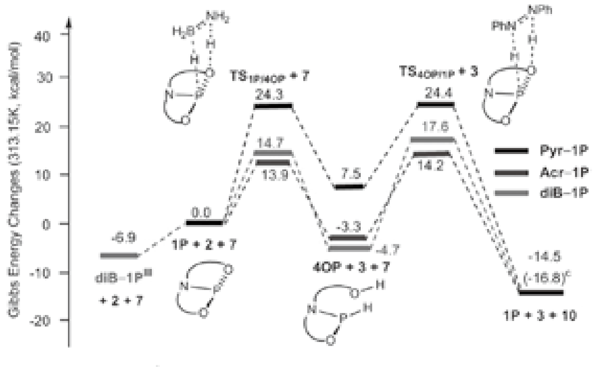
Catalysis of phosphorus compound 10-P-323,7-di(tert-butyl)-5-aza-2,8-dioxa-l-phosphabicyclo[3.3.O]octa-2,4,6-triene 1P and its analogues in transfer hydrogenation of azobenzene with ammonia-borane (NH_3BH_3) was investigated using DFT, CCSD(T), and ONIOM(CCSD(T):MP2) methods, to elucidate the electronic process of their reaction, to find a more active catalyst, and to broaden the application scope as a catalyst.



Scheme 1. Catalysts examined here.



(A)^a Substituent effects on the activity of 1P



(B)^b Framework effects on the activity of 1P

Figure 3. Hydrogenation of azobenzene by three-coordinate P compounds

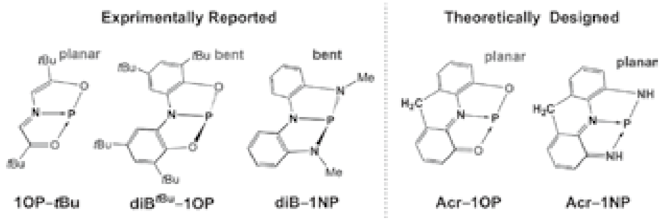
The reaction occurs through the phosphorus-ligand cooperative catalysis function, where the oxidation state of the phosphorus center changes between +I and +III. This is a characteristic difference from that of the metal–ligand cooperative function in which the oxidation state of the metal center does not change. The phosphorus–ligand cooperative function with the change in the phosphorus oxidation state should be noted as a new feature of the main-group element compound because the oxidation state does not easily change in the main group element compound in general.

In the dehydrogenation reaction of NH_3BH_3, the approach of the B–H bonding MO to the P atom induces an antibonding overlap with the P–O π MO and a bonding overlap with the P–O π* MO. As a result, the P atomic population decreases considerably in the early stage of the reaction, which corresponds to the change in the phosphorus oxidation state from +I to +III. Orbital mixing of the π* MO also engenders an increase in the electron population of the (CH=CH)-Me moiety. Because of the importance of these orbital mixings, the use of an electron-withdrawing substituent and conjugate C_6H_4 group in the ONO ligand enhances the activity for the dehydrogenation step. Simultaneously, the CT occurs from the P−O π MO to the N−H σ* MO of ammonia-borane to form the O–H bond. In the hydrogenation of azobenzene, the electronic process is almost opposite to that of dehydrogenation.

The O−H bond energy of 4OP is an important factor for determination of the catalyst activity. Acr−1P is theoretically predicted to be much more active than 1P-tBu experimentally reported. This compound is constructed by substituting two C_6H_4 groups for the (CH=CH)R moieties on the ONO ligand and connecting these C_6H_4 groups with a CH_2 linkage. This Acr−1P has the best O–H bond strength for the catalysis. The 1P-like catalyst is useful for transfer hydrogenation of substrate bearing a polar double bond. Actually, Acr−1P exhibits wide application scope as a catalyst in transfer hydrogenations of such substrates as hexafluoroacetone, benzophenone, acetophenone, acetaldehyde, and acetone. Phosphorus compounds of this type are interesting catalysts for transfer hydrogenation reactions of many substrates with ammonia-borane. Further work to investigate a new reaction is in progress in our group.

(iv) Theoretical prediction of new transfer-hydrogenation catalysis of three-coordinate phosphorus compound: Application to CO_2 Hydrogenation

The chemical conversion of carbon dioxide (CO_2) to value-added chemicals and renewable energy is an appealing strategy to address both the greenhouse effect and energy crisis issues. However, the CO_2 conversion is challenging due to the inherent thermodynamic and kinetic stabilities of CO_2. Therefore, such process usually asso-ciates with precious-metal catalysts, for which the toxicity of the catalyst brings new environmental issues. In recent years, the employment of the main-group element com-pounds, which are abundant, cheap, and gre
several Frustrated Lewis Pairs (FLPs) have been ap



Scheme 2. Three-coordinated P catalysts examined here.

In 2012, a pincer-type phosphorus compou
transfer hydrogenation of azobenzene with ammo
this reaction occurs through the phosphorus−lig
metal−ligand cooperative catalysis function that is
complexes.

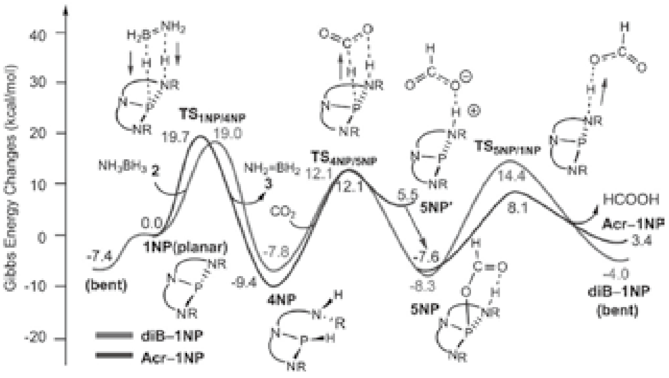


Figure 4. Energy and geometry changes in the CO_2 hydrogenation by three-coordinated P compounds

Here, we wish to report the first computatio
by the pincer-type phosphorus compounds. The us
because it has been employed in the hydrogenatio
compounds were theoretically predicted to be a
reaction occurs through a phosphorus-ligand cooperation cata-lytic cycle; see Scheme 1. The phosphorus

catalysts with the NNN ligand are more active than those with the ONO ligand and Acr−1NP is the best catalyst theoretically designed here. The activi-ty of the catalyst was greatly improved by introducing planar and the conjugate ligand. These results clearly demonstrate that the pincer-type phosphorus compound is a new promising catalyst for the metal-free conversion of CO_2.

(v) Theoretical analysis of reaction mechanism of Pd/Cu-cooperative catalysis in reductive cross-coupling of styrene and aryl bromides

Transition metal catalyzed cross-coupling reactions of alkyl and alkenyl organometallic reagents represent a powerful method for the alkylation and alkenylation, respectively, of organic electrophiles. The hydrometallation of alkenes and alkynes is an atom-efficient and practical way to prepare alkyl and alkenyl metal reagents, respectively, because a variety of main-group metal hydrides, alkenes, and alkynes are readily available. However, these organometallic nucleophiles are usually presynthesized and often purified prior to subsequent cross-coupling reactions, and such processes generally involve multistep operations. Nakao and Semba and coworkers succeeded cross-coupling reactions based on organometallic nucleophiles generated by hydrometallation of alkenes and alkynes with a catalytic amount of transition-metal hydrides in situ.

The reaction mechanism has been unclear. One of the important steps is transmetallation; if this transmetallation does not occur easily, the cross-coupling reaction is not successful. We investigated this transmetallation between Pd(II)-phenyl and Cu(I)-alkyl complexes and found that the transmetallation occurs with somewhat large activation barrier through inversion stereochemistry around the sp^3 carbon atom. It is of considerable interest to elucidate the reason why not the retention but inversion transmetallation occurs in this case and what are determining factor(s).

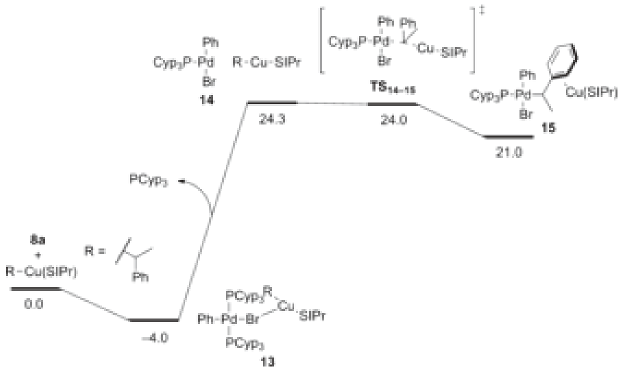


Figure 5. Changes in energy by transmetallation between Pd(II)-phenyl and Cu(I)-alkyl species.

2. Original Papers

(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, 1189−1206 (2016).

(2) Tetsuya Fukuda, Hisako Hashimoto, Shigeyoshi Sakaki, and Hiromi Tobita,
" Stabilization of a Silaaldehyde by its η^2 Coordination to Tungsten”
Angew. Chem. Int. Ed., 55, 188 –192 (2016).

(3) Yuta Takano, Tomohiro Numata, Kazuto Fujishima, Kazuaki Miyake, Kazuya Nakao, Wesley David Grove, Ryuji Inoue, Mineko Kengaku, Shigeyoshi Sakaki, Yasuo Mori, Ta-tsuya Murakami and Hiroshi Imahori
“Optical control of neuronal firing via photoinduced electron transfer in donor–acceptor conjugates”
Chem. Sci., 7, 3331-3337 (2016).

(4) H. Kameo, K. Ikeda, S. Sakaki, S. Takemoto, H. Nakazawa, H. Matsuzaka,
“Experimental and theoretical studies of Si-Cl and Ge-Cl sigma-bond activation reactions by iridium-hydride”
Dalton Trans., 45, 7570-7580 (2016).

(5) H. Kameo, T. Kawamoto, S. Sakaki, D. Bourissou, H. Nakazawa,
“Transition-Metal-Mediated Cleavage of Fluoro-Silanes under Mild Conditions”

Chem. Euro. J. 22, 2370-2375 (2016).

(6) K. Kikui, S. Hayaki, K. Kido, D. Yokogawa, K. Kasahara, Y. Matsumura, H. Sato, S. Sakaki,
"Solvent structure of ionic liquid with carbon dioxide"
A Mol. Simu., SI. **41**, 881-891 (2015).

(7) K. Semba, K. Ariyama, H. Zheng, R. Kameyama, S. Sakaki, Y. Nakao,
"Reductive Cross-Coupling of Conjugated Arylalkenes and Aryl Bromides with Hy-drosilanes by Cooperative Palladium/Copper Catalysis"
Angew. Chem., Int. Ed. 55, 6275-6278 (2016).

(8) G. Zeng, S. Maeda, T. Taketsugu, S. Sakaki,
"Theoretical Study of Hydrogenation Catalysis of Phosphorus Compound and Prediction of Catalyst with High Activity and Wide Application Scope"
ACS Cat., 6, 4859-4870 (2016).

(9) M. Nakagaki, S. Sakaki,
"Hetero-dinuclear complexes of 3d metals with a bridging dinitrogen ligand: theoretical prediction of the characteristic features of geometry and spin multiplicity"
Phys. Chem. Chem. Phys., 18, 26365-26375 (2016).

(10) GX. Zeng, S. Maeda, T. Taketsugu, S. Sakaki,
"Catalytic Hydrogenation of Carbon Dioxide with Ammonia-Borane by Pincer-Type Phosphorus Compounds: Theoretical Prediction"
J. Am. Chem. Soc., 138, 13481-13484 (2016).

(11) S. Okumura, SW. Tang, T. Saito, K. Semba, S. Sakaki, Y. Nakao,
"para-Selective Alkylation of Benzamides and Aromatic Ketones by Cooperative Nickel/Aluminum Catalysis"
J. Am. Chem. Soc., 138, 14699-14704 (2016).

3. Presentation at academic conferences

(1) S. Sakaki,
"Complex Systems Consisting of Transition Metal and Heavy Main Group Elements: Theoretical Study of Structure and Bonding Nature"
The 70th Fujihara Seminar "New Development of PhysicalOrganic Chemistry: Construction of Chemical Principles Determining Structures, Reactions, and Properties, April 18-20, 2016, Fukuoka, Japan (Invited)

(2) S. Sakaki
"Crucial Role of Lewis Acid in Enhancing Reactivity of Organometallic Complex"
The 1'st International Conference for Organometallic Chemistry (ICOC) Oct. 20-23, 2016, Beiging (Keynote lecture)

(3) 榊　茂好
「触媒の理論化学 /計算化学研究：元素戦略的触媒開発へ貢献を目指して 」
第四回元素戦略に基づいた触媒設計シンポジウム
首都大学東京 秋葉原サテライトキャンパス 2016 年 11 月 25 日（金）（招待講演）

4. Others: Review article

(1) G. Guan, GX. Zeng, H. Kameo, Y. Nakao, S. Sakaki,
Cooperative Catalysis of Combined Systems of Transition-Metal Complexes with Lewis Acids: Theoretical Understanding
Chem. Rec.. 16, 2405-2425 (2016).

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

比較的自由に電子を収容あるいは放出できる機能を持つ材料として電子化物がある。これらには電子親和力が適度に大きいことなど電子の授受に対して柔軟な電子物性を有することや、具体的な電子の収容サイトを持つ必要性がある。今年度は電子化物としての機能を備えたソフトマテリアルを得るために必要な電子を安定に補足しうる無機元素ブロックとして、無機カゴ型分子の理論的分子設計を行った。

【始めに】高分子に組み込むための部分素材として、元素ブロックの開発が現在活発に行われている1)。この元素ブロックは単に高分子の構造修飾のみならず、特異な反応性や電気・電子・光・磁気物性などにからむ有用な機能を高分子に付与するために有効な戦略を提供する。無機元素を含むカゴ型分子であるオクタシルセスキオキサンは一般には$(RSiO_{1.5})_8$と表される POSS（Polyhedral Oligomeric Silsesquioxane）の代表例であり、種々の観点から研究がなされている。POSS の電子物性として最も興味深いと考えられるものの一つに、その LUMO のエネルギー準位が低く電子親和力が大きいことがある(表 1)2)。このことは POSS が電子を捕捉しやすいという蓋然性を示すが、実際に電子を収容した POSS モノアニオンは表 1 に示すように中性状態よりも不安定であり、電子吸引基などによる修飾を行わない限りは電子を長時間安定に捕捉できる性質を示すことは考えにくい。ここでは、POSS 以上に安定な電子捕捉能を示すと期待される無機カゴ型分子である As_4S_6 及び$[HPO_3BH]_4$（POB と略）を無機元素ブロックとして提案し、それらの電子物性についての解析を行った3,4)。

【計算方法】直径が 5 Å 程度の無機カゴ状分子である As_4S_6 と POB（図 1）について、その電子捕捉の可能性についての理論的検討を行った。計算は密度汎関数理論(DFT)に基づく B3LYP 法及び UB3LYP 法によって行い、基底としては 6-31+G**を用いた。計算には Gaussian09 ソフトを使用した5)。具体的には上記の分子について、中性及びそのモノアニオン状態における構造最適化を行い、そのエネルギーを計算することによってアニオンの安定化についての予測を行った。また余剰電子を収容する SOMO（半占 MO）の軌道相などの解析も行った。

Table 1. Energetical stabilization upon the ionization

Species	LUMO level (neutral state)^a	Stabilization energy of the monoanionic state^b
As_4S_6	−2.702	46.17
POB	−0.502	11.32
POSS^c	−0.157	−11.51

^{a}in eV, ^{b}in kcal/mol, and ^{c}R = H.

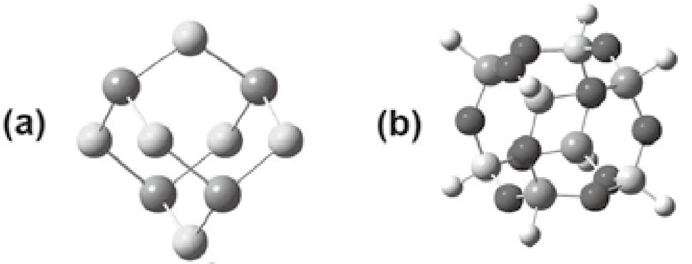


Fig. 1　Molecular structures of caged shape: (a) As_4S_6 and (b) $[HPO_3BH]_4$ (POB).

【As_4S_6とPOBの解析結果】

表1に示すAs_4S_6の計算結果では、中性状態よりもモノアニオンの方がエネルギー的にかなり安定であり、この分子は電子を安定的に捕捉する能力を持つことが分かる。また図2(a)のように、この余剰電子を収容するSOMOは中性As_4S_6分子のLUMOよりも準位が一つ上にある三重縮退したLUMO+1の一つであることが分かった。これによりJahn-Teller変形が起こって、モノアニオンでは中性状態のT_dからC_sに対称性が下がる。このSOMOを構成するのは、C_s面上にあるAsと隣接するSとの間のspσ*性の反結合性軌道である。モノアニオンの余剰電子は当該As原子の正電荷を減ずる役割をし、結果としてAs原子のローンペア性を高めている[3)]。

POBでも表1が示すように中性状態よりモノアニオンの方がエネルギー的に安定であり、やはり電子を安定的に捕捉する能力を持つことが分かる。図2(b)が示すように、POB^-のSOMOの起源となるのは中性POB分子のLUMOで縮退はしていないが、モノアニオンでは構造緩和が起こって中性状態のTからC_3に対称性が下がる。余剰電子が入るSOMOを構成するのはC_3軸上にあるPと隣接するOとの間のspσ*性の反結合性軌道である。余剰電子はこのP原子の正荷電を減ずる役割をし、結果としてP原子のローンペア性を高めている。

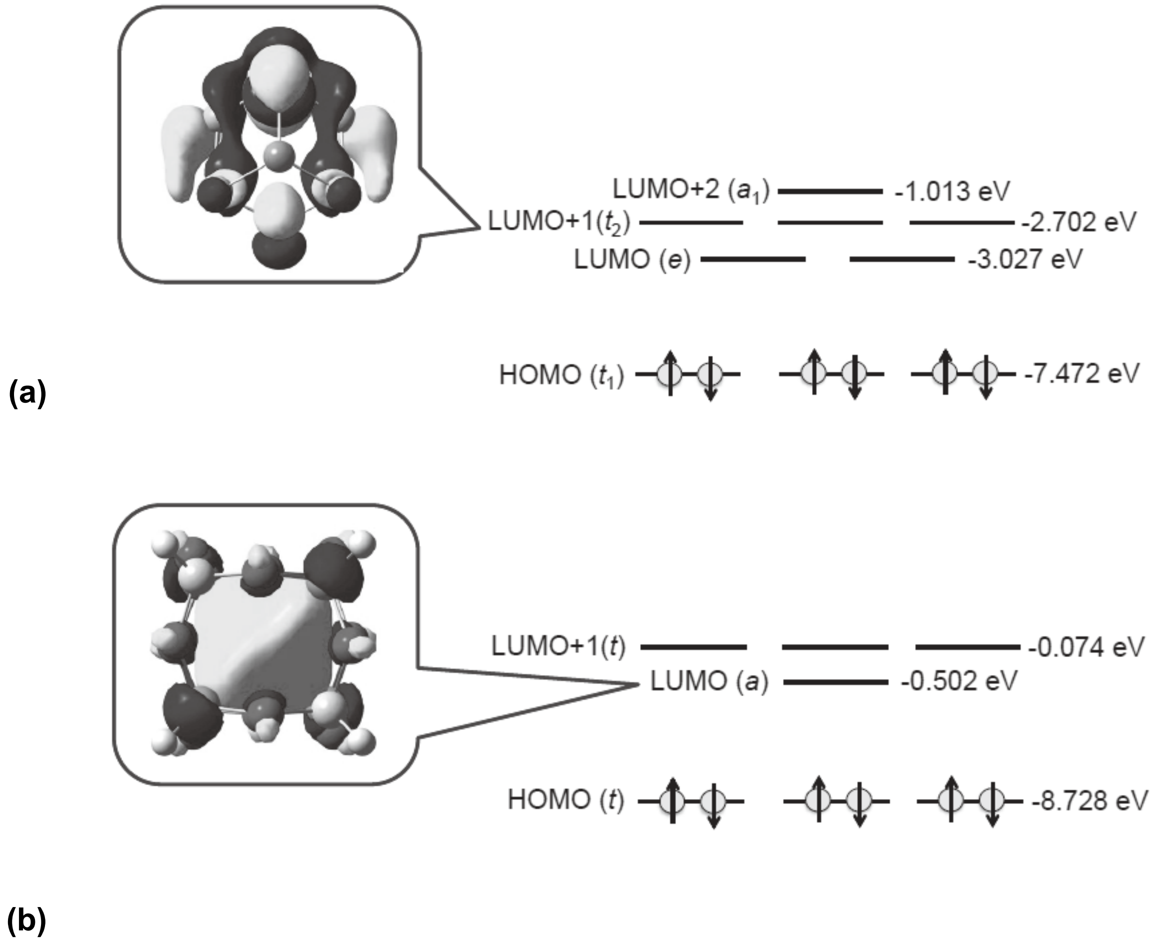


Fig. 2 Molecular-orbital energy diagrams of neutral (a) As_4S_6 and (b) POB. One of the (LUMO+1)'s of the former changes into the SOMO of $As_4S_6^-$ and the LUMO of the latter into that of POB^-. The MO patterns of those are also shown.

さらに検討したPOBのホウ素をアルミニウムに変えたPOAlや上記のPOSSでは、電子親和力は正であるが、中性状態よりもモノアニオンの方がエネルギー的に若干不安定となることも分かった。

【まとめ】

以上からAs_4S_6とPOBでは少なくとも1個の余剰電子を安定的に捕捉すると期待できる。一方、POAlとPOSSでも余剰電子の捕捉は可能であるが、同時に比較的これを放しやすい性質も持つと予想できる。すなわち電子化物を与えるカゴ状分子であっても電子の捕捉性質には差異があり、これによって相対的に電子滞留型および電子移動型の電子化物を作り分けることができよう。

つまり用いる元素の種類やカゴ状構造の選択により異なる性質を持つ元素ブロックの作り分けが可能である。これらのカゴ状分子の両側に適切な官能基をつけて図3のように高分子に組み込むことができれば、導電性、誘電性、磁性、特徴的な光物性など種々の機能を持つソフトマテリアル電子化物の作製が可能になると考えられる。現在そのような分子設計をさらに開始している。

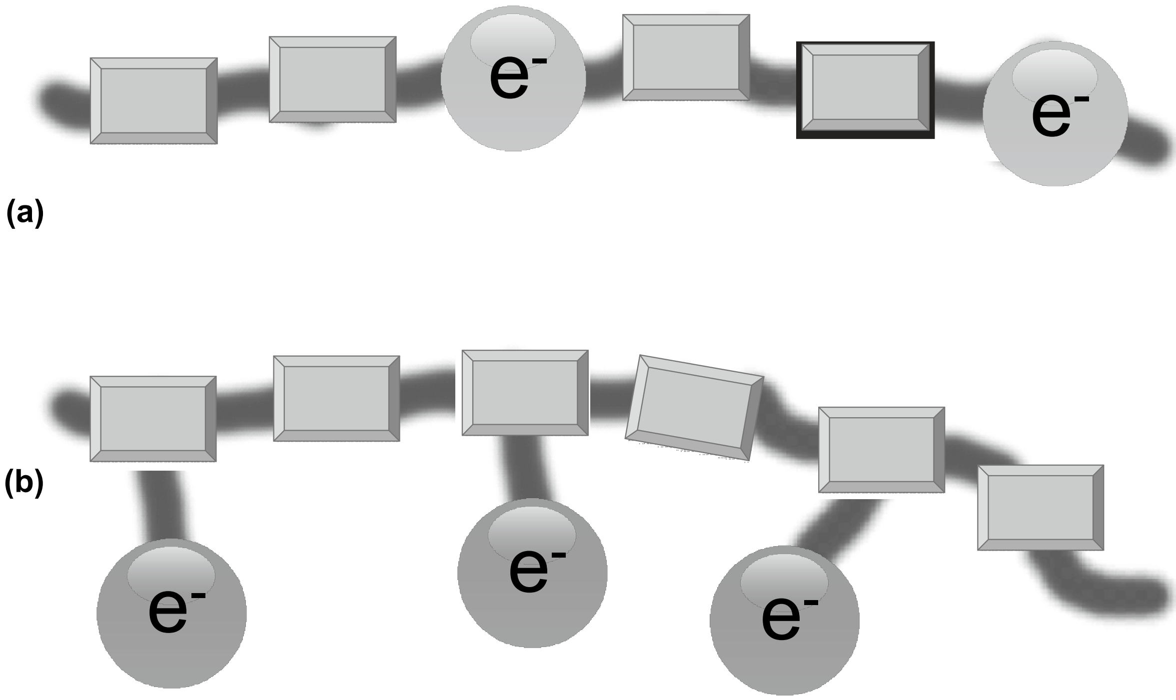


Fig. 3　Concepts of soft-material electride consisting of polymer chain and $As_4S_6^-$ or POB^- element-block. (a) Catenated and (b) suspended types.

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3G1-31

5. その他

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（2） 田中一義
「企業研究者のための計算化学」京都グリーンケミカル・ネットワーク人材育成事業第３回、京都（京都市成長産業創造センター）2016/12/6　（講演番号なし）

４．リサーチリーダー

Kazuo Takatsuka

Research Leader

1. Summary of the research of the year

Synchronizing with rapid progress in cutting-edge experimental methodologies such as ultrafast and intense pulse laser technology, we have been developing a basic framework of theoretical chemistry, which we call the theory of nonadiabatic electron wavepacket dynamics, with an aim of applications to real-time tracking of the coupled dynamics of electron and nuclear wavepakets within a molecule and to control of chemical reactions based on insights thus attained.

(i) Lorentz-force-like multidimensional effects of nonadiabatic interactions that can mechanically break the symmetric production of optical isomers [9]

The Longuett-Higgins (Berry) phase arising from nonadiabatic dynamics and the Aharonov-Bohm phase associated with the dynamics of a charged particle in electromagnetic vector potential are well known to be individually a manifestation of a class of the so-called geometrical phase. We have found and discussed another similarity between the force working on a charged particle moving in a magnetic field, the Lorentz force, and a force working on nuclei while passing across a region where they have a strong quantum mechanical kinematic (nonadiabatic) coupling with electrons in a molecule. This kinematic force is indeed akin to the Lorentz force in that its magnitude is proportional to the velocity of the relevant nuclei and works in the direction perpendicular to its translational motion. Hence this Lorentz-like nonadiabatic force is realized only in space of more or equal to three dimensions, thereby highlighting a truly multi-dimensional effect of nonadiabatic interaction. We have investigated its physical significance qualitatively in the context of breaking of molecular spatial symmetry, which is not seen otherwise without this force. This particular symmetry-breaking is demonstrated in application to a coplanar collision between a planar molecule and an atom sharing the same plane. It has been found that the atom is guided by this force to the direction out from the plane, resulting in a configuration that distinguishes one side of the mirror plane from the other. This can serve as a trigger for the dynamics towards molecular chirality.

(ii) Application of the nonadiabatic electron wavepacket theory to chemical reactions in excited states

ii-1) Chemistry beyond the notion of potential energy surface [4]

Following the previous study on nonadiabatic reaction dynamics including boron clusters [Yonehara and Takatsuka, J. Chem. Phys. 137, 22A520 (2012)], we explored deep into highly excited electronic states of the singlet boron cluster (B□□) to find the characteristic features of the densely quasi-degenerate electronic state manifold, which undergo extremely frequent nonadiabatic transitions and thereby intensive electronic state mixing among very many of the relevant states. So much so, isolating the individual adiabatic states and tracking the expected potential energy surfaces both lose the physical sense. This domain of molecular situation is far beyond the realm of the Born-Oppenheimer approximation. To survey such a violent electronic state-mixing, we applied a method of nonadiabatic electron wavepacket dynamics, here actually the semiclassical Ehrenfest method. We have tracked those electron wavepackets and found the electronic state mixing looks like an ultrafast diffusion (actually, a fractional Brownian motion) in the Hilbert space, which results in huge fluctuation in the electronic-state space. Furthermore, due to such a violent mixing, the quantum phases associated with the electronic states are swiftly randomized, and consequently the coherence among the electronic states are lost quickly. Besides, these highly excited states are mostly of highly poly-radical nature, even in the spin singlet manifold and the number of radicals amounts up to 10 electrons in the sense of unpaired electrons. Thus the electronic states are summarized to be poly-radical and decoherent with huge fluctuation in shorter time scales of vibrational motions. The present numerical study thus sets a theoretical foundation for unknown molecular properties and chemical reactivity of such densely quasi-degenerate chemical species.

ii-2) Coupled proton and electron-wavepacket transfer (CPEWT) as a universal mechanism of charge separation in organic and biological molecular systems [5,8]

We have proposed an excited-state mechanism of charge separation (proton-electron pair creation) relevant to the photoinduced water-splitting reaction ($2H_2O \rightarrow 4H^+ + 4e^- + O_2$) catalyzed by Mn-H□O systems. The water splitting is conceived to be triggered by photoinduced charge separation, in which electrons are detached from a proton in water. We here study the detailed mechanism of the charge separation by means of the theory of nonadiabatic electron wavepacket dynamics, in which all the electrons and nuclei of the molecules are considered. The mechanism has been examined in terms of simple model systems generally expressed as X--Mn--OH□···A, where X = (OH, Ca(OH)□) and A = (N-methylformamidine, guanidine, imidazole or ammonia cluster). We have found that both an electron and a proton are simultaneously transferred from donor site to the acceptors through conical intersections. In this mechanism, the electron takes different pathways from that of the proton and reach the Rydberg--like states of the acceptors, thereby inducing charge separation. We have found another crucial nonadiabatic process that deteriorates the efficiency of charge separation by rendering the created pair of proton and electron back to the originally donor site through the states of d-d band originated from Mn atom. Repetition of this process gradually annihilates the created pair of proton and electron in a way different from the usual charge recombination process. We addressed this dynamics also by means of a path--branching representation. The dynamical roles of doped Ca atom are also revealed, such as the change of the pathways of electron flow and reducing the annihilation dynamics of proton-electron pair.

ii-3) Substituent effects on photoisomerization in polyene; which double-bond will be broken to a single-bond in radiationless transition? [7]

Guided by a notion of symmetry-breaking modulation or control of the so-called symmetry allowed conical intersection by shining laser pulses [Y. Arasaki et al. PCCP, 2010, 12, 1239], we have explored a possibility of the modulation of the symmetry allowed conical intersection by chemical substitution with functional groups. As a first case study, we chose photoisomerization dynamics of s-trans-1,3-butadiene H□C=CH-CH=CH□ with one of the terminal hydrogen atom being replaced by -CF□. The target here is not the control of the rate of nonadiabatic transition but to know which one of the double bonds is more frequently isomerized in the radiationless quenching process on the way back to the ground state. We have analyzed when and how the symmetry is broken by tracking ab initio molecular dynamics paths, the mean-field paths with use of the nonadiabatic electron wavepacket dynamics, and the associated branching-paths.

(iii) Dynamics of ultrafast photoionozation and Auger process from electronic wavepacket states [10]

One of the critical difficulties in the present theory of molecular science is the lack of an appropriate method to cope with ionization dynamics of polyatomic molecules, which is induced by multiphoton electronic-state excitation due to pulse laser through wavepacket state or by electronic avalanche dynamics (the Auger process) to fill up a hole laser-created in inner shells. We have proposed a practical theory for dynamics of molecular photoionization from nonadiabatic electron wavepackets driven by intense pulse lasers Herein theime evolution of photoelectron distribution is evaluated in terms of out-going electron flux (current of the probability density of electrons) that has kinetic energy high enough to recede from the molecular system. The relevant electron flux is in turn evaluated with the complex-valued electronic wavefunctions that are time evolved in nonadiabatic electron wavepacket dynamics in laser fields. To uniquely rebuild such wavefunctions with its electronic population being lost by ionization, we adopt the complex-valued natural orbitals emerging from the electron density as building block of the total wavefunction. The method has been implemented into a quantum chemistry code, which is based on configuration state mixing for polyatomic molecules. Some of the practical aspects needed for its application will be presented. As a first illustrative example, we show the results of hydrogen molecule and its isotope substitutes (HD and DD), which are photoionized by a two-cycle pulse laser. Photon emission spectrum associated with above threshold ionization is also shown. Another example is taken from photoionization dynamics of a water molecule. Qualitatively significant effects of nonadiabatic interaction on the photoelectron spectrum are demonstrated. Thus we have opened a gate to proceed into a new field of chemical physics.

(iv) Ultrafast nuclear wavepacket dynamics driven by intense pulse lasers

iv-1) Creation of a novel molecular state created by an interplay between laser and nonadiabatic interactions [1]

When a nonadiabatic system that has an ionic state (large dipole moment) and a covalent state (small dipole moment) is located in a strong laser field, the crossing point of the two potential energy curves is forced to oscillate due to the oscillating laser field and to meet wavepackets moving on the potential curves many times. This leads to additional transitions between the two states, and under favorable conditions, the wavepacket may be confined in a spatial region rich in nonadiabatic interaction. In this paper, taking the LiF molecule system in a continuous-wave driving field as a prototypical example, the dynamical origins of the wavepacket confinement has been investigated. Identification of such new states that is not found in mother nature will extend our realm of chemistry.

iv-2) Very characteristic photon emission induced by CW laser on molecules having intramolecular electron transfer through nonadiabatic transitions [3,6]

We have proposed a theoretical principle to directly monitor the bifurcation of quantum wavepackets passing through nonadiabatic regions of a molecule that is placed in intense continuous wave (CW) laser fields. This idea makes use of the phenomenon of laser-driven photon emission from molecules that can undergo nonadiabatic transitions between ionic and covalent potential energy surfaces like Li^+ F^- and LiF. The resultant photon emission spectra are of anomalous yet characteristic frequency and intensity, if pumped to an energy level in which the nonadiabatic region is accessible and placed in a CW laser field. The proposed method is designed to take the time-frequency spectrogram with an appropriate time-window from this photon emission to detect the time evolution of the frequency and intensity, which depend on the dynamics and location of the relevant nuclear wavepackets. This method is specifically designed for the study of dynamics in intense CW laser fields and is rather limited in scope than other techniques for femtosecond chemical dynamics in vacuum. The following characteristic features of dynamics can be mapped onto the spectrogram: (1) the period of driven vibrational motion (temporally confined vibrational states in otherwise dissociative channels, the period and other states of which dramatically vary depending on the CW driving lasers applied), (2) the existence of multiple nuclear wavepackets running individually on the field-dressed potential energy surfaces, (3) the time-scale of coherent interaction between the nuclear wavepackets running on ionic and covalent electronic states after their branching (the so-called coherence time in the terminology of the theory of nonadiabatic interaction), and so on.

(v) Theory of embedding mechanics in statistical environment; real-time chemical dynamics in statistically treated solvents [2]

We have proposed a basic theory to study real-time dynamics embedded in a large environment that is treated with statistical method. In light of great progress in the molecular-level studies on time-resolved spectroscopies, chemical reaction dynamics, and so on, not only in gas phase but in condensed phases like liquid solvents and even in crowded environments in living cells, we need to bridge over a gap between statistical mechanics and microscopic real-time dynamics. For instance, an analogy to gas-phase dynamics in which molecules are driven by the gradient of the potential energy hyper-surfaces (PES) suggests that particles in condensed phases should run on the free energy surface instead. Question is whether this anticipation is correct. To answer it, we here propose a mixed dynamics and statistical representation to treat chemical dynamics embedded in statistical ensemble. We first define entropy functional, which is a function of the phase-space position of the dynamical subsystem, being dressed with statistical weights from the statistical counterpart. We then consider the functionals of temperature, free energy, and chemical potential as their extensions in statistical mechanics, through which one can clarify the relationship between real-time microscopic dynamics and statistical quantities. As an illustrative example we show that molecules in the dynamical subsystem should run on the free-energy functional surface, if and only if the spatial gradients of temperature functional are all zero. Otherwise, additional forces emerge from the gradient of the temperature functional. Numerical demonstrations are presented in the very basic level of this theory of molecular dissociation in atomic cluster solvent. This theory is being extended to treat nonadiabatic electron wavepaket dynamics in statistical solvents.

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   Y. Arasaki, Y. Mizuno, S. Scheit, and K. Takatsuka, J. Chem. Phys. **144**, 044107 (10 pages) (2016).

2. Classical and semiclassical dynamics in statistical environments with a mixed dynamical and statistical representation.
   K. Takatsuka and K. Matsumoto, PCCP, **18**, 1771-1785 (2016).

3. A perturbation theoretic approach to the Riccati equation for the Floquet energies, spectral intensities, and cutoff energy of harmonic generation in photoemission from nonadiabatic electron-transfer dynamics driven by infrared CW laser fields.
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   (Also published in Mark S. Gordon Festschrift (virtual issue))

8. Photoinduced charge separation catalyzed by Mn-oxides onto a Y-shaped branching acceptor efficiently preventing charge recombination
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10. Dynamics of photoionization from molecular electronic wavepacket states in intense pulse laser fields: A nonadiabatic electron wavepacket study.
    Takahide Matsuoka and Kazuo Takatsuka, J. Chem. Phys. **146**,134114 (14 pages) (2017).

3. Presentation at academic conferences

(1) 高塚和夫
「溶媒中の電子移動の非断熱電子動力学： Marcus 理論の分子論」
第 19 理論化学討論会，2016 年 5 月 23 日～2016 年 5 月 25 日，早稲田大学

(2) Kazuo Takatsuka
“Quantum Chemistry beyond the Born-Oppenheimer Approximation”
JFS 2016.10.26-28, FIFC, 2016 年 10 月 26 日～2016 年 10 月 28 日 福井謙一記念研究センター

(3) Kazuo Takatsuka
“Molecular Science of Nonadiabatic Electron Wavepackets: Trying to bridge between
ultrafast nonadiabatic dynamics and chemistry”
The 77th Okazaki Conference Series: International Symposium on Ultrafast Dynamics

in Molecular and Material Sciences, 2017年3月6日～2017年3月8日, 岡崎コンファレンスセンター

(4) Kazuo Takatsuka
“Chemistry of nonadiabatic electron flow : Symmetry Breaking in Chemical Reactions”
GAMESS7557, 2017.1.16-18, Kauai, Hawaii

(5) 高塚和夫
「化学反応における電子動力学 ー電子の運動が観える時代の基礎化学ー」
福井センターシンポジウム FIFC 1.27.2017

(6) 新崎康樹, 高塚和夫
“Semiclassical computation of photoelectron signals from conical intersection dynamics”
International Symposium on Ultrafast Dynamics in Molecular and Material Sciences, 2017年3月6日～2017年3月8日岡崎コンファレンスセンター

(7) Kentaro Yamamoto, Kazuo Takatsuka
“Photochemical mechanism of charge separation taken out of water molecule”
第19理論化学討論会, 2016年5月23日～2016年5月25日, 早稲田大学

(8) Kentaro Yamamoto, Kazuo Takatsuka
「光化学系 II における水分解の初期段階の機構について; Y 字型 Coupled Proton-Electron Transfer
第20回分子科学討論会」, 2016年9月13日～2016年9月15日, 神戸ファッションマート

(9) Kentaro Yamamoto, Kazuo Takatsuka
“Photoinduced Charge Separation Catalyzed by Mn-Oxides onto a Y-shaped Branching Acceptor Efficiently Preventing Charge Recombination”
JFS-Joint Symposium on Theoretical and Computational Science of Complex Systems, 2016年10月26日～2016年10月28日, 福井謙一記念研究センター

(10) Kentaro Yamamoto, Kazuo Takatsuka
“Photoinduced Charge Separation Catalyzed by Mn-Oxides onto a Y-shaped Branching Acceptor Efficiently Preventing Charge Recombination”
第14回京都大学福井謙一記念研究センターシンポジウム, 2017年1月27日, 福井謙一記念研究センター

(11)　Kentaro Yamamoto, Kazuo Takatsuka
“Photodynamical electron-wavepacket mechanism of water-splitting catalyzed by manganese oxides involving hydrogen-bond network”
The 77th Okazaki Conference Series: International Symposium on Ultrafast Dynamics in Molecular and Material Sciences, 2017年3月6日～2017年3月8日, 岡崎コンファレンスセンター

(12)　松岡貴英, 高塚和夫
「強レーザー場中の励起分子からのイオン化過程の非断熱電子動力学」
第19回　理論化学討論会, 2016年5月23日～2016年5月25日
早稲田大学

(13)　松岡貴英, 高塚和夫
「強光子場中多原子分子の電離過程における非断熱電子動力学」
第10回分子科学討論会2016神戸, 2016年9月13日～2016年9月15日, 神戸ファッションマート

(14)　Takahide Matsuoka, Kazuo Takatsuka
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(15)　松岡貴英, 高塚和夫
「高強度パルスレーザー場中のイオン化過程の非断熱電子ダイナミックス」
第14回京都大学福井謙一記念研究センターシンポジウム, 2017年1月27日, 福井謙一記念研究センター

(16)　Takahide Matsuoka, Kazuo Takatsuka
“Dynamics of photoionization from molecular electronic wavepacket states in intense pulse laser fields”
第77回岡崎コンファレンス, 2017年3月6日～2017年3月8日, 岡崎カンファレンスセンター

５．研究員

北浦　和夫

研究員

1．今年度の研究の要約

今年度は巨大分子・分子系のための新しい分子軌道計算法を開発した。

【はじめに】ナノサイズ物質の構造・機能を解明・予測・設計するための基盤的ツールのひとつとして、大規模分子系の電子状態計算法がある。1990年頃から巨大系の計算法の研究が活発に展開され、さまざまな方法が提案されている 1)。我々は、Huzinagaのサブシステム SCF 法 2)に基づいて、数千～数万原子系からなる巨大分子系の計算法として、Group molecular orbital (GMO)法を開発した。

【理論】系を *N* 個のグループに分割する。分子集合体の場合は、各分子を１グループとし(図 1a の G*i*)、共有結合系はで、フラグメント分子軌道法に習って、結合電子対を保ったまま切断してグループに分ける(図 1b の G*i*)。

グループ *I* の分子軌道は、Huzinaga のサブシステム SCF 方程式を一部修正した式(1)で求める。

$$\widetilde{\mathbf{F}}^I\mathbf{C}^I = \mathbf{S}^I\mathbf{C}^I\boldsymbol{\varepsilon}^I \quad (1)$$

$$\widetilde{F}^I_{\mu\nu} = F^I_{\mu\nu} + P^I_{\mu\nu} \quad (2)$$

$$F^I_{\mu\nu} = H^I_{\mu\nu} + V^{2,I}_{\mu\nu} + \sum_{J\neq I}\left(V^{1,J}_{\mu\nu} + V^{2,J}_{\mu\nu}\right) \quad (3)$$

$$V^{1,I}_{\mu\nu} = \sum_{A\in I}\langle\mu|\frac{-Z_A}{|\mathbf{r}-\mathbf{R}_A|}|\nu\rangle \quad (4)$$

$$V^{2,I}_{\mu\nu} = \sum_{\lambda,\sigma\in I} D^I_{\lambda\sigma}\left[(\mu\nu\,|\,\lambda\sigma) - \frac{1}{2}(\mu\lambda\,|\,\nu\sigma)\right] \quad (5)$$

$$P^I_{\mu\nu} = -\frac{\alpha}{4}\sum_{J\neq I}^{N^I_{\rm ovl}}\sum_{\mu',\nu'\in J} D^J_{\mu'\nu'}\left(F^J_{\mu\mu'}S^J_{\nu'\nu} + S^J_{\mu\mu'}F^J_{\nu'\nu}\right) \quad (6)$$

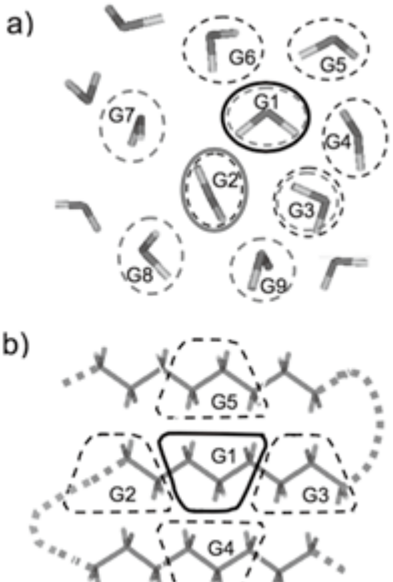

図 1 グループの定義。a)分子集合系の例、b)共有結合系の例。

F^I、H^I 、$\mathrm{V}^{1,I}$ 、と $\mathrm{V}^{2,I}$ と P^Iは、それぞれ、Fock、コアハミルトニアン、核引力、電子ー電子反発と射影演算子である。α はパラメータで、通常 2 である。 $N^I_{\rm ovl}$は overlapping group（後述）の数を示す。
グループ *I* の全電子エネルギー$E^{\rm ele}_I$と系の全エネルギーEは、それぞれ、次式と次次式となる（$E^{\rm nr}$は核間反発エネルギー）。

$$E^{\rm ele}_I = \frac{1}{2}\mathrm{Tr}\left\{\mathbf{D}^I\cdot\left(\widetilde{\mathbf{F}}^I + \mathbf{H}^I + \mathbf{P}^I\right)\right\} \quad (7)$$

$$E = \sum_{I}^{N} E_I^{\mathrm{ele}} + E^{\mathrm{nr}} \qquad (8)$$

グループIの基底関数は、グループの原子の基底関数と、Iとの距離がR-TAILS以内にあるグループ（tail groupと呼ぶ。図1aのG2-G6がG1のtail group）の原子の基底関数の和集合を用いる。基底関数がグループIのものと重なりがあるグループを、Iのoverlapping groupと呼ぶ。

GMO計算の流れは次のとおりである（図1)。

1）全グループについて、初期GMOを準備する。分子集合系の場合は、独立分子個々のab initio MO、共有結合系の場合は、切断端を適切な基（メチル基など）でキャップしたモデル分子のab initio MOをLMOに変換した後、キャップ基の電子に対応する不要なLMOを除いたLMOを初期GMOとする。

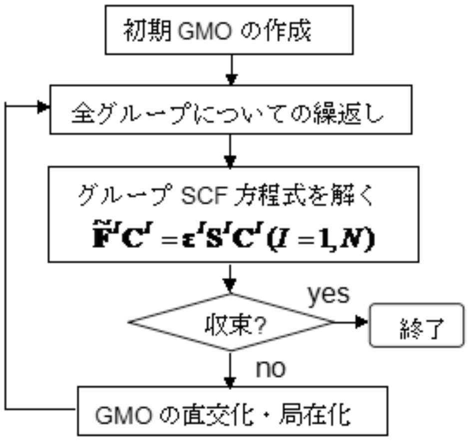

図2 GMO計算のフローチャート

2）全グループについて、式(1)を解く。

3）全グループについて、各groupのGMOとそのoverlap groupのGMOを直交化（局所直交化近似）した後、LMOに変換して当該groupの電子のLMOをそのグループのGMOとする。

4）全グループで、GMOの密度行列の前回との差が閾値以下になるまで、2)と3)を繰り返す。

【結果】GMOの精度と計算速度を検証した。GMO計算プログラムは、Pythonで作成しLotus[3)]に組み込んだものを用いた。

1）水分子集合体

$(H_2O)_n$（n=20、40、80。すべて球状クラスター)について、R-TAILS=3.2ÅでGMO計算を行った結果の全エネルギーの誤差（ab initio MOの値との差）を図3a)に示す。システムサイズが大きくいなるにつれて、誤差は大きくなるが､n=80で1分子あたり0.013(STO-3G), 0.067(6-31G), 0.072(6-31G*) kacl/molと十分小さい（R-TAILSを大きくとると誤差が小さくなる)。

2）n-alkaneの精度

C_nH_{2n+2}(n=20、40、60。すべて直鎖構造）について、$(CH_2)_4$を1グループにとり、R-TAILS=2.2ÅによるGMO計算の精度を図3b)に示す。水分子クラスターと異なって、この系ではGMOの誤差は負である。1グループあたりの全エネルギーの誤差は、-0.022(STO-3G)、-0.011(&-31G)、-0.014(6-31G*) kcal/molである。

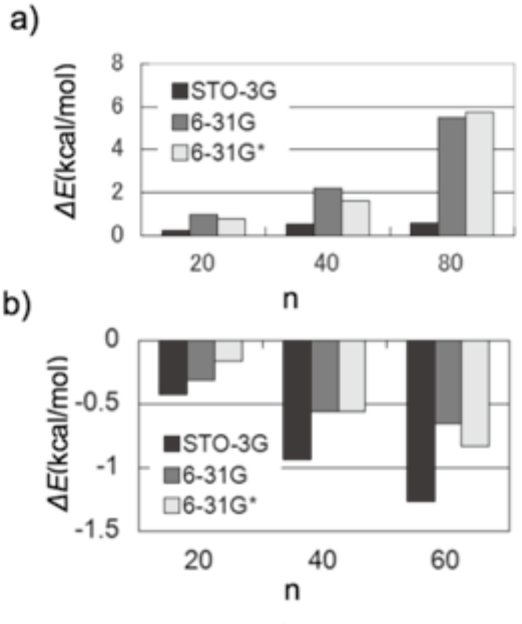

図3 全エネルギーの誤差。a)$(H_2O)_n$、b)C_nH_{2n+2}。

3）計算時間

$(H_2O)_n$球状クラスターの１分子あたりの計算時間を図 4 に示す。用いた基底関数は STO-3G である。GMO の計算時間のシステムサイズに対するべき乗依存性は 1.92 であり、ab initio MO のそれ 2.93 より低い。おおよそ、n=270 で交差し、n=500 では GMO が 2.6 倍高速である。

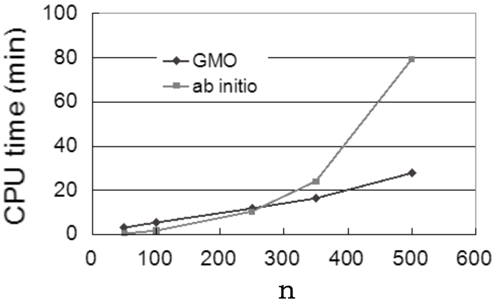

図 4 GMO と ab initio 計算時間の比較。系は$(H_2O)_n$、基底関数は STO-3G。

【まとめ】GMO 法は、満足できる精度を持ち、大きな系で伝統的な ab initio MO 法より高速であることから、巨大分子の実用的な計算法として有望であることが分かった。現在、さらに高速化するために、GMO のリニアスケーリング化を行っている。また、並列計算に向けてプログラムを改良中である。

【文献】 1) Gordon, M. S.; Pruitt, S. R.; Fedorov, D. G.; Slipchenko, L. V. *Chem. Rev.* **2012**, *112*, 632–672, 2) S. Huzinaga and A. A. Cantu, J. Chem. Phys. 55,5543 (1971), 3) T. Shimazaki, M. Hashimoto and T. Maeda, Proceedings of the 3rd International Workshop on Software Engineering for High Performance Computing in Computational Science and Engineering, Association for Computing Machinery 9(2015).

