PHYSICAL ORGANIC CHEMISTRY

Annual Research Highlights

(1) "Effect of Electron-vibration Coupling in Electron Transfer through Rigid Planar COPV"

We have recently developed a rigid planar π-electron system, carbon-bridged oligo(*p*-phenylenevinylene)s (COPVs), that possess unique photophysical and electronic properties as well as high stability. To examine the electron transfer ability through COPVs, we have synthesized a zinc porphyrin (electron donor)–COPV*n*–C_{60} (electron acceptor) conjugate (**ZnP–COPV*n*–C_{60}**), and studied dynamics in the excited-state in collaboration with Prof. Guldi's group in FAU, Germany. We found that charge separation (CS) and charge recombination (CR) rates were enhanced by 6.5 and 840 times, respectively, compared to phenylenevinylene-linked counterparts. The significant increase in the CR rate has been rationalized by the contribution of electron-vibration coupling as indicated in the semi-classical Marcus formalism, which has been clearly observed in the present experiments.

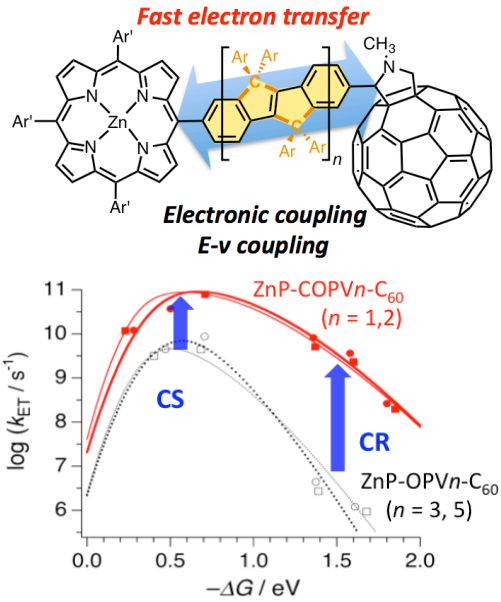

Fig. 1 Structure of porphyrin-COPV-C_{60} conjugates and semi-classical Marcus plot that indicates the contribution of electron-vibration coupling in the Marcus inverted region
1. (1)-4) *Nat. Chem.*, **6**, 899 (2014).

(2) "Iron-Catalyzed C-H Functionalization with Organoboranes"

We discovered that an inexpensive and non-toxic iron salt and a diphosphine ligand catalyze the reaction of a carboxamide bearing a bidentate directing group with an organoborate, in the presence of and a crucial Zn(II) additive that promotes the difficult iron/boron transmetalation. The key to the success of this reaction is the creation of a high-valent iron catalyst by the design of the directing group, diphosphine ligand, and mild organoborate reagent. This catalyst surpasses the versatility of any other catalyst to date, and a large variety of substrates could be coupled, including the unprecedented stereospecific alkenylation of an alkenamide to yield stereodefined dienes and alkenes.

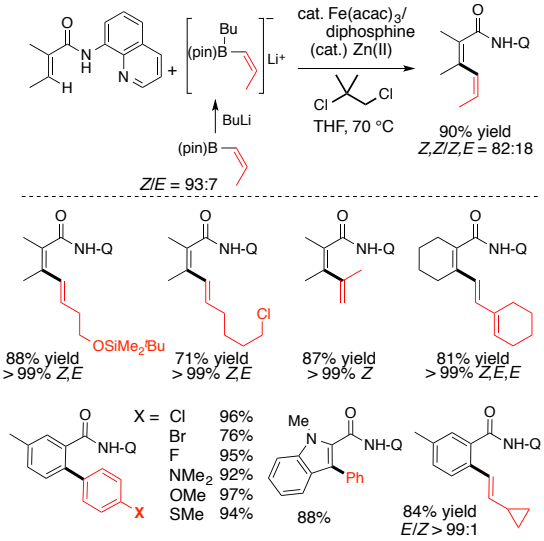

Fig. 2 Iron-catalyzed reaction of carboxamides with organo-boron compounds via directed C–H bond activation.
1.(1)-2) *J. Am. Chem. Soc.*, **136**, 14349 (2014).

(3) "Conformational Analysis of Single Alkyl Chains by Electron Microscopy"

After discovery of the gauche conformation of 1,2-dichloroethane by San-ichiro Mizushima, et al., conformational analysis of organic molecules is based on time- and molecular-average as determined for ensembles. In the current work, we demonstrated a proof-of-principle study of the determination of the conformation of each C−C bond in single alkyl and perfluoroalkyl fullerene molecules encapsulated in a single-walled carbon nanotube. Analysis of 82 individual molecules indicated that 6% of the CF_2−CF_2 bonds and about 20% of the CH_2−CH_2 bonds in the corresponding hydrocarbon analogue are in the gauche conformation. We expect that the experimental protocol reported here will serve as a standard model for future study of the static and dynamic behaviors of organic molecules

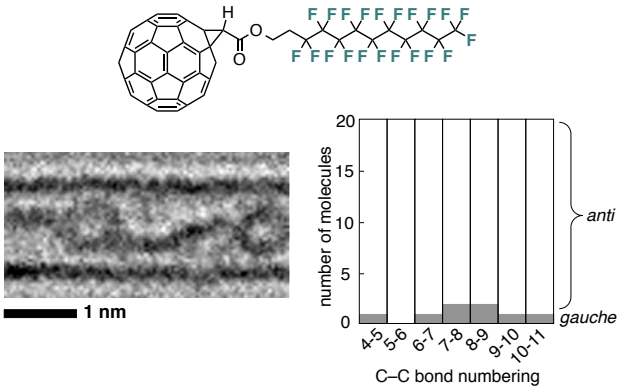

Fig. 3 Transmission electron microscopic image of a perfluorofullerene molecule in a single-walled carbon nanotube and anti/gauche ratio of individual C-C bonds.
1.(1)-21) *J. Am. Chem. Soc.*, **136**, 466-473 (2014).

物理有機化学研究室

研究ハイライト

(1) 剛直平面構造を有する炭素架橋 *p*-フェニレンビニレン（COPV）をリンカーとした光誘起電子移動系における振電相互作用の発現

我々は以前に剛直な平面構造を有する炭素架橋オリゴフェニレンビニレン化合物 COPV を独自に開発し，強い光吸収等の興味深い光物性と高い安定性など様々な興味深い物性を有することを見出している．今回，亜鉛ポルフィリン（電子供与体）と C_{60}（電子受容体）を COPV で連結した **ZnP–COPV*n*–C$_{60}$** を合成