2．論文

(1) Tomomi Shimazaki, Kazuo Kitaura, Dmitri G. Fedorov, Takeshi Nakajima
“Gropup molecular orbital approarch to solve Huzinaga subsystem self-consistent-field equations”
J. Chem. Phys. 146(8) 084109(2017).

(2) Dmitri G. Fedorov, Kazuo Kitaura
"Many-body expansion of the Fock matrix in the fragment molecular orbital method"
J. Chem. Phys. 147(10)104106(2017).

６．博士研究員

Takuya Saito

FIFC Fellow

1. Summary of the research of the year

Complementary mode analyses for sub- and superdiffusion

A tagged monomer of a polymer undergoes anomalous diffusion. Through the fluctuation-dissipation relation, the diffusion is associated with a response. To verify the relation between the diffusion and response, there are two typical protocols; (i) observing the position while pulling with the constant force, (ii) the momentum transfer while pulling with the constant velocity (the momentum transfer is monitored by integrating the force acting on the tagged monomer with respect to time). The generalized Langevin equations with the power-law kernels describe those dynamics. The one kernel is converted into the other with the Laplace transform so that the sum of the exponents for sub- and superdiffusion is constant value 2, i.e., $\left\langle \delta\Delta x(t)^2 \right\rangle \sim t^{\alpha}$, $\left\langle \delta\Delta p(t)^2 \right\rangle \sim t^{2-\alpha}$. This means that, if the one shows subdiffusion, the other does invariably superdiffusion.

In the protocol (i) for the polymer, the tagged monomer shows the subdiffusion. The GLE generating the subdiffusion is decomposed into equations of motion in mode space with the restoring force. On the other hand, the superdiffusion is observed at the constant velocity protocol (ii). The mode analysis for the subdiffusion is no longer applied to the superdiffusion, since the subdiffusion mode analysis generates the subdiffusion, but not the superdiffusion even if tuning the exponents of the power law in the coefficients.

We then proposed the mode analysis for the superdiffusion. Equation of motion in the mode space for the superdiffusion has the form of the underdamped Langevin equation, which is derived by investigating the decomposition of the kernel in the generalized Langevin equation. Superimposing the modes, the GLE for the superdiffusion of the momentum transfer is reproduced. In a similar way, the numerical verifications suggested that the mode analysis for the superdiffusion generates the superdiffusion, but not the subdiffusion.

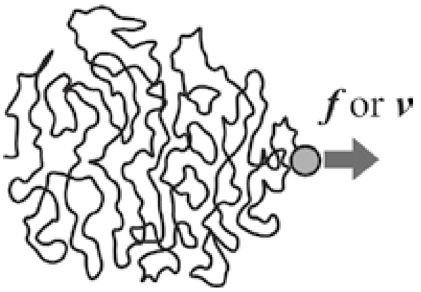

Fig 1. Schematic representation of a polymer in near-equilibrium state when weakly pulling at constant force f or velocity v.

The mode analyses for the sub- and superdiffusion is complimentary, totally covering the exponents range $0 < \alpha < 2$.

Nonequilibrium mode analyses for superdiffusion

The fluctuation-dissipation relation (FDR) is not ensured in the nonequilibrium condition. Indeed, the FDR derivation was found in the polymer stretching at the constant force protocol, where the subdiffusion was observed. The mode analysis for the subdiffusion can qualitatively describe the FDR derivation by giving the Langevin equation for the stretching state, which has the form of the overdamped Langevin equation with harmonic potential in the normal mode.

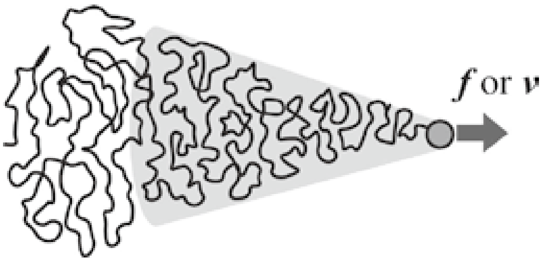

Fig 2. Schematic representation of a polymer in transient stretching process.

However, as clarified in the equilibrium mode analyses, the mode for the subdiffusion cannot be applied to dynamics for the superdiffusion and vice versa. To describe superdiffusion in the nonequilibrium, we then need the different approach and studying the nonequilibrium mode analysis for the superdiffusion.

First we performed the molecular dynamics (MD) simulation for the polymer stretching at the constant velocity protocol. To achieve the nonequilibrium, the operation velocity is set to be high. We established the plot of the normalized ratio of the variance to the average momentum, which takes a value 2 if the FDR holds. The results show that (1) the ratio almost retains the value 2 at the beginning, but (2) it goes upward and peaks, (3) it eventually turns back to the value 2. This is interpreted by the following scenario: (1) the equilibrium modes are monitored until the first blob forms. As a result, the FDR is maintained. (2) The transient nonequilibrium modes show up and the ratio deviates from the value 2. (3) The center of mass mode dominates after the internal modes relax. The FDR then finally recovers. To explain the simulation results, we discussed the mode analysis for the superdiffusion.

Active diffusion driven by athermal noise

Besides the thermal noise, studying athermal noise could shed a new insight into the fluctuation in a living cell. We then theoretically investigate the active diffusion driven by athermal noise. By introducing the effective friction, we drive the scaling laws for the athermally driven system. In addition, in the presence of the active noise, we discussed the various polymeric characteristics or situations, which include the self-avoiding effect, hydrodynamic interactions, branching and the viscoelastic conditions.

2. Original papers

(1) Takahiro Sakaue, and Takuya Saito,
“Active diffusion of model chromosomal loci driven by athermal noise”
Soft matter 13, 81(2017).

3. Presentation at academic conferences

(1) Takuya Saito and Takahiro Sakaue
“Fluctuations in driven polymer stretching with constant velocity”
Kakuma Campus, Kanazawa University, Ishikawa, Sep 16, 2017

4. Others

(1) Takuya Saito
“駆動される高分子の標識されたモノマーの異常拡散”
ERI, The University of Tokyo, Tokyo, Sep. 21, 2016.

Mitsusuke Tarama

FIFC Fellow

1. Summary of the research of the year

Swinging motion of active deformable particles in Poiseuille flow

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 microswimmers such 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 the 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.

Although by breaking symmetry active particles achieve spontaneous motion, in most practical situations this motion is influenced by the environment in various manners. Indeed it is an interesting problem how active particles behave as a consequence of the interplay between active motion and external stimuli. For active particles swimming in a fluid environment the effect of the external flow field is crucial. A simple linear shear flow, Poiseuille flow, and swirl flow are characteristic flow profiles. Here we discuss the case of a Poisueille flow, which often appears in a flow channel.

In particular, we are interested in the effect on deformable active particles such as liquid droplets that self-propel due to Marangoni effect. Based on symmetry considerations, we have derived a set of coupled nonlinear time-evolution equations that models active deformable particles under an external flow field [1]. Here we considered the Poiseuille flow profile of the form **u** = (u_0(1-Y), 0), as sketched in Fig. 1(a). The effect of the boundary walls placed at Y = ±1 are taken into account by a soft repulsive potential and the hydrodynamic interaction is omitted. For simplicity, we take into consideration the lowest mode deformation, i.e., the second-mode deformation which represents an elliptical (ellipsoidal in 3d) deformation, and we confine ourselves to a two-dimensional space. From symmetry, the particles tend to self-propel in either parallel or perpendicular direction with respect to the longitudinal axis of the elliptical shape deformation, as sketched in Figs. 1(b) and 1(c). We refer to these cases as parallel and perpendicular particles, respectively.

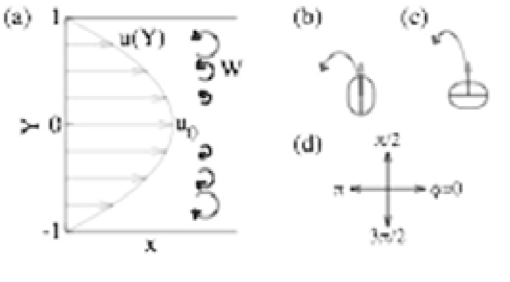

Fig. 1: Sketches of (a) the flow velocity u(Y) and vorticity W, the particles with (b) parallel and (c) perpendicular configurations, and (d) the value of the angle φ. This figure is reproduced from Ref. [3].

For the case of rigid active particles, or active colloids, the dynamics in Poiseuille flow have been studied in detail [2]. Zöttl and Stark showed that both, the circular active colloids and the slender elliptical active colloids, that correspond to the parallel particles, undergo swinging motion around the centerline of the flow as well as tumbling motion. In the limit of a rigid elliptical shape and in the over-damped limit, our model is reduced to the one studied by Zöttl and Stark. Then, we solved the equations of motion analytically. The solutions are characterized by the vertical position Y to the streamline and the direction of the active velocity φ, as shown in Fig. 2. See Fig. 1(d) for the definition of φ. We found that the parallel and perpendicular particles show qualitatively the same dynamics. Namely, in both cases the particles exhibit swinging motion around the centerline and tumbling motion, which are displayed by the gray solid lines and the black broken lines in Fig. 2. Those solutions are divided by the separatrix plotted by the blue solid line in Fig. 2.

When the active particle is deformable, the time-evolution equations are too complicated to solve analytically and therefore we integrated them numerically [3]. We varied the strength of the self-propulsion α and the external Poiseuille flow u_0. We found that the parallel and perpendicular particles exhibit different dynamics. Note that, in the absence of the external flow, there is a bifurcation from straight motion to circular motion at $\alpha = \alpha_c$ [4].

First, we explain the motion of the parallel particles. The results are summarized in the phase diagram in Fig. 3(a). For $0 < \alpha < \alpha_c$, these particles showed swinging motion around the centreline for the parameters indicated by the black open circles in Fig. 3(a). Although most swinging particles moved downstream as depicted in Fig. 3(d), upstream swinging motion was also found for a relatively small flow velocity as shown in Fig. 3(c). For very small u_0 as indicated by the pluses in Fig. 3(a), the particle touched the confinement at $Y = \pm 1$, as displayed in Fig. 3(b). These solutions coexisted with tumbling

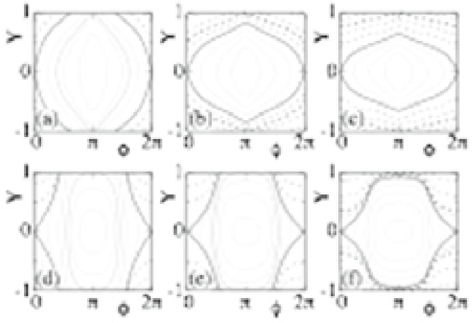

Fig. 2: The trajectories in the Y-φ space of the solutions of rigid active particles with [(a)–(c)] the parallel configuration and [(d)–(f)] the perpendicular configuration. The gray solid lines and the black broken lines correspond to the swinging motion around the centerline and the tumbling motion, respectively, which are separated by the separatrix displayed by the dark gray solid line. The flow velocity is chosen as $u_0 = 0.25$ for (a) and (d), 0.6 for (b) and (e), and 1 for (c) and (f). This figure is reproduced from Ref. [3].

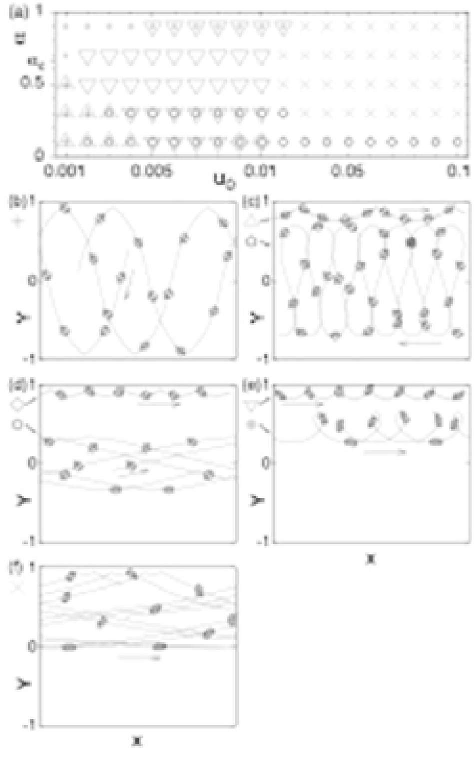

Fig. 3: Dynamics of parallel particles in the Poiseuille flow. (a) Dynamical phase diagram. (b)–(f) Characteristic real-space trajectories of (b) bouncing motion between the two channel walls; (c) upstream swinging motion [dark gray line] and bouncing motion against the wall with the shape oscillating around $\theta = 0$ [light gray line]; (d) downstream swinging motion [dark gray line] and bouncing motion against the wall with the shape oscillating around the diagonal direction [light gray line]; (e) cycloidal motion [dark gray line] and tumbling motion at the wall [light gray line]; (f) bouncing motion with excursion to the middle of the channel. This figure is reproduced from Ref. [3].

motion, as shown in Fig. 3(e), and two types of bouncing motion, as in Figs. 3(c) and 3(d), which were obtained for the parameters indicated by the magenta down triangles, pink up triangles, and purple diamonds in Fig. 3(a), respectively. For $\alpha > \alpha_c$, the particles exhibited cycloidal motion, as shown in Fig. 3(e) for cyan dots in Fig. 3(a). At the orange crosses in Fig. 3(a), the particle underwent bouncing motion against one wall with an excursion to the middle of the channel, as shown in Fig. 3(f).

Next, we discuss the motion of the perpendicular particles. The results are summarized in the phase diagram displayed in Fig. 4(a). In this case, swinging motion was not observed. For $\alpha < \alpha_c$, the perpendicular particles showed bouncing motion between two walls as shown in Fig. 4(b), which were obtained for the red plusses in Fig. 4(a). For large u_0, at the purple pentagons in Fig. 4(a), the particles bounced against one wall as displayed in Fig. 4(c). Interestingly, for further increased u_0, the perpendicular particles exhibited straight motion along a streamline far from the channel walls as depicted in Fig. 4(d). Such solution was observed at the blue squares in Fig. 4(a). For $\alpha > \alpha_c$, cycloidal motion and tumbling motion are obtained, as shown in Fig. 4(e), at the cyan dotes and at the magenta down triangles in Fig. 4(a). At the orange cross in Fig. 4(a), the particle bounced against the one wall with an excursion to the middle of the channel, as shown in Fig. 4(f).

In summary, we investigated the dynamics of active deformable particles in an external Poiseuille flow. First, we clarified the relation of our model to that of rigid active particles. Then, we studied the dynamical modes that active deformable particles exhibit by changing the strength of the external flow. We emphasized the difference between the active particles that tend to self-propel parallel to the elliptical shape deformation and those self-propelling perpendicularly. In particular, we found that the parallel particles exhibit the swinging motion, whereas the perpendicular particles show a straight motion along the stream line.

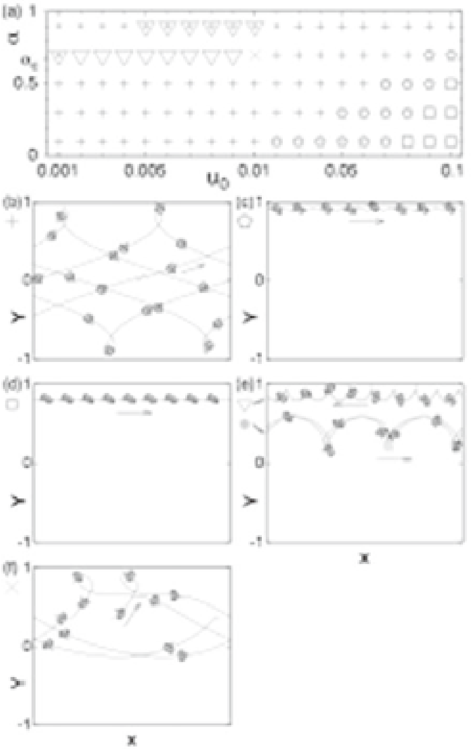

Fig. 4: Dynamics of perpendicular particles in the Poiseuille flow. (a) Dynamical phase diagram. (b)–(f) Characteristic trajectories of each dynamical motion in real space. (b) Bouncing between the two channel walls; (c) Bouncing motion against one of the two walls; (d) Straight motion far from the channel wall; (e) Cycloidal motion [dark gray line] and tumbling motion at the wall [light gray line]; (f) Bouncing against the wall with an excursion to the middle of the channel. This figure is reproduced from Ref. [3].

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2. Original papers

(1) Mitsusuke Tarama and Takao Ohta
"Reciprocating motion of active deformable particles"
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3. Presentation at academic conferences

(1) Mitsusuke Tarama, and Takao Ohta,
"Appearance of reciprocating motion of active deformable particles"
Synergy of Fluctuation and Structure: Quest for Universal Laws in Non-Equilibrium Systems: The third research area meeting, Kyushu University, Japan, 18 Jun., 2016 (poster).

(2) Mitsusuke Tarama, and Takao Ohta,
"Reciprocating motion of active deformable particles in homogeneous media"
Statphys26, the Palais des Congrès de Lyon, Lyon, France, 18-22 Jul., 2016 (poster).

(3) Mitsusuke Tarama, and Takao Ohta,
"Back-and-forth motion of active soft particle"
The 4th International Soft Matter Conference, the centre Alpes-Congrès at Alpexpo, Grenoble, France, 15 Sep., 2016 (poster).

(4) Mitsusuke Tarama, and Takao Ohta
"Back-and-forth motion of active deformable particles"
Microswimmers – From Single Particle Motion to Collective Behaviour, the Forschungszentrum caesar, Bonn, Germany, 6 Oct., 2016 (poster).

(5) Mitsusuke Tarama and Takao Ohta
"Reciprocating motion of active deformable particles"
Patterns in Nature Functions, Variations and Control, University of Bayreuth, Bayreuth, Germany, 10 Oct., 2016 (poster).

(6) Mitsusuke Tarama,
"Dynamics of active deformable particles: from swimming droplets to crawling cells"
Structured Soft Interfaces: Caught Between Multi-Scale Simulation and Application , Lorentz Center, Leiden University, the Netherlands, 23 Jan., 2017 (poster).

(7) 多羅間充輔,
"ポアズイユ流中での変形するアクティブマターのダイナミクス"
日本物理学会第72回年次大会, 大阪大学 豊中キャンパス, 17 Mar., 2017 (oral).

4. Others

(1) Mitsusuke Tarama
"アクティブマターの非線形ダイナミクス"
郡研セミナー, 御茶ノ水女子大学, 12 Apr., 2016.

Masato Itami

FIFC Fellow

1. Summary of the research of the year

Universal Form of Stochastic Evolution for Slow Variables in Equilibrium Systems

The main purpose of the present work is to re-derive nonlinear, multiplicative Langevin equations for a complete set of slow variables in equilibrium systems with particular emphasis of the separation of time scales and a universal asymptotic form of the probability density for time-averaged fluxes. We first assume a complete set of slow variables. Let τ_{macro} be the shortest time scale of the slow variables and τ_{micro} be the largest time scale of the other dynamical variables. Then, from the separation of time scales $\tau_{\mathrm{micro}} \ll \tau_{\mathrm{macro}}$ we can find Δt such that $\tau_{\mathrm{micro}} \ll \Delta t \ll \tau_{\mathrm{macro}}$. This Δt plays two crucial roles in the derivation of the equation for slow variables. First, because $\tau_{\mathrm{micro}} \ll \Delta t$, we can consider the central limit theorem for the time averaged flux as a universal form of the asymptotic behavior of the transition probability of the slow variables during a time interval Δt. The time reversibility in microscopic Hamiltonian systems provides a restriction on the transition probability. Second, because $\Delta t \ll \tau_{\mathrm{macro}}$, this universal form of the transition probability leads to the path integral form of a stochastic system. This stochastic system is nothing but the nonlinear, multiplicative Langevin equations. This concept is quite natural and general. Indeed, one can interpret the arguments of Onsager and Green through this concept. Nevertheless, as far as we know, there is no explicit presentation of the derivation of the nonlinear, multiplicative Langevin equations with the universal asymptotic form of the probability density for time-averaged fluxes and the path integral formulation under $\tau_{\mathrm{micro}} \ll \Delta t \ll \tau_{\mathrm{macro}}$. We thus expect that this result will be instructive for understanding the universal form, and will also be useful for deriving the equation for slow variables even in systems out of equilibrium.

Here, we point out the difference between our and previous approaches. Our final goal is to establish a firm connection between a Langevin equation and a microscopic mechanical system. The previous studies using a projection operator method or a nonequilibrium statistical operator method have the same motivation as ours. Their methods use some physical approximation (such as a markovian approximation) just before obtaining a Langevin equation. The validity of the approximation depends on observation time scales and details of a system, and their formulation is based on only an identity, which is useful but far from a physical principle. Thus, their assumptions are out of scope of the theories. Then, we aim to achieve our goal with physical principles. From this motivation, we use the central limit theorem with the separation of time scales for connecting a microscopic mechanical and mesoscopic stochastic description in a mathematically and physically clear way. This work also differs from another type of derivation of the Langevin equation on the basis of arguments within stochastic processes. Their derivation is self-contained and elegant, but arguments relating to microscopic descriptions are out of scope of their theory. As a technical remark, we note that they used the Kolmogorov forward and backward equations for restricting the form of the Langevin equation by imposing a detailed balance condition, while we directly use the transition probabilities. Although we do not completely achieve our aim, we believe that it is important to show the outline of our approach even without a rigorous proof. Our approach is not simply another derivation of known results, but provides a new direction of future studies.

Setup and basic concept

We consider fluctuations of a system in equilibrium. There is a special set of variables whose time scales are well separated from those of the other dynamical degrees of freedom. We refer to such a set as a complete set of slow variables and denote it by $\boldsymbol{X} = (X^1, X^2, \dots, X^N)$. For simplicity, we assume that the Hamiltonian of the microscopic mechanical system is symmetric with respect to the time-reversal operation. For such a system, the probability density of $\boldsymbol{X}$ is denoted by $P_{eq}(\boldsymbol{X}) = \exp[S(\boldsymbol{X})]/Z$, where Z is the normalization constant, and $S(\boldsymbol{X}^*) = S(\boldsymbol{X})$ for the time reversal $\boldsymbol{X}^*$ of $\boldsymbol{X}$. The physical interpretation of S depends on the system being studied. For example, $S(\boldsymbol{X})$ corresponds to entropy when thermodynamic fluctuations in an isolated system are considered. For other cases, $S(\boldsymbol{X})$ should be read from the form of the stationary distribution. Suppose that the system is in equilibrium. We then expect that the time evolution of $\boldsymbol{X}$ can be described by a Langevin equation.

On the basis of a microscopic mechanical description, we can define the conditional probability density of $\boldsymbol{X} = \boldsymbol{X}_\mathrm{f}$ at time t, denoted by $P_t(\boldsymbol{X}_\mathrm{f}|\boldsymbol{X}_\mathrm{i})$, provided that $\boldsymbol{X} = \boldsymbol{X}_\mathrm{i}$ at time 0. There are two important properties of this probability density. First, following the central limit theorem, we assume the Gaussian form of form of the probability density for the time averaged flux written as $(\boldsymbol{X}_{\Delta t} - \boldsymbol{X})/\Delta t$. The result is given by

$$P_{\Delta t}(\boldsymbol{X}_\mathrm{f}|\boldsymbol{X}_\mathrm{i}) = \frac{1}{\sqrt{(4\pi\Delta t)^N \det L(\boldsymbol{X}_\mathrm{i})}} \exp\left[-\frac{\Delta t}{4}\sum_{i,j}(L^{-1})^{ij}(\boldsymbol{X}_\mathrm{i})\left[\frac{X_\mathrm{f}^i - X_\mathrm{i}^i}{\Delta t} - J^i(\boldsymbol{X}_\mathrm{i})\right]\left[\frac{X_\mathrm{f}^j - X_\mathrm{i}^j}{\Delta t} - J^j(\boldsymbol{X}_\mathrm{i})\right]\right], \quad (1)$$

where J^i is the most probable value of the time averaged flux, and $2L^{ij}$ is the dispersion matrix. We assume that the matrix $L = (L^{ij})$ is positive definite. Second, from the reversibility of microscopic Hamiltonian systems, we can obtain

$$P_{\Delta t}(\boldsymbol{X}_\mathrm{f}|\boldsymbol{X}_\mathrm{i})P_{eq}(\boldsymbol{X}_\mathrm{i}) = P_{\Delta t}(\boldsymbol{X}_\mathrm{i}^*|\boldsymbol{X}_\mathrm{f}^*)P_{eq}(\boldsymbol{X}_\mathrm{f}). \quad (2)$$

Then, by substituting (1) into (2), we obtain a possible form of $J^i(\boldsymbol{X})$ and a symmetry property of L. For convenience, we denote $\boldsymbol{X}^*$ by $\boldsymbol{\epsilon X} = (\epsilon^1 X^1, \epsilon^2 X^2, \dots, \epsilon^N X^N)$, where $\epsilon^i = +1 \text{ or } -1$ for X^i. We decompose $J^i(\boldsymbol{X})$ into two parts, $J^i(\boldsymbol{X}) = J^i_\mathrm{rev}(\boldsymbol{X}) + J^i_\mathrm{irr}(\boldsymbol{X})$ with $J^i_\mathrm{rev}(\boldsymbol{X}) = [J^i(\boldsymbol{X}) - \epsilon^i J^i(\boldsymbol{X}^*)]/2$ and $J^i_\mathrm{irr}(\boldsymbol{X}) = [J^i(\boldsymbol{X}) + \epsilon^i J^i(\boldsymbol{X}^*)]/2$, which satisfy $J^i_\mathrm{rev}(\boldsymbol{X}^*) = -\epsilon^i J^i_\mathrm{rev}(\boldsymbol{X})$ and $J^i_\mathrm{irr}(\boldsymbol{X}^*) = \epsilon^i J^i_\mathrm{irr}(\boldsymbol{X})$. We also define the matrix $L_\mathrm{T} = \left(L_\mathrm{T}^{ij}\right)$ by $L_\mathrm{T}^{ij}(\boldsymbol{X}) = \epsilon^i \epsilon^j L^{ij}(\boldsymbol{X}^*)$. Note that $\det L_\mathrm{T}(\boldsymbol{X}) = \det L(\boldsymbol{X}^*)$.

Results

Direct substitution of (1) into (2) would result in a complicated form, so we use a trick. Using the relations between different discretization schemes in a path integral formulation as first derived by Wissel, we can rewrite (1) in terms of $\boldsymbol{X}_\mathrm{m} = (\boldsymbol{X}_\mathrm{i} + \boldsymbol{X}_\mathrm{f})/2$ as

$$P_{\Delta t}(\boldsymbol{X}_{\mathrm{f}}|\boldsymbol{X}_{\mathrm{i}}) = \frac{1}{\sqrt{(4\pi\Delta t)^N \det L(\boldsymbol{X}_{\mathrm{m}})}} \exp\left[-\frac{\Delta t}{4}\sum_{i,j}(L^{-1})^{ij}(\boldsymbol{X}_{\mathrm{m}})\left[\frac{X_{\mathrm{f}}^i - X_{\mathrm{i}}^i}{\Delta t} - \tilde{J}^i(\boldsymbol{X}_{\mathrm{m}})\right]\left[\frac{X_{\mathrm{f}}^j - X_{\mathrm{i}}^j}{\Delta t} - \tilde{J}^j(\boldsymbol{X}_{\mathrm{m}})\right] - \frac{\Delta t}{2}\sum_i \frac{\partial J_{\mathrm{rev}}^i(\boldsymbol{X}_{\mathrm{m}})}{\partial X_{\mathrm{m}}^i} - \frac{\Delta t}{2}\sum_i \frac{\partial J_{\mathrm{irr}}^i(\boldsymbol{X}_{\mathrm{m}})}{\partial X_{\mathrm{m}}^i} + \frac{\Delta t}{4}\sum_{i,j}\frac{\partial L^{ij}(\boldsymbol{X}_{\mathrm{m}})}{\partial X_{\mathrm{m}}^i \partial X_{\mathrm{m}}^j}\right]$$

with

$$\tilde{J}^i(\boldsymbol{X}) = J_{\mathrm{rev}}^i(\boldsymbol{X}) + J_{\mathrm{irr}}^i(\boldsymbol{X}) - \sum_j \frac{\partial L^{ij}(\boldsymbol{X})}{\partial X^j}.$$

Substituting this into (2) with $P_{eq}(\boldsymbol{X}) = \exp[S(\boldsymbol{X})]/Z$, we obtain

$$0 = \frac{\Delta t}{4}\sum_{i,j}(L^{-1})^{ij}(\boldsymbol{X}_{\mathrm{m}})\left[\frac{X_{\mathrm{f}}^i - X_{\mathrm{i}}^i}{\Delta t} - \tilde{J}^i(\boldsymbol{X}_{\mathrm{m}})\right]\left[\frac{X_{\mathrm{f}}^j - X_{\mathrm{i}}^j}{\Delta t} - \tilde{J}^j(\boldsymbol{X}_{\mathrm{m}})\right]$$

$$- \frac{\Delta t}{4}\sum_{i,j}\left(L_{\mathrm{T}}^{-1}\right)^{ij}(\boldsymbol{X}_{\mathrm{m}})\left[\frac{X_{\mathrm{f}}^i - X_{\mathrm{i}}^i}{\Delta t} - \tilde{J}_{\mathrm{T}}^i(\boldsymbol{X}_{\mathrm{m}})\right]\left[\frac{X_{\mathrm{f}}^j - X_{\mathrm{i}}^j}{\Delta t} - \tilde{J}_{\mathrm{T}}^j(\boldsymbol{X}_{\mathrm{m}})\right] + \Delta t\sum_i \frac{\partial J_{\mathrm{rev}}^i(\boldsymbol{X}_{\mathrm{m}})}{\partial X_{\mathrm{m}}^i}$$

$$- \frac{\Delta t}{4}\sum_{i,j}\frac{\partial}{\partial X_{\mathrm{m}}^i \partial X_{\mathrm{m}}^j}\left[L^{ij}(\boldsymbol{X}_{\mathrm{m}}) - L_{\mathrm{T}}^{ij}(\boldsymbol{X}_{\mathrm{m}})\right] + \frac{1}{2}\log\frac{\det L(\boldsymbol{X}_{\mathrm{m}})}{\det L_{\mathrm{T}}(\boldsymbol{X}_{\mathrm{m}})} + \Delta t\sum_i \frac{X_{\mathrm{f}}^i - X_{\mathrm{i}}^i}{\Delta t}\frac{\partial S(\boldsymbol{X}_{\mathrm{m}})}{\partial X_{\mathrm{m}}^i}, \quad (3)$$

where $\tilde{J}_{\mathrm{T}}^i(\boldsymbol{X}) = J_{\mathrm{rev}}^i(\boldsymbol{X}) - J_{\mathrm{irr}}^i(\boldsymbol{X}) + \sum_j \frac{\partial L_{\mathrm{T}}^{ij}(\boldsymbol{X})}{\partial X^j}$, and we have used $S(\boldsymbol{X}_{\mathrm{f}}) - S(\boldsymbol{X}_{\mathrm{i}}) = \Delta t \sum_i \frac{X_{\mathrm{f}}^i - X_{\mathrm{i}}^i}{\Delta t}\frac{\partial S(\boldsymbol{X}_{\mathrm{m}})}{\partial X_{\mathrm{m}}^i} + O\left(\left(X_{\mathrm{f}}^i - X_{\mathrm{i}}^i\right)^2\right)$. Note that the $O\left(\left(X_{\mathrm{f}}^i - X_{\mathrm{i}}^i\right)^2\right)$ terms in (3) are irrelevant in the limit $\Delta t/\tau_{\mathrm{macro}} \to 0$. Because (3) holds for any $X_{\mathrm{f}}^i - X_{\mathrm{i}}^i$ and X_{m}^i, comparing the quadratic terms in $X_{\mathrm{f}}^i - X_{\mathrm{i}}^i$ in (3) yields $L^{ij}(\boldsymbol{X}) = L_{\mathrm{T}}^{ij}(\boldsymbol{X})$. Comparing the first terms in $X_{\mathrm{f}}^i - X_{\mathrm{i}}^i$ in (3), we also have

$$J_{\mathrm{irr}}^i(\boldsymbol{X}) = \sum_j L^{ij}(\boldsymbol{X})\frac{\partial S(\boldsymbol{X})}{\partial X^j} + \sum_j \frac{\partial L^{ij}(\boldsymbol{X})}{\partial X^j},$$

which is called the fluctuation dissipation relation of the second kind. Comparing the zero-order terms in $X_{\mathrm{f}}^i - X_{\mathrm{i}}^i$ in (3), we finally obtain $\sum_i \frac{\partial}{\partial X^i}\left[J_{\mathrm{rev}}^i(\boldsymbol{X})P_{eq}(\boldsymbol{X})\right]$.

Now we go back to (1). This is interpreted as the transition probability for the discrete time Langevin equation. By taking the limit $\Delta t/\tau_{\mathrm{macro}} \to 0$, we obtain

$$\frac{dX^i}{dt} = J_{\mathrm{rev}}^i(\boldsymbol{X}) + \sum_j L^{ij}(\boldsymbol{X})\frac{\partial S(\boldsymbol{X})}{\partial X^j} + \sum_j \frac{\partial L^{ij}(\boldsymbol{X})}{\partial X^j} + \sum_j l^{ij}(\boldsymbol{X}) \cdot \xi^j,$$

where $l^{ij}(\boldsymbol{X})$ satisfies $L^{ij}(\boldsymbol{X}) = \frac{1}{2}\sum_k l^{ik}(\boldsymbol{X})l^{jk}(\boldsymbol{X})$, ξ^i is the zero-mean Gaussian white noise with covariance $\langle \xi^i(t)\xi^j(s)\rangle = \delta^{ij}\delta(t-s)$, and · denotes multiplication with the Ito rule. The form of this equation is universal and equivalent to that obtained by Green.

2. Original papers

(1) Masato Itami and Shin-ichi Sasa,
“Universal Form of Stochastic Evolution for Slow Variables in Equilibrium Systems”
J. Stat. Phys. **167**(1), 46–63 (2017).

3. Presentation at academic conferences

(1) Masato Itami and Shin-ichi Sasa
“Derivation of Stokes’ law without the hydrodynamic equations”
STATPHYS26, Lyon, France, July 18-22, 2016 (poster).
(2) 伊丹將人、佐々真一
「平衡系における遅い変数の発展方程式の微視的導出」
日本物理学会第72回年次大会、大阪大学、2017年3月17-20日（口頭）

4. Others

(1) Masato Itami and Shin-ichi Sasa
“Universal Form of Stochastic Evolution for Slow Variables in Equilibrium Systems”
The 14th symposium of Fukui Institute for Fundamental Chemistry, Kyoto, Jan. 27, 2017 (poster).

Shunsuke Yabunaka

FIFC Fellow

1. Summary of the research of the year

Dynamics of electric double layers in the presence of selective solvation effects

Structure formation due to ions plays an important role in dynamics of biomaterials, such as proteins, and soft materials such as colloidal suspensions. There have been many theoretical studies on this topic without taking into account ion-solvent interactions and physical significance of ion-solvent interaction remains still elusive.

In liquid water, small metallic ions are surrounded by several water molecules to form a hydration shell due to the ion-dipole interaction. As a result, such ions are strongly hydrophilic. On the other hand, some ions are strongly hydrophobic. As an example, tetraphenylborate BPh4- with an 0.9nm has four phenyl rings and, due to its large size, it deforms hydrogen bonding, leading to strong hydrophobicity.

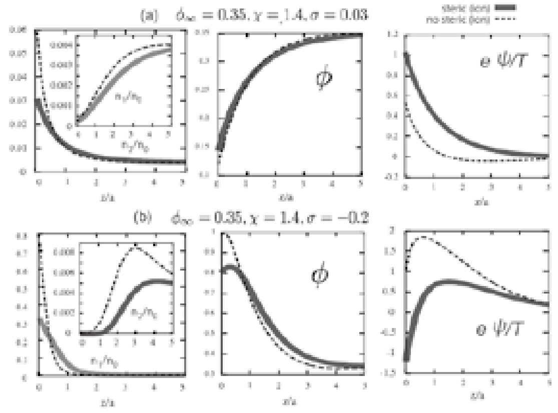


Fig. 1 Calculated profiles of ions (left), composition of polar component (middle) and electric potential (right) around the metallic wall with positive (top) and negative (bottom) surface charge.

I considered a mixture solvent (water-oil) with hydrophilic and hydrophobic ions near a charged metal wall in collaboration with Prof. Onuki (Kyoto University) (A. Onuki, S. Yabunaka, T. Araki and R. Okamoto, Current Opinion in Collioid Interface Science (2016)). Assuming that the system is uniform parallel to the wall, it reduces to a one-dimensional problem. I calculated equilibrium profiles of ion concentrations and composition as shown in Fig.1.

After completing this paper, we found that the surface voltage generally behaves as a nonmonotonous function of the surface charge due to the inversion of the electric double layer near the wall. This behavior indicates thermodynamic instability of laterally uniform one-dimensional solution. The simplest possible situation is illustrated in Fig. 1. We actually calculated 2 dimensional coexistence profile of two kinds of electric double layers (S. Yabunaka and A. Onuki submitted).

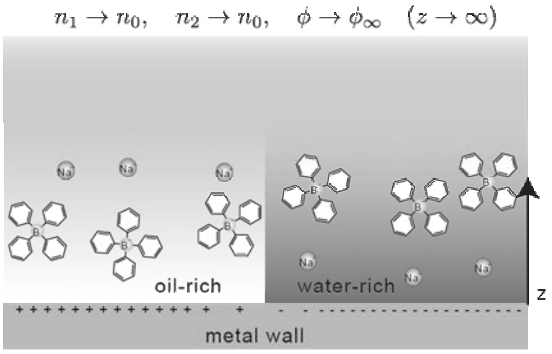


Fig. 2 Schematic representation of coexistence of two kinds of electric double layer containing small hydrophobic cations (Na+) and large hydrophobic anions (BPh4-) in an aqueous mixture on a metal wall.

Collective motion of fluid droplets under chemical reaction

Recently, collective motion of self-propelled particles has attracted much attention because such system may describe some universal features in collective motion of several biological systems, such as herd of animals, fish school etc. However, in theoretical studies, the self-propulsion and the interaction between droplets are introduced phenomenologically without deriving them from hydrodynamic equations.

As a first step toward understanding of collective motion, in collaboration with Dr. Yoshinaga, I theoretically derived the interaction between two self-propelling droplets (S. Yabunaka and N. Yoshinaga, Journal of Fluid Mechanics (2016)). As shown in Fig. 3, there are two contributions: (1) the hydrodynamic interaction due to the flow field and (2) the concentration-mediated interaction due to the overlap between the cloud-like profiles of the third component.

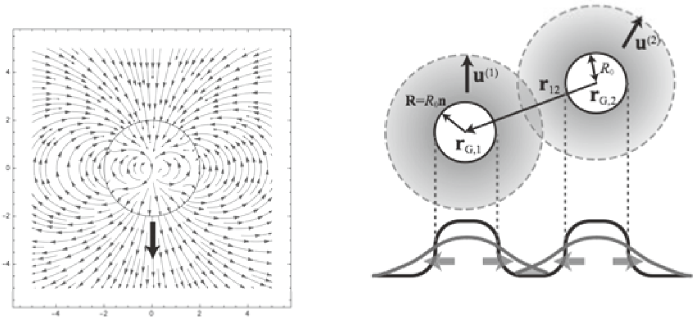


Fig. 3 Schematic explanations of the hydrodynamic interaction (Left) and the concentration-mediated interaction (Right)

Continuum theory of growing tissues

Cellular tissues are soft viscoelastic materials, similar to conventional soft materials. However there are several striking differences between tissues and conventional soft materials: (a) Cells generate active contractile forces consuming energy. (b) Cell motility. (c) Cell polarity. (d) Cell proliferation and death. To investigate properties of such active materials is of paramount importance not only for fundamental science but also for medical applications such as controlling organ formation in vitro, wound healing and cure for cancer etc.

However, there had been no continuum theory for tissues that takes the features (a-d) into account. Recently, I constructed hydrodynamic equation describing (a-d) for tissues in one-dimensional space with Dr. Philippe Marcq (Curie Institute) (S. Yabunaka and P. Marcq, submitted). We applied the framework of active gel theory, which has succeeded in describing several biomaterials such as motility assays, to tissues. In this paper, we calculated tissue growth speed by taking into account a coupling between stress and growth rate and we showed that this coupling can lead to significant increase of the front velocity near the stability threshold of the bulk uniform state. We also examined emergence of mechanical wave, which has been observed in many experiments (for example X. Serra-Picamal Nature Physics 2012). We found that mechanical wave appears via Hopf bifurcation above threshold of active parameters.

2. Original papers

(1) Akira Onuki, Shunsuke YABUNAKA, Takeaki ARAKI and Ryuichi OKAMOTO,
“Structure formation due to antagonistic salts”
Current Opinion in Collioid Interface Science Volume 22, April 2016, Pages 59–64

(2) Shunsuke Yabunaka and Natsuhiko Yoshinaga, "Collision between chemically-driven self-propelled drops”
Journal of Fluid Mechanics, November 2016, Pages 205-233

3. Presentation at academic conferences

(1) 藪中俊介、義永那津人,
“化学反応で自己推進運動する液滴の衝突”
日本物理学会 2016 年秋季大会 15pBE, Kanazawa, Sep.15, 2016

(2) 藪中俊介、Bertrand Delamotte,
“O(N)*O(2)模型における多重臨界固定点の非摂動繰り込み群による研究”
日本物理学会2016年秋季大会16aAK, Kanazawa, Sep.16, 2016

4. Others

(1) Shunsuke Yabunaka
“Self-propelled motion of a droplet under chemical reaction”
Bio/Softmatter Seminar, Tokyo Metropolitan University, July 29, 2016

(2) 藪中俊介
“増殖を取り入れたアクティブマターの連続体理論”、京都若手ソフトマター研究会,
Kyoto,Mar. 8, 2016.

Simon K. Schnyder

FIFC Fellow

1. Summary of the research of the year 2016

a) Dynamic heterogeneities and non-Gaussian behavior in two-dimensional randomly confined colloidal fluids

Slow relaxation phenomena are often linked to the appearance of a diverging length scale. While for the arrest of particles in glass-forming fluids the relevance of a divergent length scale is a highly controversial issue, the existence of such a length scale is obvious if the slowing down of the relaxation dynamics is associated with an underlying continuous phase transition, such as, e.g., the critical point of a liquid-gas transition or a percolation transition.

A paradigm for slow relaxation in combination with a percolation transition is the Lorentz gas where a single tracer particle moves through the free volume provided by an disordered matrix of obstacles. If the density of obstacles is sufficiently high the tracer does not find any percolating path through the system and is thus localized in a finite volume. At the percolation transition of the free volume, where the tracer particle exhibits a localization transition from a delocalized to a localized state, the tracer particle probes the fractal structure of the free volume. This is associated with an anomalous diffusion dynamics, as reflected in a sublinear growth of the mean-squared displacement (MSD). Generalizations of the Lorentz model, for instance with many interacting particles, soft interaction potentials, or correlated matrix structures, have been investigated in both simulation and theory.

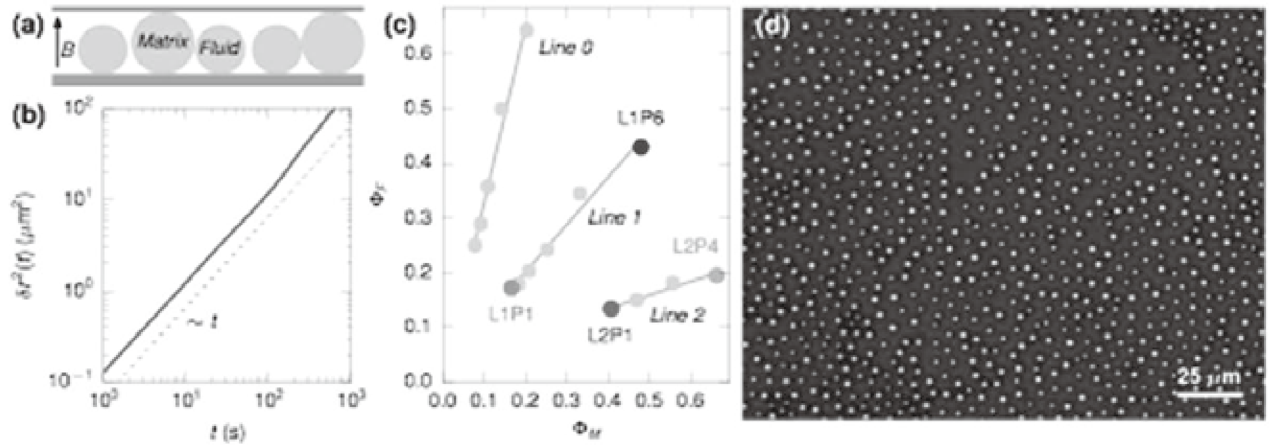


Fig. 1 (a) Schematic of the experiment, a binary system of small and large particles confined between two glass slides (particle diameters to scale). The large particles support the top slide. The magnetic field B tunes the effective interaction between the particles. (b) Mean-squared displacement for the fluid particles in a very dilute cell. A dashed line indicating diffusive behavior, $\delta r^2(t) \sim t$, is shown as a guide to the eye. (c) State diagram for the effective area fractions of the fluid (φ_F) vs the matrix particles (φ_M). (d) Snapshot of the system at state point L1P6 in a quadrant of size 214 × 171 μm.

The original classical Lorentz-gas model assumes Newtonian dynamics for the tracer particle and a hard-sphere potential for its interaction with the obstacles. Here, the “energy barriers” that the tracer sees when it travels through the arrangement of obstacles are infinitely high. However, in a modified model with soft interactions between the tracer and the obstacles this is no longer the case and the effective barrier height provided by the obstacles depends on the energy of the tracer particle. Thus, for a given obstacle configuration, the effective free volume that the tracer can explore is strongly correlated with its energy.

As shown in a series of molecular dynamics (MD) simulations [1], in an ideal gas of tracer particles in a random arrangement of soft obstacles each particle sees a different percolation transition of the free volume according to the kinetic energy that has been assigned initially to each of the tracer particles. As a consequence, quantities like the self-diffusion coefficient, which have to be averaged over all particles, do not show the singular behavior expected at the localization transition. Instead, all quantities exhibit nonuniversal behavior: the transition is rounded. Only if a special average over tracer particles with the same energy is performed, a sharp transition as in the hard-sphere Lorentz gas is recovered. These results suggest that the rounding of the transition is a generic feature of realistic, soft systems. The heterogeneous structure of the matrix leads to heterogeneous or non-Gaussian dynamics, as exemplified by the anomalous diffusion at the localization transition and other signatures such as a large non-Gaussian parameter. The non-Gaussian parameter is often used to characterize dynamical heterogeneities and in the Lorentz model has a weak divergence at the localization transition In a soft system, in which each particle sees a different matrix structure according to its energy, it can be expected that the dynamics are even more heterogeneous. However, the connection between this rounding of the transition in a soft heterogeneous medium and its dynamical heterogeneities has not been explored, yet.

Recently, we have presented an experimental realization of a two-dimensional (2D) Lorentz-gas-like system [2], see also Fig. 1. It consists of a binary mixture of superparamagnetic colloidal particles confined between two glass plates such that the larger colloidal particles are immobilized and the smaller particles can move through the matrix formed by the larger ones. In this experiment, the effective size of the particles is varied by exposing the particles to an external magnetic field that induces magnetic dipoles in the particles, leading to a repulsive r^{-3} interaction between them (here r is the distance between two particles). By varying the strength of the external magnetic field, the effective density of the matrix is changed while the structure of the matrix remains unaffected. We have demonstrated that the tracer particles, i.e., the smaller particles, exhibit a transition from a delocalized state at low effective matrix densities to a localized state at high matrix densities [2]. This transition is rounded because the energy of the Brownian particles is a fluctuating quantity and, due to the soft r^{-3} interaction with the obstacles, the barriers seen by the tracers are not infinitely high as for hard interactions.

We discuss generic features of the structure and dynamics in heterogeneous media by comparing the results of colloidal experiments and MD simulations. First, we qualitatively characterize the tracer dynamics by calculating the single-particle probability distributions and discuss the structure of the matrix and fluid particles in terms of the partial pair distribution functions. We then show that around the transition from a delocalized to a localized state, the dynamics of the tracer particles in both simulation and experiment exhibit strong dynamic heterogeneities that are associated with strong non-Gaussian fluctuations. To this end, we

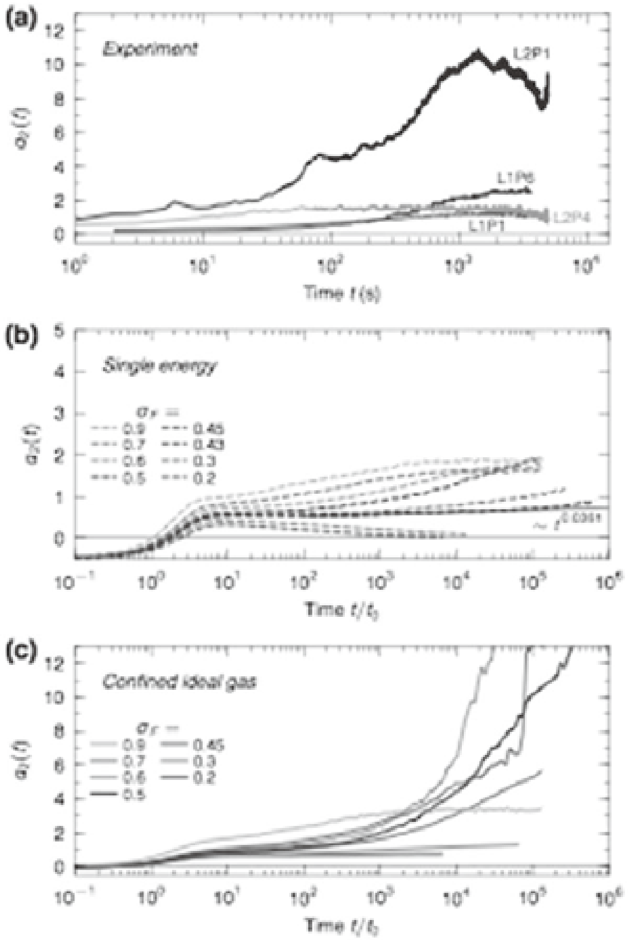


Fig. 2 Non-Gaussian parameter $\alpha^2(t)$ for the experiment (a), and for the simulation in the (b) single-energy and (c) confined-ideal-gas cases.

provide a detailed analysis of simulation and experiment in terms of the self-part of the intermediate scattering function (SISF), $F_s(q,t)$, the mean-quartic displacement (MQD), $\delta r^4(t)$, and the non-Gaussian parameter (NGP), $\alpha^2(t)$, thereby extending upon our previous work [2]. We find that a large fraction of particles can already be localized while the MSD still appears diffusive. While this heterogeneity is typical for the Lorentz gas, we find it to be enhanced when the artificial constraint of assigning the same energy to all particles in the simulation is removed. As a consequence, the rounded delocalized-to-localized transition of the tracer particles is associated with a strong increase of $\alpha^2(t)$ on rather small and intermediate time scales, whereas the α^2 of the Lorentz gas indicates only small deviations from Gaussian behavior, see Fig. 2. This strong increase of $\alpha^2(t)$ is found in the experiment as well.

References

[1] S. K. Schnyder, M. Spanner, F. Höfling, T. Franosch, and J. Horbach, Soft Matter 11, 701 (2015).

[2] T. O. E. Skinner, S. K. Schnyder, D. G. A. L. Aarts, J. Horbach, and R. P. A. Dullens, Phys. Rev. Lett. 111, 128301 (2013).

b) Collective motion of cells crawling on a substrate

Directional collective motion of cells is of fundamental importance for embryogenesis, wound healing and tumor invasion. Cells move in clusters, strands or sheets to cover empty area, to grow or invade tissues. How the cells coordinate and control their motion, is the subject of ongoing research. At the level of a single cell, it is well established that its motion is intricately linked to its shape. The shape of crawling cells is highly variable, depending on the type of cell, the substrate, as well as a result of the migration process itself.

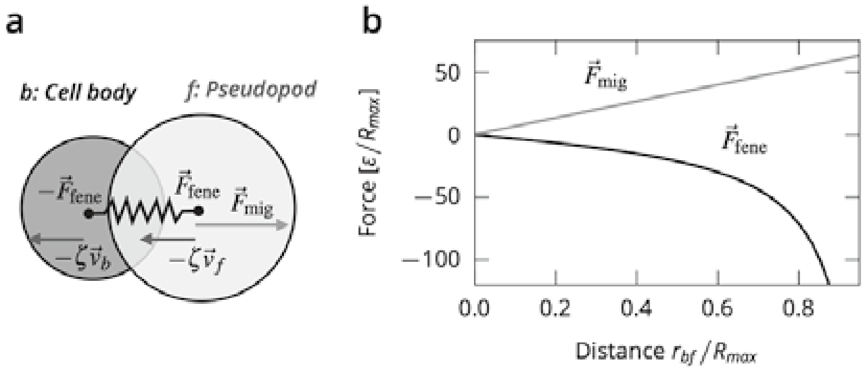


Fig. 3 (a) Schematic of the cell model. (b) Forces acting on the two disks being at distance r_{bf}.

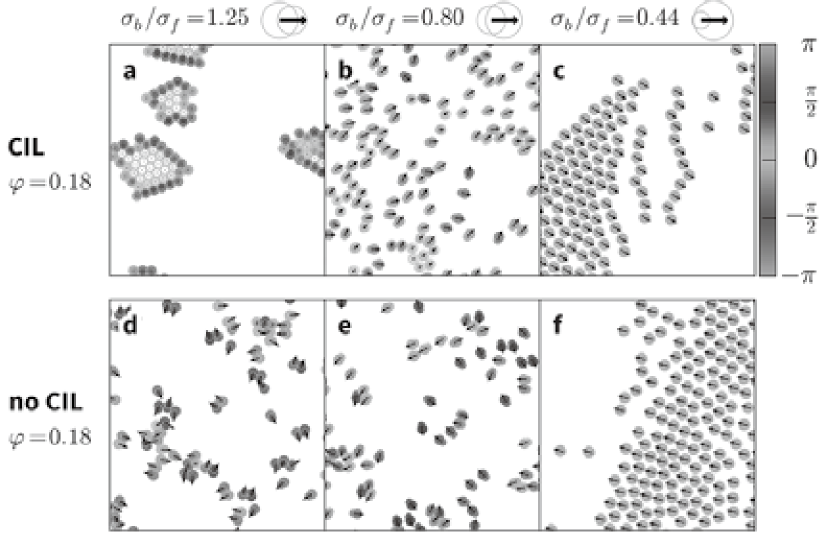


Fig. 4 Snapshots of CIL and no-CIL cells for a range of cell shapes. Cell velocities are given as arrows and color. Hue indicates deviation from average direction, and slower cells are lighter in color. The cells undergo a transition from a clustering/disordered state to an ordered state upon change of the cell shape.

When a cell starts moving, its shape breaks symmetry, whereas circular cells typically cannot move. While there is evidence that shape has a strong influence on scattering and can lead to clustering and collective directed motion of swimmers, less is known about the role of cell shape in organizing collective crawling. It has been shown in simulations that inelastic collisions between crawling cells, e.g. due to deformation, can lead to coherent migration, suggesting the importance of deformability for collective behavior. When crawling cells come into contact, it inhibits their protrusions, which tends to change their shape and reorient them. It was shown that this effect, called contact inhibition of locomotion (CIL), enables cells to follow chemical gradients more effectively by aligning them. In growing colonies, CIL leads to a slowing down of the motility of individual cells when the density of their environment crosses a certain threshold. Thus, CIL is believed to play a crucial role in the control of collective tissue migration, tissue growth, morphogenesis, wound healing and in tumors. So, we built a minimal, mechanical model of cells crawling on a substrate, aiming to isolate behavior purely caused by the interplay of contact inhibition and deformable shape, while neglecting properties such as cell-cell adhesion or chemotaxis.

By mimicking the mechanical motion of cells crawling on a substrate using a pseudopod, we constructed a minimal model for migrating cells which gives rise to contact inhibition of locomotion (CIL) naturally. The model cell consists of two disks, one in the front (a pseudopod) and the other one in the back (cell body), connected by a finitely extensible spring, see Fig. 3. Despite the simplicity of the model, the cells' collective behavior is highly nontrivial, depending on the shape of cells and whether CIL is enabled or not. Cells with a small front disk (i.e. a narrow pseudopod) form immobile colonies. In contrast, cells with a large front disk (i.e. such as a lamellipodium) exhibit coherent migration without any explicit alignment mechanism being present in the model, see Fig. 4. This suggests that crawling cells often exhibit broad fronts because it helps them align.

2. Original papers

(1) S. K. Schnyder, T. O. E. Skinner, A. Thorneywork, D. G. A. L. Aarts, J. Horbach, R. P. A. Dullens, "Dynamic heterogeneities and non-Gaussian behaviour in 2D randomly confined colloidal fluids", Physical Review E (2017).

3. Presentations at academic conferences

(1) Simon K. Schnyder, John J. Molina, Ryoichi Yamamoto, "Collective dynamics of migrating cells", Workshop, Fukuoka, January 2017.

4. Others

(1) Seminar, Simon K. Schnyder, John J. Molina, Ryoichi Yamamoto, "Collective dynamics of migrating cells", R Lab, Nonlinear Physics Group, University of Nagoya, May 2016.

(2) Talk, Simon K. Schnyder, John J. Molina, Ryoichi Yamamoto, "Collective dynamics of migrating cells", Summer School: Active Complex Matter, Cargèse, Corsica Island, France, July 2016.

Miho Isegawa

FIFC Fellow

1. Summary of the research of the year

Copper-catalyzed Enantioselective Boron Conjugate Addition: DFT and AFIR Study on Different Selectivities of Cu(I) and Cu(II) Catalysts

We present a mechanistic survey on the LCu-catalyzed (L = chiral 2,2′-bipyridine ligand) enantioselective boron conjugate addition reaction, carried out using density functional theory (DFT) and the artificial force induced reaction (AFIR) methods. The computed catalytic cycle for Cu(I)- and Cu(II)-based catalysts consists of three steps: (a) boron–boron bond cleavage of $B_2(pin)_2$, (b) boron conjugate addition on the β-carbon of chalcone, and (c) protonation. The enantioselectivity of the reaction with LCu(I) or LCu(II) catalysts is solely governed at the boron conjugate addition step. The multicomponent (MC)-AFIR search and the subsequent DFT calculations for the LCu(I) catalyst determined transition states (TSs), which lead to Cu(I)-O-enolate and Cu(I)-C-enolate, and both equally contribute to the C–B bond formation with no enantioselectivity. On the other hand, a MC-AFIR search and the subsequent DFT calculations for the analogous LCu(II) catalyst showed that only the transition state (TS) leading to Cu(II)-O-enolate contributes to the reaction. Furthermore, the TSs leading to the *R*- and *S*-forms of Cu(II)-O-enolates are energetically well separated, with the *R*-form being of lower energy, which is consistent with experimental observations. Our study provides important mechanistic insights for designing transition metal catalysts for Cu-catalyzed enantioselective boron conjugate addition reaction.

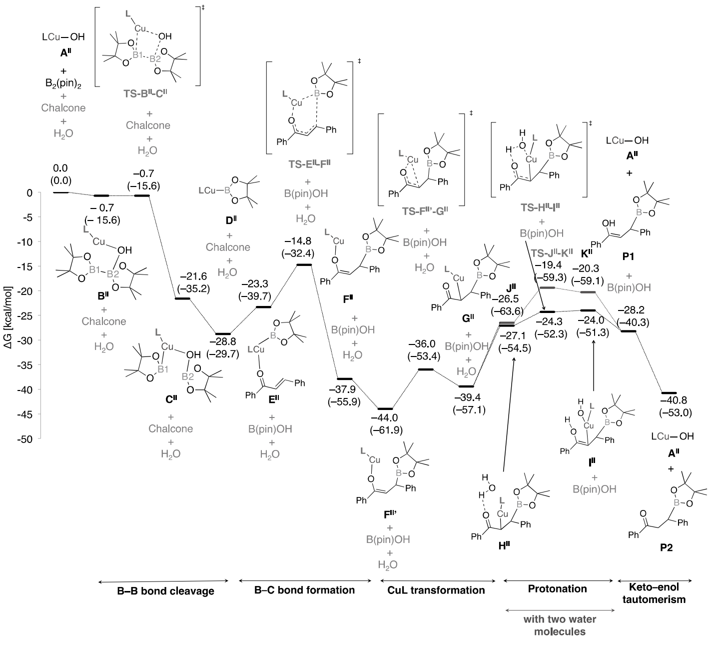


Figure 1. Calculated free energy profile for Cu(II)-based catalyst. Δ*G* and Δ*H* (in parentheses)

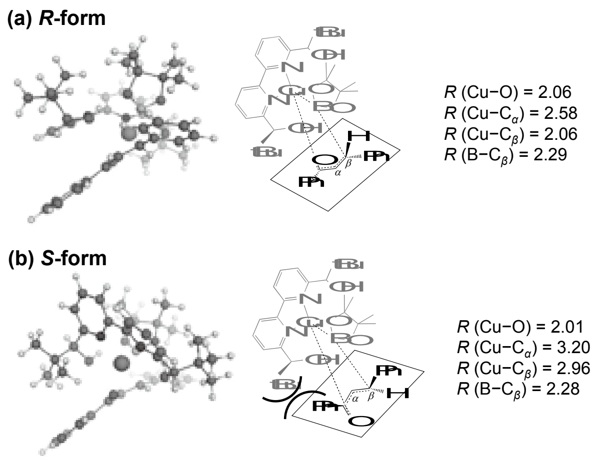


Figure 2. The lowest energy transition state for each *R*-form (favorable) (**TS1-*R*-b(II)**) and *S*-form (unfavorable) (**TS10-*S*-b(II)**) in the Cu(II) system. Selected bond lengths are given in **Å**.

Hydride Attack in Dioxygen Activation by a Biomimetic Model for Oxygen-Tolerant [NiFe] Hydrogenase: A Density Functional Study for the Reaction Mechanism

The mechanism for the dioxygen activation by a biomimetic model complex of O_2-tolerant [NiFe]-hydrogenase, $[NiLFe(\eta^5\text{-}C_5Me_5)]^+$ **[**L=N, N'-diethyl-3,7,-diazabiomimnonate-1,9-dithiolato] was established by using density functional theory (DFT) and artificial force induced reaction (AFIR) method. Particularly, the AFIR method was employed by combining DFT for obtaining "approximate" transition state structures. Our computational results suggests that the dioxygen activation is initiated by O_2 binding to the electron rich Fe(II) center in end-on fashion. Then reduction of O_2 coordinated complex occurs in the presence of strong acid of BH_4^-, through hydride transfer. Once the hydride transfer occurs, the BH_3 immediately attacks on the electron rich oxygen, giving rise to BH_3OH^-. The mechanistic insights of the O_2 activation in this study are important in interpreting the mechanism of the O_2-tolerant hydrogenase and developing superior molecular catalyst that combines "self-repairing" function from the oxidized state to recover the catalytic function.

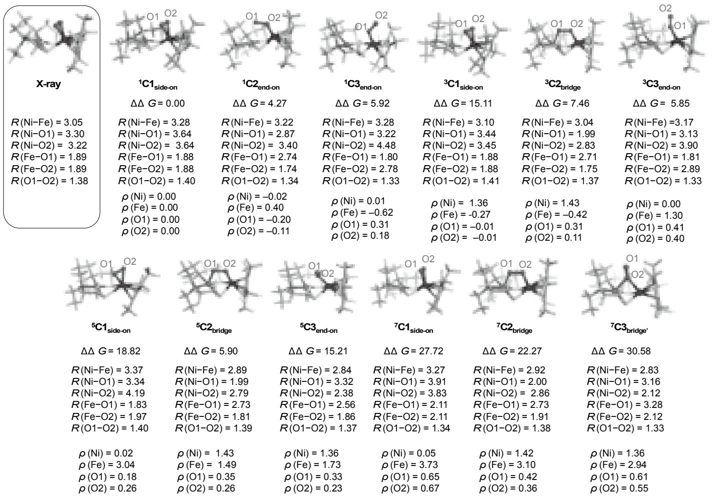


Figure 3. Binding modes of oxygen on [NiFe] core. Relative free energy ΔΔ *G* (kcal/mol), bond length, and spin densities are shown. The free energies are given relative to the most stable orientations $^{1}\mathbf{C1}_{\textbf{side-on}}$.

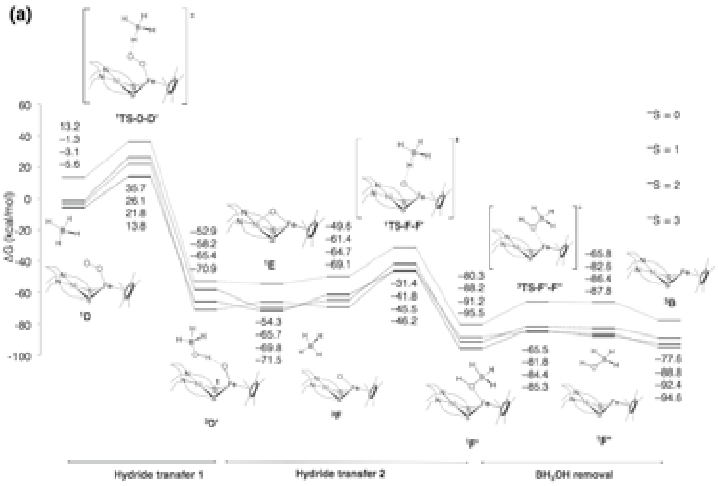


Figure 4 (a) Free energy profiles for four spin states (S = 0, 1, 2, and 3) in (i) the first hydride transfer, (ii) the second hydride transfer, and (iii) BH_3OH^- removal.

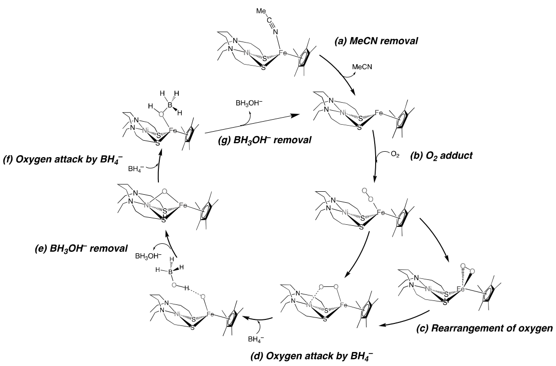


Figure 5. Summary of catalytic cycle for O_2 activation by [NiFe]-complex.

Fe centered H_2 Molecule Activation by [NiFe] core: Density Functional Study for the Reaction Mechanism

We performed theoretical study for a bio-inspired model of [NiFe] hydrogenase, using density functional theory (DFT) and artificial force induced reaction (AFIR) methodology. The model system is the first NiFe molecular catalyst which successfully extracts electrons from hydrogen molecule in addition to the hydride transfer and hydrogen generation with addition of acid. Our aim in this study is to precisely reveal the reaction mechanism for the whole catalytic cycle and to corroborate the experimental observations; spin state, oxidation state, and the function. Our calculated free energy profile for the full catalytic cycle revealed that the NiFe complex is not significantly stabilized by the H_2 binding on the metal center, therefore the simultaneous addition of base with bubbling the H_2 is crucial. The generated hydride complex is binding to the Fe, and not binding both Ni and Fe which has been observed in the Ni-R state of hydrogenase. From the hydride complex, the hydride transfer process by is low barrier process and the proton transfer process from acid is barrierless process. Following one-electron oxidation of NiFe hydride complex by ferrocene, the hydrogen atom transfer (HAT) process or proton coupled electron transfer process (PECT) is favored, and the both proton transfer (PT)/electron transfer (ET) and ET/PT are less likely. Our study in the hydrogen activation process give the chemical insights to understand the function and reaction mechanism of hydrogenase and to create more efficient H_2 activation catalyst.

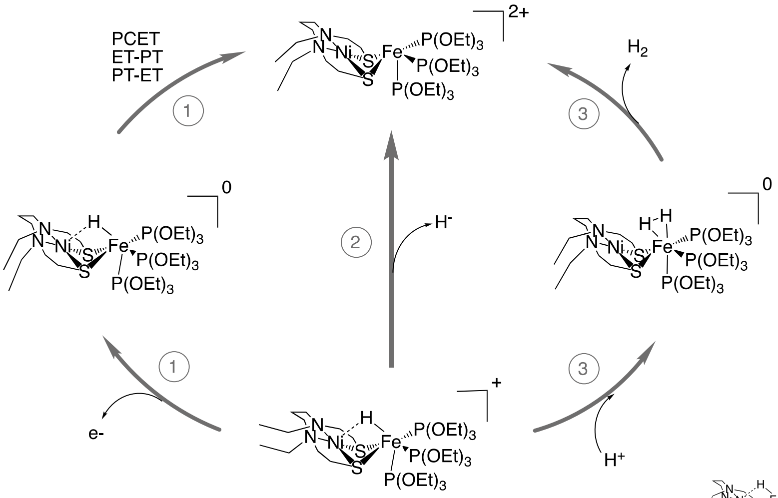


Figure 6. Three pathways from [NiFe] hydride complex to [NiFe] core. (1) PECT/HAT following electron transfer, (2) hydride transfer, and (3) generation of H_2 with proton transfer.

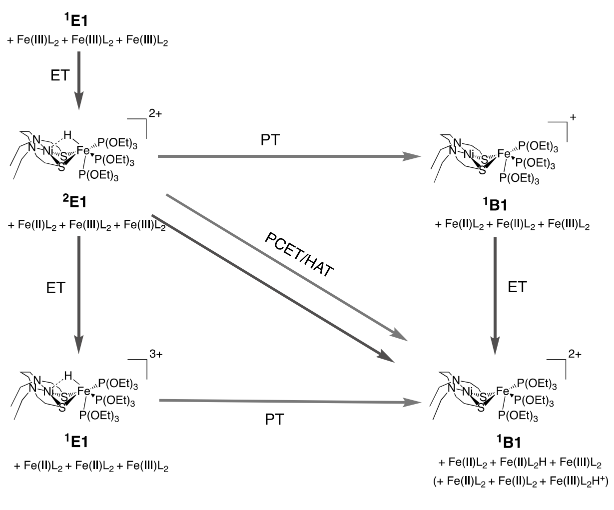


Figure 7. Three pathways following electron transfer; (i) PT → ET (ii) PCET/HAT and (iii) ET → PT.

2. Presentation at academic conferences

(1) Miho Isegawa, W. M. C. Sameera, Akhilesh K. Sharma, Taku Kitanosono, Shū Kobayashi, Keiji Morokuma “Copper-catalyzed Enantioselective Boron Conjugate Addition: DFT and AFIR Study on Different Selectivities of Cu(I) and Cu(II) Catalysts”
Japan-France-Spain Joint-Symposium on Theoretical and Computational Science of Complex Systems, Oct. 26 to 28, 2016, Kyoto

(2) Miho Isegawa, W. M. C. Sameera, Akhilesh K. Sharma, Taku Kitanosono, Shū Kobayashi, Keiji Morokuma “Copper-catalyzed Enantioselective Boron Conjugate Addition: DFT and AFIR Study on Different Selectivities of Cu(I) and Cu(II) Catalysts” The 10th Annual Meeting of Japan Society for Molecular Science, Sept. 13 to 15, 2016, Kobe.

(3) Miho Isegawa, W. M. C. Sameera, Akhilesh K. Sharma, Seiji Ogo, Keiji Morokuma, “Hydride Attack in Dioxygen Activation by a Biomimetic Model for Oxygen-Tolerant [NiFe] Hydrogenase: A Density Functional Study for the Reaction Mechanism”, FIFC annual meeting, Jan. 27, 2017, Kyoto

(4) Miho Isegawa, W. M. C. Sameera, Akhilesh K. Sharma, Taku Kitanosono, Shū Kobayashi, Keiji Morokuma “Copper-catalyzed Enantioselective Boron Conjugate Addition: DFT and AFIR Study on Different Selectivities of Cu(I) and Cu(II) Catalysts”, stimuli-responsive chemical species for the creation of functional molecules, Mar. 6-7, 2017, Hiroshima.

Satoshi Suzuki

Research Fellow

1. Summary of the research of the year

1.1 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

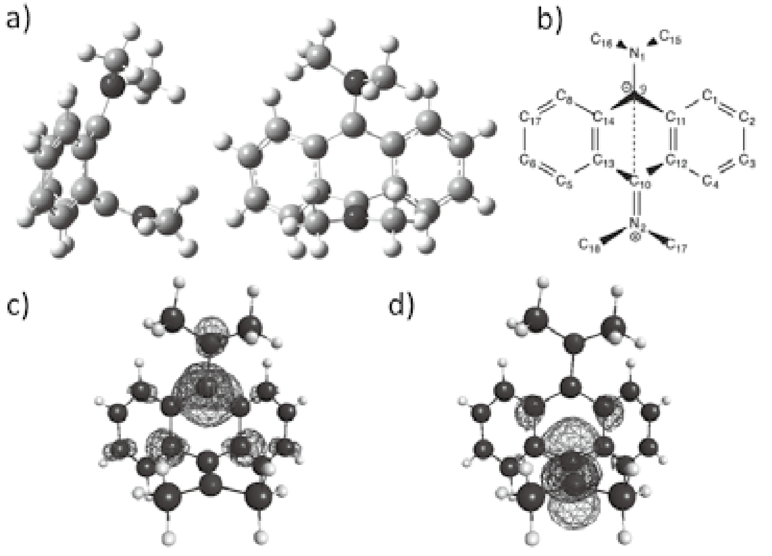
9,10-bis(N,N-dialkylamino)anthracene(BDAA) はアルキルアミノ基で置換されたアントラセンであり、そのシンプルな分子構造にもかかわらず凝集誘起発光(aggregation-induced emission:AIE) を起こす。多くの蛍光分子では凝集により発光性は低下する。AIE は非蛍光性の分子が凝集により蛍光性を持つようになる。一連の BDAA において、大きなストークスシフトが観測され、自己吸収が起こりにくいことが AIE の一因であると実験的に示唆された。
まず、大きなストークスシフトがどのような構造変化によって起こるのかを計算によって確認した。また、BDAA 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。

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。

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。



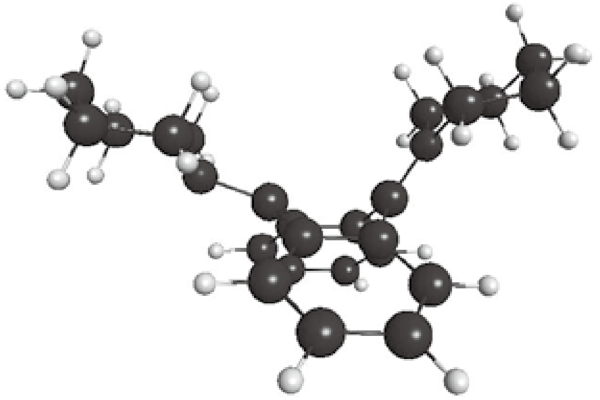
固相中での円錐交差

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。

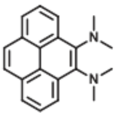


BDAA-piperidyl の気相中での円錐交差構造

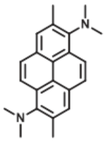
一方、変位の比較的小さい、アントラセン部分の面外変角による円錐交差も存在するが、こちらは気相中でも固相中でもエネルギーが高く内部転換には関わらないと考えられる。以上のことからこの分子における固相での発光しやすさについて、定性的には説明ができた。

1.2 ビスジアルキルアミノアレーン類における凝集誘起発光(AIE)の起源

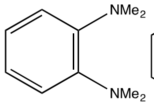
ピレン骨格の特定の位置にアルキルアミノ基を導入した分子 **1** は AIE 特性を示すのに対し、**2** は溶液中でも発光し AIE 特性を持たないことが実験グループにより明らかにされた。このことから、適当な芳香族炭化水素の適当な位置をアルキルアミノ基で置換すれば AIE 特性を示すのではないかと予想される。そこで、モデル化合物としてアルキルアミノ基で二置換されたベンゼン、ナフタレン(**1a**,**1b** と呼ぶ)と、アルキルアミノ基とメチル基を持つベンゼン、ナフタレン(**2a**,**2b** と呼ぶ)を考え、失活過程を議論する。モデル化合物の失活過程から重要な反応座標がわかれば一般の芳香族化合物への応用は容易に可能であると期待できる。



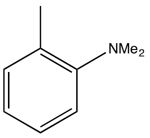
1



2



1a



2a

1a,**2a** の MECI を(10e,8o)CASSCF/6-31G で最適化した。得られた MECI と S_1 フランクコンドン状態の間に遷移状態があることが示唆されたので、S_1 面上での極小点と遷移状態の探索を TD-B3LYP/6-31G(d)レベルで行った。CASSCF の計算は GAMESS, TDDFT 計算は Gaussian16 を用いて行った。**1a**,**2a** の PES は似通っており、どちらもフランクコンドン状態からアルキルアミノ基に置換された炭素位置における ring-puckering mode に沿って MECI に到達するということがわかった。図 1 に **1a**,**1b**,**2a**,**2b** の基底状態の安定構造を 0kJ/mol とした、S_1 状態のポテンシャル面を示す。違いとして、**2a** の場合に比べて **1a** の方が遷移状態が低い。このことから **1a** の方が **2a** よりも溶液中で失活しやすく光りにくいと考えられる。これは変位するアルキルアミノ基の隣のもう一つのアルキルアミノ基が遷移状態を安定化しているからだとわかった。同様に **1b** と **2b** の比較からも **1b** の方が光りにくいと考えられる。実際の分子 **1**,**2** において **2** が発光性であり **1** は溶液中では非発光性である理由はモデル分子からの演繹で概ね説明できることがわかった。

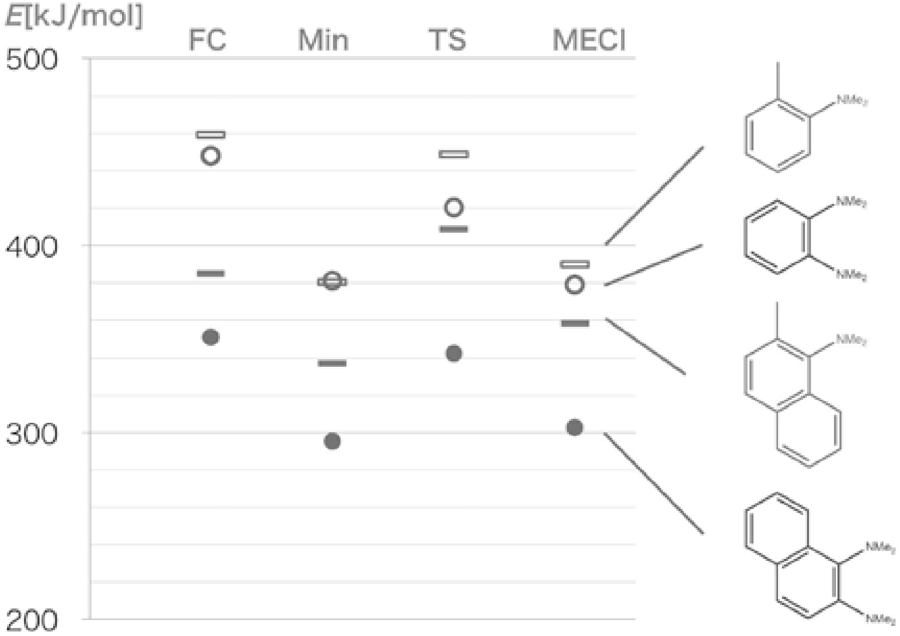


図 1　**1a,1b,2a,2b** の S_1 状態ポテンシャルエネルギー面

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**, 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., **138**, 8194-8206

3. Presentation at academic conferences

(1) ビスアルキルアミノアントラセンの凝集誘起発光
◯鈴木聡　諸熊奎治　理論化学討論会 2016　東京

Akhilesh Kumar Sharma

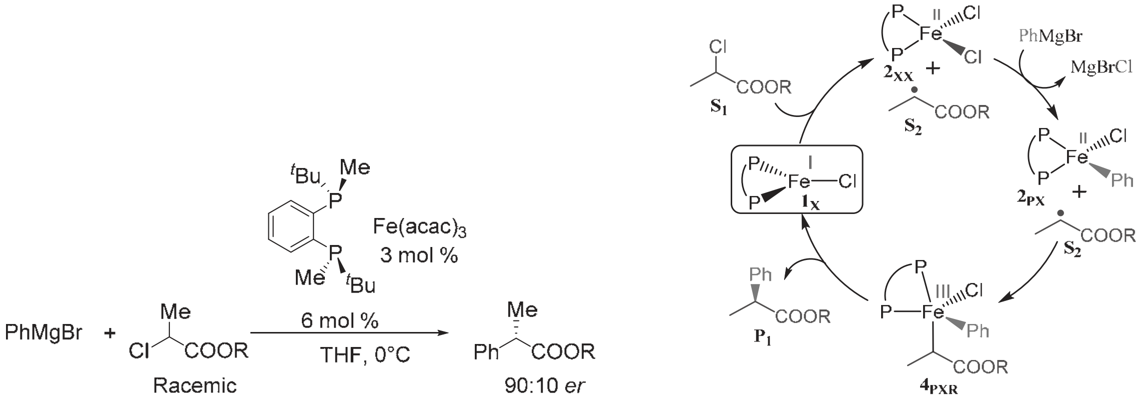
Postdoctoral Fellow

1. Summary of the Research of FY2016

Transition metals are being used in homogenous catalysis for variety cross-coupling reactions and formation of asymmetric compounds. 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 mechanistic understanding of Fe–catalyzed reactions is important for further development in this field. M. Nakamura and coworkers have been developing variety of Fe-phosphine catalyzed coupling reaction. The mechanism of these reactions is not established and there is no clear understanding on the origin of enantioselectivity. We have studied the mechanism of reactions using DFT methods. The AFIR method as implemented in GRRM program is used to explore potential energy surface of the important steps in the reaction.

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

In current study we have studied the mechanism of chiral Fe-Phosphine catalyzed cross-coupling reaction (Scheme 1). The favorable mechanism involves first formation C-Cl activation by Fe(I) species ($\mathbf{1_X}$), followed by transmetalation. The Fe(II) species ($\mathbf{2_{PX}}$) then undergo Fe(III) formation by coordination of radical ($\mathbf{S_2}$) to Fe-center. The resultant species ($\mathbf{4_{PXR}}$) undergo reductive elimination leading to the formation of coupling product.

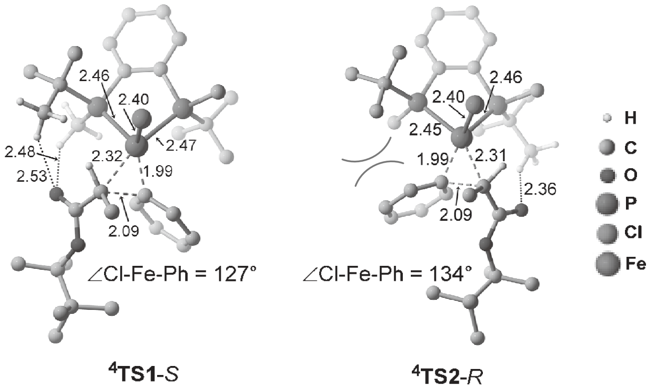


(a) (b)

Scheme 1. (a) Fe-catalyzed enantioselective cross-coupling reaction. (b) The lowest energy pathway based on computational results.

Among different steps, the formation of $\mathbf{4_{PXR}}$ or C–C coupling can be stereoselectivity determining. We have studied these two steps systematically through Multi Component Artificial Force Induced Reaction (MC-AFIR) method. More than 50 distinct TSs were optimized for these two steps. These two steps occurs in quartet spin state, with Fe quintet for Fe(II) and quartet in Fe(III) spin state. The radical coordination to Fe-center is not enantioselectivity determining, as the activation free energy barrier for lowest diastereomeric TSs is very small (0.3 kcal/mol). The C–C bond formation is stereoselectivity determining. In the lower energy TSs methyl and bulky phenyl groups of substrate are away from phosphine and chloride ligand. Further carbonyl group of substrate interacts with C–H hydrogens of phosphine ligands (Figure 1). Such interaction are absent in higher energy TSs.

The computed enantiomeric ratio determined by Boltzmann distribution of TSs is 92:8, which is in good agreement with experimentally reported ratio (90:10). The lowest energy diastereomeric TSs differ by 1.5 kcal/mol free energy (Figure 1). From EDA (energy decomposition analysis) it is clear that the **TS2** is higher in energy due to more distortion in Fe-Phosphine-Phenyl fragment, which occur due to bulky *tert*-butyl fragment. Our study will be helpful in further development of asymmetric Fe-catalysts.

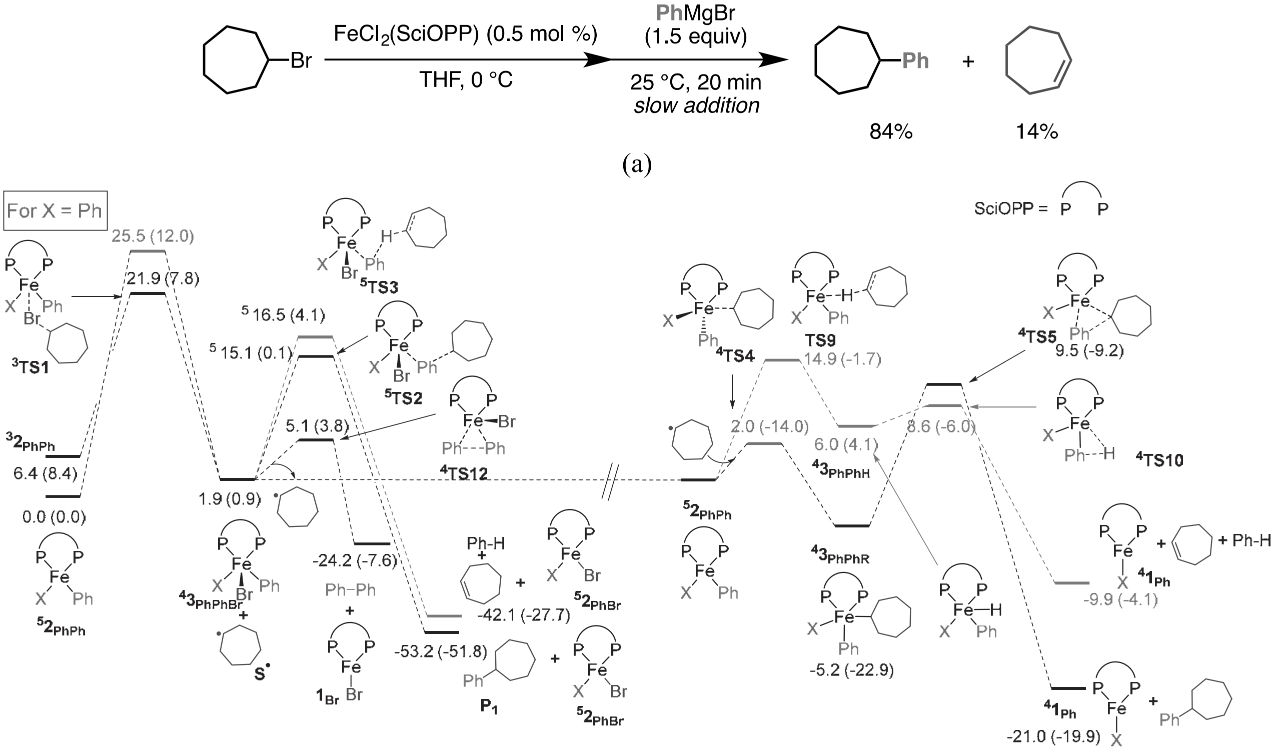


^{4}**TS1**-*S* ^{4}**TS2**-*R*

Figure 1. Optimized geometries of lowest energy TSs leading to *S* and *R* forms of the products.

Computational Insights on Mechanism of Iron-SciOPP-Catalyzed Alkyl–Aryl Coupling Reaction

Fe-bisphosphine, -amine and -NHC complexes have been used extensively for cross-coupling reactions. To gain mechanistic insight we have studied Fe-SciOPP-Catalyzed Kumada-Tamao-Corriu coupling between alkyl-halides and aryl Grignard reagents trough DFT methods. In this study the mechanism of cross-coupling-product and byproduct formation is explored.



(a)

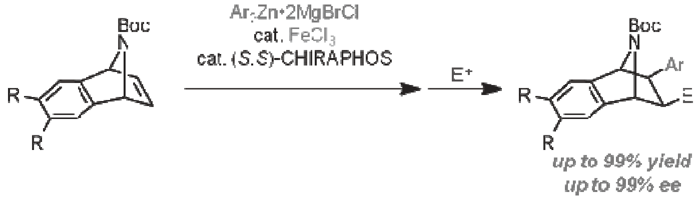
(b)

Figure 2. (a) Fe(SciOPP) catalyzed coupling reaction. (b) Free energy profile for mechanism of cross-coupling product formation from Fe(SciOPP)Ph$_2$.

We found that Fe(II) species (Fe(SciOPP)Ph$_2$) helps in C–Cl activation at the start of the reaction. It will be followed by generation of Fe(I) species ($^{4}\mathbf{1}_{\mathbf{Br}}$) by reductive elimination from $^{4}\mathbf{3}_{\mathbf{PhPhBr}}$ (Figure 2). Afterwards, C–Cl activation will occur by Fe(I) species, as activation barrier through it is only 4 kcal/mol. The reaction of alkyl radical to Fe(II) species ($^{5}\mathbf{2}_{\mathbf{PhPh}}$) is more favorable. The C–C coupling occurs through Fe(III) intermediate ($\mathbf{3}_{\mathbf{PhPhR}}$) (Figure 2). Formation of alkene involves hydrogen abstraction by Fe(II) species, followed by benzene formation. Similar mechanism has been found for Fe(SciOPP)PhBr. The calculation for exploring missing stationary points is in progress and manuscript is in preparation.

Computational Insights on Mechanism of Iron-Catalyzed Enantioselective Carbometalation of Azabycyclic Alkenes

Recently Prof. Nakamura and group have explored carbometalation of azabycyclic alkenes. We have studied mechanism of carbometalation step through DFT methods. First we have studied the different spin states of Fe(II) species, which is proposed to be the active species in this reaction. We found that Fe(II) with tetrahedral geometry is the ground state and the triplet Fe(II) species (with square-planar geometry) is higher in energy by 2.5 kcal/mol. THF coordination slightly lower the energy of quintet Fe(II) complex (-1.5 kcal/mol).



The azabycyclic alkenes coordinates weakly to Fe(II) in quintet spin state (Figure 3). We found that the carbometalation occurs in triplet spin state. Hence, this step involves two state reactivity, as both **I2** and **I3** have quintet as ground state and TS have triplet spin state. For the enantioselectivity study, we are exploring different conformations of **TS2** through MC-AFIR method in quintet and triplet spin state. Till now >12 distinct TSs are optimized each for triplet and quintet spin state. Further sampling of TSs is in progress and manuscript is in preparation.

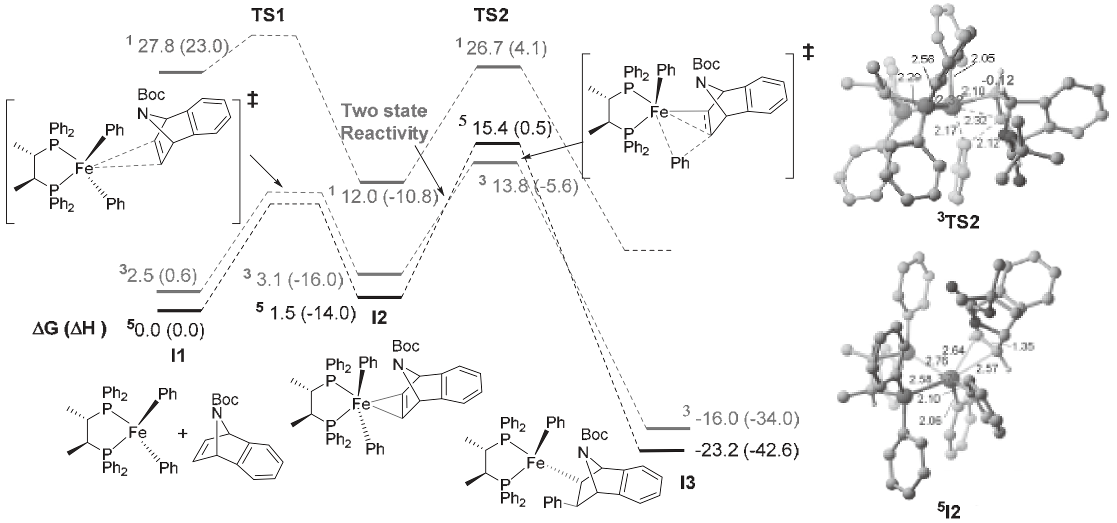


Figure 3. Free energy profile for Fe-catalyzed carbometalation and two important stationary points in the reaction.

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(1) Ming-Chung Yang, Akhilesh K. Sharma, W. M. C. Sameera, Keiji Morokuma, and Ming-Der Su
"Theoretical Study of Addition Reactions of L4M(M = Rh, Ir) and L2M(M = Pd, Pt) to Li+@C60"
J. Phys. Chem. A 121(13), 2665-2673 (2017).

(2) Miho Isegawa, W. M. C. Sameera, Akhilesh K. Sharma, Taku Kitanosono, Masako Kato, Shu Kobayashi, and Keiji Morokuma
"Copper-catalyzed Enantioselective Boron Conjugate Addition: DFT and AFIR Study on Different Selectivities of Cu(I) and Cu(II) Catalysts"
ACS Catal. DOI: 10.1021/acscatal.7b01152.

(3) Akhilesh K. Sharma, W. M. C. Sameera, Masayoshi Jin, Laksmikanta Adak, Chiemi Okuzono, Takahiro Iwamoto, Masako Kato, Masaharu Nakamura and Keiji Morokuma
"DFT and AFIR Study on the Mechanism and the Origin of Enantiose-lectivity in Iron-Catalyzed Cross-Coupling Reactions"
(Submitted)

3. Review Article

(1) W. M. C. Sameera, Akhilesh K. Sharma, Satoshi Maeda, Keiji Morokuma
"Artificial Force Induced Reaction Method for Systematic Determination of Complex Reaction Mechanisms"
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4. Presentation at academic conferences

(1) Akhilesh kumar Sharma, W. M. C. Sameera, Masaharu Nakamura, Keiji Morokuma
"Computational insights on the mechanism and the origin of enantioselectivity in Fe-catalyzed cross-coupling reaction"
The 10th Annual Meeting of Japan Society for Molecular Science, Sept. 13-15, 2016.

(2) Akhilesh K. Sharma, W. M. C. Sameera, Masaharu Nakamura, Keiji Morokuma
"Computational Insights on the Mechanism and the Origin of Enantioselectivity in Fe-catalyzed Cross-Coupling Reaction"
Japan-France-Spain Joint-Symposium on Theoretical and Computational Science of Complex Systems, Kyoto, Oct. 26-28, 2016.

5. Others

(1) Akhilesh K. Sharma, W. M. C. Sameera, Masaharu Nakamura, Keiji Morokuma
"Computational Insights on Iron-Catalyzed enantioselective Carbometalation of Azabycyclic Alkenes"
The 14th symposium of Fukui Institute for Fundamental Chemistry, Kyoto, Jan. 27, 2017.

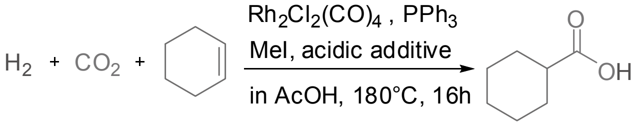
Maneeporn Puripat

Research Fellow

1. Summary of the research of the year

Theoretical Investigation of Catalytic Hydrocarboxylation of Olefins with CO_2

The CO_2 is an attractive C1 building block which leads carboxylic acids and their derivatives. To establish the catalytic systems to form the carboxylic acids from CO_2, the mechanical understanding is indispensable. One of the effective catalytic systems is the hydrocarboxylation of olefin with CO_2 catalyzed by the Rhodium complex.[1] (See Scheme 1) Though the reaction mechanism was partly investigated by the experimental measurements, there are still remaining questions.



Scheme 1 Catalytic Hydrocarboxylation of Olefins with CO_2

To understand the catalytic reaction mechanism, one of the methods in the Global Reaction Route Mapping (GRRM) strategy, called the artificial force induced reaction (AFIR) method,[2] was employed to search systematically all possible pathways for the reaction of catalytic hydrocarboxylation of cyclohexene with CO_2.

Herein, the mechanism of the Rh complex-catalyzed Hydrocarboxylation will be studied systematically using the AFIR method. A preliminary search for the Wilkinson catalyst showed that it required the high barrier; we did not pursue this approach further.

In this research, we looked for all possible pathways including the oxidative addition, carbonylation step, reductive elimination, and final transformation step into Cyclohexanecarboxylic acid (CA). The Rh complexes with different coordination number of the phosphine ligand are used to model the catalysts of this reaction. These complexes is used to interact with the simple starting reagents; olefin, H_2, and CO_2, leading to the CA as the final product. The detailed multi-component (MC)-AFIR calculation is as follows. Firstly, approximate local minimums (LMs) and transition states (TSs) between each catalyst and a hydrogen molecule were explored by the MC-AFIR method. The AFIR functions were minimized with γ = 300 KJ mol^{-1}. At this stage, M06-L/Def2SVP/Def2SVP level of theory was used to speed up the calculation. We found that M06-L reproduced the results of hybrid functional since all of them provided the same trend. In all calculations, the solvation Gibbs free energy was included by the polarized continuum model (PCM). For the initial AFIR search with M06-L/Def2SVP/Def2SVP, a PCM model using the dielectric constant of 6.3 for acetic acid was employed. Then, all the approximate LMs and TSs obtained by the initial MC-AFIR search were re-optimized without artificial force at the B3LYP-D3/SDD (Rh & I); 6-31g(d) (for other atoms) level using the same PCM model. We report in the results section the Gibbs free energy at (453.15 K, 69.085 atm), and the electronic energy with zero-point correction (ZPE, in parentheses). After optimization of a TS, the intrinsic reaction coordinate (IRC) was calculated to confirm the reaction pathway. All these AFIR search, optimizations and IRC calculations were performed with the Global Reaction Route Mapping (GRRM) program using energies, first, and second energy derivatives computed with the Gaussian09 program.

The reaction was determined into two cycles separately as shown in Figure 1: Cycle B starts the reaction with the oxidative addition of H_2 and Rh complex, and Cycle A with the oxidative addition of Iodocyclohexane (CI) and Rh complex. In each cycle, we followed the oxidative addition, carbonylation step, reductive elimination, dehydration step, and final transformation step into Cyclohexanecarboxylic acid (CA). It is important to emphasize that for Rh complex, we considered the types of ligands coordinated to Rh atom carefully to examine their effect.

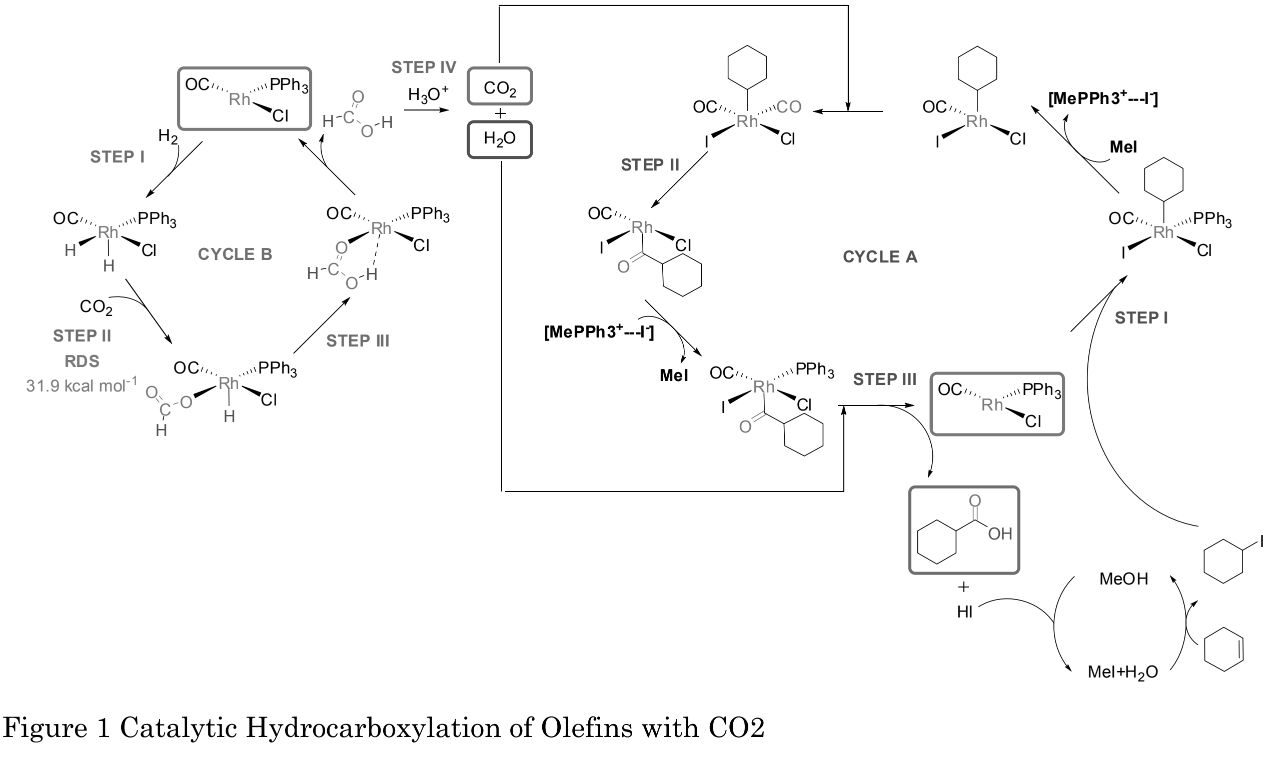


Figure 1 Catalytic Hydrocarboxylation of Olefins with CO2

In Cycle B, firstly, the reaction pathways of the oxidative addition of H_2 to the Rh complexes were examined and it was found that the coordination number of the phosphine ligand affects the reaction barriers. The most favorable pathway starts from the dissociation one of the phosphine ligands of the Rh catalyst, followed by the oxidative addition of H_2, and the formation of the formic acid. The decomposition of the formic acid can provide CO and H_2O, which will be utilized with olefin in Cycle A to form carboxylic acid.

In Cycle A, we purposed that the cyclohexyl iodide was simply formed from the coupling among I^- and cyclohexene. In this step, the cyclohexyl iodide and MeOH will be formed. In this cycle, the reaction started with the oxidative addition between the cyclohexyl iodide and the Rh complex. This was consistent with the experimental result that carboxylic acid will be formed after the cyclohexyl iodide existence. Then, the PPh_3 ligand was removed due to steric effect. This will provide the vacant site for CO to adduct. Then, the carbonylation step took place. After that, the PPh_3 ligand interacts to the Rh complex again to stabilize the intermediate. At this stage, the water molecule directly activated to the cyclohexanecarbonyl ligand to form the carboxylic acid and HI. In this case, HI will be consumed with MeOH to give MeI and H_2O.

From calculation, the active species was found to be the monomeric Rh complex. This consistent with the single-crystal X-ray diffraction, which the monomeric complex and $MePPh3^+$ were detected. The task of MeI and PPh_3 help to stabilize the intermediates and transition states along the reaction. The purposed mechanism is consistent with the result of NMR spectroscopy, which observed that the carbonyl group of the carboxylic acid functionality was caused by CO, while the –OH group was resulted from water molecule. The rate-determining step (RDS) of the process is the carbonylation step (step II) in Cycle B, whose reaction barrier is 31.9 kcal mol^{-1}.

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[1] Ostapowicz, T. G.; Schmitz, M.; Krystof, M.; Klankermayer, J.; Leitner, W., Angew. Chemie - Int. Ed. 52 (2013) page 12119–12123.

[2] Maeda, S.; Ohno, K.; Morokuma, K., Phys. Chem. Chem. Phys. 15 (2013) page 3683-3701.

2. Original papers

(1) -

3. Presentation at academic conferences

(1) Maneeporn Puripat, Miho Hatanaka, and Keiji Morokuma, “Theoretical Investigation of Catalytic Hydrocarboxylation of Olefins with CO_2” Second Circular of Computational Sciences and Workshop 2017 (CSW2017), Kanagawa, March 6-8, 2017

(2) Maneeporn Puripat, Romain Ramozzi, Miho Hatanaka, Waraporn Parasuk, Vudhichai Parasuk, and Keiji Morokuma, “The Biginelli reaction is a urea-catalyzed organocatalytic multicomponent reaction” The 14th symposium of Fukui Institute for Fundamental Chemistry, Kyoto, Jan. 27, 2017.

青野　信治

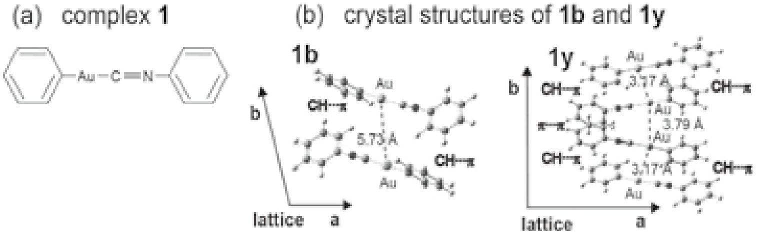
センターフェロー（榊研）

1. 今年度の研究の要約

今年度は金(I)-イソシアニド錯体によって構成される多型結晶の相対安定性および吸収・発光スペクトルの研究を行った。

【序】 金(I)-イソシアニド錯体は複数の単結晶構造を持ち、熱や光照射でなく機械的刺激によって相転移を起こし、各々の単結晶構造で異なる発光色を示す事から分子科学的にも、また材料化学的にも興味深い系である。 phenyl(phenyl-isocyanide) Gold(I)錯体 **1** は、溶媒中から高速で結晶化させると単結晶構造 **1b** が、ゆっくり結晶化させると単結晶構造 **1y** が生成する事が実験的に報告されている（Scheme 1）[1]。**1b** では最小単位格子が２個の分子から構成されているのに対して、**1y** では１６個の分子（Scheme 1b において c 軸方向に更に３層が方向性を各々90 度変えて存在する。）から構成されている。特に **1b** では PhNC 基と Ph 基の平面角τが 70 度ほど捻じれた単量体から構成されるのに対し、**1y** では PhNC 基と Ph 基がほぼ並行な単量体から構成されている。また **1b** では隣り合う分子間の Au-Au 距離は 4.7～5.7Å と長く、PhNC 基と Ph 基は CH-π相互作用しているのに対し、**1y** では隣り合う分子間の Au-Au 距離は 3.2～3.7Å と短く、PhNC 基と Ph 基の CH-π相互作用に加えて、PhNC 基のπ-π相互作用も存在している。

吸収・発光スペクトルのピーク位置は、これらの単結晶構造の間で大きく異なり、吸収スペクトルにおいて **1y** は **1b** よりも 1.0 eV、発光スペクトルにおいて **1y** は **1b** よりも 0.3 eV 以上低エネルギー側へのシフトが観測されている[1]。本研究では、QM/MM 法で結晶効果を考慮し、気相、溶液、結晶中での比較・検討を行い、この原因の究明を試みた。



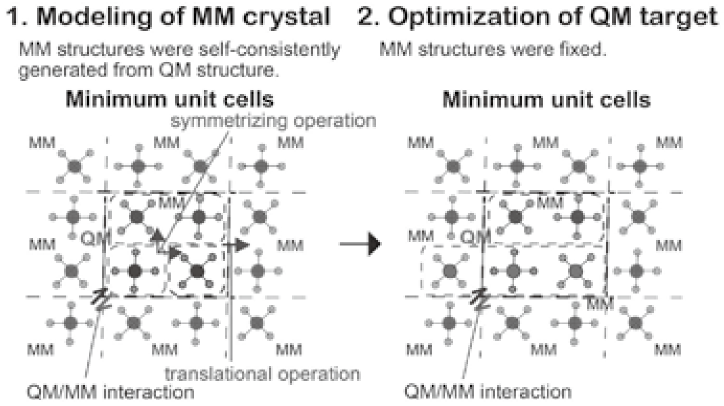
Scheme 1: 金(I)-イソシアニド錯体の構造

【方法】構造最適化には B3LYP-D3 汎関数による DFT 法を用い、吸収エネルギーは B3LYP 汎関数による TDDFT 法で求め、発光エネルギーは B3LYP-D3 汎関数を用いた３重項-１重項のエネルギー差で求めた。Au の原子価電子には(2111111/411/2111/1)基底を用い、内殻電子は Stuttgart グループの ECP で置き換え、f 軌道の分極関数を１つ加えた。他の原子については 6-31++G**基底を用いた。$CHCl_3$ 中の溶媒効果は 3D-RISM 法、結晶効果は周期境界条件に基づく QM/MM 法によって考慮した[2]。

本研究の QM/MM 法に基づく結晶中の構造決定は、次のように構築されている（Scheme 2)。まず、基底状態結晶を点電荷と LJ パラメータを用いてモデル化した。ここで、対称操

作と格子ベクトルによる並進操作を用いる事で全結晶部分を再構成できる領域を QM 領域に選び、計算された RESP 電荷を MM 領域に再分布させる事で自己無撞着的に MM 領域の点電荷と構造を決めた^2。これによって得られた基底状態結晶中での吸収エネルギーを求めた。

基底状態結晶の MM モデルは固定したまま、式(1)のエネルギー E_{crystal}が最少となるように反応中心部分の３重項状態の構造を決定して、発光エネルギーを求めた。



Scheme 2: QM/MM 法による結晶中３重項構造の決定

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

本研究では、格子ベクトルと基底状態結晶の Au 原子の位置を実験結果に固定した。

またスペクトルに対する結晶内部と結晶表面の結果を調べるため、結晶内部で定めた構造について、スラブモデルを適用し、結晶表面での吸収・発光スペクトルを求めた。

【結果と考察】 基底状態の単量体では、Ph 基と PhNC 基の分子内平面角τ に対する気相中のエネルギー、$\mathrm{CHCl_3}$ 中の自由エネルギーは B3LYP-D3 汎関数を用いた DFT 計算レベルでほぼ一定であり、CCSD(T)計算レベルでも平面角τ＝90度のねじれ構造がτ＝0度の平行構造に比べて 0.5 kcal/mol だけ安定であるという結果から、常温では自由回転していると考えられる。（図１）

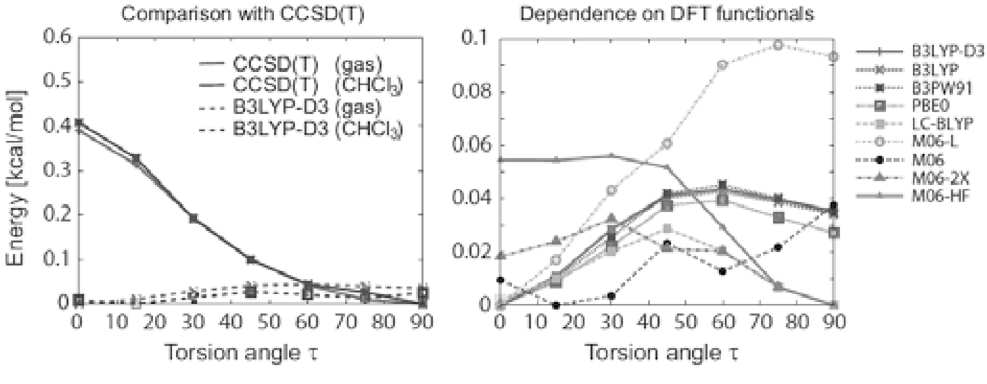


図１：分子内平面角τ に対するエネルギー安定性

そこで、吸収スペクトルと平面角τの関係性をみる為、τ＝0、30、60、90度の構造について TDDFT 計算を行った結果、Ph 基のπ軌道から PhNC 基のπ*軌道への LLCT 励起が最低励起状態となるが、その振動子強度は平面角τに強く依存する事が分かった（図２）。また最低励起エネルギーは気相中で 3.2-3.3 eV、$\mathrm{CHCl_3}$ 中で 3.7-3.8 eV と後者の方が 0.5 eV 高い。また、第二ピークは Ph 基のπ軌道から PhNC 基の面内π_{in}*軌道への LLCT 励起であり、第一ピークが平面角τ=0 度で大きな強度を持つのに対して、第二ピークは平面角τ=90 度で大きな強度を持つ。この第二ピークについても、気相中で 4.2 eV、$\mathrm{CHCl_3}$ 中で 4.6 eV と後者の

方が 0.4 eV 高い。この溶媒中における励起エネルギーの増加は、錯体 **1** の PhNC 基は中性であるのに対して Ph 基はアニオン性であるので、より強い CH-π相互作用の溶媒和が Ph 基に生じ、この溶媒和によって Ph 基のπ軌道が相対的に安定化するため、Ph 基のπ軌道から PhNC 基のπ*軌道への LLCT 励起などの励起エネルギーは $CHCl_3$ 中でより高くなる事が原因である。

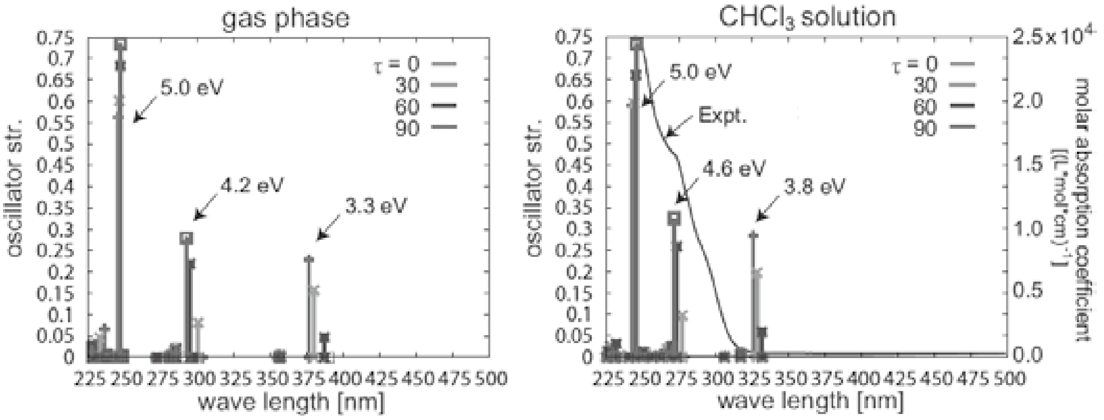


図２：気相、液相の励起エネルギーと振動子強度

結晶中の **1b** と **1y** についても、四量体を QM 領域に選び、自己無撞着点電荷を用いた QM/MM 計算によって構造を決定した。計算された単量体当りの結晶エネルギーは **1b** よりも **1y** の方が約 1 kcal/mol ほど安定であり、この傾向は実験において **1b** から **1y** への単結晶-単結晶相転移を不可逆的に起こす事が出来る事に合致する。また、得られた結晶構造における四量体について TDDFT 計算を行う事で吸収スペクトルを計算した（図３）。

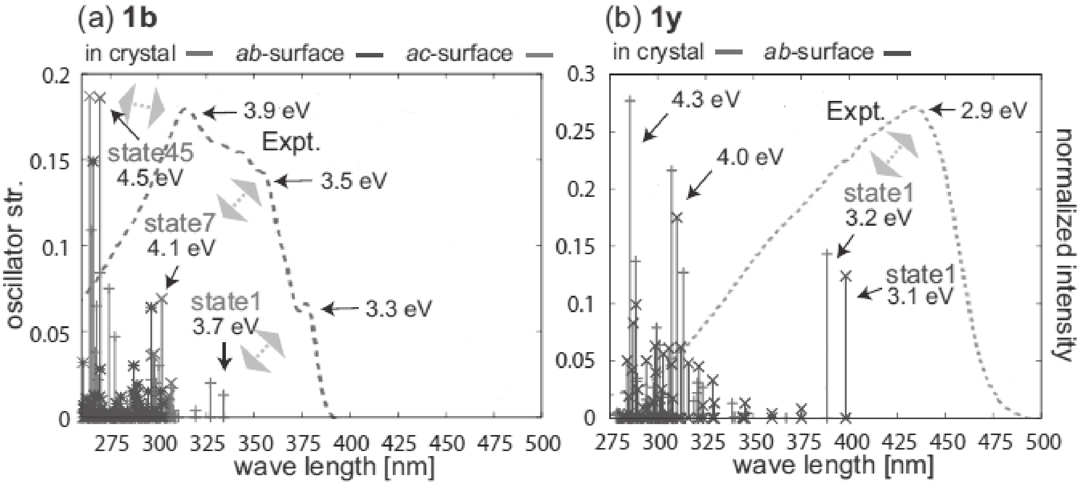


図３：結晶中の励起エネルギーと振動子強度

1b で計算された 4.1 eV の第一ピークは Ph 基のπ軌道から PhNC 基のπ*軌道への分子内および分子間 LLCT 励起であり、気相中の分子内 LLCT 励起に比べて 0.8 eV ほど高く、また 4.5 eV の第二ピークは Ph 基のπ軌道から PhNC 基の面内π_{in}*軌道への LLCT 励起であり、起草中の分子内 LLCT 励起に比べて 0.3 eV ほど高い。これらの増加は、Ph 基が隣り合う２つの分子の PhNC 基と CH-π相互作用している事が原因である。実際、CH-π相互作用が１つ

しかない結晶表面の場合は、特にこの前者のLLCT励起は3.7 eVに計算される。実験結果では3.9 eVに大きなピークがある他、3.5 eVにショルダーと3.2 eVに小さな吸収が観測されているが、これらは各々、結晶内分子のPh基のπ軌道からPhNC基の面内π_{in}*軌道へのLLCT励起、結晶内分子のPh基のπ軌道からPhNC基のπ*軌道へのLLCT励起、結晶表面の分子のPh基のπ軌道からPhNC基のπ*軌道へのLLCT励起に対応すると帰属できる。

一方、**1y**での結晶中と結晶表面で計算された3.2 eV、3.1 eVの第一ピークはAuのd軌道からPhNC基のπ*軌道へのMLCT励起であり、実験値2.9 eVのピークに対応している。**1y**では隣り合う分子のAu-Au距離が短いので、anti-bonding combination型のd軌道が生じ、そのエネルギーが相対的に高くなるため、π-π*型LLCT励起よりもMLCT励起が低く、**1b**の第一ピークとは異なる励起状態となる。**1b**から**1y**への単結晶-単結晶相転移による吸収スペクトルのレッドシフトについて、実験値1.0 eVに対して計算値1.4 eVであり、傾向を再現している。

また、気相、$CHCl_3$中の単量体の３重項状態は、PhNC基のπ-π*局所的励起構造が求まった。このπ-π*局所的励起は基底状態と電荷分布が大きく変化しておらず、発光エネルギーは気相、$CHCl_3$中ともに2.72 eVであり、環境の影響を受けない。二量体も検証したが、π-π*局所的励起よりもanti-bonding combination型Auのd軌道からbonding combination型PhNC基のπ*軌道へのMLCT励起構造が安定であった（図４）。π-π相互作用構造は、CH-π相互作用構造よりも気相中で3 kcal/mol安定であり、発光エネルギーも前者が1.95 eV、後者が2.45 eVとなり、発光エネルギーはAu-Au距離だけでなく、２つのPhNC基の向きにも大きく依存する。

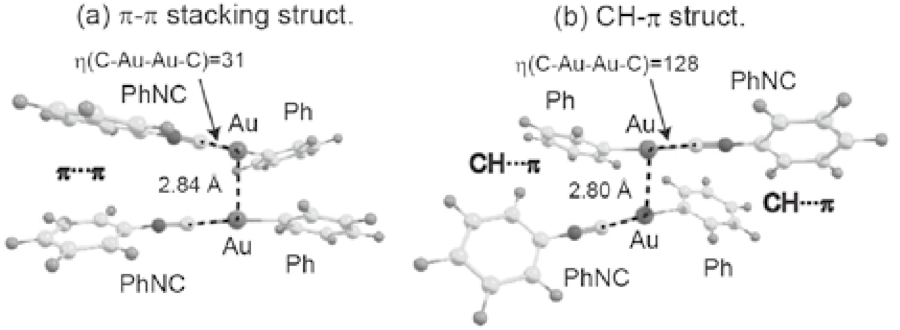


図４：MLCT型３重項の２つの安定構造

1bでは、周囲の分子の配向性のためMLCT型３重項構造を二量体間で作る事ができず、PhNC基のπ-π*局所的励起構造からの発光エネルギーが2.72 eVに求まった。一方、**1y**ではMLCT型３重項のCH-π相互作用構造を二量体間で作り、両側の隣り合う二量体も近付く事で、その発光は2.38 eVに求まった。これは実験値2.19 eVに比べて高い結果になっているが、**1b**から**1y**への単結晶-単結晶相転移による発光スペクトルのレッドシフトについて、実験値0.34 eVに対して計算値0.35 eVであり、良い一致を与えている。

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Japn・France・Spain-Joint Symposium on Theoretical and Computational Science of Complex System　京都　2016/10/26　P37

4. その他

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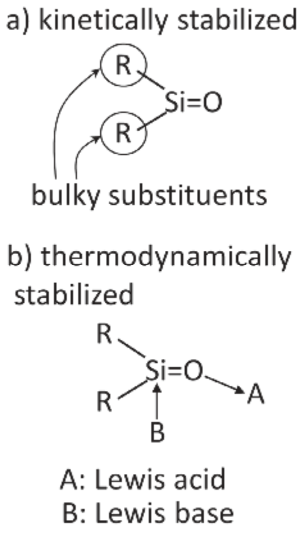
「金(I)-イソシアニド錯体の吸収・発光スペクトル：QM/MM法による分子結晶効果の研究」福井謙一京都大学第１４回京都大学福井謙一記念研究センターシンポジウム　京都　2017/1/27　P16

中垣　雅之

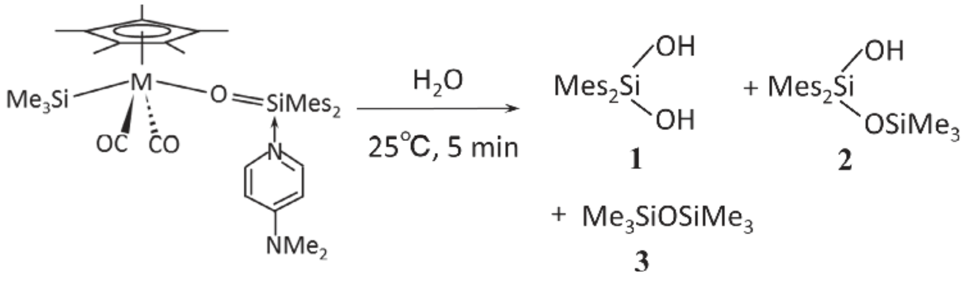
FIFC フェロー

1. 今年度の研究の要約

【緒言】遷移金属と典型元素の結合を含む化合物は錯体、有機・無機金属化合物など多岐に渡り、其々に異なった結合の性質を有する。シラノンはケイ素－酸素二重結合を持つ化合物であるが、高い分極や弱いπ結合性のため、かさ高い置換基やルイス酸・塩基の配位による安定化を必要とする(スキーム 1)。近年、村岡らによってモリブデン及びタングステン原子にシラノンが配位した錯体(スキーム 2)が合成された。[1] この錯体は水分子との反応によって複数の生成物が生じるが、金属原子や用いる溶媒の種類によってその生成比が大きく変化する(スキーム 2)。これらの結果は選択的反応やその制御の観点から非常に興味深いが、その違いを生む要因だけでなく、それぞれの生成物に至る反応機構も明らかにされていない。また水分子との反応機構を理解することは安定な Si-O 二重結合を生成する上で極めて重要である。本研究では、電子状態計算を用いて**シラノン−金属錯体の水分子との反応機構を明らかにし、反応を制御する支配的要因の解明を試みた。**



スキーム 1

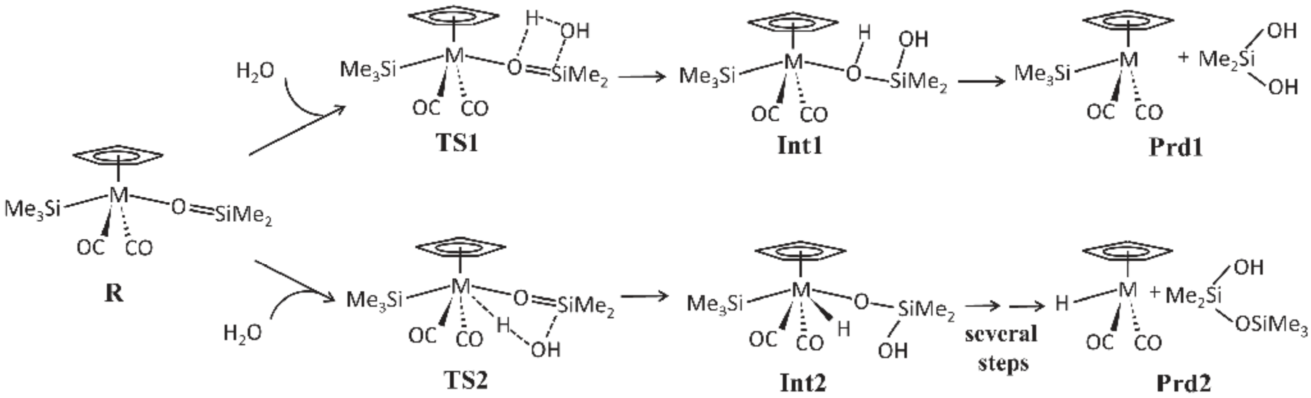


M	Solvent	NMR yield 1	2	3
Mo	C_6D_6	86 %	7 %	-
	CD_3CN	51 %	34 %	28 %
W	C_6D_6	-	82 %	-
	CD_3CN	63 %	9 %	34 %

スキーム 2

【計算方法】構造最適化には DFT(B3PW91)法を用い、エネルギー計算には SCS-MP2 法を用いた。また、PCM 法を用い溶媒効果を取り入れた。基底関数は、構造最適化及び振動数計算には遷移金属に LANL2DZ その他の原子には 6-31G*を用い、エネルギー計算には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、その他の原子には 6-311G*を用いた。

【結果及び考察】構造最適化の結果、生成物 1 及び生成物 2 を生じるそれぞれの反応経路が得られた(スキーム３)。反応経路 1 では水分子の OH 及び H がシリレンの Si 及び O に反応し生成物 1 を生じる。一方、反応経路 2 では水の H 原子はシリレンではなく金属原子に配位する。配位構造の異なるいくつかの中間体を経由した後に反応物 2 を生じる。ルイス塩基であるジメチルアミノピリジン(DMAP)がシリレンに配位していない場合、反応経路 1 の遷移状態 TS1 は、反応経路 2 の初めの遷移状態である TS2 よりも 10kcal/mol 以上不安定である。



スキーム 3　２つの反応経路

DMAP が配位することで２つの反応経路の相対安定性は大きく変化する。反応経路 1 では水分子と反応した後も DMAP はシラレンケイ素原子上に配位しているが、反応経路２では TS2 において既に DMAP が解離している(図１)。そのため、DMAP 配位による安定化のため反応経路１と２の遷移状態のエネルギー差は小さくなる。

また図１に示すような、H 原子と OH 基を供給する水分子が異なる水２分子による橋かけ構造を考えることで遷移状態の高さは大きく減少する（表１）。

表１. 水分子数と Gibbs エネルギー変化(kcal/mol)

	Int1	TS1	R	TS2	Int2
M=Mo, $(H_2O)_1$	−0.9	+15.0	0.0	+14.6	+4.2
M=Mo, $(H_2O)_2$	−3.5	+8.9	0.0	+7.6	+4.3
M=W, $(H_2O)_1$	+1.4	+15.7	0.0	+12.2	+0.0
M=W, $(H_2O)_2$	−0.3	+10.2	0.0	+8.2	+1.7

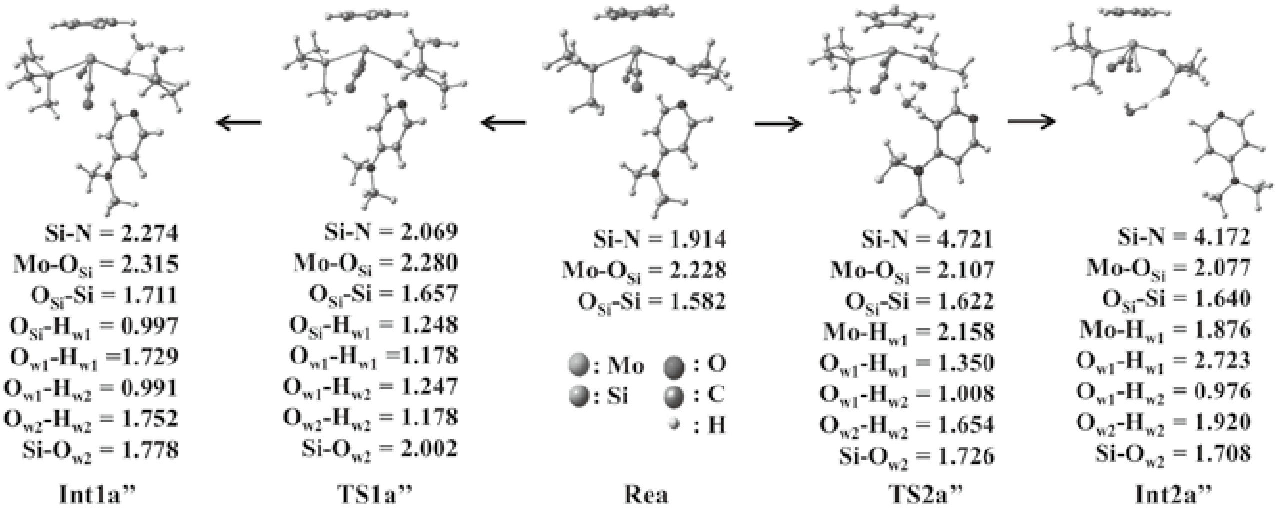


図 1 **DMAP** 配位した **Mo** 錯体と水２分子の反応

中間体２以降の反応経路２の最適化構造を図２に示す。立体障害の小さいＨ原子が動くことにより配位構造が変化し、$SiMe_3$ 基が一旦金属原子から解離しＨ原子と結合した(Int4)後に、金属原子との再結合を経由してシラレンと反応する(Int6)。中間体２以降の反応においては Si-Mo 結合が切断される TS4 の反応障壁が最も高い。

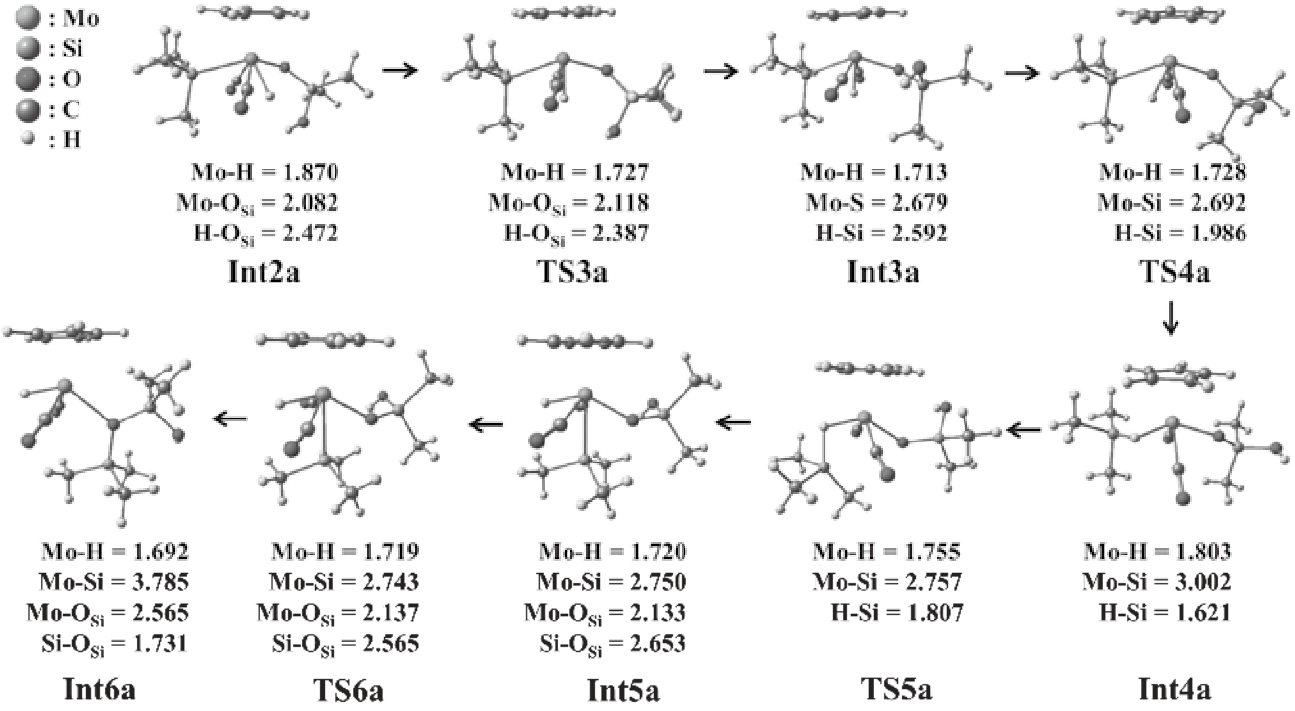
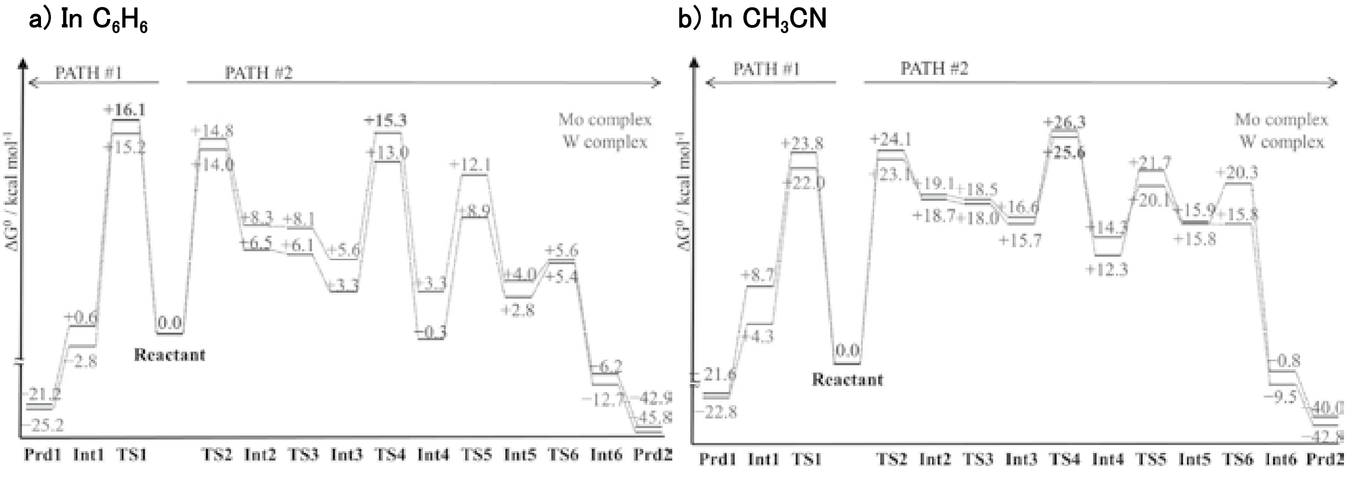


図２　反応経路２の中間体２以降の最適化構造

溶媒効果を取り入れた２つの反応経路の Gibbs エネルギー変化を図３に示す。ベンゼン溶液中では Mo 錯体は TS4 が最も高く(15.3 kcal/mol)、反応は経路１が有利である。一方、W 錯体では TS1 が最も高く(16.1 kcal/mol)、経路２が有利である。一方、アセトニトリル溶液中では Mo 錯体 W 錯体共に TS4 が最も高く(26.3, 25.6 kcal/mol)、経路１が有利である。これらの結果は金属原子や溶媒の種類による主生成物の変化をよく再現している。


a) In C_6H_6

b) In CH_3CN

図3　溶媒中での Gibbs エネルギー変化（SCS-MP2 法, kcal/mol）

２つの金属錯体を比較すると、反応経路1ではMo錯体がW錯体よりも有利である。反応経路1では水分子のH及びOH共にシラノンに結合することから金属原子は直接は関与しない。Si=O π軌道のエネルギーはMo錯体で−8.86 eVとW錯体の−8.89eVよりも高い。従って、Mo錯体のシラノンの方がプロトンライクな水素原子の求電子攻撃を受けやすいと考えられる。シラノンの配位を取り除いた金属錯体のHOMO及びLUMOを図4に示す。HOMOはdπ軌道であり、LUMOはdσ軌道であり、その軌道エネルギーは、W錯体の方がHOMOは高くLUMOは低い。そのためシラノンから金属へのσ供与はW錯体で大きい、その結果π軌道エネルギーが下がる。そのため、水との反応はMo錯体の方が有利であると考えられる。一方、反応経路2ではMo錯体よりもW錯体が有利である。経路2では金属原子にH原子が結合することからTS2の反応は水分子による金属−シラノン錯体への酸化付加反応とみることができる。HOMOの軌道エネルギーはW錯体の方が高いことから酸化付加反応が起こりやすいと考えられる。

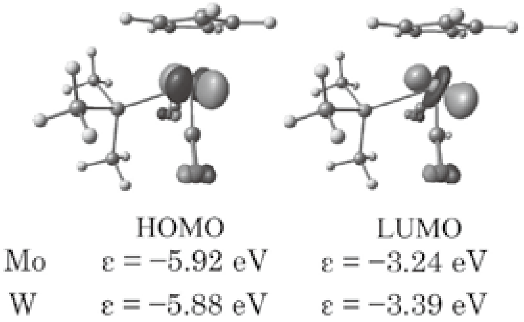


図4 Mo, W錯体のHOMOとLUMO

本研究により、シラノン−金属錯体と水との複数の反応機構が明らかになった。シラレンと水の付加反応と金属錯体への酸化付加反応は競争的に起こり、金属錯体の軌道エネルギーが反応の進行方向に大きく寄与していることから配位子を化学的に修飾し軌道エネルギーを変化させることで反応を制御できると考えられる。

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第14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, 2017/1/27

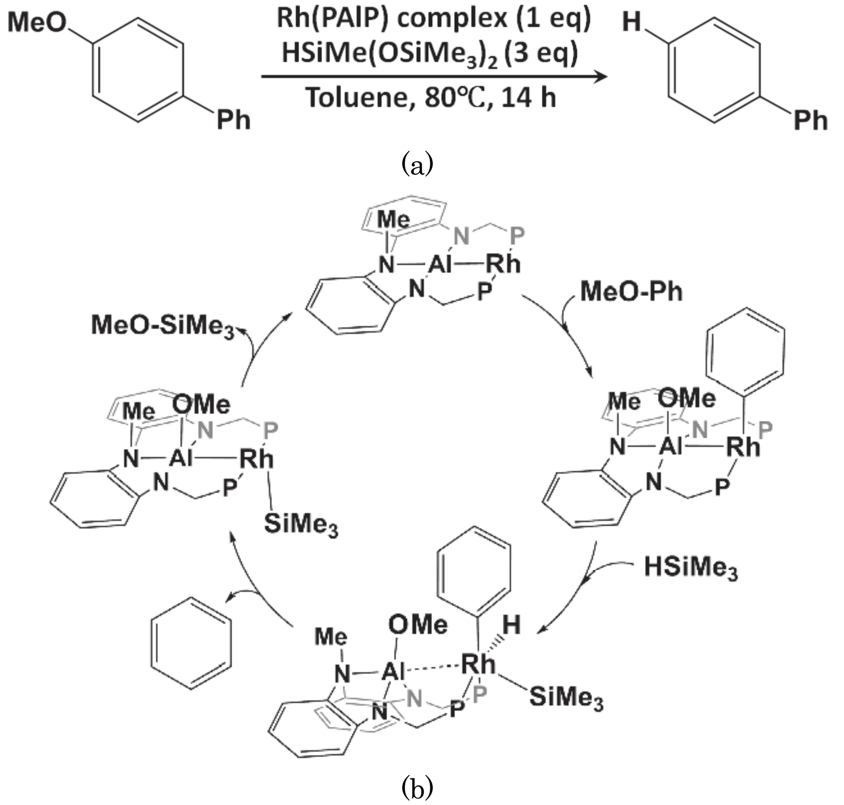
Hong Zheng

SPR Fellow

1. Summary of the research of the year

Why can Rhodium-Aluminum Bonded Complex Cleave very Strong C-O Bond? Theoretical Study

X-type ligands with a lone pair of electrons and a formally vacant π-orbital can coordinate with a transition metal via a σ-bond between low-valent group 13 element and transition metal atom and have been investigated well, with the expectation that they have unique bifunctional nucleophilic/electrophilic properties. In previous reports the multidentate supporting X-type ligands such as X-type boryl donor (PBP) ligand have been synthesized. Though the boryl ligands have been studied well, the X-type alumanyl ligands have been rear with only two examples coordinated with $FeCp(CO)_2$.



(a)

(b)

Scheme 1. (a) C-O activation catalyzed by Rh-(PAlP) complex followed by hydrogenation. (b) Proposed reaction mechanism.

Recently a series of Rhodium complex with X-type alumanyl ligand (Rh-(PAlP)) were synthesized by Nakao and coworkers. The alumanyl ligands were expected to activate and/or functionalize organic compounds due to their σ-donation and the high Lewis acidity. Actually, the conventionally difficult C-O activation was experimentally succeeded by the Rh-(PAlP) complex, as shown in Scheme 1. In this reaction, the C-O bond in Ar-OMe compound is activated in the presence of hydrosilanes and Ar-H compound is afforded. However, the reaction mechanism is not clear and thus theoretical investigation is indispensable.

In this work, we firstly investigated the reaction mechanism of the reaction cycle with Rh-(PAlP) complexes by means of DFT calculations. The purposes here are to elucidate the characteristic features of C-O activation and the following Si-H activation. Also, to clarify what is important factor for the C-O activation and to increase the field of application of Rh-(PAlP), we focus on the first step of the reaction cycle and predicted a series of C-X (X = OMe, F, NMe_2) activation by Rh-(PAlP).

Reaction mechanism of the reaction cycle.

As shown in Figure 1, in the first step of catalytic cycle via C-O bond cleavage by Rh-Al, the Rh-(PAlP) complex firstly form an adduct complex **AD1a** with anisole, in which the O atom and the phenyl group weakly coordinates with the Al and Rh atoms, respectively. The O-Ph distance increases by 0.105 Å in **AD1a** compared to free PhOMe compound, indicating strong interaction occurs between the Rh-Al and C-O bonds. Then, the C-O bond between the Ph and OMe groups is cleaved through one transition state **TS1a**. In **TS1a**, the O-Ph distance increases by 0.348 Å but the Al-O and Rh-Ph distances decrease by 0.226 Å and 0.111 Å, respectively, meaning the O-Ph bond is broken and Al-O and Rh-Ph bonds are somehow formed. Hence, **TS1a** is the transition state of C-O bond activation. Moreover, the Rh-Al bond becomes longer by 0.222 Å as going from **AD1a** to **TS1a**, implying the Rh-Al bond is weakened due to formation of Al-O and Rh-Ph bonds. The O-Ph bond cleavage is completed in **P1a**, in which O-Ph distance increases to 3.560 Å, whereas Rh-Al bond is almost broken due to a large distance of 2.595 Å.

In the second step, one $HSiMe_3$ compound approaches **P1a** to afford an adduct **AD2**, in which Rh(Ph)-Al(OMe) complex is distant from hydrosilane. Then, the Rh-H and Rh-Si distances decreases dramatically but the H-Si bond increases by 0.073 Å in **TS2**. The Rh-Al further increases by 0.446 Å because of the oxidative addition on Rh. The Si-H bond is completely cleaved in **P2**, in which Rh atom has Ph, H, and $SiMe_3$ groups. Hence **TS2** is the transition state of Si-H activation. The H starts to bond with Ph in **TS3**, in which the Ph-H distance decreases by 0.687 Å but the Rh-Ph distance increases by 0.082 Å as going from **P2** to **TS3**. The Ph is changing its orientation to interact with the H in **TS3**. One benzene compound is formed in **P3**. The Rh-Al distance decreases to 2.600 Å and the C_6H_6 species detaches from the Rh center in **P3**. Herein, a Rh($SiMe_3$)-Al(OMe) complex **P4** is formed. However, reductive elimination of Si-O bond can not occur in **P4** directly and the Rh-$SiMe_3$ bond must rotates by nearly 180°, leading to another geometry **P5**. The reductive elimination of Si-O bond occurs through **TS4**. In **TS4**, the Si-O distance decreases by 1.619 Å but Rh-Si increases by 1.035 Å. The Al-O bond changes little in **TS4**. Finally, the Si-O bond is formed in **P6**. The Rh-Al bond is formed in **P6** and hence the reaction cycle is completed.

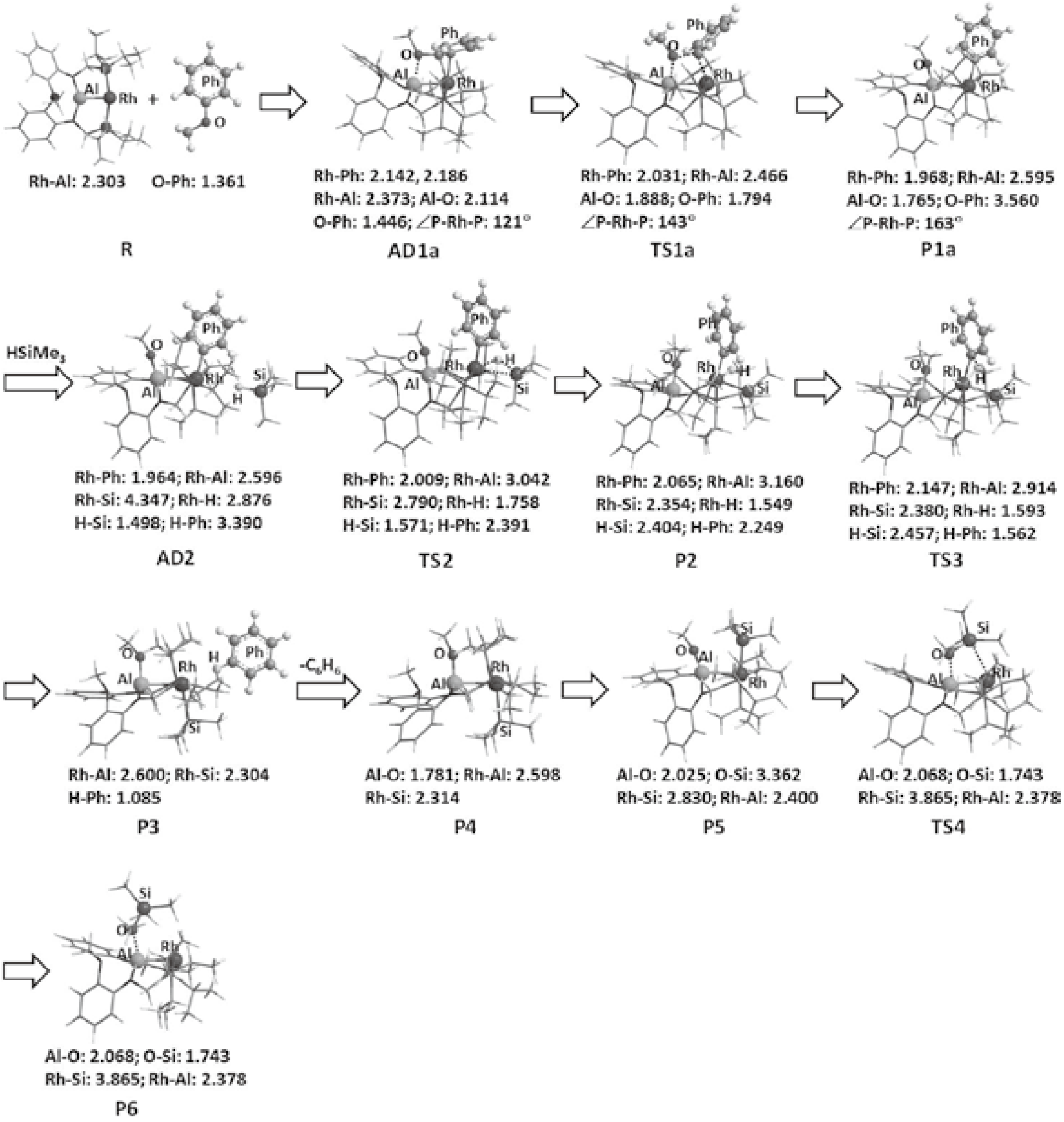


Fig 1. Geometrical parameters of complexes in the C-O activation followed by Si-H activation by Rh-(PAlP). The bond distances are represented in Angstrom.

The **AD1a** is moderately higher than reactant, as shown in Figure 2. The activation energy of **TS1a** is 9.9 kcal/mol, implying that C-O activation is easy. The **P1a** complexes is much more stable than reactant by -26.5 kcal/mol, suggesting that the Al-O and Rh-Ph bonds are strong. In Si-H activation, the activation energy of **TS2** is 23.2 kcal/mol relative to **AD2**. The product of Si-H activation **P2** is only 1.1 kcal/mol lower than **TS2** due to steric repulsion and geometry distortion around the Rh atom. The activation energy of **TS3** is 31.5 kcal/mol but **P3** is 10.0 kcal/mol more stable than **AD2**. Considering that the activation energy of Si-O reductive elimination TS is 22.4 kcal/mol relative to **P3**, the benzene formation step is the rate-determining step in this reaction cycle. In general, C-O activation can easily occur by employing the Rh-Al complex, which is consistant with the experimental observation.

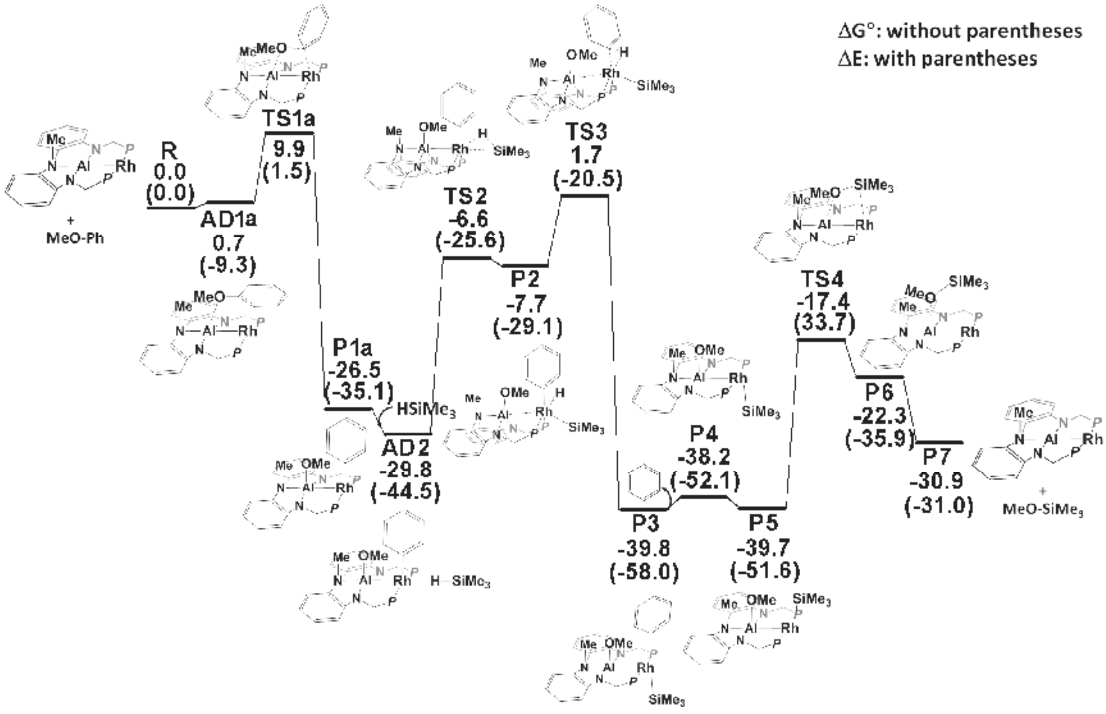


Fig 2. Energy changes (in kcal/mol) of the reaction cycle.

C-X activations by Rh-(PAlP). It is very special that the strong C-O bond can be cleaved by the Rh-(PAlP) complex with small activation energy and the product is very stable. To understand why C-O activation is easy and what factor is important for this reaction, we performed investigations of C-F and C-N activations with Ph-F and Ph-NMe$_2$ compounds. Also, since C-O activation in Cy-OMe is useful for synthesis of sugar, the Cy-O activation of Cy-OMe by Rh-(PAlP) was predicted.

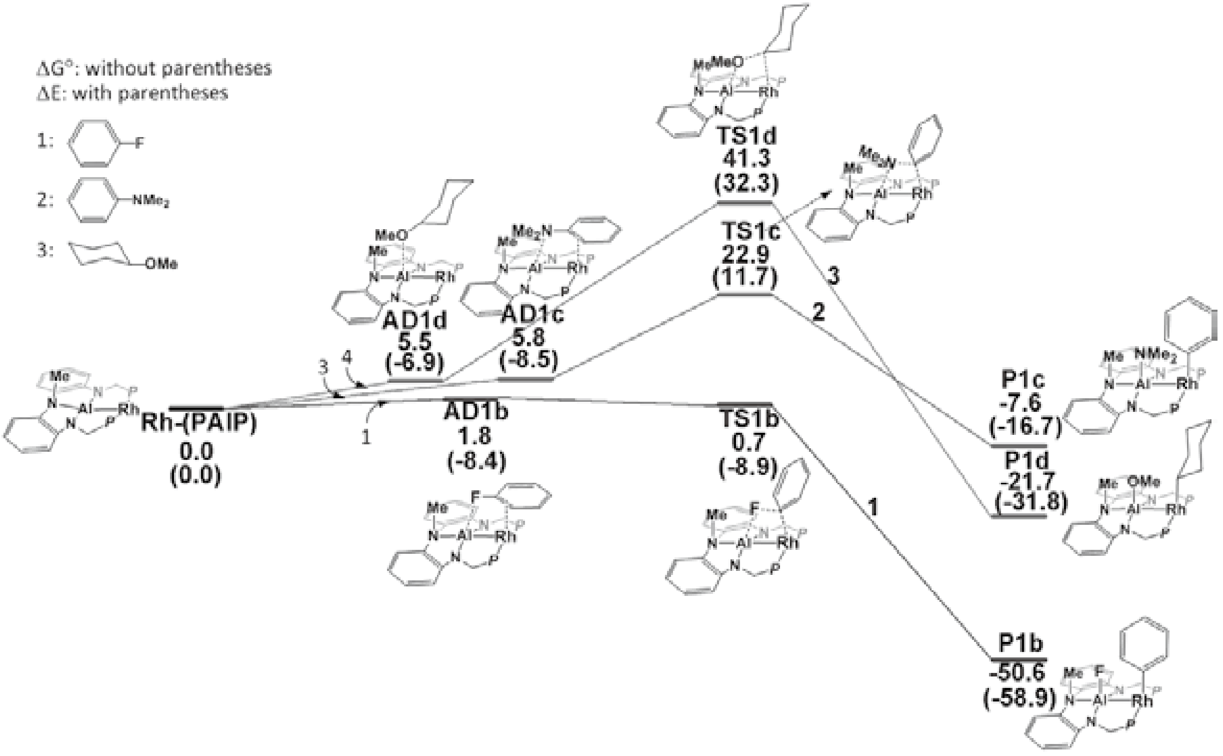
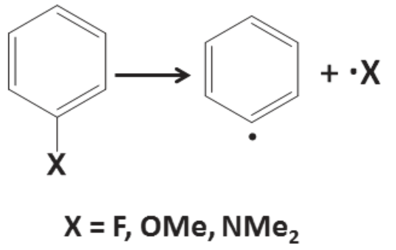


Fig 3. Energy changes (in kcal/mol) of C-F, C-N, and Cy-O activations.

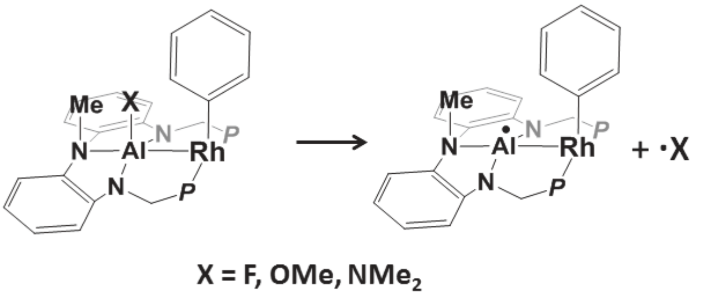
As shown in figure 3, in the C-F activation, the adduct complex **AD1b** is 1.8 kcal/mol higher than reactant, whereas the transition state **TS1b** is 1.1 kcal/mol lower than **AD1b**. These results indicate that the C-F activation is much easier than the C-O activation of anisole without an activation barrier from adduct. The C-F activation product **P1b** is 24.1 kcal/mol more stable than **P1a**, suggesting Al-F bond is much stronger than Al-O bond. In contrast, the activation energy of **TS1c** in C-N activation is 13.0 kcal/mol higher than **TS1a** and the product **P1c** is 18.9 kcal/mol less stable than **P1a**. These results imply that Al-N bond is weak and therefore C-N activation can hardly occur. In the Cy-O activation, very weak interaction occurs between Cy-OMe and Rh-Al complexes in the adduct **AD1d** since the Cy group does not coordinate with the Rh. In the Cy-O activation transition state **TS1d**, the Cy-Rh distance is still large and its activation energy is 41.3 kcal/mol, meaning this reaction can hardly occur. Herein, Rh-(PAlP) is useful for C-F activation but can not be used for C-N and Cy-O activations.

Several important factors for C-X (X=F, OMe, NMe_2) and Cy-O activations. Here we firstly analysed the C-X (X = F, OMe, NMe_2) bond energies (BE). The calculation mode is shown in Scheme 2a. The BE values of C-X and Cy-O bonds decreases in the order C-F > C-OMe > C-NMe_2 > Cy-OMe, meaning bond cleavage becomes easier as going from C-F to Cy-OMe. However, the lowest-unoccupied-molecular-orbital (LUMO) level becomes higher in the order C-F < C-OMe < C-NMe_2 < Cy-OMe. In the reaction with σ-donating alumanyl ligand, a lower LUMO level is good for the reaction and hence C-F is can easily react with the Rh-Al bond.



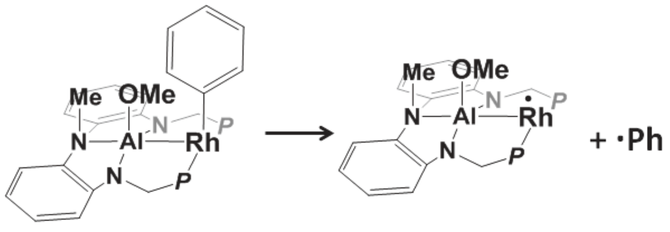
(C-X)/(Cy-O) bond	BE	LUMO/eV
C-F	129.5	-0.11
C-OMe	108.0	0.30
C-NMe_2	104.4	0.51
Cy-OMe	98.2	1.13

(a)



Al-X bond	BE
Al-F	162.0
Al-OMe	123.1
Al-NMe_2	96.1

(b)



bond	BE
Rh-Ph	82.0
Rh-Cy	61.0

(c)

Scheme 2. Bond energy (in kcal/mol) calculation modes: (a) Calculation mode and bond energies of C-X (X=F, OMe, NMe_2) bonds and LUMO energies of Ph-X and Cy-OMe species;[a] (b) Calculation mode and bond energies of Al-X (X=F, OMe, NMe_2) bonds; (C) Calculation mode and bond energies of Rh-Ph and Rh-Cy bonds.[b]

[a] The bond energy of Cy-O bond was calculated with the same mode as that of C-X bonds.

[b] The bond energy of Rh-Cy bond was calculated with the same mode as that of Rh-Ph bond.

The BE values of Al-X bonds decrease in the order Al-F > Al-OMe > Al-NMe_2, as shown in Scheme 1b, which agree with the order of LUMO in Scheme 1a. The difference between Al-X and C-X bonds $\Delta BE(X)$ ($\Delta BE(X) = BE(Al\text{-}X) - BE(C\text{-}X)$) decreases in the order $\Delta BE(F) > \Delta BE(OMe) > \Delta BE(NMe_2)$, indicating that the large Al-F bond energy is an important factor for the smooth C-F activation.

The BE of Rh-Cy bond is 21.0 kcal/mol smaller than that of Rh-Ph bond, as depicted in Scheme 1c, implying that weak Rh-Cy bond is one factor for the instability of **TS1d**.

Based on these results, it is concluded that the LUMO of Ph-X compounds and the BE of Al-X bonds are important factors for the C-X activations. The high LUMO of Cy-OMe and small BE of Rh-Cy bond are the reasons why Cy-O activation is difficult.

In conclusion, C-O activation can occur easily with a small activation energy (9.9 kcal/mol) by using Rh-(PAlP) complex. The rate-determining step in the whole reaction cycle is the formation of C_6H_6 species with an activation energy of 31.5 kcal/mol. The C-F activation can easily occur but C-N and Cy-O activations are difficult with large activation energies. The Lower LUMO of Ph-F and strong Al-F bond are the main reasons of stable **TS1b**. The high LUMO of Ph-NMe_2 and weak Al-N bond are the reasons of unstable **TS1c**. The instability of **TS1d** is assigned to the high LUMO of Cy-OMe and weak Rh-Cy bond.

2. Original papers

(1) Hong Zheng, Yoshiaki Nakao, Shigeyoshi Sakaki,
"Why can Rhodium-Aluminum Bonded Complex Cleave very Strong C-O Bond? Theoretical Study" *In preperation*.

3. Others

(1) Teruhiko Saito, Hong Zheng, Naofumi Hara, Nishamol Kuriakose, Shigeyoshi Sakaki, Yoshiaki Nakao,
"Rhodium Complexes Bearing PAlP Pincer Ligands" *In preparation*.

Lu Jing

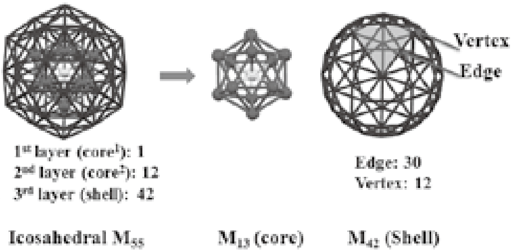
Research Fellow

1. Summary of the research of the year

DFT insight into core-shell preferences for bimetallic $Pt_{42}M_{13}$ (M=Mo, Tc, Ru, Rh, Pd, W, Re, Os, and Ir) clusters

Platinum (Pt)-based clusters/particles have been playing a major role in many industrial application, such as catalyzing the oxygen reduction reaction (ORR) in proton exchange membrane fuel cells. Great efforts are being made to decrease Pt content with increasing Pt dispersion and enhancing catalytic activity. One approach is based on the core−shell structure consisting of a thin layer of Pt deposited on the surface of nanoparticles made of a less expensive and/or a more abundant metal. Currently, bimetallic Fe-Pt, Co-Pt, Ni-Pt, Cu-Pt, and Ru-Pt with core-shell structure have been reported as good catalytic candidates both experimentally and theoretically. However, the systematically study about the determining factors influencing core-shell structure for bimetallic alloyed cluster/particle and their electronic structure have been rarely presented.

For the icosahedral bimetallic $Pt_{42}M_{13}$ (M = Mo, Tc, Ru, Rh, Pd, W, Re, Os, and Ir) clusters, a comprehensive analysis of the determining factors influencing core-shell structure, such as cohesive energy, stability of the core and shell, together with charge transfer, are elucidated. Also, the electronic structures of the investigated bimetallic core-shell $M_{13}@Pt_{42}$ clusters are clarified.



Scheme 1. Model systems of icosahedral 55-atom clusters with corresponding M_{13} core and M_{42} shell.

Relative energy. For the icosahedral $Pt_{42}M_{13}$ (M = Ru and Os) clusters, the most stable structure is the core-shell structural $M_{13}@Pt_{42}$ cluster, the next stable one is $Pt_{42}M_{12}^{core}M^{vertex}$ cluster, and the least stable one is $Pt_{42}M_{12}^{core}M^{edge}$ cluster. Similarly, the icosahedral core-shell structural $Rh_{13}@Pt_{42}$ cluster is the most stable among these three isomers. The energies difference between the $Pt_{42}Rh_{12}^{core}Rh^{edge}$ ($Pt_{42}Rh_{12}^{core}Rh^{vertex}$) and $Rh_{13}@Pt_{42}$ is 11.42 kcal/mol (6.88 kcal/mol). For the icosahedral Pt-Ir combination, the stability decreases in the order of $Ir_{13}@Pt_{42}$ (0.00 kcal/mol) > $Pt_{42}Ir_{12}^{core}Ir^{edge}$ (+41.45 kcal/mol) > $Pt_{42}Ir_{12}^{core}Ir^{vertex}$ (+48.59 kcal/mol). In a word, the icosahedral core-shell structural $M_{13}@Pt_{42}$ (M = Ru, Rh, Os, and Ir) clusters are favorable. However, in the cases of M = Mo, Tc, Pd, Re, and W, the icosahedral core-shell structural $M_{13}@Pt_{42}$ clusters are not stable. For the combinations of Pt-Mo, Pt-W, and Pt-Re, the $Pt_{42}M_{12}^{core}M^{edge}$ isomer have the lowest energy, which are lower by 47.76 kcal/mol, 25.02 kcal/mol, and 10.53 kcal/mol than

$M_{13}@Pt_{42}$, respectively. For the $Pt_{42}Tc_{13}$ and $Pt_{42}Pd_{13}$ clusters, the stability decreases in the order of $Pt_{42}M_{12}^{core}M^{vertex} > Pt_{42}M_{12}^{core}M^{edge} > M_{13}@Pt_{42}$ (see Table 1).

Table 1. Relative energy (in kcal/mol) of three isomers in the most stable spin states.

M	$M_{13}@Pt_{42}$	$Pt_{42}M_{12}^{core}M^{edge}$	$Pt_{42}M_{12}^{core}M^{vertex}$
Mo	0.00 (Singlet)	-47.76 (Singlet)	-36.53 (Quintet)
Tc	0.00 (Octet)	-18.38 (Doublet)	-18.59 (Octet)
Ru	0.00 (Septet)	+37.96 (Septet)	+31.03 (Septet)
Rh	0.00 (20et)	+11.42 (20et)	+6.88 (20et)
Pd	0.00 (23et)	-31.07 (15et)	-31.37 (15et)
W	0.00 (Singlet)	-25.02 (Singlet)	-8.49 (Triplet)
Re	0.00 (Doublet)	-10.53 (Doublet)	+3.24 (Dectet)
Os	0.00 (Septet)	+65.64 (Triplet)	+61.16 (Septet)
Ir	0.00 (Dectet)	+41.45 (Quartet)	+48.59 (12et)

Segregation energy. The calculated segregation energies are positive in the cases of M = Ru, Rh, Os, and Ir, showing that M-core and Pt-shell structure is preferred (see in Figure 1). The minimum segregation energies for the Ru-Pt, Rh-Pt, Os-Pt, and Ir-Pt are 1.35 eV, 0.30 eV, 2.65 eV, and 1.80 eV, respectively. For the combinations of Mo-Pt, Tc-Pt, Pd-Pt, W-Pt, and Re-Pt, however, the segregation energies are -2.07 eV, -0.81 eV, -1.35 eV, -1.09 eV, and -0.46 eV, respectively. The negative segregation energy indicates that $M_{13}@Pt_{42}$ (M = Mo, Tc, Pd, W, and Re) structure is not stable. For the 4*d* metals, the segregation energy increases as going from Mo to Ru and then decreases as going from Ru to Pd. Though the same trend is found for the 5*d* metals, the value shifts to more positive (or less negative).

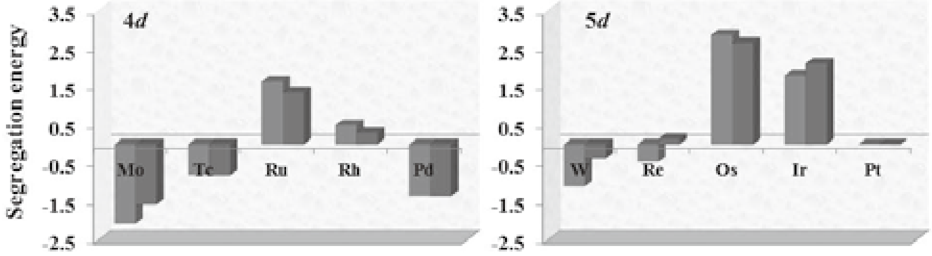


Figure 1. Calculated segregation energy (in eV) for icosahedral $Pt_{42}M_{13}$ (M = Mo, Tc, Ru, Rh, Pd, W, Re, Os, and Ir) clusters.

Cohesive energy. The cohesive energy of icosahedral Ru_{13}, Rh_{13}, Os_{13}, and Ir_{13} are 4.86 eV, 4.28 eV, 5.41 eV, and 5.29 eV, respectively, which are larger than that of Pt_{13} (3.95 eV). It means that the M (M = Ru, Rh, Os, and Ir) prefers to occupy the core positions to achieve the greater binding energies. Also, 5*d* metal (Os or Ir) has larger cohesive energy than 4*d* metal (Ru or Rh) in the same group. On the other hand, the cohesive energy of Pd_{13} (2.43 eV) is smaller than that of Pt_{13}. It means that Pd is unfavorable to reside in the core position for the combination of Pd and Pt.

M_{13} core and Pt_{42} shell. For the icosahedral M_{13} (M = Ru, Rh, Os, and Ir) core, the RMSD values for the Ru_{13}, Rh_{13}, Os_{13}, and Ir_{13} are 0.023 Å, 0.045 Å, 0.002 Å, and 0.006 Å, respectively. Meanwhile, the calculated distortion energies of Ru_{13}, Rh_{13}, Os_{13}, and Ir_{13} using the B3LYP functional are 0.52 eV, 1.08 eV, -0.05 eV, and 0.28 eV, respectively. The smallest distortion energy is observed in the Os_{13}, verifying that the Os_{13} core is the most stable. The next stable core is Ir_{13}, and the least stable cores are Ru_{13} and Rh_{13}. It is reasonable to infer that, smaller RMSD and distortion energy of M_{13} core will result in the stabilization of M_{13} core, which is beneficial to form the core-shell structure.

In the cases of metals in group VI and VII, the optimized structure of isolate M_{13} is significantly different from icosahedral structure, indicating that the icosahedral M_{13} (M = Mo, Tc, W, and Re) is unfavorable. The instability of icosahedral M_{13} core is the major reason why these metals do not have $M_{13}@Pt_{42}$ structure. It suggests that the M_{13} cluster in the core positions must have the same structure as the total $M_{13}@Pt_{42}$ cluster.

Also, the distortion energy of the icosahedral Pt_{42} surface in the $M_{13}@Pt_{42}$ cluster is lower than that in the Pt_{55} cluster, which also contributes to the stability of Pt_{42} shell. These factors are important for stabilizing the $M_{13}@Pt_{42}$ core-shell structure.

Charge transfer. Charge distribution and *d*-orbital population are also important factors influencing core-shell structure. NBO charge distributions for the icosahedral $M_{13}@Pt_{42}$ and Pt_{55} clusters are given in Table 2. The NBO charge of Pt atom in the core1 position for the pure Pt_{55} cluster is +0.638 *e*. However, the charges of Ru, Rh, Os, and Ir atoms in the core1 position of the stable core-shell structural $M_{13}@Pt_{42}$ clusters are -3.246 *e*, -1.575 *e*, -1.467 *e*, and -0.619 *e*, respectively, indicating that the charge transfer (CT) is occurred from Pt to M (M = Ru, Rh, Os, and Ir) metals with incompletely occupied *d* orbital. Similarly, the charges of M atom in the core2 position are also negative (-2.946 *e*, -2.515 *e*, -1.577 *e*, and -0.220 *e*, respectively). On the other hand, the NBO charge of Pt in the edge position of the Pt_{55} cluster is -0.122 *e*. The charges of M in the same position are much more negative, and the most negative charge is found in the Os. For the position of vertex, the Pt has a positive charge. On the contrary, the Ru, Rh, Os, and Ir have negative charges.

The *d*-orbital population of Pt atom, which is located in the core1 position of Pt_{55} cluster, decreases by 0.21 *e* compared to d^9 electron configuration in the atomic ground state. However, the *d*-orbital populations of Ru, Rh, Os, and Ir in the stable icosahedral core-shell structural $Ru_{13}@Pt_{42}$, $Rh_{13}@Pt_{42}$, $Os_{13}@Pt_{42}$, and $Ir_{13}@Pt_{42}$ clusters increase by 2.49 e, 1.75 e, 3.19 e, and 1.94 e, respectively, compared with the atomic electron configurations. The difference of *d*-orbital population for the 5*d* metal (Os or Ir) is larger than that for the 4*d* metal (Ru or Rh) in the same group. The large difference of *d*-orbital population between M in the $M_{13}@Pt_{42}$ cluster and M in the atomic ground state is benefit to obtain large segregation energy, and then increase the tendency of core-shell structure.

Table 2. NBO charge (*q*), *s*, *p*, and *d* orbital populations of M, and difference in electron population from the atomic ground states.

$M_{13}@Pt_{42}$		**$Pt_{42}M_{12}^{core}M^{edge}$**	**$Pt_{42}M_{12}^{core}M^{vertex}$**
$q(M^{core1})$	**$q(M^{core2})$**	**$q(M^{edge})$**	**$q(M^{vertex})$**
Ru $5s^14d^7$			
-3.246	-2.946	-1.777	-1.364
5*s*: 0.24 [-0.76]	0.41 [-0.59]	5*s*: 0.60 [-0.40]	5*s*: 0.62 [-0.38]
4*d*: 9.49 [**+2.49**]	9.09 [+2.09]	4*d*: 8.26 [+1.26]	4*d*: 7.65 [+0.65]
5*p*: 1.73 [+1.73]	1.74 [+1.74]	5*p*: 1.41 [+1.41]	5*p*: 1.77 [+1.77]
Rh $5s^14d^8$			
-1.575	-2.515	-1.281	-0.993
5*s*: 0.33 [-0.67]	0.41 [-0.59]	5*s*: 0.56 [-0.44]	5*s*: 0.61 [-0.39]
4*d*: 9.75 [**+1.75**]	9.51 [+1.51]	4*d*: 8.89 [+0.89]	4*d*: 8.63 [+0.63]
5*p*: 2.40 [+2.40]	1.90 [+1.90]	5*p*: 1.35 [+1.35]	5*p*: 1.44 [+1.44]

Os $6s^25d^6$			
-1.467	-1.577	-2.013	-2.496
6s: 0.58 [-1.42]	0.50 [-0.50]	*6s*: 0.63 [-1.37]	*6s*: 0.73 [-1.27]
5d: 9.19 [**+3.19**]	8.85 [+2.85]	*5d*: 8.29 [+2.29]	*5d*: 8.13 [+2.13]
6p: 2.42 [+2.42]	1.76 [+1.76]	*6p*: 1.40 [+1.40]	*6p*: 2.03 [+2.03]
Ir $6s^25d^7$			
-0.619	-0.220	-1.326	-1.123
6s: 0.55 [-1.45]	0.47 [-1.53]	*6s*: 0.73 [-1.27]	*6s*: 0.81 [-1.19]
5d: 8.94 [**+1.94**]	9.07 [+2.07]	*5d*: 8.99 [+1.99]	*5d*: 8.79 [+1.79]
6p: 2.21 [+2.21]	1.52 [+1.52]	*6p*: 1.22 [+1.22]	*6p*: 1.12 [+1.12]
Pt $6s^15d^9$			
+0.638	-0.170	-0.122	+0.083
6s: 0.48 [-0.52]	0.48 [-0.52]	*6s*: 0.62 [-0.38]	*6s*: 0.70 [-0.30]
5d: 8.79 [**-0.21**]	9.10 [+0.10]	*5d*: 8.88 [-0.12]	*5d*: 8.70 [-0.30]
6p: 1.29 [+1.29]	1.49 [+1.49]	*6p*: 1.31 [+1.31]	*6p*: 1.22 [+1.22]

In summary, the crucial factors influencing core-shell structure, such as cohesive energy, stability of the icosahedral M$_{13}$ core and Pt$_{42}$ shell, and electronic properties are systematically explored for the icosahedral Pt$_{42}$M$_{13}$ (M = Mo, Tc, Ru, Rh, Pd, W, Re, Os, and Ir) clusters. The icosahedral core-shell structural M$_{13}$@Pt$_{42}$ clusters are stable in the case of M = Ru, Os, and Ir. However, the core-shell structural Mo$_{13}$@Pt$_{42}$, Tc$_{13}$@Pt$_{42}$, Pd$_{13}$@Pt$_{42}$, W$_{13}$@Pt$_{42}$, and Re$_{13}$@Pt$_{42}$ clusters are not stable.

Our results suggest that the M with larger cohesive energy prefers to occupy the core position. The stability of icosahedral M$_{13}$ core and Pt$_{42}$ shell are also important for the formation of core-shell structure. In addition, the large difference of *d*-orbital population between M in the M$_{13}$@Pt$_{42}$ cluster and M in the atomic ground state is benefit to obtain positive segregation energy. We expect that our study can provide useful understanding of the core-shell preferences for the bimetallic Pt-shell clusters/particles, and then predict whether the bimetallic Pt-M clusters have a stable core-shell structure or not.

2. Original papers

(1) Jing Lu, Kazuya Ishimura, and Shigeyoshi Sakaki,
“DFT insight into core-shell preferences for bimetallic Pt$_{42}$M$_{13}$ (M = Ru, Rh, Os, and Ir) clusters”
In preparation.

3. Presentation at academic conferences

(1) Jing Lu, Kazuya Ishimura, and Shigeyoshi Sakaki,
“DFT insight into core-shell preferences for bimetallic Pt$_{42}$M$_{13}$ (M=Mo, Tc, Ru, Rh, Pd, W, Re, Os, and Ir) clusters”
第 20 回理論化学討論会 (P24), Kyoto, May 17, 2016

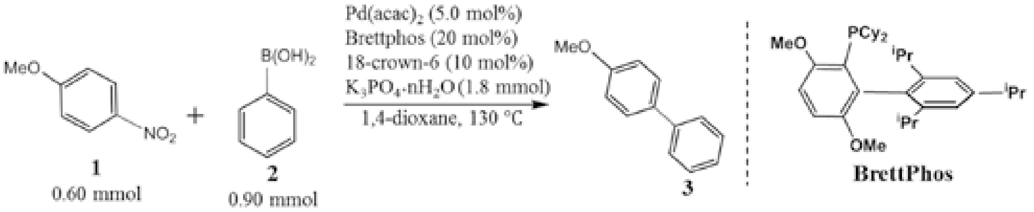
Rong-Lin Zhong

SPR Fellow

1. Summary of the research of the year

How to Succeed Oxidative Addition of Nitrobenzene to Palladium(0) Complex: Characteristic Features in Electronic Process

The Pd-catalyzed Suzuki-Miyaura cross-coupling reaction is one of efficient and versatile methods for constructing carbon–carbon bonds in biaryls and substituted aromatics. In the conventional Suzuki-Miyaura cross-coupling reaction, aryl halides are employed as electrophilic coupling reagent. Recently, substantial efforts have been devoted to the use of alternatives of aryl halides as the electrophilic coupling reagent because aryl halides are difficult to be regioselectively synthesized from arenes. For example, the use of aryl ethers, aryl esters, and arenols have been succeeded in the Suzuki-Miyaura cross-coupling reaction. On the other hand, the use of nitroarenes for the Suzuki-Miyaura cross-coupling reaction has not been succeeded for a long time despite that nitroarenes are highly versatile aromatic building blocks in organic synthesis, and directly obtained though nitration which is generally highly selective toward mono-functionalization. Very recently, the Suzuki-Miyaura cross-coupling reaction of nitroarenes with phenylboronic acid has been succeeded by Nakao group as shown in Scheme 1. The catalytic cycle of this reaction is initiated by the concerted oxidative addition of the Ar–NO_2 bond to Pd(0) complex.



Scheme 1. Suzuki-Miyaura cross-coupling reaction of 1-methoxy-4-nitrobenzene.

In the Suzuki-Miyaura cross-coupling reaction, the first step is the oxidative addition of aryl–halide (Ar^1-X) to Pd(0) complex, the second step is transmetalation between Ar^1-Pd(II)-X complex and aryl-boronic acid (Ar^2-$B(OH)_2$), and the last step is reductive elimination of Ar^1-Ar^2. In previously reported Pd-catalyzed Suzuki–Miyaura cross-coupling reaction of nitro-halo arenes, the aryl group of phenyl boronic acid was introduced at the halide site and the nitro group was not substituted. This suggests that the oxidative addition of the Ar-NO_2 bond is difficult. Therefore, it is of considerable interests to get a fundamental understanding of the reason(s) why the Ar-NO_2 bond activation is more difficult than the Ar-X. On the other hand, usual phosphine ligand is effective for Ar-X bond activation and generally a bulky monophosphine ligand is more favorable for the Ar-X (X=Cl and Br) bond activation than a bi-phosphine ligand according to previous investigations. Another characteristic feature of the Suzuki-Miyaura cross-coupling reaction of nitroarenes is the use of unique BrettPhos while usual phosphine ligand, such as PMe_3 could not. We wonder why not usual phosphine ligand but BrettPhos was successfully used in the Suzuki-Miyaura cross-coupling reaction of nitroarenes.

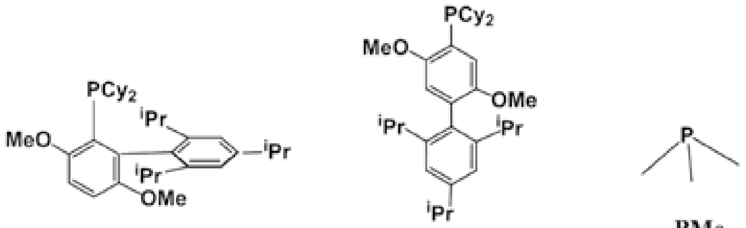
In this work, we theoretically investigated the characteristic features of the concerted oxidative addition of nitrobenzene to Pd(Brettphos) complex. Our purposes here are to elucidate the reasons why the Ph-NO_2 bond activation is more difficult than Ph-X bond (X=halide), why unique BrettPhos is used as ligand, and why usual phosphine is not useful for the Ph-NO_2 bond activation.

Models and Computational Details

All geometry optimizations were performed by ωB97XD functional in gas phase, using the Stuttgart-Dresden-Bonn basis set for Pd with the effective core potentials and the 6-31G(d) basis sets for other atoms were used. Single-point calculations were performed by the ωB97XD functional, using a better basis set system (BS-II) to provide a better potential energy change. In BS-II, two f polarization functions were added to Pd and 6-311G(d) basis sets were used for other atoms, where diffuse functions were added to anionic Br atom, N and O atom of NO_2 group. Solvation effects (1,4-dioxane) were evaluated with polarizable continuum model (PCM) method, where the geometries optimized in gas phase were employed.

In this work, discussion is presented based on the Gibbs energy, where the translation entropy in solution was corrected by the method of Whiteside *et al.* because the reactions occur in solution. Thermal correction and entropy contribution to the Gibbs energy were taken from the frequency calculation in gas phase at 298.15 K and 1 atm. In this work, the Gibbs activation energy ($\Delta G^{o\ddagger}$) is defined as a difference in Gibbs energy between the transition state (TS) and the most stable intermediate before TS. The Gibbs reaction energy (ΔG^{o}) is defined as a difference in Gibbs energy between the product and the reactants. All these calculations were carried out with Gaussian09 program.

Since the usual phosphine ligand is not useful while the unique BrettPhos was successfully used in the Suzuki-Miyaura cross-coupling reaction of nitroarenes. The ligand effect on the oxidative addition reaction of nitrobenzene is important to be considered. In this work, we compare BrettPhos with BrettPhos isomer and PMe_3 ligands to reveal the characteristic features of BrettPhos. The molecule structures of the three ligands are shown in Scheme 2. The BrettPhos isomer is a bulky monophosphine and designed by change the position of tri-^{i}Pr-Ph group from *ortho* to *para* of the phenyl ring of BrettPhos.



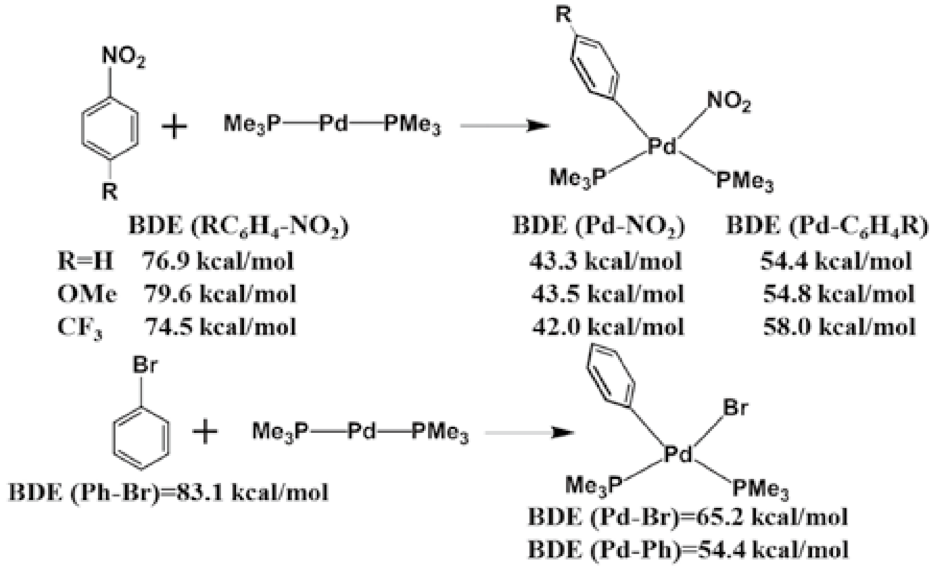
BrettPhos BrettPhos isomer PMe_3

Scheme 2. The molecular structure of BrettPhos, BrettPhos isomer, and phosphine (PMe_3) ligand.

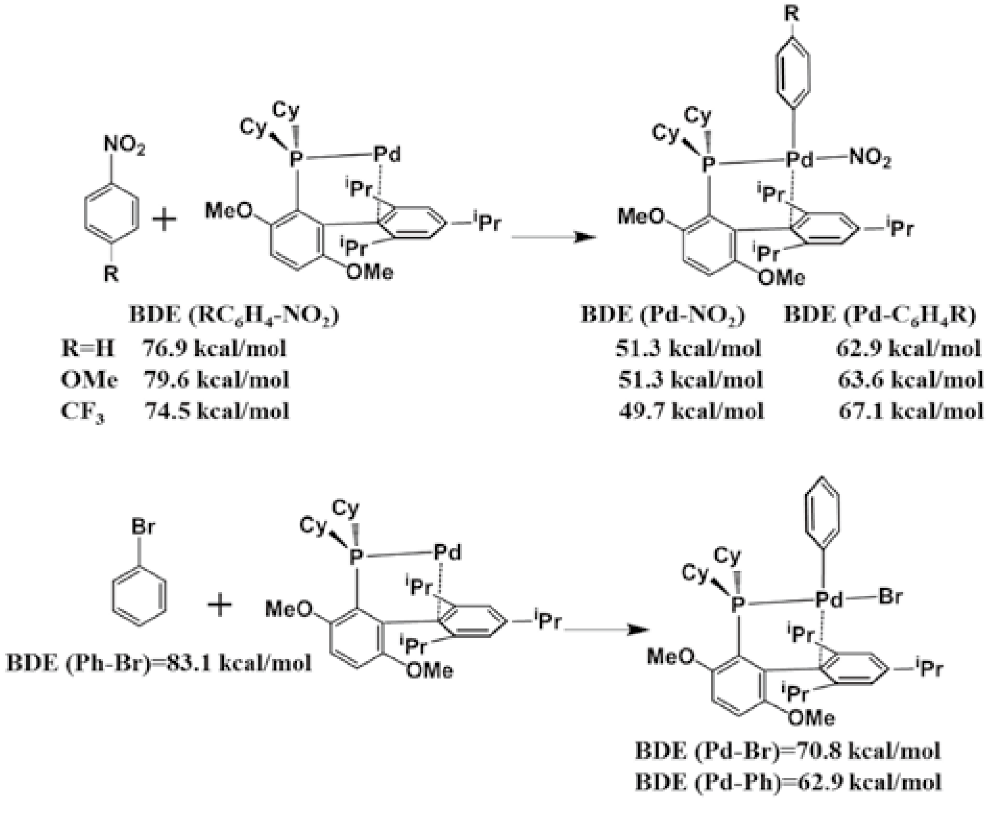
Results and Discussion

Thermodynamics of Oxidative Addition of Nitrobenzene and Bromobenzene Derivatives to $Pd(PMe_3)_2$ and Pd(BrettPhos)

The catalytic cycle of the Suzuki-Miyaura cross-coupling reaction of nitrobenzene is initiated by the oxidative addition of $Ph\text{-}NO_2$ bond to Pd(BrettPhos) complex. According to experiments and our theoretical examinations, the single electron transfer mechanism and stepwise oxidative addition via the nucleophilic attack mechanism were unlikely. Therefore, here the concerted oxidative addition of $Ph\text{-}NO_2$ bond to Pd(0) complex was investigated, which is an unprecedented elemental reaction with considerable interests. To understand the oxidative addition of nitrobenzene, we firstly evaluated the $Ph\text{-}NO_2$ bond dissociation energy (BDE) compared with Ph-Br bond. As shown in Scheme 3, the BDE($Ph\text{-}NO_2$) is 76.9 kcal/mol and the BDE(Ph-Br) is 83.1 kcal/mol. The $Ph\text{-}NO_2$ bond is moderately weaker than the Ph-Br, which is in consistent with experiments. However, the $Ph\text{-}NO_2$ bond activation is more difficult than Ph-Br even though $Ph\text{-}NO_2$ bond is weaker. To investigate these differences between $Ph\text{-}NO_2$ and Ph-Br bond activation, we evaluated the BDE($Pd\text{-}NO_2$) and BDE(Pd-Br) in the product of oxidative addition with $(PMe_3)_2$ ligands. As shown in Scheme 3, the BDE($Pd\text{-}NO_2$) is 43.3 kcal/mol and the BDE(Pd-Br) is 65.2 kcal/mol. Though the Ph-Br bond is stronger than $Ph\text{-}NO_2$ bond by 6.2 kcal/mol, the Pd-Br bond is much stronger than that of $Pd\text{-}NO_2$ by 21.9 kcal/mol. This is an important reason why the oxidative addition of bromobenzene to $Pd(PMe_3)_2$ is more exothermic than that of nitrobenzene. Furthermore, we also evaluated the BDE($Pd\text{-}NO_2$) and BDE(Pd-Ph) in the product of oxidative addition with BrettPhos. The $Pd\text{-}NO_2$ and Pd-Ph bond with BrettPhos ligand are considerably stronger than that with $(PMe_3)_2$ ligand by 8.0 kcal/mol and 8.5 kcal/mol, respectively. Therefore the oxidative addition of nitrobenzene to Pd(BrettPhos) is more exothermic than to $Pd(PMe_3)_2$. On the other hand, we also considered the *para* substituted effect of electron donating (OMe) and electron withdrawing group (CF_3) on the oxidative addition of nitrobenzene. As shown in Scheme 3 and Scheme 4, the effect of OMe group on Pd-Ph and $Pd\text{-}NO_2$ is very small, while slightly strengthen the $Ph\text{-}NO_2$ bond. On the other hand, the $Ph\text{-}NO_2$ bond is slightly weakened together with Pd-Ph bond is moderately strengthened by substitution of the CF_3 group, which is independent on the ligands. It indicates that the oxidative addition of nitrobenzene is more exothermic with the substitution of electron withdrawing group.



Scheme 3. Bond dissociation energy (BDE) of Ph-NO_2, Ph-Br, Pd-Ph, Pd-NO_2, and Pd-Br with $(PMe_3)_2$ ligand. The substituted effect of OMe and CF_3 group on Ph-NO_2 has been considered.



Scheme 4. Bond dissociation energy (BDE) of Ph-NO_2, Ph-Br, Pd-Ph, Pd-NO_2, and Pd-Br with BrettPhos ligand. The substituted effect of OMe and CF_3 group on Ph-NO_2 has been considered.

Geometry and Energy Changes in Oxidative Addition of 1-methoxy-4-nitrobenzene and 1-methoxy-4-bromobenzene

We investigated the oxidative addition of 1-methoxy-4-nitrobenzene to Pd(BrettPhos) complex **1**, because this substrate was used in the experiment of transmetalation. 1-methoxy-4-nitrobenzene approaches **1** to form a stable η^2-coordinated adduct (**AD1a**), in which the *meta* C-C bond of the phenyl ring coordinates with the Pd atom, as shown in Figure 1. The binding energy is significantly large (27.9 kcal/mol in the Gibbs energy). **AD1a** is not connected to the transition state of the oxidative addition, as will be shown below, because the C-NO_2 bond is distant from the Pd. Prior to the oxidative addition, the Pd atom moves to the *ortho* C-C bond of the phenyl ring to form **AD2a**, which is less stable than **AD1a** by 5.5 kcal/mol. Starting from **AD2a**, the oxidative addition occurs through the three-membered transition state (**TSa**) to afford the four-coordinated Pd (II)(NO_2)(C_6H_4-OMe^p)(Brettphos) (**PRDa**). In **TSa**, the C1-N bond is elongated to 1.784 Å from 1.455 Å, indicating that the C1-N bond cleavage is in progress. Though the Pd-C1 distance becomes shorter to 2.119, which is close to that of product; the Pd-C2-C3 angle still deviates from that of the **PRDa**, indicating that the orientation of the phenyl group is changing in **TSa**. On the other hand, the Pd-N distances become shorter to 2.072 Å, which is close to that of **PRDa**, and also the NO_2 group has already changed its orientation toward the Pd. This means that the Pd-NO_2 bond is almost formed in **TSa**. The **PRDa** is a pseudo-square-planar Pd(II) complex.

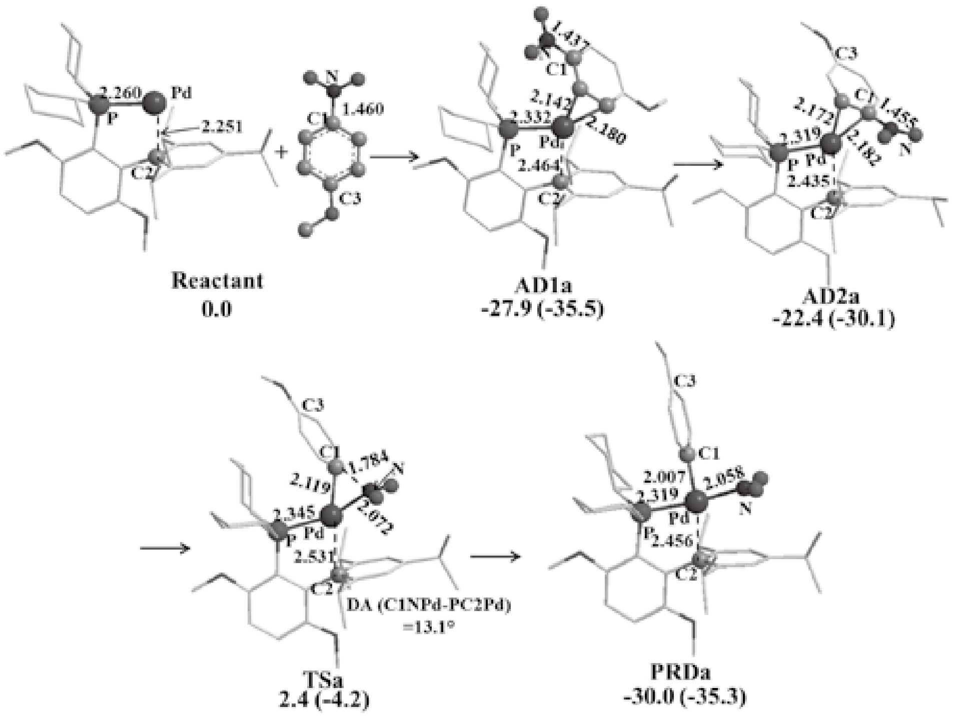


Figure 1. Optimized geometries in oxidative addition of 1-methoxy-4-nitrobenzene to Pd(BrettPhos) complex (distance [Å], hydrogen atoms are omitted for clarity), Gibbs energy relative to that of separated reactants are provided (potential energies are in the parentheses).

The Gibbs activation energy ($\Delta G^{o\ddagger}$) of this reaction is 30.3 kcal/mol (relative to the most stable reactant adduct **AD1**) and the Gibbs reaction energy (ΔG^{o}) is -30.0 kcal/mol (relative to the sum of reactant complex **1** and p-methoxynitrobenzene).

We investigated the oxidative addition of 1-methoxy-4-bromobenzene to Pd(BrettPhos) complex for comparison as shown in Figure 2. This reaction proceeds through a similar η^2-coordinated adducts (**AD1b** and **AD2b**) and transition state (**TSb**) to afford a palladium(II) complex Pd (II)(Br)(C_6H_4-OMe^p)(Brettphos) (**PRDb**), as shown in Figure 2. Though **AD1b** and **AD2b** are similar to **AD1a** and **AD2a**, we found some of interesting differences between **TSa** and **TSb**. In **TSb**, the Pd-C1 distance is longer than that in **TSa** by 0.118 and the Pd-Br distance is somewhat longer than in **PRDb**, suggesting that **TSb** is less product-like than **TSa**. Correspondingly, the dihedral angle between plane C1BrPd and plane PC2Pd in **TSb** is 27.9°, while the dihedral angle (13.1°) between plane C1NPd and plane PC2Pd in **TSa** is smaller (more product-like). The $\Delta G^{o\ddagger}$ is 16.3 kcal/mol, which is much smaller than that for Ph-NO_2 bond activation, and the ΔG^{o} is -50.0 kcal/mol, which is much more negative than that for Ph-NO_2 bond activation. These results indicate clearly that the oxidative addition of nitroarene is more difficult than that of bromoarene, which is consistent with previous experiments.

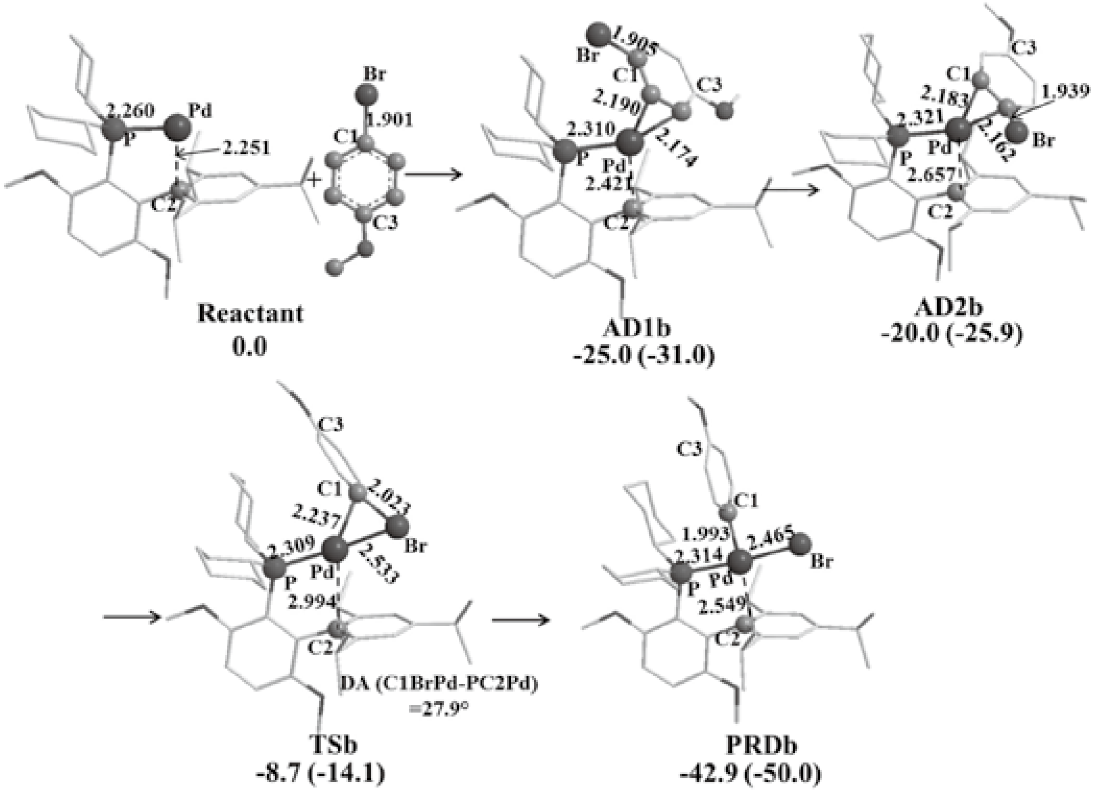
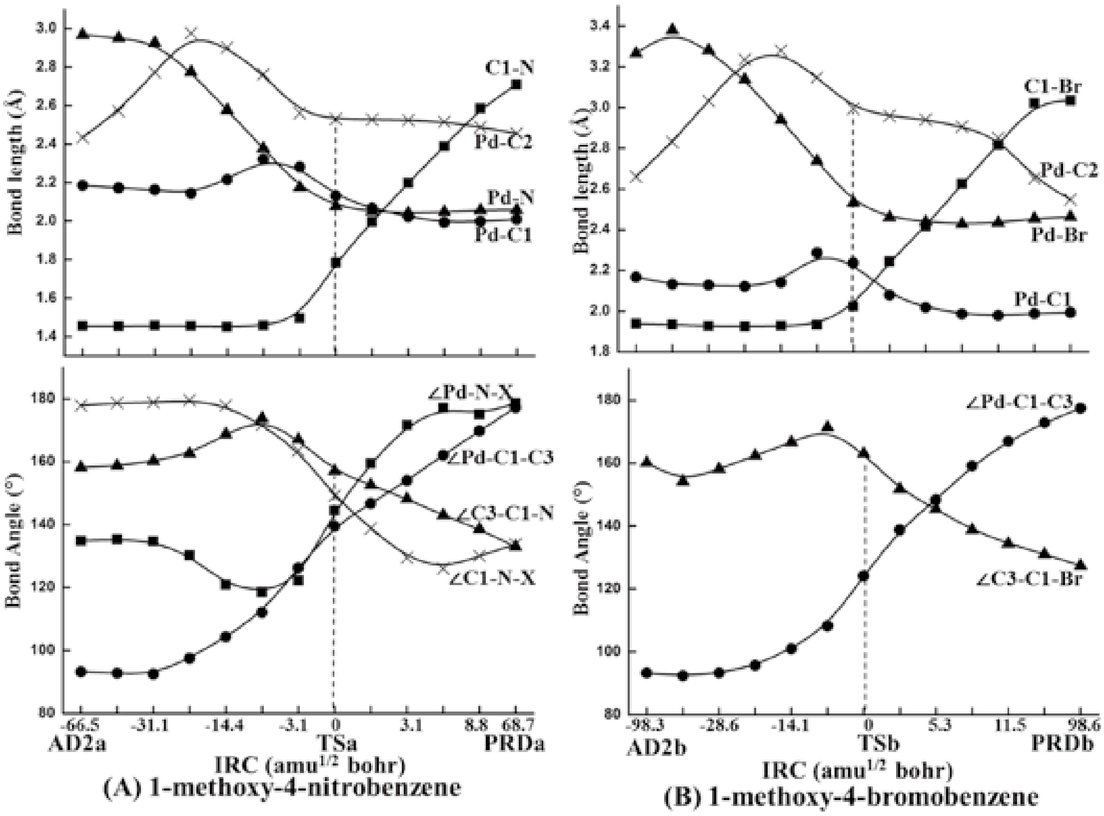


Figure 2. Optimized geometries in oxidative addition of 1-methoxy-4-bromobenzene to Pd(BrettPhos) complex (distance [Å], hydrogen atoms are omitted for clarity), Gibbs energy relative to that of separated reactants are provided (potential energies are in the parentheses).

Characteristic Features of Oxidative Addition of 1-methoxy-4-nitrobenzene

To gain an insight into characteristic features of oxidative addition of 1-methoxy-4-nitrobenzene, we focused on the main difference in several important bond distance, angle and potential energy changes along the intrinsic reaction coordinate (IRC) between the Ph-NO_2 and Ph-Br bond activation. As shown in Figure 3, the first stage of the reaction is the increase of Pd-C2 distance, which means the dissociation of the η^1 coordination between Pd center and the C2 atom of the tri-^{i}Pr-phenyl ring of BrettPhos ligand. The second stage is the decrease of Pd-C2 and the increase of Pd-C1 distance, which means the re-coordination of between Pd center and the tri-^{i}Pr-phenyl ring together with dissociation of the η^2 coordination between Pd center and *ortho* C-C bond of 1-methoxy-4-nitrobenzene. The third stage is the decrease of Pd-C1 and the increase of C-N1 distance, which means coordination (η^1) between C1 and Pd together with the dissociation of C-N1 bond to form **TSa**; in this stage the orientation change of phenyl and NO_2 group is in progress because the ∠Pd-C1-C3 increase from 112° to 139° and Pd-N-X (X is the center between two O atoms) increase from 118° to 144°, which means Pd-Ph and Pd-N bond formation is in progress. The last stage is continuous increase of C1-N distance together with the increase of the angel Pd-C1-C3 and Pd-N-X to form the **PRDa**. Compared with Ph-NO_2 bond activation, two differences in geometry change were found in the Ph-Br bond activation; 1. The C1-Br bond elongates by 0.085 Å and the ∠Pd-C1-C3 (Ph orientation) increases by 30.85° from **AD2b** to **TSb**, smaller than that of Ph-NO_2 bond activation case, in which C1-NO_2 bond elongates by 0.329 Å and the ∠Pd-C1-C3 (Ph orientation) increases by 46.12° together with the ∠Pd-N-X (NO_2 orientation) increase 9.63°. It shows that the distortion of 1-methoxy-4-nitrobenzene in **TSa** is larger than that of 1-methoxy-4-bromobenzene in **TSb**. 2. The Pd-C2 distance of **TSb** have not decreased to that of **PRDb**, while in Ph-NO_2 bond activation case, the re-coordinate of Pd-C2 has almost finished in **TSa**. In this context, the **TSa** is more product-like than **TSb**.

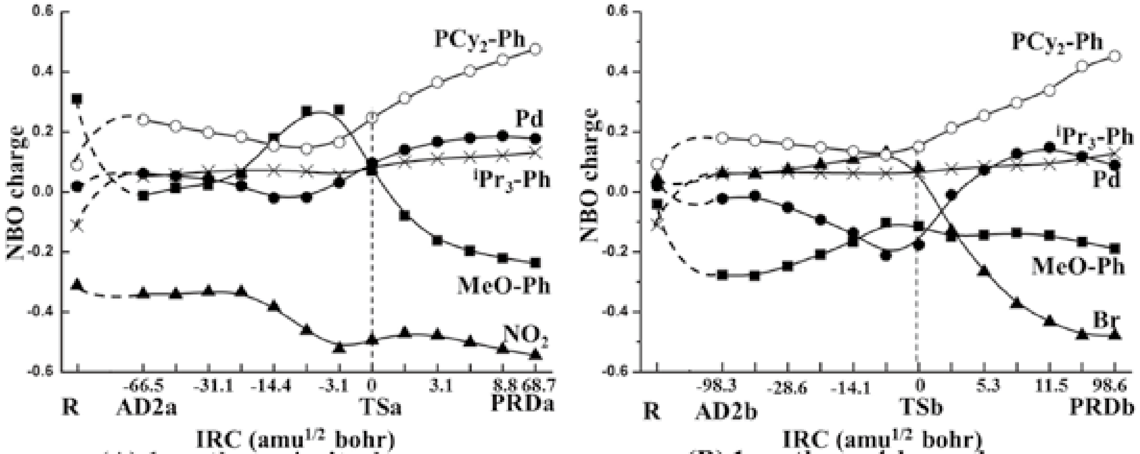


(A) 1-methoxy-4-nitrobenzene

(B) 1-methoxy-4-bromobenzene

Figure 3. Change in several important bond distance, angle and potential energy along the IRC of the oxidative addition reaction of 1-methoxy-4-nitrobenzene and 1-methoxy-4-bromobenzene.

The natural bond orbital (NBO) charge changes along IRC are obviously different in the Ph-NO_2 bond activation and Ph-Br bond activation as presented in Figure 4. In **AD2a**, the NBO charge of NO_2 is more negative than MeO-Ph group, while the NBO charge of Br atom is less negative than MeO-Ph group in **AD2b**, because NO_2 is a strong electron withdrawing group. In the dissociation of Pd-C2 η^1 coordination stage (first stage), the charge of MeO-Ph and NO_2 group slightly increase together with that of Pd decreases; similar trend that the charge of MeO-Ph and Br group slightly increase are also shown in the Ph-Br bond activation in this stage. However, in the second stage, the charge of NO_2 considerably decreases together with that of the MeO-Ph group increases, while that of Br atom and MeO-Ph group continuously increase. It indicates that, the $Ph^{\delta+}$-$NO_2{}^{\delta-}$ polarization decreases the NBO charge of NO_2 while the polarization of $Ph^{\delta+}$-$Br^{\delta-}$ did not occur in this stage. After that, the NBO charge of NO_2 in **TSa** is almost close to that of **PRDa** while that of Br in **TSb** is considerably larger than that of **PRDb**. On the other hand, the charge of MeO-Ph group of **TSa** is 0.07, which is considerably larger than that (-0.23) of **PRDa**, while the charge of MeO-Ph group of **TSb** is -0.11, which is almost close to that (-0.19) of **PRDb**. Therefore, the charge transfer from Pd to NO_2 is almost finished in **TSa**, while the charge transfer process to Br occurs after **TSb**. On the other hand, the charge transfer from Pd to MeO-Ph group is in progress in **TSa**, while the charge transfer process to MeO-Ph group has already occurred in **AD2b**. In this context, the electronic process in the oxidative addition of 1-methoxy-4-nitrobenzene to Pd(BrettPhos) exhibits a unique feature, which is significantly different with that of 1-methoxy-4-bromobenzene.



(A) 1-methoxy-4-nitrobenzene **(B) 1-methoxy-4-bromobenzene**

Figure 4. Change in NBO charge along the IRC of the oxidative addition reaction of 1-methoxy-4-nitrobenzene and 1-methoxy-4-bromobenzene.

The orbital interactions in the TS of the oxidative addition of 1-methoxy-4-nitrobenzene and 1-methoxy-4-bromobenzene to Pd(BrettPhos) complex are shown in Figure 5. In the HOMO of **TSa**, charge transfer occur from the Pd dπ orbital to the σ*+π* orbital of the Ph-NO_2, which consists the σ*-antibonding orbital of the C-NO_2 bond and the π* orbital of the NO_2 group (LUMO); together with charge transfer from the Pd dπ orbital to another σ*+π* orbital of the Ph-NO_2, which consists the σ*-antibonding orbital of the C-NO_2 bond and the π* orbital of the Ph group (LUMO+1). However, in the HOMO of **TSb**, a smaller charge transfer occur from the Pd dπ orbital to the σ*+π* orbital of the Ph-Br, which consists the σ*-antibonding orbital of the C-Br bond and the π* orbital of the Ph group (LUMO). Therefore, charge transfer from Pd to NO_2 is earlier than the charge transfer from Pd to MeO-Ph group because the π* orbital of the NO_2 group participates in the charge transfer interaction of **TSa**, while in the Ph-Br bond activation, the charge transfer from Pd to Br is later than the charge transfer from Pd to MeO-Ph group.

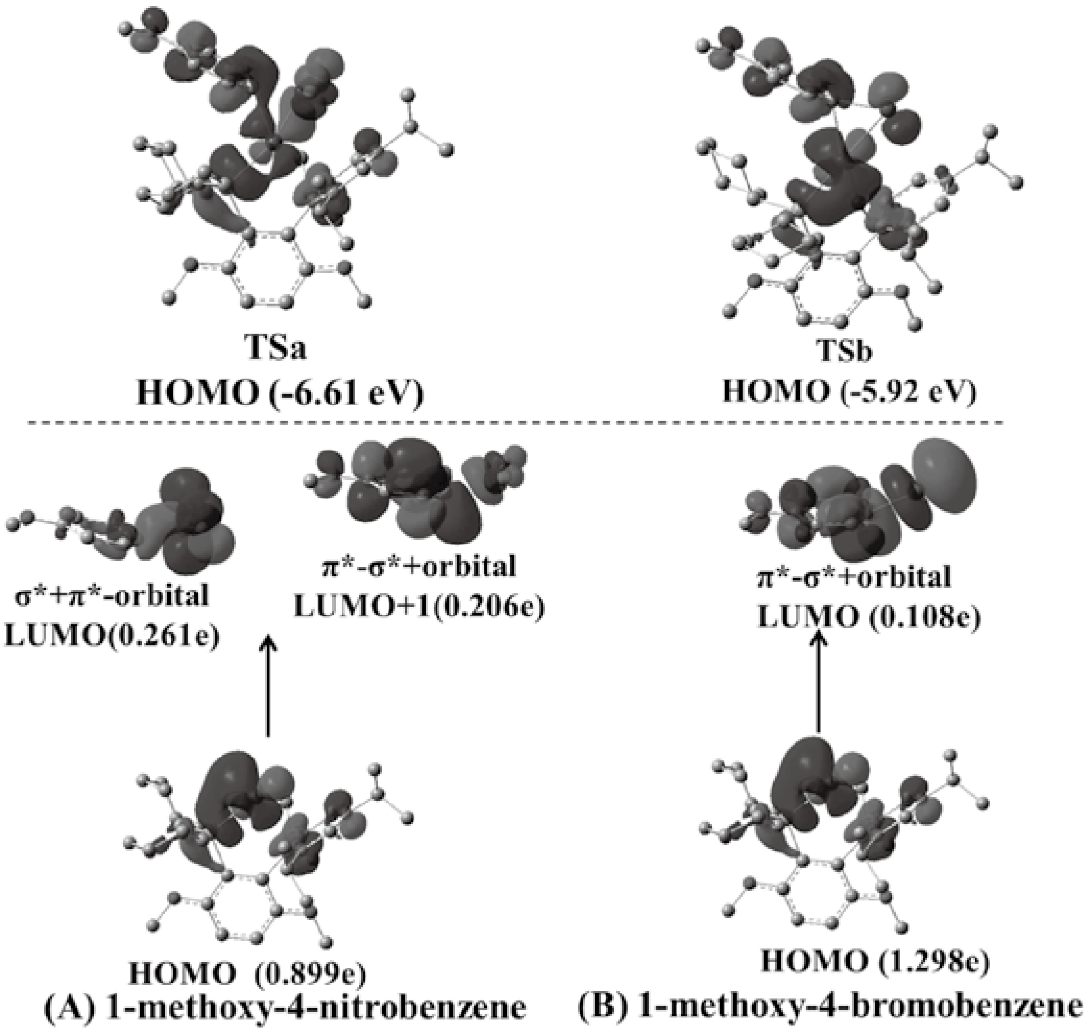


Figure 5. HOMO of **TSa** and **TSb,** and charge transfer interactions in **TSa** and **TSb**.

Furthermore, the potential energy (E), deformation energy (E_D) of each moiety and interaction energy (E_{int}) between them are listed in Table 1. The difference between the potential energy of **AD1a** and **AD1b** is 4.5 kcal/mol. It suggests that **AD1a** and **AD1b** are similarly stable. However, in **TSa**, the E_D of 1-methoxy-4-nitrobenzene moiety is larger than that of 1-methoxy-4-bromobenzene moiety in **TSb** by 27.0 kcal/mol even though the E_{int} in **TSa** is larger than that in **TSb** by 17.5 kcal/mol. Therefore, the larger E_D of 1-methoxy-4-nitrobenzene moiety is the origin of larger Ph-NO_2 bond activation barrier. This is because the sp^2 orbital of NO_2 must change its direction toward Pd to form bonding interaction. However, Br has spherical valence orbital, which can form the interaction with dπ of Pd by keeping the Ph-Br σ-bond.

Characteristic Feature of BrettPhos

According to previous reports, mono-phosphine ligands are generally more favorable for the Ph-Br bond activation than bis-phosphine ligands. Therefore, we take a BrettPhos isomer by change the position of tri-^{i}Pr-Ph group from *ortho* to *para* of the phenyl ring as an example to consider the mono-phosphine ligands for Ph-NO_2 bond activation. As shown in Figure 6, the **PRDc** is less stable than **AD1c**, which suggests that Ph-NO_2 bond activation with BrettPhos isomer is an endergonic reaction. Besides, intermediates, transition state and product of BrettPhos isomer are less stable than those of BrettPhos. Therefore, a mono-phosphine ligand is not favorable for the Ph-NO_2 bond activation even though it is effective for Ph-Br bond activation. As shown in Figure 7, dπ orbital of Pd provided by Brettphos is at a higher energy than that provide by Brettphos isomer, which is favorable for charge transfer to Ph-NO_2 moiety because the π of phenyl moiety in BrettPhos interacts with dπ of Pd in an antibonding way.

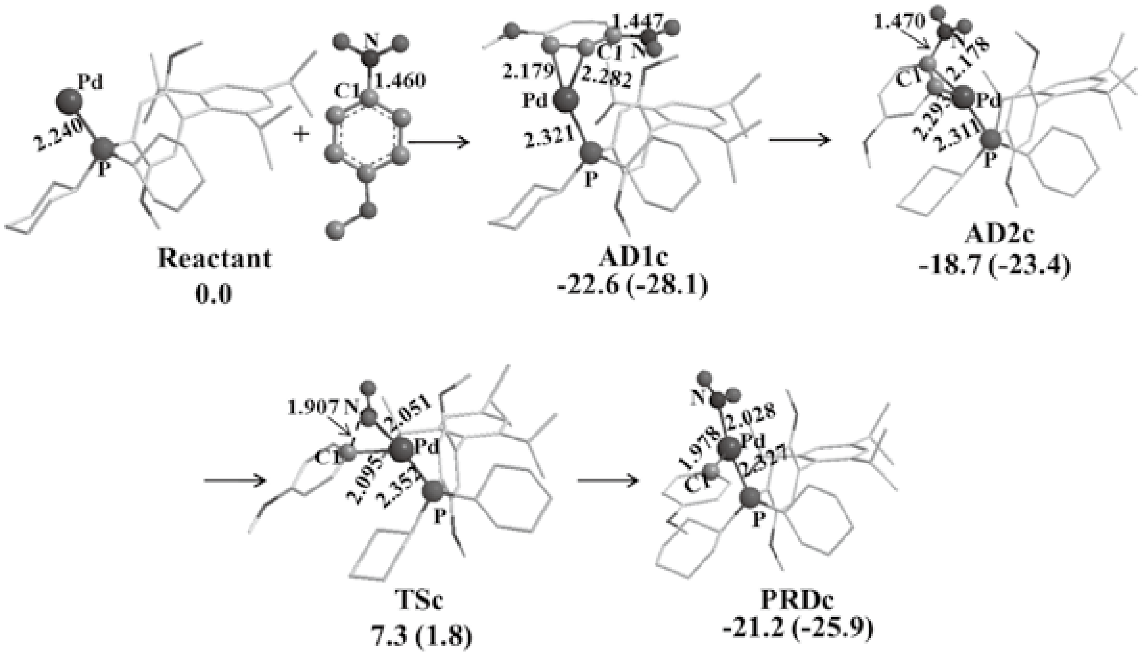


Figure 6. Optimized geometries in oxidative addition of 1-methoxy-4-nitrobenzene to Pd(BrettPhos isomer) (distance [Å], hydrogen atoms are omitted for clarity), Gibbs energy relative to that of separated reactants are provided (potential energies are in the parentheses).

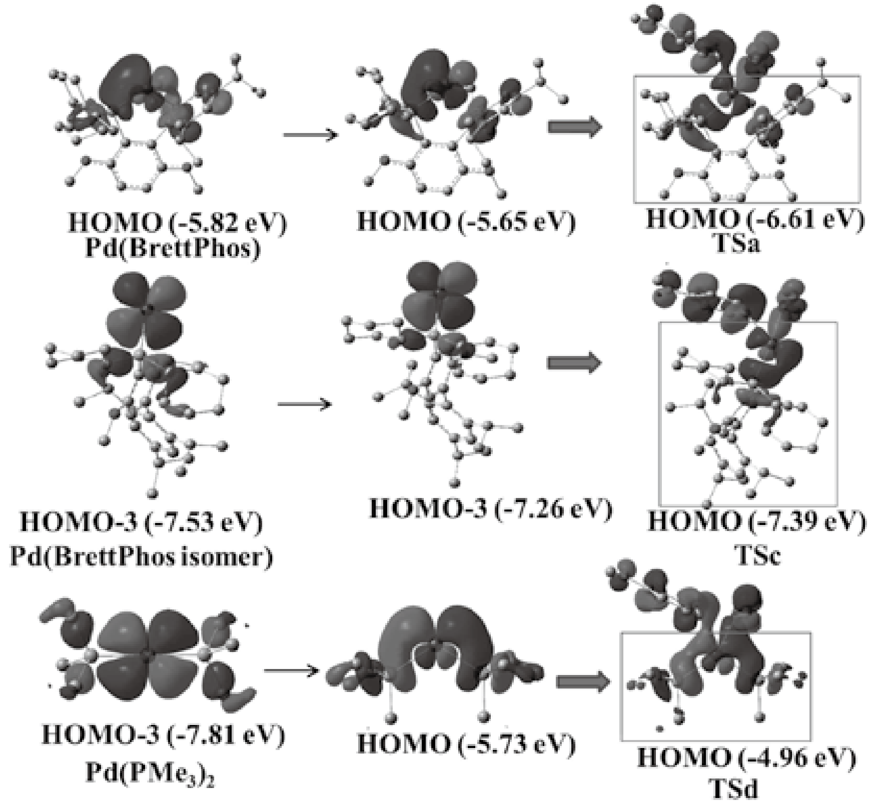


Figure 7. HOMO **(**d$_\pi$**)** orbital in Pd(BrettPhos), Pd(BrettPhos isomer), and Pd(PMe$_3$)$_2$ moieties in reactant and TS.

To further reveal the characteristic feature of BrettPhos ligand, we also compared BrettPhos with (PMe$_3$)$_2$ ligand. The geometry and energy change in oxidative addition of 1-methoxy-4-nitrobenzene with Pd(PMe$_3$)$_2$ is shown in Figure 8. Results indicate that BrettPhos is more favorable than (PMe$_3$)$_2$, because the intermediates, transition state, and product of BrettPhos are relatively more stable than those of (PMe$_3$)$_2$ by 20.0 kcal/mol. It is worthy of note that, from reactant to **TSd**, the P-Pd-P angle decrease from 180° to 114.56°. Correspondingly, the deformation energy of Pd(PMe$_3$)$_2$ moiety in **TSd** is 19.0 kcal/mol because of the bending, which is larger than that (4.7 kcal/mol) of Pd(BrettPhos) moiety in **TSa**. In this context, larger deformation energy of Pd(PMe$_3$)$_2$ is response for corresponding less stable intermediates, transition state, and product. The dπ orbital of Pd provided by (PMe$_3$)$_2$ in **TSd** is shown in Figure 7. The dπ orbital of Pd(PMe$_3$)$_2$ is -7.81 eV considerably increase to -5.73 eV of **TSd** with a larger deformation energy (19.0 kcal/mol). However, the dπ orbital of Pd(BrettPhos) is -5.82 eV slightly increase to -5.65 eV of **TSa** with a smaller deformation energy (4.7 kcal/mol). In this context, the dπ orbital of Pd(BrettPhos) is more reactive at a higher energy while the dπ orbital of Pd(PMe$_3$)$_2$ is more stable that need a larger deformation energy to activate it. Therefore, the dπ orbital of Pd(BrettPhos) is more reactive than Pd(PMe$_3$)$_2$, which provide a better charge transfer to form a stable precursor and transition state that is an important reason why BrettPhos is more favorable than (PMe$_3$)$_2$. Furthermore, the activation energy of Ph-NO_2 bond is 29.1 kcal/mol with $(PMe_3)_2$ ligand, which is larger than BDE(Pd-P) in **AD1d**, 20.8 kcal/mol. In this context, prior to TS, PMe_3 ligand might dissociate, which is another reason why $(PMe_3)_2$ is unfavorable for Ph-NO_2 bond activation.

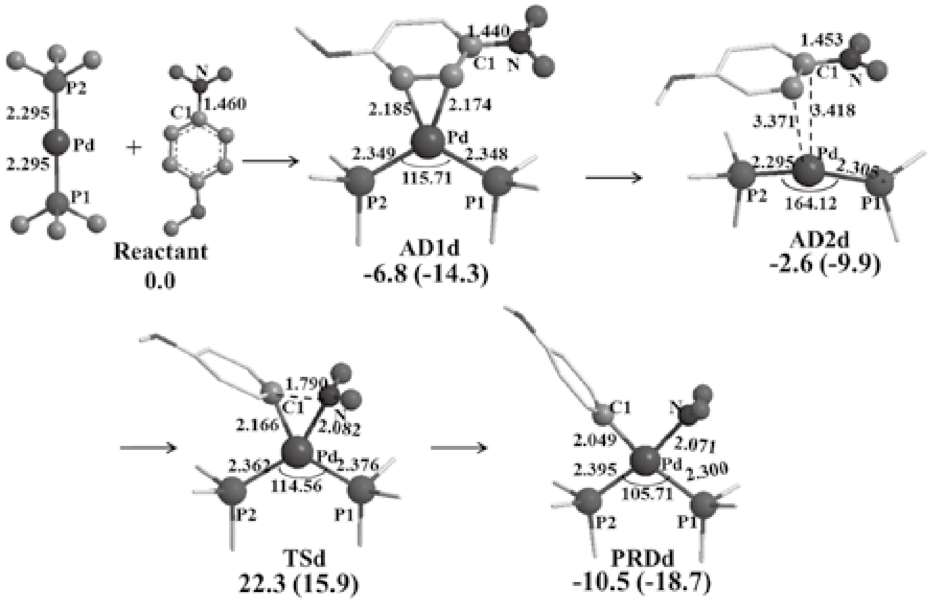


Figure 8. Optimized geometries in oxidative addition of 1-methoxy-4-nitrobenzene to $Pd(PMe_3)_2$ isomer (distance [Å], hydrogen atoms are omitted for clarity), Gibbs energy relative to that of separated reactants are provided (potential energies are in the parentheses).

Conclusions

In this work, we theoretically investigated the characteristic features of the oxidative addition of nitrobenzene to Pd(BrettPhos) complex with the density functional theory method. The Ph-NO_2 bond activation energy is 30.3 kcal/mol, which is larger than that (16.3 kcal/mol) of Ph-Br. Results indicate that the Ph-NO_2 bond activation is more difficult than Ph-Br, which is in consistent with previous experiments. Interestingly, the electronic process of the oxidative addition of nitrobenzene exhibits characteristic feature that is significantly different with bromobenzene. In Ph-NO_2 bond activation, charge transfer from Pd to NO_2 is earlier than the charge transfer from Pd to Ph group, while in the Ph-Br bond activation, the charge transfer from Pd to Br is later than the charge transfer from Pd to Ph group. This is because the π* orbital of the NO_2 group participates in the charge transfer interaction of transition state. In this context, the characteristic feature in electronic process of Ph-NO_2 bond activation originates from the participation of the π* orbital of the NO_2 group. Correspondingly, the distortion of nitrobenzene moiety in transition state is larger than bromobenzene moiety because the sp^2 orbital of NO_2 must change its direction toward dπ orbital of Pd to form bond interaction while Br does not change the direction of orbital, which is responsible for the larger Ph-NO_2 bond activation barrier. On the other hand, the BrettPhos isomer (mono-phosphine) is unfavorable for the Ph-NO_2 bond activation because dπ of Pd provided by BrettPhos is at higher energy than that provided by BrettPhos isomer, which is more favorable for charge transfer to Ph-NO_2 moiety because the π of Ph interacts with dπ of Pd in an antibonding way. On the other hand, the dπ orbital of $Pd(PMe_3)_2$ is more stable that need a larger distortion to activate it. Therefore, the better dπ of Pd provided by BrettPhos effectively stabilizes intermediates, transition state, and product of Ph-NO_2 bond activation that is an important reason why BrettPhos is better than usual phosphine ligands.

2. Original papers

(1) Rong-Lin Zhong, Masahiro Nagaoka, Yoshiaki Nakao, and Shigeyoshi Sakaki,“ How to Succeed Oxidative Addition of Nitrobenzene to Palladium(0) Complex: Characteristic Features in Electronic Process”，*in preparation.*

(2) Rong-Lin Zhong, Hong-Liang Xu, and Zhi-Ru Li, “The polar 2e/12c bond in phenalenyl-azaphenalenyl hetero-dimers: Stronger stacking interaction and fascinating interlayer charge transfer”，J. Chem. Phys. 145, 054304 (2016).

(3) Rong-Lin Zhong, Hong-Liang Xu, and Zhong-Min Su, “Connecting effect on the first hyperpolarizability of armchair carbon–boron–nitride heteronanotubes: pattern versus proportion”，Phys. Chem. Chem. Phys., 18, 13954-13959 (2016)

3. Presentation at academic conferences

Rong-Lin Zhong, Masahiro Nagaoka, Yoshiaki Nakao, and Shigeyoshi Sakaki, “Theoretical Study on Oxidative Addition of Nitrobenzene to Palladium(0)-Brettphos Complex” 多元素協働触媒による分子変換手法創出のための勉強会, Kyoto, March 15, 2017

Takahide Matsuoka

Research Fellow

1. Summary of the research of the year

Electron dynamics of photoionization of H_2 in intense pulse laser fields

Photoionization process in intense pulse laser field, involves complex interplays among electrons, nuclei, and laser-field. Namely, the charge resonance enhanced ionization, the interatomic Coulombic decay and the above-threshold ionization are processes, which involves the electronic continuum states. Moreover, the availability of X-ray laser pulse allows further investigations of auto-ionization and Auger effect, which involves electronic correlations. Our present method effectively includes the ionization processes and dynamical correlations.

The outgoing electron flow from the molecular region per unit time is given as electron flux $\vec{j}$ at boundary surface ∂V. The time-dependent electron wavepacket $\Psi(t)$ is a complex wavefunction and thus the natural orbitals ϕ_λ of the wavepacket are also complex. Thereby the fluxes of the natural orbitals are given as,

$$\vec{j}^{(\lambda)} = \frac{\hbar}{2\mathrm{i}}\left[\phi_\lambda^*\vec{\nabla}\phi_\lambda - \phi_\lambda\vec{\nabla}\phi_\lambda^*\right]$$

The outgoing electron flux $\vec{j}^{(\lambda)}$ from each natural orbital ϕ_λ reduces the occupation number $n^{(\lambda)}$ of the natural orbital per unit time.

$$\frac{\partial n^{(\lambda)}}{\partial t} = \int_{\partial V} \vec{j}^{(\lambda)} \cdot \mathrm{d}\vec{S}$$

By scaling the norm of the complex natural orbitals ϕ_λ with the reduced occupation number, the outgoing electron flow is effectively taken into account by the reduced electron density of the wavepacket $\Psi(t)$. The scaling of the natural orbitals is incorporated by scaling the Slater determinants of the natural orbitals, in which the wavepacket $\Psi(t)$ is expanded, as follows [1],

$$\Psi(t) = \sum_I C_I\Phi_I \to \Psi'(t) = \sum_I \left(\prod_i \sqrt{\frac{n_{I,i}(t')}{n_{I,i}(t)}}\right) C_I\Phi_I$$

The continuity equation is integrated only for electron flux which is above threshold j_{thresh} for ionization with external field taken into consideration.

The occupation number of hydrogen molecule in 580 TW/ cm^2 two-cycle laser pulse with wavelength 760 nm shows significant decrease while at the peak of the laser pulse (Fig. 1). The radiation spectra of hydrogen molecule showed odd-order peaks (due to rapid acceleration of dipole in Fig. 2 (a)) with fine structures, which is unique in molecular systems (Fig. 2 (b)). The fine structures are also seen in the electron flux of the time-dependent wavepacket, which reflect the recollision process between the electron and parent

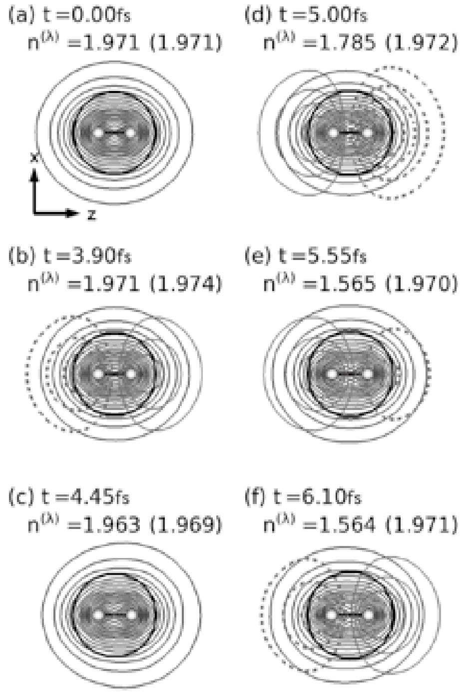


Figure 1. Time propagation of the natural orbital with largest occupation number of H_2 in intense laser field. The real part and imaginary part are shown in blue and red, respectively. The occupation numbers in parentheses are the ones one the normalized wavepacket.

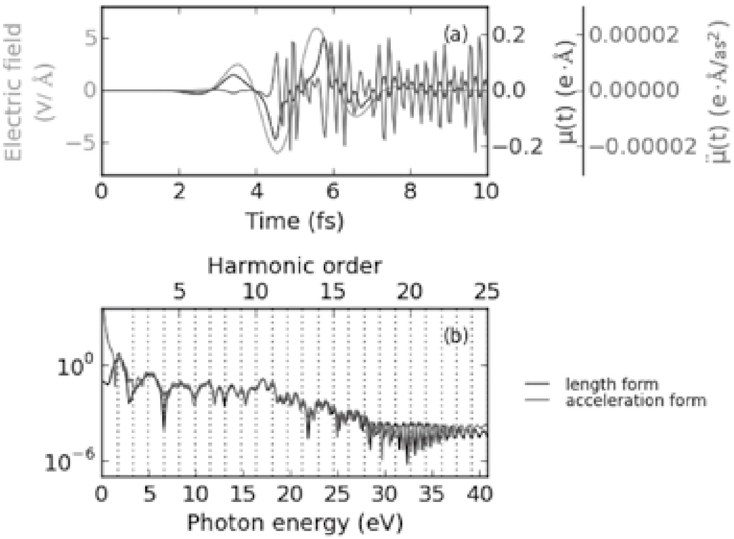


Figure 2. (a) Electric field (green), dipole moment of the system (blue), and dipole acceleration (red). (b) Power spectra of H_2 molecule.

ion. The rapid stroke of acceleration is seen during the second half cycle of the laser field, which eventually is when the first recollision of the electron and the parent ion takes place, and the electron is accelerated. The repetitive recollision thus results in high-order harmonic generation process in the intense laser field (Fig. 2(b)). The contribution of the nonadiabatic effect introduces isotope effect to the ionization process. A significant anisotropic behavior of the angular distribution of photoelectron of HD in intense field is seen due to the electron flux induced by nuclear motion differs between proton and deuteron.

Photoionization of H_2O in intense pulse laser fields

The photoionization process of 1^1B_1 state H_2O molecule with two 100 TW/cm^2 185 nm laser pulses (FWHM being 8.27 fs) has also been calculated with the nonadiabatic electron dynamics method. HOH bond angle flips at t=20 fs and returns at t=40 fs, hence becomes linear at t=10 fs and 30 fs. The laser polarization is fixed along the symmetry axis of H_2O and the center of the laser pulse is set at t=10 fs and 30 fs. Therefore, the laser intensity is at its maximum when H_2O have a linear structure perpendicular to the laser polarization. While the nuclear configuration is linear, the theoretical calculation counterintuitively resulted in significant flux perpendicular to the laser polarization (Fig. 3 (a) thru (j)). Without the nonadiabatic interaction due to the nuclear motion, the electron flux perpendicular to laser polarization is zero. Therefore, the perpendicular electron flux arises from the bending motion of the nuclei. The angular distribution of the photoelectron flux, which is the integrated electron flux at the boundary surface, also shows the strongest intensity at the linear structure (Fig. 3 (k and l)).

Comparison between the results with and without nonadiabatic interaction due to nuclear motion indicates strong contribution of the bending motion to the photoionization process. The bending motion effects the direction of the electron flux, i.e. with the interaction, electron flows along the OH bond, hence the angular distribution of the photoelectron is also seen along the OH bond. Without the nonadiabatic effect, the electron flux becomes negligible and thus also the photoelectron cross-section. The result implicates the significant role of nonadiabatic interaction of nuclear motion in photoionization processes for general cases of polyatomic molecules.

[1] K. Takatsuka, J. Phys. B 47, 124038 (2014).

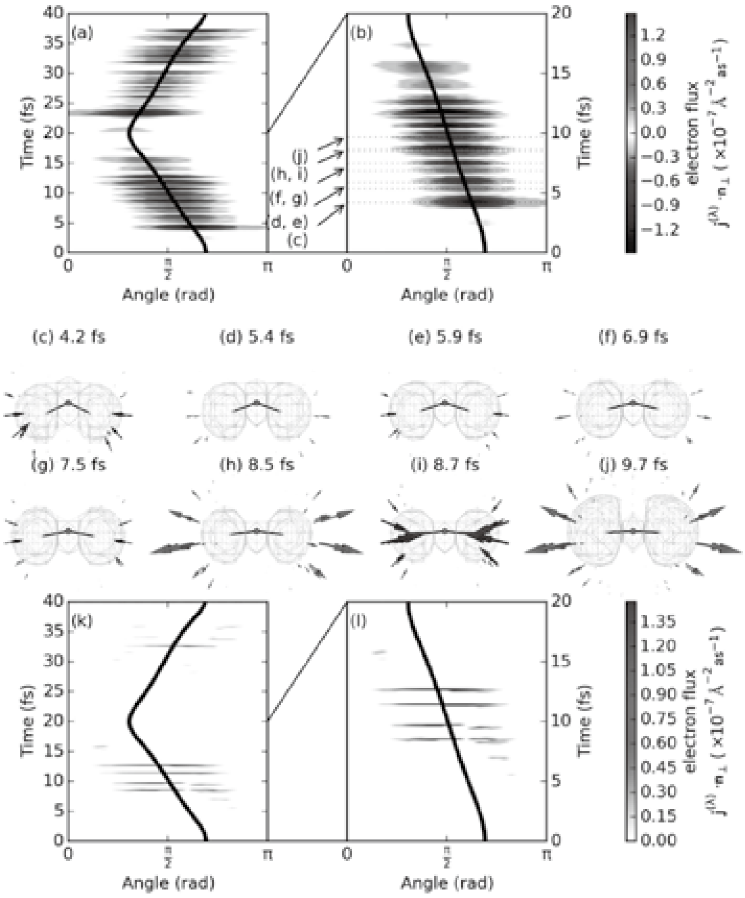


Figure 3. (a and b) Angular distribution of electron flux of H_2O. The thick solid curves indicate the polar angle of H coordinates. (c thru j) Fluxes at selected times. Blue and red indicate inward and outward fluxes, respectively. (k and l) Angular distribution of photoelectron.

2. Original papers

(1) Takahide Matsuoka, and Kazuo Takatsuka,
“Dynamics of photoionization from molecular electronic wavepacket states in intense pulse laser fields: A nonadiabatic electron wavepacket study”
J. Chem. Phys. 146, 134114 (2017).

3. Presentation at academic conferences

(1) 松岡貴英・高塚和夫
「強レーザー場中の励起分子からのイオン化過程の非断熱電子動力学」
第 19 回理論化学討論会 新宿 2016/5/25 3B19

(2) 松岡貴英・高塚和夫

「強光子場中多原子分子の電離過程における非断熱電子動力学」
第 10 回分子科学討論会 2016 神戸　2016/9/14 2A15

(3) Takahide Matsuoka, and Kazuo Takatsuka,
“Dynamics of photoionization from molecular electronic wavepacket states in intense pulse laser fields”
77th Okazaki Conference Series: International Symposium on Ultrafast Dynamics in Molecular and Material Sciences (P03), Okazaki, May 6, 2017

山本　憲太郎

研究フェロー（高塚グループ）

１．今年度の研究の要約

今年度は，Mn を含む触媒系における非断熱動力学的な電荷分離の機構の理論的研究を行った．

【序】光触媒的な電荷分離は，光のエネルギーを別の形に変換して固定するための，鍵となる反応である．天然光合成系では，最終的に水を分解してプロトンと電子を取り出し，このような電荷分離状態を実現する．この反応は，光化学系 II (PSII) 中の oxygen-evolving complex (OEC) に触媒される．今日では，OEC は Mn_4CaO_5 だと考えられている. [1] 我々は，この水分解サイクルの動力学的機構の解明を進めている．本講演では，Mn クラスターによる電荷分離の基本的な機構，coupled proton-electron transfer [2] に基づいて，その初期段階であるプロトンと電子の分離について考察し，特にアクセプター側の役割に注目する．

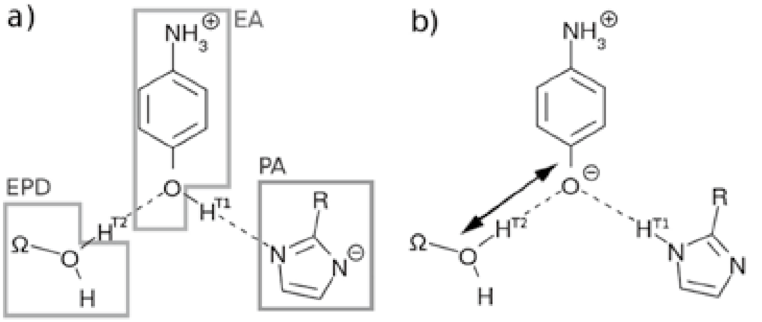


図 1 モデル系の概念図．EPD，EA，そして PA はそれぞれ，electron-proton donor，electron acceptor，そして proton acceptor を意味する． H^{Tn} (n = 1, 2) とラベルさ

【方法論】OEC 周辺の X 線構造 [1] に基づいて，図 1a に示すようなモデル系を考える．このモデル系は，$\Omega-OH_2$ (Ω = MnOH or $MnCa(OH)_3$)，$HO-C_6H_4-NH_3^+$，そして$[R-C_3N_2H_2]^-$ (R = H) からなり，PSII の OEC，P680 + Y_Z，そして D1-H190 にそれぞれ対応する．OEC による水分解にさきがけて，P680 からは電子が，D1-H190 からはプロトンが，それぞれ移動済みであると仮定し，それを正および負電荷で表現する．図 1b に示すように，H^{T1} は基底状態で PA 側に移動する．図 1b の構造から光励起状態を考え，全自由度の非断熱動力学を解析する．特に H^{T2} の運動と，それにカップルする電子の運動に注目する．

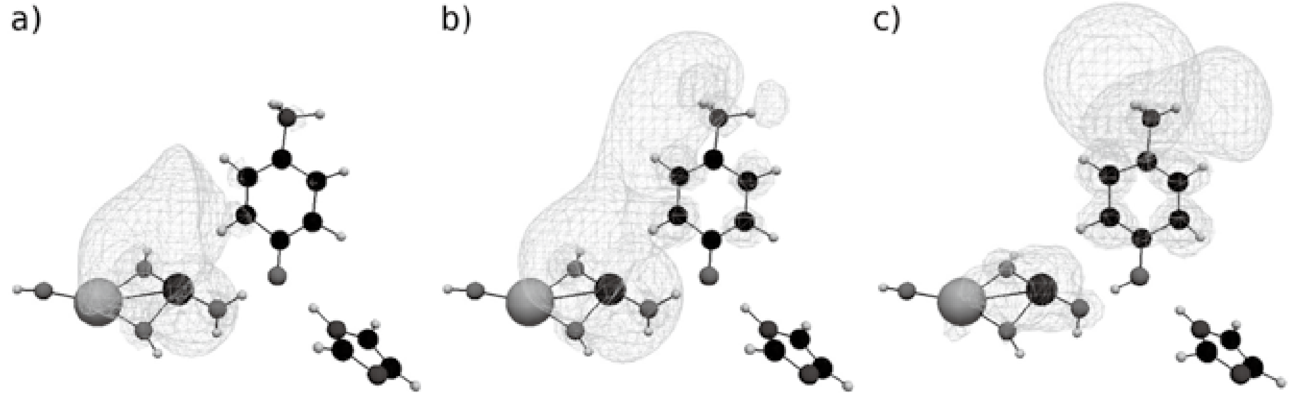


図 2 Ω = MnCa(OH)$_3$ の場合の，励起状態の反応経路に沿った構造の時間変化と，それと couple する不対電子密度の空間分布の時間変化のスナップショット．

動力学計算は，path-branching representation に基づく.[3] この理論では，電子波束 $\Psi(\mathbf{R},\mathbf{r},t)=\sum_I C_I(t)\Phi_I(\mathbf{r};\mathbf{R}(t))$ が，反応経路に沿って時間発展する．ここで，$\mathbf{R},\mathbf{r},t$ はそれぞれ原子核，電子，時間の座標である．$\Phi_I(\mathbf{r};\mathbf{R}(t))$は核座標$\mathbf{R}(t)$をパラメータとする量子化学計算によって求める．そして，電子の運動方程式は次式で表される．

$$i\hbar\dot{C}_I=\sum_J\left(H_{IJ}^{(el)}-i\hbar\sum_k\dot{R}_k X_{IJ}^k-\frac{\hbar^2}{4}\sum_k\left(Y_{IJ}^k+Y_{JI}^{k^*}\right)\right)C_J$$

ここで，$H_{IJ}^{(el)}$は電子の Hamiltonian で，$X_{IJ}^k=\langle\Phi_I|\partial\Phi_J/\partial R_k\rangle$，$Y_{IJ}^k=\langle\Phi_I|\partial^2\Phi_J/\partial R_k^2\rangle$である．また，原子核は force matrix $F_{IJ}=\langle\Phi_I|\partial H^{(el)}/\partial R_k|\Phi_J\rangle$に駆動される．

【結果と考察】光励起状態の非断熱動力学の解析から，図 2 に示すような，プロトンと電子が別々の経路を通って，別々の場所に移動する機構が得られた．Ω = MnOH の場合にも，定性的に同じ機構が得られる．EPD と EA の間プロトン移動は，局所的に見れば，基底状態に類似する．一方で電子は，プロトンを迂回するように移動し，EA の Rydberg-like state に至る．図 1a の状態から考えると，プロトンはリレーによって結果的に PA に移動し，電子は EA に移動する．そして，それぞれ負および正電荷をキャンセルする．プロトンと電子の分岐点は，形式的には EA の O 原子であり，その周辺の構造が Y の字を連想させることから，この機構を Y-shaped coupled proton electron-wavepacket transfer (Y-shaped CPEWT) と呼ぶ．基底状態では，プロトン移動は起こるものの，このような電子移動は起こらない．

アクセプターがこのように Y 字型である利点のひとつは，d-d state への非断熱遷移に伴う電荷再結合が抑制されることである．Ω = MnOH の場合，Schiff 塩基をアクセプターとした先行研究 [2] では一回で 25%程度が d-d state に非断熱遷移するが，Y 字型では 3%程度になる．さらに，Ca が加わることによってそれは 0.3%程度まで抑えられる．

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2. 論文

(1) Kentaro YAMAMOTO and Kazuo TAKATSUKA,

“Dynamical mechanism of charge separation by photoexcited generation of proton–electron pairs in organic molecular systems. A nonadiabatic electron wavepacket dynamics study”

Chem. Phys. 475, 39-53 (2016)

(2) Kentaro YAMAMOTO and Kazuo TAKATSUKA,

“Photoinduced Charge Separation Catalyzed by Manganese Oxides onto a Y-Shaped Branching Acceptor Efficiently Preventing Charge Recombination”

ChemPhysChem. 18, 537-548 (2016)

3. 学会発表

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「Photochemical mechanism of charge separation taken out of water molecule」第 19 回理論化学討論会，東京 2016/5/23-25 3B18.

(2) 山本憲太郎，高塚和夫
「光化学系 II における水分解の初期段階の機構について；Y 字型 Coupled Proton-Electron Transfer」第 10 回分子科学討論会，神戸 2016/9/13-15 1F13.

(3) Kentaro Yamamoto and Kazuo Takatsuka “Photoinduced Charge Separation Catalyzed by Mn-Oxides onto a Y-shaped Branching Acceptor Efficiently Preventing Charge Recombination”, 第 14 回京都大学福井謙一記念研究センターシンポジウム，Kyoto, Japan 2017/1/27 P9.

(4) Kentaro Yamamoto and Kazuo Takatsuka “Photodynamical electron-wavepacket mechanism of water-splitting catalyzed by manganese oxides involving hydrogen-bond network”, The 77th Okazaki Conference Series: International Symposium on Ultrafast Dynamics in Molecular and Material Sciences”, Okazaki, Japan, 2017/3/6-8 P06.

７．共同研究員

Yanying Zhao

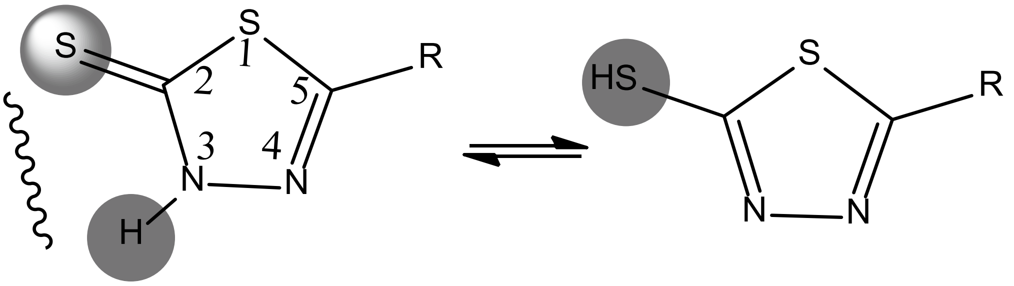
Visiting Scholar

1. Summary of the research of the year

(1) 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 $T_1/S_0 \rightarrow S_0'$.

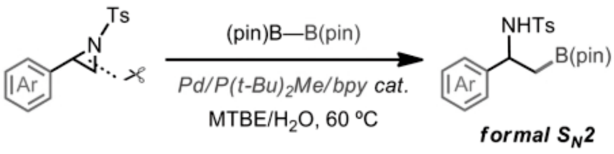


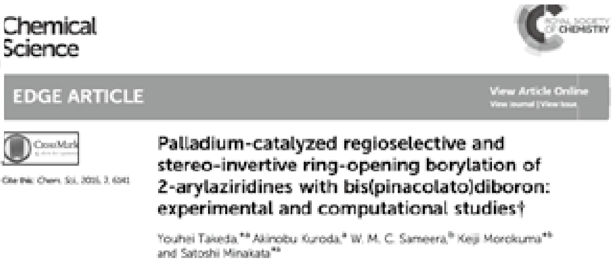
Scheme 1

(2) Exploring water micro-solvation role in Pd-Catalyzed Ring-Opening Borylation of 2-Arylaziridines(AZ) by Artificial Force-Induced Reaction method in the global reaction route mapping (GRRM)

The active species PdL_2 initiates the aziridine ring opening borylation reaction of 2-arylaziridines by experiments and calculations, which opens up and avenue to the further development of transition metal-catalyzed ring opening C-E bond forming cross couplings of aziridines. H_2O illustrates fundamentally important role in Pd-catalyzed regioselective borylative ring-opening rection. The multi-component artificial force-induced reaction (MC-AFIR) method in the global reaction route mapping (GRRM) strategy determines all of the local minima (LMs) of the hydrogen-bonding equilibrium structures of intermediates III and VI and transition states (TSs) for subsequent reaction paths systematically. The mechanism proposed herein indicates the amount of water does not affect the ring-opening regioselectivity both in the experiments and calculations, however, definite amount of H_2O molecules can stabilize the reaction intermediates via hydrogen bonding chain of H_2O cluster and push the subsequent reaction. At the same time, H_2O increase the barrier for the side reaction. And the important role of H_2O are further explained in aziridine ring-opening, the proton transfer, ligand dissociation/association and B-B bond cleavage reaction process. The revised catalytic cycle is proposed.

The full catalytic cycle consists of a selectivity-determining aziridine ring opening (oxidative addition), a proton transfer, phosphine ligand dissociation from the catalyst, boron–boron bond cleavage, and reductive elimination. Importantly, H_2O plays an indespensible role in the proton transfer step by H_2O hydrogen bond chain, including to quench TSN^- as a proton source, and form the [Pd(OH)] species as an internal base, and further stabilize the reaction intermediates and pushing subsequent reactions, such as B-B bond cleavage.




Chemical Science

EDGE ARTICLE

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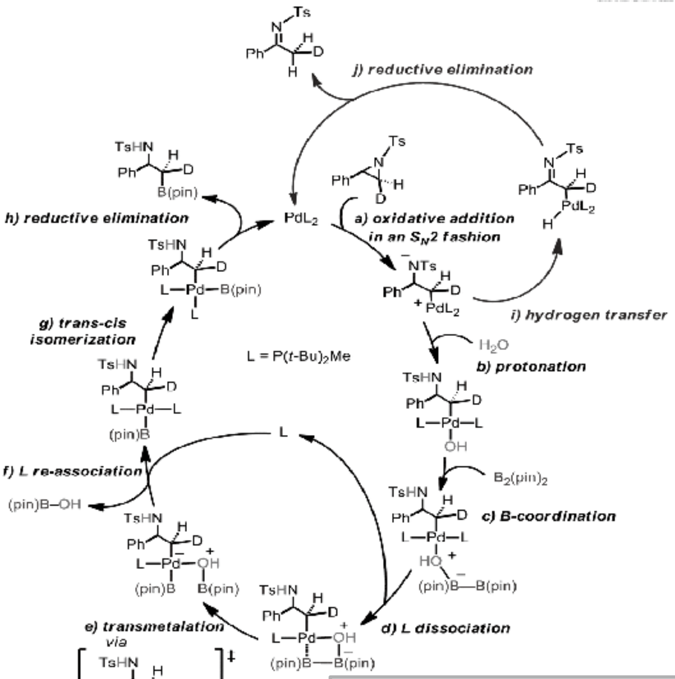
Cite this: Chem. Sci., 2016, 7, 6141

Palladium-catalyzed regioselective and stereo-invertive ring-opening borylation of 2-arylaziridines with bis(pinacolato)diboron: experimental and computational studies†

Youhei Takeda,*a Akinobu Kuroda,a W. M. C. Sameera,b Keiji Morokuma*b and Satoshi Minakata*a



Water plays important roles in the reaction process:

(1) As a proton source toe quench TsN$^-$.

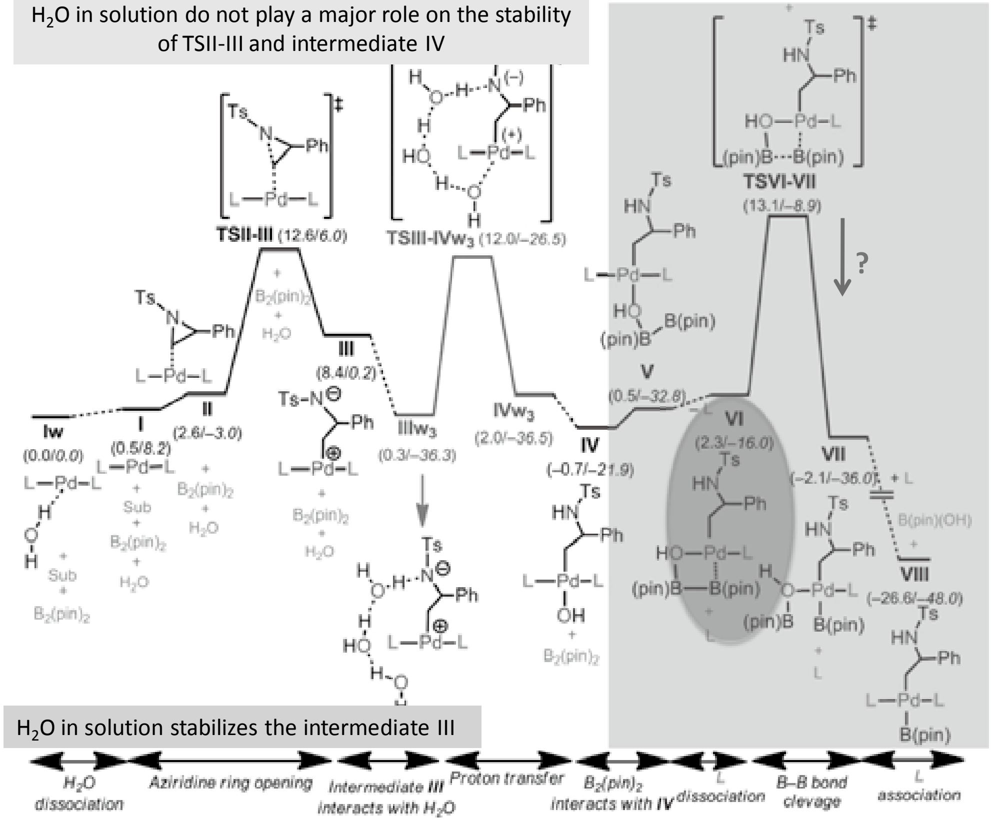
(2) As an internal base to form the [Pd(OH)] species.

(3) Stabilize the reaction intermediates.

Propose catalytic cycle.

Chem. Sci., 2016, 7, 6141

Mechanism



H_2O in solution do not play a major role on the stability of TSII-III and intermediate IV

H_2O in solution stabilizes the intermediate III

Energies are indicated in kcal/mol^{-1}. ΔG values are in plain text, and ΔE values are in italics.

Chem. Sci., 2016, 7, 6141.

Our Objective:

(1) Confirm the important role of the H_2O on the reaction process.

(2) Explain the mechanism of water driving on the phosphine ligand dissociation and B-B bond cleavage.

2. Original papers

(1) Pang, Sumei, Zhao Yanying*, Xue Jiadan, Zheng Xuming. "Solvent-dependent dynamics of hydrogen bonding structure 5-(methylthio)-1, 3, 4-thiadiazole-2 (3H)-thione as determined by Raman spectroscopy and theoretical calculation." Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 171 (2017): 470-477.

(2) Liu, Xin, and Yanying Zhao*. "Adsorption Kinetics of Methylene Blue on Synthesized DMF-MIL-101 (Cr), a DMF-functionalized Metal-organic Framework." Key Engineering Materials 671 (2016).

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

(4) 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.

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

(6) Zhao Yanying*, Zhang Yuchen, Liu Xin, Zheng Xuming Formation, characterization, structure and bonding analysis of the metal-carbon bond $OM-(\eta^6-C_6H_6)$ (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

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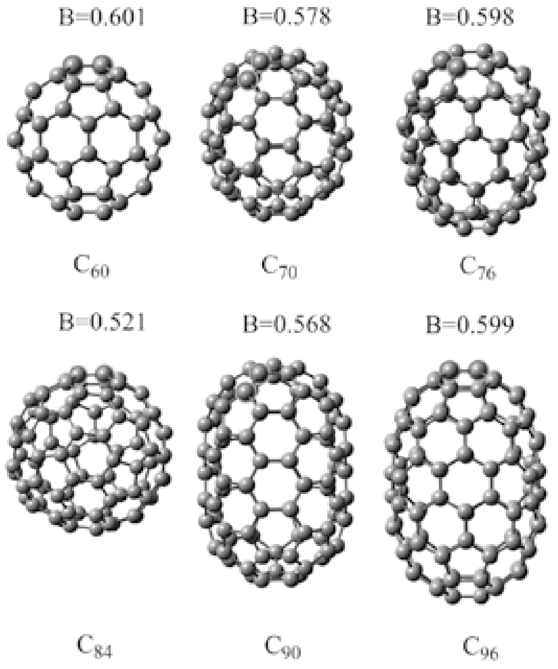
1. Summary of the research of the year

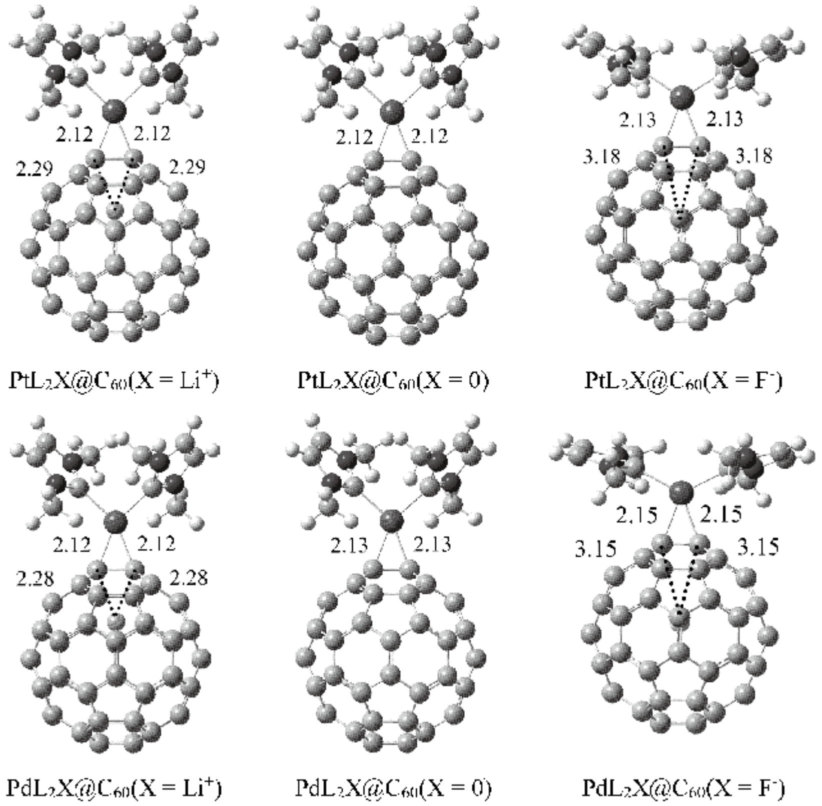
The importance of Metal-Carbon Back-Bonding to the Stability of Fullerene-Transition metal complexes and the role of Cage Sizes, Encapsulated Ions and Metal Fragments

A density functional study of $\{\eta^2\text{-}(X@C_n)\}ML_2$ complexes with various cage sizes (C_{60}、C_{70}、C_{76}、C_{84}、C_{90}、C_{96}), encapsulated ions ($X = F^-$, 0, Li^+) and metal fragments (M = Pt、Pd) is performed, using M06/LANL2DZ levels of theory. The importance of π back-bonding to the thermodynamic stability of fullerene-transition metal complexes ($\{\eta^2\text{-}(X@C_n)\}ML_2$) and the effect of encapsulated ions, metal fragments and cage sizes on the π back-bonding are determined in this study. The theoretical computations suggest that π back-bonding plays an essential role in the formation of fullerene-transition metal complexes. The theoretical evidence also suggests that there is no linear correlation between cage sizes and π back-bonding, but the encapsulated Li^+ ion enhances π back-bonding and F^- ion results in its deterioration. These computations also show that a platinum center produces stronger π back-bonding than a palladium center. It is hoped that the conclusions that are provided by this study can be used in the design, synthesis and growth of novel fullerene-transition complexes.



Scheme 1. The sites of attack for addition to the fullerenes Ih-C_{60}, D_{5h}-C_{70}, D_2-C_{76}, D_{2d}(23)-C_{84}, D_{5h}(1)-C_{90} and D_{5h}(1)-C_{96}. The Hückel π bond orders (B) were calculated using the freeware

program, HuLiS.



$PtL_2X@C_{60}(X = Li^+)$ $PtL_2X@C_{60}(X = 0)$ $PtL_2X@C_{60}(X = F^-)$

$PdL_2X@C_{60}(X = Li^+)$ $PdL_2X@C_{60}(X = 0)$ $PdL_2X@C_{60}(X = F^-)$

Figure 1. Optimized geometries for $\{\eta^2\text{-}(X@C_{60})\}ML_2$ (M = Pt, Pd; X = Li^+, 0 , F^-)

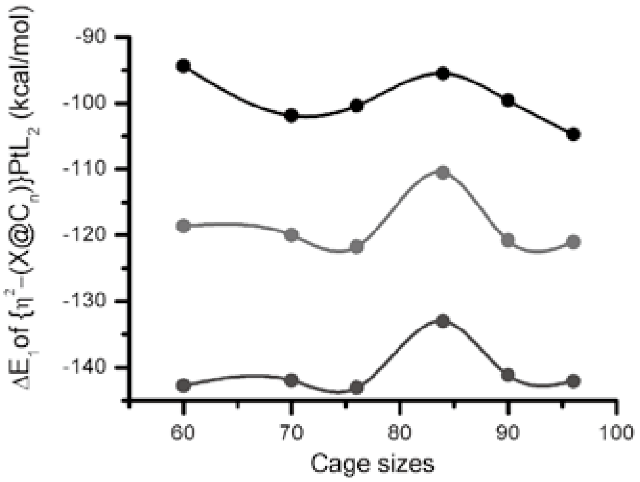


Figure 2. The correlation between ΔE_1 and cage sizes for $\{\eta^2\text{-}(X@C_n)\}PtL_2$ (n = 60, 70, 76, 84, 90 and 96) complexes. The blue, red and black lines represent the respective values for ΔE_1 for X = Li^+, 0 and F^-.

2. Original papers

(1) Ming-Chung Yang, Akhilesh K. Sharma, W. M. C. Sameera, Keiji Morokuma, and Ming-Der Su Theoretical Study of Addition Reactions of L_4M (M = Rh, Ir) and L_2M (M = Pd, Pt) to $Li^+@C_{60}$. The Journal of Physical Chemistry A, 2017, 121, 2665-2673.

(2) Jia-Syun Lu, Ming-Chung Yang, and Ming-Der Su Indium–Arsenic Molecules with an In≡As Triple Bond: A Theoretical Approach. ACS Omega, 2017, 2, 1172–1179.

(3) Jia-Syun Lu, Ming-Chung Yang and Ming-Der Su. The effect of substituents on triply bonded boron≡antimony molecules: a theoretical approach. Phys. Chem. Chem. Phys., 2017, 19, 8026-8033.

(4) Jia-Syun Lu, Ming-Chung Yang and Ming-Der Su. The Effect of Substituents on the Stability of Triply Bonded Gallium≡Antimony Molecules: A New Target for Synthesis. Dalton Transactions, 2017, 46, 1848-1856.

(5) Jia-Syun Lu, Shih-Hao Su, Ming-Chung Yang, Xiang-Ting Wen, Jia-Zhen Xie, and Ming-Der Su Substituent Effects on Boron–Bismuth Triple Bond: A New Target for Synthesis. Organometallics, 2016, 35, 3924–3931.

８．日本学術振興会外国人特別研究員

Xue-Feng Ren

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1. Summary of the research of the year

Computational Insights on the Emission Decay Way of Facial and Meridional Tris-cyclometalated Iridium(III) Complexes

Significant attractions have been focused on synthesis d^6 complexes due to theirs extreme widely used in variety photocatalysis and photoelectrochemistry. The Ir(III) chelates complexes have been widely synthesized because of their long excited-state lifetimes and high efficiencies. In viewing this, a series of tris-cyclometalates of Ir(III) had been reported by either facial (fac) meridional (mer) isomers. The photophysical properties of both facial and meridional complexes have also been examined and show distinct differences between the two forms, especially for the properties of excited state. The emission wavelengths of meridional forms are red shifted compared with its facial complexes. Furthermore, the luminescent quantum efficiencies (Φ) and lifetimes (t) of fac-Ir(III) complexes are ten times larger than that of mer-Ir(III) complexes. The radiative decay rates (K_r) of these complexes under fac− and me- configurations are similar with each other, while the nonradiative decay rates (K_{nr}) of mer-Ir(III) complexes are ten times larger than that of fac-Ir(III) complexes. The mechanism of emission decay is not established and there is no clear understanding on the origin of the dramatically differences on the K_{nr}. We have studied the emission decay of this kind of isomers using DFT methods. The SC-AFIR method is implemented in GRRM program is employed to locate the minimum energy seam of crossing (MESXs).

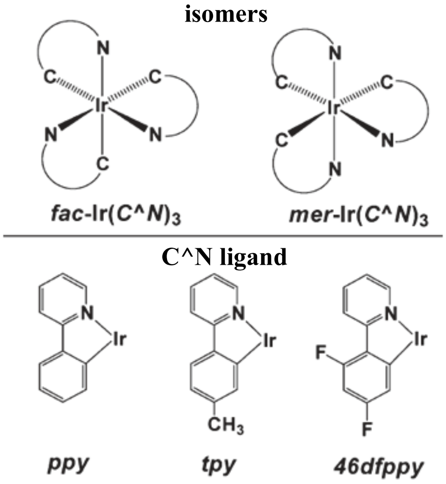
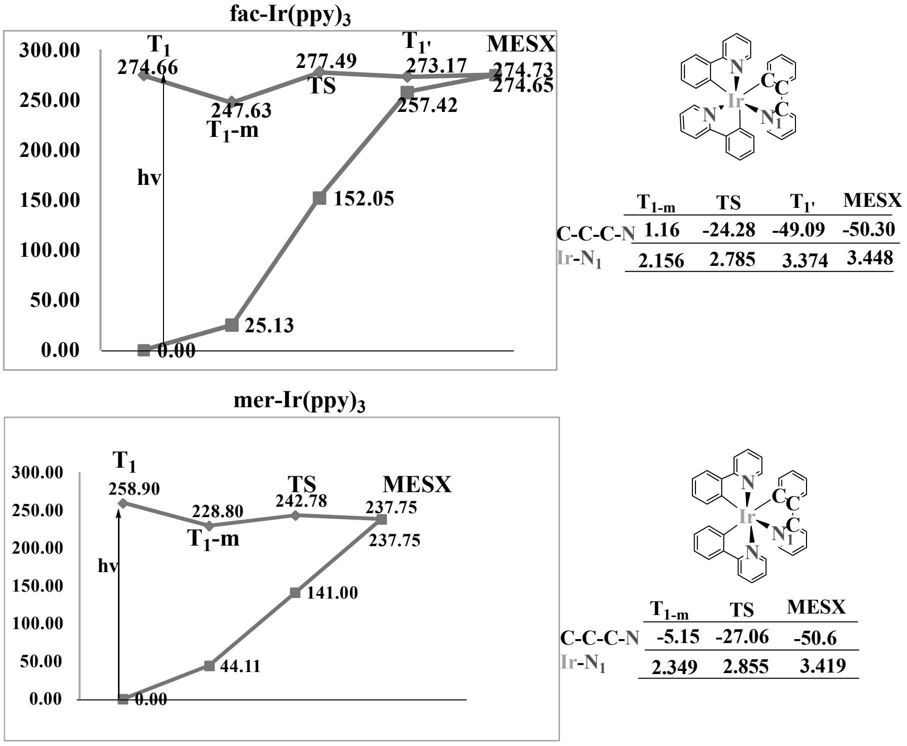


Figure 1. The scheme of studied molecules

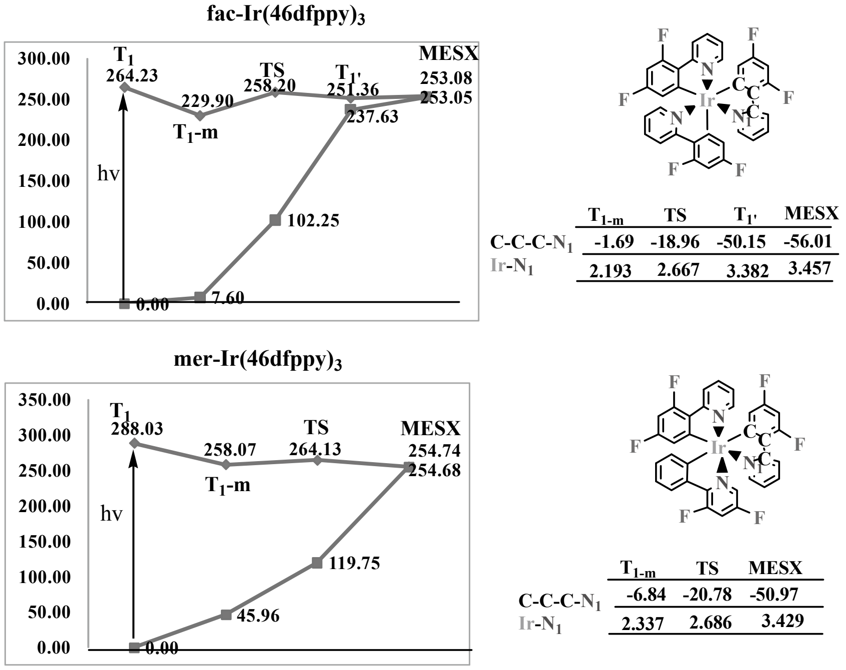
The emission decay leads to distort the phenyl ring of the ppy ligand and Ir-N_1 bond break. The MESX of mer-Ir(ppy)$_3$ is lower than T_1 state at the FC region by 21.15kJ/mol, while the energy differences between the MESX of fac-Ir(ppy)$_3$ and T_1 at the FC state is less than 1 kJ/mol. This means that the quenching pathway of mer-Ir(ppy)$_3$ is favorable compared with its facial isomer. Furthermore, the energy barrier from the $T_{1\text{-}m}$ to MESX of mer-Ir(ppy)$_3$ is found to be much lower than that of fac-Ir(ppy)$_3$. Therefore, the calculated results can fully explain the experimental data(K_{nr} is 3.2×10^5 and 6.4×10^6 for fac-Ir(ppy)$_3$ and mer-Ir(ppy)$_3$, respectively).



	$T_{1\text{-m}}$	TS	$T_{1'}$	MESX
C-C-C-N	1.16	-24.28	-49.09	-50.30
Ir-N_1	2.156	2.785	3.374	3.448

	$T_{1\text{-m}}$	TS	MESX
C-C-C-N	-5.15	-27.06	-50.6
Ir-N_1	2.349	2.855	3.419

Figure 2. The emission decay of fac-Ir(ppy)$_3$ and mer-Ir(ppy)$_3$ obtained by B3LYP method



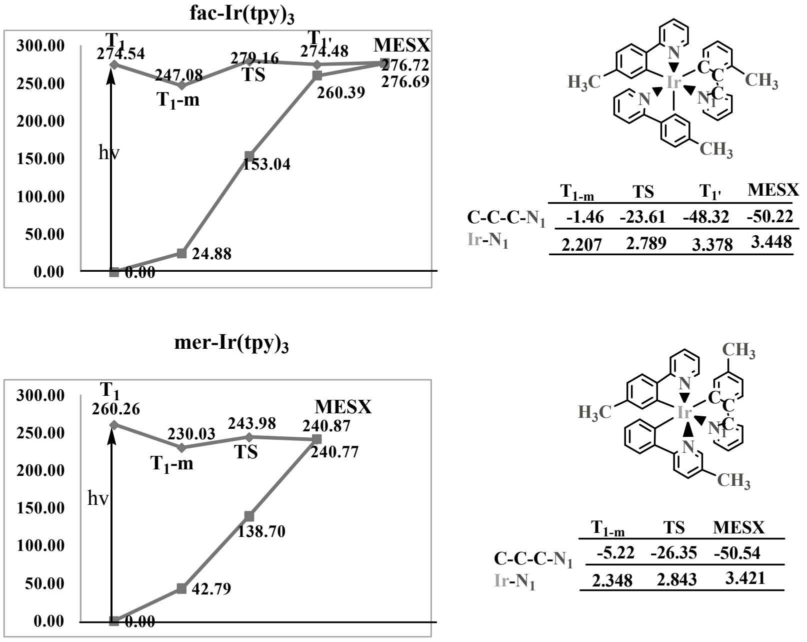
	$T_{1\text{-m}}$	TS	$T_{1'}$	MESX
C-C-C-N_1	-1.69	-18.96	-50.15	-56.01
Ir-N_1	2.193	2.667	3.382	3.457

	$T_{1\text{-m}}$	TS	MESX
C-C-C-N_1	-6.84	-20.78	-50.97
Ir-N_1	2.337	2.686	3.429

Figure 3. The emission decay of fac-Ir(46dfppy)$_3$ and mer-Ir(46dfppy)$_3$ obtained by B3LYP method

As depicted in Figure 3, by the introduction of the fluorine at the ppy ligand, the MESX of fac-Ir(46dfppy)$_3$ is 11.15kJ/mol lower than corresponding T_1 state at the FC geometry, and the energy barrier is 28.30 kJ/mol. This means the decay process of fac-Ir(46dfppy)$_3$ from the T_1 state is more probable compared with fac-Ir(ppy)$_3$, which is consistent with the large K_{nr} value (3.6×10^5)

relative to fac-Ir(ppy)$_3$. Follow this coordinate, the mer-Ir(46dfppy)$_3$ has much small MESX lower than the FC state(33.28kJ/mol) and smaller energy barrier (6.06kJ/mol), thus it has efficient quenching pathway.



	$T_{1\text{-m}}$	TS	$T_{1'}$	MESX
C-C-C-N_1	-1.46	-23.61	-48.32	-50.22
Ir-N_1	2.207	2.789	3.378	3.448

	$T_{1\text{-m}}$	TS	MESX
C-C-C-N_1	-5.22	-26.35	-50.54
Ir-N_1	2.348	2.843	3.421

Figure 4. The emission decay of fac-Ir(tpy)$_3$ and mer-Ir(tpy)$_3$ obtained by B3LYP method

As depicted in Figure 4, by the introduction of the methyl at the ppy ligand, the MESX of fac-Ir(tpy)$_3$ is larger than corresponding T_1 state at the FC geometry, and the energy barrier is 32.08kJ/mol. This means the decay process of fac-Ir(tpy)$_3$ from the T_1 state is less probable compared with fac-Ir(ppy)$_3$, which is consistent with the small K_{nr} value (2.5×10^5) relative to fac-Ir(ppy)$_3$. The mer-Ir(tpy)$_3$ has small energy lower than FC (19.39kJ/mol) and energy barrier (13.95kJ/mol) compared with fac-Ir(tpy)$_3$, therefore the quenching pathway is more favorable compared with that of fac-Ir(tpy)$_3$.

2. Original papers

Xue Feng Ren and Keiji Morokumma, “Emission Decay Way of a series of Facial and Meridional Tris-cyclometalated Iridium(III) Complexes”, In preparation.

3. Presentation at academic conferences

(1) Xue Feng Ren and Keiji Morokumma
“The effect of intramolecular Hydrogen Bond on the Mechanism of Exicted state Decay of Iridium(III) Complexes”, The 10th Annual Meeting of Japan Society for Molecular Science, 2016,9,13-15, KOBE fashion mart, Poster

Ⅴ　資料

1．研究業績一覧（平成 28 年度）

№	Authors	Title	Journal	Volume (Number), first page to last page	year
水野　英如					
1	H. Mizuno, L. E. Silbert, and M. Sperl	Spatial Distributions of Local Elastic Moduli Near the Jamming Transition	*Physical Review Letters*	Vol.116, p.068302 (5pages)	2016
2	K. Saitoh and H. Mizuno	Anomalous energy cascades in dense granular materials yielding under simple shear deformations	*Soft Matter*	Vol.12, p.1360-1367 (8pages)	2016
3	H. Mizuno, L. E. Silbert, M. Sperl, S. Mossa, and J.-L. Barrat	Cut-off nonlinearities in the low-temperature vibrations of glasses and crystals	*Physical Review E*	Vol.93, p.043314 (18pages)	2016
4	H. Mizuno, K. Saitoh, and L. E. Silbert	Elastic moduli and vibrational modes in jammed particulate packings	*Physical Review E*	Vol.93, p.062905 (21pages)	2016
5	K. Saitoh and H. Mizuno	Enstrophy cascades in two-dimensional dense granular flows	*Physical Review E*	Vol.94, p.022908 (11pages)	2016
6	H. Mizuno, S. Mossa, and J.-L. Barrat	Relation of vibrational excitations and thermal conductivity to elastic heterogeneities in disordered solids	*Physical Review B*	Vol.94, p.144303 (22pages)	2016
西本　佳央					
7	Yoshio Nishimoto and Dmitri G. Fedorov	The fragment molecular orbital method combined with density-functional tight-binding and the polarizable continuum model	*Phys. Chem. Chem. Phys.*	18(32), 21997-22734	2016
8	Hiroya Nakata, Yoshio Nishimoto, and Dmitri G. Fedorov	Analytic second derivative of the energy for density-functional tight-binding combined with the fragment molecular orbital method	*J. Chem. Phys.*	145(4), 044113	2016
9	Yoshio Nishimoto and Stephan Irle	Quantum Chemical Prediction of Vibrational Spectra of Large Molecular Systems with Radial or Metallic Electronic Structure	*Chem. Phys. Lett.*	667, 317-321	2017
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11	Yoshio Nishimoto	Analytic Hyperpolarizability and Polarizability Derivative with Fractional Occupation Numbers for Large Extended Systems	*J. Chem. Phys.*	146(8), 084101	2017
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12	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*	16, 2349-2363	2016

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13	Youhei Takeda, Akinobu Kuroda, W. M. C. Sameera, Keiji Morokuma, Satoshi Minakata	Palladium-catalyzed regioselective and stereo-invertive ring-opening borylation of 2-arylaziridines with bis(pinacolato) diboron: experimental and computational studies	*Chem. Sci.,*	7, 6141-6152	2016
14	W. M. C. Sameera, Satoshi Maeda, Keiji Morokuma	Computational Catalysis Using the Artificial Force Induced Reaction Method	*Acc. Chem. Res.*	49 (4), 763-773	2016
15	Shunsuke Sasaki, Satoshi Suzuki, W. M. C. Sameera, Kazunobu Igawa, Keiji Morokuma, Gen-ichi 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 (26), 8194-8206	2016
16	Hu-Jun Qian, Ying Wang Keiji Morokuma	Quantum mechanical simulation reveals the role of cold helium atoms and the coexistence of bottom-up and top-down formation mechanisms of buckminsterfullerene from carbon vapor	*Carbon*	14, 635-641	2017
17	Ryo Nakano, Lung Wa Chun, Yumiko Watanabe, Yoshishige Okuno, Yoshikuni Okumura, Shingo Ito, Keiji Morokuma, and Kyoko Nozaki	Elucidating the Key Role of Phosphine−Sulfonate Ligands in Palladium-Catalyzed Ethylene Polymerization: Effect of Ligand Structure on the Molecular Weight and Linearity of Polyethylene	*ACS Catal.,*	6, 6101-6113	2016
18	Menggai Jiao, Wei Song, Hu-Jun Qian, Ying Wang, Zhijian Wu, Stephan Irle, Keiji Morokuma	QM/MD studies on graphene growth from small islands on the Ni(111) surface	*Nanoscale*	8, 3067-3074	2016
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21	Anna V. Pomogaeva, Keiji Morokuma, and Alexey Y. Timoshkin	Trimeric Cluster of Lithium Amidoborane—The Smallest Unit for the Modeling of Hydrogen Release Mechanism	*Journal of Computational Chemistry*	37, 1259-1264	2016
22	Miho Hatanaka, Yuichi Hirai, Yuichi Kitagawa, Takayuki Nakanishi, Yasuchika Hasegawa, Keiji Morokuma	Organic linkers control the thermosensitivity of the emission intensities from Tb(III) and Eu(III) in a chameleon polymer	*Chem. Sci.,*	8, 423-429	2017
23	Naokazu Kano, Nathan J. O'Brien, Ryohei Uematsu, Romain Ramozzi, Keiji Morokuma	Trihydroborates and Dihydroboranes Bearing a Pentacoordinated Phosphorus Atom: Double Ring Expansion To Balance the Coordination States	*Angew. Chem.*	129, 5976-5979	2017
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26	Z. Slanina, F. Uhlík, S. Nagase, X. Lu, T. Akasaka, and L. Adamowicz	Computed Relative Populations of D_2(22)-$\mathrm{C_{84}}$ Endohedrals with Encapsulated Monomeric and Dimeric Water	*Chem. Phys. Chem.*	17, 1109-1111	2016
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28	Y. Takano, R. Tashita, M. Suzuki, S. Nagase, H. Imahori, and T. Akasaka	Molecular Location Sensing by Anisotropic Magnetism of an Endohedral Metallofullerene	*J. Am. Chem. Soc.*	138, 8000-8005	2016
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30	J. –S. Dang, W. –W. Wang X. Zhao, and S. Nagase	Unconventional Electronic Structure and Chlorination/Dechlorination Mechanisms of $^{\#1911}\mathrm{C_{64}}$ Fullerene	*Inorg. Chem.*	55, 6827-6829	2016
31	Q. –Z. Li, J. –J. Zheng, L. He, S. Nagase, and X. Zhao	Stabilization of a Chlorinated $^{\#4348}\mathrm{C_{66}}$:$\mathrm{C_{2v}}$ Cage by Encapsulating Monometal Species: Coordination between Metal and Double Hexagon-Condensed Pentalenes	*Inorg. Chem.*	55, 7667-7675	2016
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33	C. L. Wagner, L. Tao, E. J. Thompson, T. A. Stich, J. –D. Guo, J. C. Fettinger, L. A. Berben, R. D. Britt, S. Nagase, and P. P. Power	Dispersion-Force-Assisted Disproportionation: A Stable Two-Coordinate Copper (II) Complex	*Angew. Chem. Int. Ed.*	55, 10444-10447	2016
34	T. Kuwabara, M. Nakada, J. Hamada, J. –D. Guo, S. Nagase, and M. Saito	(h^4-Butadiene)Sn(0) Complexes: A New Approach for Zero-Valent p-Block Elements Utilizing a Butadiene as a 4π-Electron Donor	*J. Am. Chem. Soc.*	138, 11378-11382	2016
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39	T. Sugahara, J. –D. Guo, T. Sasamori, Y. Karatsu, Y. Furukawa, A. E. Ferao, S. Nagase, and N. Tokitoh	Reaction of a Stable Digermyne with Acetylenes: Synthesis of a 1,2-Digermabenzene and a 1,4-Digermabarrelene	*Bull. Chem. Soc. Jpn.*	89, 1375-1384	2016
40	D. J. Liptrot, J. –D. Guo, S. Nagase, and P. P. Power	Dispersion Forces, Disproportionation, and Stable High-Valent Late Transition Metal Alkyls	*Angew. Chem. Int. Ed.*	55, 14766-14769	2016
41	S. Tsukada, N. J. O'Brien, N. Kano, T. Kawashima, J. –D. Guo, and S. Nagase	The Synthesis and Structure of a Dianionic Species with a Bond between Pentacoordinated Tin Atoms: Bonding Property of the Tin-Tin Bond	*Dalton Trans.*	45, 19374-19379	2016
42	M. Suzuki, M. Yamada, Y. Maeda, S. Sato, Y. Takano, F. Uhlík, Z. Slanina, Y. Lian, X. Lu, S. Nagase, M. M. Olmstead, A. L. Balch, and T. Akasaka	The Unanticipated Dimerization of Ce@C_{2v}(9)-C_{82} upon Cocrystallization with Ni(octaethyporphyrin) and Comparison with Monomeric M@C_{2v}(9)-C_{82} (M = La, Sc, and Y)	*Chem. Eur. J.*	22, 18115-18122	2016
43	M. Yamada, Y. Tanabe, J. –S. Dang, S. Sato, N. Mizorogi, M. Hachiya, M. Suzuki, T. Abe, H. Kurihara, Y. Maeda, X. Zhao, Y. Lian, S. Nagase, and T. Akasaka	D_{2d}(23)-C_{84} versus Sc_2C_2@D_{2d}(23)-C_{84}: Impact of Endohedral Sc_2C_2 Doping on Chemical Reactivity in the Photolysis of Diazirine	*J. Am. Chem. Soc.*	138, 16523-16532	2016
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45	Tetsuya Fukuda, Hisako Hashimoto, Shigeyoshi Sakaki, and Hiromi Tobita	Stabilization of a Silaaldehyde by its η2 Coordination to Tungsten	*Inorg. Chem.*	55, 188-192	2016
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47	Yuta Takano, Tomohiro Numata, Kazuto Fujishima, Kazuaki Miyake, Kazuya Nakao, Wesley David Grove, Ryuji Inoue, Mineko Kengaku, Shigeyoshi Sakaki, Yasuo Mori, Tatsuya Murakami and Hiroshi Imahori	Optical control of neuronal firing via photoinduced electron transfer in donor–acceptor conjugates	*Chem. Sci.*	7, 3331-3337	2016

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49	Hajime Kameo, Tatsuya Kawamoto, Shigeyoshi Sakaki, Didir Bourissou, Hiroshi Nakazawa	Transition-Metal-Mediated Cleavage of Fluoro-Silanes under Mild ConditionsTransition-Metal-Mediated Cleavage of Fluoro-Silanes under Mild Conditions	*Chem. A Euro. J.*	22, 2370-2375	2016
50	Hajime Kameo, Koki Ikeda, Didir Bourissou, Shgeyoshi Sakaki, Shin Takemoto, Hiroshi Nakazawa, Hiroyuki Matsuzaka	Transition-Metal-Mediated Germanium-Fluorine Activation: Inverse Electron Flow in sigma-Bond Metathesis	*Organometallics*	35, 713-719	2016
51	Koki Kikui, S. Hayaki, K. Kido, Daisuke Yokogawa, K. Kasahara, Y. Matsumura, Hirofumi Sato, Shigeyoshi Sakaki,	Solvent structure of ionic liquid with carbon dioxide	*J. Mol. Liq.*	217, 12-16	2016
52	Kazuhiko Semba, Kenta Ariyama, Hong Zheng, Ryohei Kameyama, Shigeyoshi Sakaki, Yoshiaki Nakao	Reductive Cross-Coupling of Conjugated Arylalkenes and Aryl Bromides with Hydrosilanes by Cooperative Palladium/Copper Catalysis	*Angew. Chem., Int. Ed.*	55, 6275-6278	2016
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54	Masayuki Nakagaki, Shigeyoshi Sakaki,	Hetero-dinuclear complexes of 3d metals with a bridging dinitrogen ligand: theoretical prediction of the characteristic features of geometry and spin multiplicity	*Phys. Chem. Chem. Phys.*	18, 26365-26375	2016
55	Guixiang Zeng, Satoshi Maeda, Tetsuya Taketsugu, Shigeyoshi Sakaki,	Catalytic Hydrogenation of Carbon Dioxide with Ammonia-Borane by Pincer-Type Phosphorus Compounds: Theoretical Prediction	*J. Am. Chem. Soc.*	138, 13481-13484	2016
56	Shogo Okumura, Shuwei. Tang, Teruya Saito, K. Semba, Shigeyoshi Sakaki, Yoshiaki Nakao	para-Selective Alkylation of Benzamides and Aromatic Ketones by Cooperative Nick-el/Aluminum Catalysis	*J. Am. Chem. Soc.*	138, 14699-14704	2016
57	Wei Guan, Guixinag Zeng, Hajime Kameo, Yoshiaki Nakao, Shigeyoshi Sakaki	Cooperative Catalysis of Combined Systems of Transition-Metal Complexes with Lewis Acids: Theoretical UnderstandingCooperative Catalysis of Combined Systems of Transition-Metal Complexes with Lewis Acids: Theoretical Understanding	*Chem. Rec.*	16, 2405-2425	2016

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58	Shun Goda, Masanori Nikai, Mikinao Ito, Daisuke Hashizume, Kohei Tamao, Atsushi Okazawa, Norimichi Kojima, Hiroyuki Fueno, Kazuyoshi Tanaka, Yoshio Kobayashi, and Tsukasa Matsuo	Synthesis and Magnetic Properties of Linear Two-Coordinate Monomeric Diaryliron (II) Complexes Bearing Fused-Ring Bulky “Rind” Groups	*Chem. Lett.*	45(6), 634-636	2016
59	Tohru Sato, Naoki Haruta, and Kazuyoshi Tanaka	Thermodynamical Vibronic Coupling Constant and Density: Chemical Potential and Vibronic Coupling in Reactions	*Chem. Phys. Lett.*	652, 157-161	2016
60	Hiroyuki Watanabe, Masataka Hirose, Kazuyoshi Tanaka, Kazuo Tanaka, and Yoshiki Chujo	Color Tuning of Alternating Conjugated Polymers Composed of Pentaazaphenanthrene by Modulating Their Unique Electronic Structures Involving Isolated-LUMOs	*Polym. Chem.*	7, 3674-3680	2016
61	Yoshimasa Matsumura, Makoto Ishidoshiro, Yasuyuki Irie, Hiroaki Imoto, Kensuke Naka, Kazuyoshi Tanaka, Shinsuke Inagi, and Ikuyoshi Tomita	Arsole-Containing p-Conjugated Polymer by the Post-Element-Transformation Technique	*Angew. Chem. Int. Ed.*	55(48), 15040-15043	2016
62	Akihiro Ito, Ryohei Kurata, Yusuke Noma, Yasukazu Hirao, and Kazuyoshi Tanaka	Radical Cation of an Oligoarylamine Having a Nitroxide Radical Substituent: A Coexistent Molecular System of Localized and Delocalized Spins	*J. Org. Chem.*	81(22), 11416-11420	2016
63	Julián Zapico, Marie Shirai, Ryo Sugiura, Naokazu Idota, Hiroyuki Fueno, Kazuyoshi Tanaka, and Yoshiyuki Sugahara	Borophosphonate Cages as Element-Blocks: Ab Initio Calculation of the Electronic Structure of a Simple Borophosphonate, [HPO3BH]4, and Synthesis of Two Novel Borophosphonate Cages with Polymerizable Groups	*Chem. Lett.*	46(2), 181-184	2017
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65	K. Takatsuka, K. Matsumoto	Classical and semiclassical dynamics in statistical environments with a mixed dynamical and statistical representation	*PCCP*	18, 1771-1785	2016
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69	Yuta Mizuno, Yasuki Arasaki, Kazuo Takatsuka,	Real-time observation of wavepacket bifurcation on nonadiabatically coupled field-dressed potential energy curves by means of spectrogram of induced photon-emission from molecules driven by CW laser	*J. Chem. Phys.*	145, 184305 (11 pages)	2016
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72	Kazuo Takatsuka	Lorentz-like force emerging from kinematic interactions between electrons and nuclei in molecules. A quantum mechanical origin of symmetry breaking that can trigger molecular chirality	*J. Chem. Phys.*	146, 084312 (10 pages)	2017
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78	Masato Itami and Shin-ichi Sasa	Universal Form of Stochastic Evolution for Slow Variables in Equilibrium Systems	*J. Stat. Phys.*	167(1), 46-63	2017

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85	Ming-Chung Yang, Akhilesh K. Sharma, W. M. C. Sameera, Keiji Morokuma, and Ming-Der Su	Theoretical Study of Addition Reactions of L4M(M = Rh, Ir) and L2M(M = Pd, Pt) to Li+@C60	*J. Phys. Chem. A*	121(13), 2665-2673	2017
86	Miho Isegawa, W. M. C. Sameera, Akhilesh K. Sharma, Taku Kitanosono, Masako Kato, Shu Kobayashi, and Keiji Morokuma	Copper-catalyzed Enantioselective Boron Conjugate Addition: DFT and AFIR Study on Different Selectivities of Cu(I) and Cu(II) Catalysts	*ACS Catal.*	DOI: 10.1021/acscatal.7b01152.	2017
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87	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

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中垣　雅之					
89	Masayuki Nakagaki, Shigeyoshi Sakaki	Hetero-dinuclear complexes of 3d metals with a bridging dinitrogen ligand: theoretical prediction of the characteristic features of geometry and spin multiplicity	*Phys. Chem. Chem. Phys.*	18, 26365-26375	2016
90	Takako Muraoka, Haruhiko Kimura, Gama Trigagema, Masayuki Nakagaki, Shigeyoshi Sakaki, and Keiji Ueno	Reactions of Silanone(silyl)tungsten and -molybdenum Complexes with MesCNO, $(Me_2SiO)_3$, MeOH, and H_2O: Experimental and Theoretical Studies	*Organometallics*	36, 1009-1018	2016
Zheng, Hong					
91	Kazuhiko Semba, Kenta Ariyama, Hong Zheng, Ryohei Kameyama, Shigeyoshi Sakaki, Yoshiaki Nakao	Reductive Cross-Coupling of Conjugated Arylalkenes and Aryl Bromides with Hydrosilanes by Cooperative Palladium/Copper Catalysis	*Angew. Chem., Int. Ed.*	55, 6275-6278	2016
Lu Jing					
92	Jing Lu, Yiying Zheng, and Jingping Zhang	Computational design of benzo [1,2-b:4,5-b'] dithiophene based thermally activated delayed fluorescent materials	*Dyes and pigments*	127, 189-196	2016
Rong-Lin Zhong					
93	Rong-Lin Zhong, Hong-Liang Xu, and Zhi-Ru Li	The polar 2e/12c bond in phenalenyl-azaphenalenyl hetero-dimers: Stronger stacking interaction and fascinating interlayer charge transfer	*J. Chem. Phys.*	145, 054304	2016
94	Rong-Lin Zhong, Hong-Liang Xu, and Zhong-Min Su	Connecting effect on the first hyperpolarizability of armchair carbon–boron–nitride heteronanotubes: pattern versus proportion	*Phys. Chem. Chem. Phys.*	18, 13954-13959	2016
松岡　貴英					
95	Takahide Matsuoka, and Kazuo Takatsuka	Dynamics of photoionization from molecular electronic wavepacket states in intense pulse laser fields: A nonadiabatic electron wavepacket study	*J. Chem. Phys.*	146(13), 134114	2017

№	Authors	Title	Journal	Volume (Number), first page to last page	year
山本　憲太郎					
96	Kentaro Yamamoto and Kazuo Takatsuka	Dynamical mechanism of charge separation by photoexcited generation of proton–electron pairs in organic molecular systems. A nonadiabatic electron wavepacket dynamics study	*Chem. Phys.*	475, 39-53	2016
97	Kentaro Yamamoto and Kazuo Takatsuka	Photoinduced Charge Separation Catalyzed by Manganese Oxides onto a Y-Shaped Branching Acceptor Efficiently Preventing Charge Recombination	*Chem. Phys. Chem*	18(5), 537-548	2017
Yanying Zhao					
98	Pang, Sumei, Zhao Yanying*, Xue Jiadan, Zheng Xuming.	"Solvent-dependent dynamics of hydrogen bonding structure 5-(methylthio)-1, 3, 4-thiadiazole-2 (3H)-thione as determined by Raman spectroscopy and theoretical calculation."	*Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*	171, 470-477.	2017
99	Liu, Xin, and Yanying Zhao.*	"Adsorption Kinetics of Methylene Blue on Synthesized DMF-MIL-101 (Cr), a DMF-functionalized Metal-organic Framework."	*Key Engineering Materials*	671	2016
Ming-Chung Yang					
100	Ming-Chung Yang, Akhilesh K. Sharma, W. M. C. Sameera, Keiji Morokuma, and Ming-Der Su	Theoretical Study of Addition Reactions of L_4M (M = Rh, Ir) and L_2M(M = Pd, Pt) to $Li^+@C_{60}$.	*J. Phys. Chem. A*	121, 2665-2673	2017
101	Jia-Syun Lu, Ming-Chung Yang and Ming-Der Su	Triply-bonded indium phosphorus molecules: theoretical designs and characterization.	*RSC Advances*	7, 20597-20603	2017
102	Jia-Syun Lu, Ming-Chung Yang and Ming-Der Su	Indium–Arsenic Molecules with an In≡As Triple Bond: A Theoretical Approach.	*ACS Omega*	2, 1172–1179	2017
103	Jia-Syun Lu, Ming-Chung Yang and Ming-Der Su	The effect of substituents on triply bonded boron≡antimony molecules: a theoretical approach.	*Phys. Chem. Chem. Phys.*	19, 8026-8033	2017
104	Jia-Syun Lu, Ming-Chung Yang and Ming-Der Su	The Effect of Substituents on the Stability of Triply Bonded Gallium≡Antimony Molecules: A New Target for Synthesis.	*Dalton Transactions*	46, 1848-1856	2017

2．共同研究者受入れ状況（平成 28 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	SAMEERA, W.M.C.	外国人 共同研究者	平成 26 年 9 月 16 日～ 平成 28 年 9 月 15 日	日本学術振興会・ 外国人特別研究員	合成キラル金属ポルフィリンの反応機構と選択性の計算化学による研究
諸熊奎治	鈴木　机倫	共同研究者	平成 27 年 3 月 1 日～ 平成 29 年 2 月 28 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	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
諸熊奎治	ZHAO Yanying	外国人 共同研究者	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	招へい 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
諸熊奎治	REN, Xuefeng	招へい 外国人学者	平成 28 年 6 月 18 日～ 平成 30 年 6 月 17 日	中国鉱山技術大学 （中国）・准教授	光機能性分子の発行阻害機構の理論化学的研究
諸熊奎治 榊　茂好	畑中　美穂	共同研究者	平成 28 年 8 月 1 日～ 平成 29 年 7 月 31 日	奈良先端科学技術大学院大学（日本）・特任准教授	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
永瀬　茂	ＬＩ, Qiao-Zhi	外国人 共同研究者	平成 28 年 9 月 19 日～ 平成 29 年 3 月 19 日	西安交通大学 （中国）・PhD 学生	金属内包フラーレンの理論的研究
諸熊奎治	PRABHAKAR, Rajeev	招へい 外国人学者	平成 29 年 2 月 15 日～ 平成 29 年 3 月 9 日	University of Miami （アメリカ）・准教授	理論計算の基づく生体から着想を得た触媒、物質、薬の開発
榊　茂好	GUPTA, Ashutosh	招へい 外国人学者	平成 29 年 3 月 2 日～ 平成 29 年 3 月 16 日	Udai Pratap (Autonomous) College （インド）・准教授	分子間相互作用と化学反応に関する理論計算化学研究

３．海外渡航一覧（平成 28 年度）

職　　名	氏　　名	期間（自）	期間（至）	目 的 地
研　究　員	榊　　茂好	2016/6/12	2016/6/22	チェコ、ドイツ
特定研究員	多羅間　充輔	2016/7/7	2016/8/5	ドイツ、フランス
特定研究員	伊丹　将人	2016/7/17	2016/7/24	フランス
研　究　員	榊　　茂好	2016/8/30	2016/9/4	中　国
特定研究員	多羅間　充輔	2016/9/11	2016/9/27	ドイツ、フランス
特定研究員	多羅間　充輔	2016/10/3	2016/11/4	ドイツ
研　究　員	榊　　茂好	2016/10/19	2016/10/23	中　国
研　究　員	高塚　和夫	2017/1/14	2017/1/20	アメリカ合衆国
特定研究員	多羅間　充輔	2017/1/23	2017/2/12	オランダ、ドイツ
特定研究員	藪中　俊介	2017/3/15	2017/4/30	フランス
特定研究員	SCHNYDER, Simon Kaspar	2017/3/15	2017/3/31	フランス

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

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FIFC

第14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］北村 隆行（工学研究科長）　10:05-10:15

講演会（Lecture session）

高塚 和夫（京都大学 福井謙一記念研究センター）　10:15-11:15

「化学反応における電子動力学
－電子の運動が観える時代の基礎化学－」

八島 栄次（名古屋大学 大学院工学研究科）　11:25-12:25

「らせん構造を基本骨格とする
超分子・高分子の創成、構造と機能」

高田 彰二（京都大学 大学院理学研究科）　12:35-13:35

「複雑生体分子系のマルチスケールシミュレーション」

－ 昼食 －　13:35-15:00

「福井謙一奨励賞」表彰式
（Ceremony of Kenichi Fukui Encouragement Award）　15:00-15:30

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29年1月27日㊎

会場：京都大学 福井謙一記念研究センター

2017.1.27　Fukui Institute for Fundamental Chemistry (FIFC), Kyoto University

京都大学福井謙一記念研究センター
〒606-8103　京都市左京区高野西開町34-4
問合せ先：西本佳央 / E-mail:nishimoto.yoshio@fukui.kyoto-u.ac.jp　Tel:075-711-7894
事務室 / Tel:075-711-7708　Fax:075-781-4757

http://www.fukui.kyoto-u.ac.jp

第14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　2017年1月27日（金） 10:00~19:00
場所　京都大学 福井謙一記念研究センター

開会式 (Opening)： 3階大会議室

[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]　北村 隆行（京都大学 工学研究科長）　10:05 – 10:15

講演会 (Lecture Session) ： 3階大会議室

- 高塚 和夫 （京都大学 福井謙一記念研究センター）　10:15 – 11:15
  「化学反応における電子動力学 ー電子の運動が観える時代の基礎化学ー」
  司会：榊 茂好（福井センター）

- 八島 栄次 （名古屋大学 大学院工学研究科）　11:25 – 12:25
  「らせん構造を基本骨格とする超分子・高分子の創成、構造と機能」
  司会：赤木 和夫（福井センター）

- 高田 彰二 （京都大学 大学院理学研究科）　12:35 – 13:35
  「複雑生体分子系のマルチスケールシミュレーション」
  司会：林 重彦（京大院理）

— 昼食 —

「福井謙一奨励賞」表彰式 (Ceremony of Kenichi Fukui Encouragement Award) ： 3階大会議室

15:00 – 15:30

ポスターセッション (Poster Session) ： 3階大会議室

15:30 – 17:20

懇親会 (Banquet) ： 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. **A computational study on luminescent $[Cu(POP)(dmp)]^+$ and $[Cu(xantphos)(dmp)]^+$ complexes**
Sae Yanagida, ○W. M. C. Sameera, Masaki Yoshida, Atsushi Kobayashi, and Masako Kato (Dept. of Chem., Faculty of Sci., Hokkaido Univ.)

2. **レナードジョーンズクラスター LJ7 における固液転移とカオス**
○馬場 朋広、清水 寧（立命館理工）

3. **小数軌道占有数を用いた解析的微分法の開発**
○西本 佳央（京大福井セ）

4. **Universal Form of Stochastic Evolution for Slow Variables in Equilibrium Systems**
○伊丹 將人[1]、佐々 真一[2]（京大福井セ[1]、京大理[2]）

5. **Collective Dynamics of Migrating Cells**
○Simon K. Schnyder[1], John J. Molina[2], and Ryoichi Yamamoto[2] (FIFC[1], Grad. School of Eng., Kyoto Univ.[2])

6. **化学反応で自己推進運動する液滴の衝突**
○藪中 俊介[1]、義永 那津人[2]（京大福井セ[1]、東北大 AIMR[2]）

7. **Aggregation-induced Emission of bis(dialkylamino)anthracene**
○鈴木 聡、諸熊 奎治（京大福井セ）

8. **DFT investigations for activation process of dioxygen by a model of [NiFe] hydrogenase**
○伊勢川 美穂[1]、W. M. C. Sameera[2]、A. K. Sharma[1]、小江 誠司[3]、諸熊 奎治[1]（京大福井セ[1]、北大院理[2]、九大 I^2CNER[3]）

9. **Theoretical study on ring opening and closing mechanism of diarylethene derivatives**
○Kimichi Suzuki[1], Satoshi Maeda[1], and Keiji Morokuma[2] (Grad. School of Sci., Hokkaido Univ.[1], FIFC[2])

10. **The Biginelli reaction is a urea-catalyzed organocatalytic multicomponent reaction**
○ Maneeporn Puripat[1], Romain Ramozzi[1], Miho Hatanaka[2,3], Waraporn Parasuk[4], Vudhichai Parasuk[5], and Keiji Morokuma[1] (FIFC[1], Kindai Univ.[2], JST PRESTO[3], Kasetsart Univ.[4], Chulalongkorn Univ.[5])

11. **Computational Insights on Iron-Catalyzed Enantioselective Carbometalation of Azabycyclic Alkenes**
○Akhilesh K. Sharma[1], W. M. C. Sameera[1], M. Nakamura[2], and K. Morokuma[1] (FIFC[1], Dept. of Energy and Hydrocarbon Chem., Grad. School of Eng., Kyoto Univ.[2])

12. **Theoretical Study on Oxidative Addition of Nitrobenzene to Palladium(0)-Brettphos Complex**
○Rong-Lin Zhong[1], Masahiro Nagaoka[2], Yoshiaki Nakao[2], and Shigeyoshi Sakaki[1] (FIFC [1], Grad. School of Eng., Kyoto Univ.[2])

13. **Rational design of phenoxazine-based thermally activated delayed fluorescent materials with high performance**
○Jing Lu[1,2], Yiying Zheng[2], and Jingping Zhang [2] (FIFC [1], Northeast Normal Univ. [2])

14. **Characteristic Features Transmetallation of Pd(II)–Ph Complex with Cu(I)–alkyl Complexes: Theoretical Study**
○Hong Zheng[1], Kazuhiko Semba[2], Yoshiaki Nakao[2], and Shigeyoshi Sakaki[1] (FIFC [1], Dept. of Mat. Chem., Kyoto Univ.[2])

15. **三中心多重金属結合を持つクロム(II)三核錯体の構造と電子状態**
○中垣 雅之[1]、中谷 直輝[2]、長谷川 淳也[2]、榊 茂好[1]（京大福井セ[1]、北大触媒研[2]）

16. **金(I)-イソシアニド錯体の吸収・発光スペクトル：QM/MM 法による分子結晶効果の研究**
○青野 信治、榊 茂好（京大福井セ）

17. **高強度パルスレーザー場中のイオン化過程の非断熱電子ダイナミックス**
○松岡 貴英、高塚 和夫（京大福井セ）

18. **浮動ガウシアン基底を用いた水素分子の原子核−電子波動関数における非断熱ダイナミクスの研究**
○市川 雄一[1]、加藤 毅[2]、山内 薫[2]（京大福井セ[1]、東大院理[2]）

19. **Photoinduced Charge Separation Catalyzed by Mn-Oxides onto a Y-shaped Branching Acceptor Efficiently Preventing Charge Recombination**
○Kentaro Yamamoto and Kazuo Takatsuka (FIFC)

20. **液体の統計力学と原子間力顕微鏡で見るカルサイト上の三次元水和構造**
○天野 健一[1]、宮澤 佳甫[2]、西 直哉[1]、福間 剛士[2]、作花 哲夫[1]（京大院工[1]、金大院自然[2]）

21. **キラルネマチック相を示す液晶性イオン液体の合成と不斉電解重合への応用**
○和田 浩平、山川 勝平、赤木 和夫（京大院工）

22. **キラル側鎖を有するポリジフェニルアセチレン誘導体の合成と光学特性**
○松山 大起、大田 冬木、赤木 和夫（京大院工）

23. **π–π 相互作用と水素結合を利用した芳香族共役系ポリマー凝集体の構築とその光学特性**
○原田 恭佑、野津 賢祐、赤木 和夫（京大院工）

24. **メソポーラスシリカで被覆したアルミニウムナノ粒子アレイのプラズモン特性と薄膜内への光閉じ込め**
○阪本 浩之[1]、村井 俊介[1,2]、藤田 晃司[1]、田中 勝久[1]（京大院工[1]、JST さきがけ[2]）

25. **Why Na Cannot Be Intercalated into Graphite**
○大田 航[1]、Maxim Shishkin[2]、佐藤 啓文[1,2]（京大院工[1]、京大 ESICB[2]）

26. **HIV-1 protease に関する理論的研究**
○金曽 将弘、林 重彦（京大院理）

27. **液体ピレンの分子動力学シミュレーションと理論的解析**
○山本 裕生[1]、Lu Fengniu[2]、中西 尚志[2]、林 重彦[1]（京大院理[1]、国際ナノアーキテクトニクス研究拠点[2]）

28. **光誘起チャネルロドプシンに関する理論研究**
○成 せい[1]、神谷 基司[2]、吉田 紀生[3]、林 重彦[1]（京大院理[1]、理研[2]、九大院理[3]）

29. **LOV 光受容タンパク質の光活性化機構の理論的研究**
○田口 真彦、成 鉞、東村 智佳、林 重彦（京大院理）

30. **Theoretical study on molecular mechanism of a light-driven ion transport of Halorhodopsin**
○小山 糧、長谷川 太祐、林 重彦（京大院理）

31. **周期的静電ポテンシャルを考慮した埋め込みクラスターモデルの開発**
○松井 正冬[1]、榊 茂好[1,2]（京大 ESICB[1]、京大福井セ[2]）

32. Theoretical Study of NO–CO Reaction on Cu_{38} Cluster

○ Nozomi Takagi[1], Kazuya Ishimura[2], Ryoichi Fukuda[1], Masahiro Ehara[1,2], and Shigeyoshi Sakaki[1,3] (ESICB, Kyoto Univ.[1], IMS[2], FIFC[3])

33. Adsorption of CO_2 and C_2H_2 in a Flexible Porous Coordination Polymer: QM and Classical Monte-Carlo Study

○Jia-Jia Zheng[1,2], Shinpei Kusaka[1], Ryotaro Matsuda[1,3], Susumu Kitagawa[1], and Shigeyoshi Sakaki[2] (iCeMS[1], FIFC[2], Grad. School of Eng., Nagoya Univ.[3])

34. 光駆動イオン輸送型ロドプシンのイオン輸送メカニズムの解明

○宮原 友夫、中辻 博（量子化学研究協会研究所）

35. 太陽電池設計のための非断熱分子動力学シミュレーションの実装

○嶺澤 範行（理研 AICS）

36. TD-DFT 法を用いた $Ir(ppy)_3$ 錯体およびその類縁体の光吸収特性に関する理論研究

○名取 圭紀、浅岡 瑞稀、北河 康隆、中野 雅由（阪大院基礎工）

37. Theoretical study on third-order nonlinear optical property of carbon-bridged oligo para-phenylenevinylene (COPV)

○Yusuke Nishigaki[1], Hiroshi Matsui[1], Tsuji Hayato[2], and Masayoshi Nakano[1] (Grad. School of Eng. Sci., Osaka Univ.[1], Faculty of Sci., Kanagawa Univ.[2])

38. イリジウム二核錯体を用いる第一級アルコールの酸化反応に関する理論的研究

○瀬川 実礼[1]、畑中 美穂[1,2]、中井 英隆[1]、若林 知成[1]（近大理工[1]、JST さきがけ[2]）

39. 不斉亜鉛錯体を触媒とするアルドール反応の立体選択性発現機構の解明

○日下部 彩[1]、畑中 美穂[1,2]、若林 知成[1]（近大理工[1]、JST さきがけ[2]）

40. P=P double bond cleavage by N-heterocyclic carbenes

Naoki Hayakawa[1], Kazuya Sadamori[1], Shota Tsujimoto[1], ○ Miho Hatanaka[1,2], Tomonari Wakabayashi[1], and Tsukasa Matsuo[1] (Kindai Univ.[1], JST PRESTO[2])

５．福井センターセミナー　ポスター・プログラム

第14回
福井センターセミナー (春季)

The 14th Fukui Center Seminar-Spring

2016年4月13日(水) 13:30-17:00
April 13, 2016

〒606-8103 京都市左京区高野西開町34-4 (TEL: 075-711-7708)
京都大学福井謙一記念研究センター (1階106室）

Fukui Institute for Fundamental Chemistry (1F, room 106)
Kyoto Univ. (http://www.fukui.kyoto-u.ac.jp/)

13:30～14:20 Takahiro Sasamori (Kyoto Univ.)
"What is the Difference of Multiple Bonds between Carbon and heavier Group 14 Elements?"

14:20～15:10 Atsushi Wakamiya (Kyoto Univ.)
"Materials Design for Highly Efficient Perovskite Solar Cells"

15:10～15:25 Break

15:25～16:15 Hideki Yorimitsu (Kyoto Univ.)
"Journey from Discovery of New Pummerer Chemistry to Catalytic C-S Bond Cleavage"

16:15～17:00 Shigeyoshi Sakaki (Kyoto Univ.)
"The Present and Future of Molecular Theory and Calculations in Transition Metal Chemistry"

皆様のご来場を歓迎します
We welcome all of you to join.

６．複雑・複合系の理論計算科学に関する日・仏・スペイン合同シンポジウムを開催

雑・複合系の理論計算科学に関する 日・仏・スペイン合同シンポジウム

日　程

2016年10月26日（水）～ 28日（金）

場　所

京都大学福井謙一記念研究センター（〒606-8103 京都府京都市左京区高野西開町34-4）

趣　旨

理論計算科学は、理論的手法、計算機、計算アルゴリズムの進歩により、長足の発展を遂げ、今や化学、物理、生命科学分野の研究で欠くことの出来ない研究手法となっている。特に、実験的な手段が限られている複雑・複合系の研究分野では、理論計算科学への期待が大きい。たとえば、化学分野では触媒が、物理分野では無限系と孤立系が相互作用している複合系、金属と複合金属クラスターの境界などがその例である。生命科学では、酵素や細胞などが化学、物理から見た場合の複雑・複合系である。これらの研究対象は、化学、物理、生命科学の中で互いに離れているが、その理論計算科学的手法には共通性も多く、理論計算を中心とした領域融合は、これらの研究に大きな成果を生み出すはずである。本学は、福井謙一博士の存在により、特に化学および生命科学分野で計算科学研究が歴史的に盛んであり、わが国はもとより世界レベルで先導的な研究を進めてきた。本シンポジウムは、わが国の窓口となり、わが国の若手、中堅研究者に、フランス、スペインからの若手、中堅研究者を加え、複雑・複合系に関する理論計算科学に関する研究成果を互いに紹介しあい、理論計算科学を機軸とする融合研究の更なる展開を目指し、このシンポジウムを企画した。将来的には、より多くの国と国際連携も広げる予定である。

内　容

Plenary Talk, Invited Talk, Poster Session を行います。Speaker（別ページ）と Program（PDF）はそれぞれのリンクをご参照ください（2016/10/22 更新）。

Poster Session (PDF)の発表者一覧を作成しました（2016/10/22 更新）。

ポスターセッション詳細

お申し込み期限は9月23日（金）

題目、発表者氏名〔所属〕、連絡先、Poster Short Talk 希望の有無を記載し、要旨（word-file と pdf-file 双方）と共に JFSsymp@fukui.kyoto-u.ac.jp にメールをお送りください。

要旨は例をダウンロードして、それを書きつぶして、作成ください。

Poster Short Talk は件数が限られていますので、御希望に添えない場合があります。御了承ください。

要旨の例は右をクリックしてください： Abstract_Example (word-file)
なお、ポスターボードのサイズはA0縦型です（2016/10/22更新）。

参加申し込み

お名前、御所属、連絡先、懇親会参加の有無を記載したメールを JFSsymp@fukui.kyoto-u.ac.jp にお送りください。

参加費

10,000円 〔当日会場にてお支払いください〕
学生、博士研究員の方には免除制度(*)がございますので、申請の際はメールに「参加費免除希望」とご記入ください（2016/09/24更新)。
(*)対象： 所属機関にて支払い可能な財源をお持ちでない方

懇親会

10月27日（木）夕方を予定しています（当センターにて開催します)。
会費：5,000円 （当日会場にてお支払いください）

組織委員会

Honorary Chair: Keiji Morokuma
International Committee Members:
Odile Eisenstein, Feliu Maseras, Koichi Yamashita, Shigeyoshi Sakaki

実行委員会（Local Committee Members）

江原正博、榊 茂好、佐藤啓文、高塚和夫、長岡正隆、永瀬 茂、長谷川淳也、林 重彦、山下晃一、吉澤一成 （敬称略）

連絡先

京都大学福井謙一記念研究センター 榊茂好
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７．日本－ブラジル　理論化学・計算化学交流会を開催

日本－ブラジル　理論化学･計算化学交流会を開催

趣　旨

JSPSとサンパウロ研究財団（São Paulo Research Foundation : 略称FAPESP）のサポートにより、JSPS-FAPESP Joint Research Workshop として国際シンポジウム”Multi-scale Simulation of Condensed-phase Reacting Systems 2016″（MSCRS2016)が名古屋大学で開催されます。

その一環として、ブラジルからの参加者が京都大学福井謙一記念研究センター（FIFC）を訪問して当センターを見学すると共に、センター研究者と理論化学･計算化学に関する研究紹介と意見・情報交換を行います。

日　時

2016年10月13日〔木〕　9:30から12:45まで

場　所

京都大学福井謙一記念研究センター（〒606-8103 京都府京都市左京区高野西開町34-4）多目的室（参加者が多い場合、３階大ホール）

プログラム

09:30　FIFC到着;会場へ
09:40　開会挨拶（FIFCセンター長代理；田中一義先生）
09:50　挨拶と講演　Prof. Sylvio Canuto（ブラジル側代表、サンパウロ大教授）
10:50　講演　榊　茂好（FIFC）
11:20　講演　永瀬　茂（FIFC）
11:50　閉会挨拶　（長岡正隆名大教授）
12:00　記念撮影
12:15　センター見学
12:45　交流会終了

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（無断転載を禁ず）

Fukui Institute for Fundamental Chemistry Kyoto University

Annual Report 2016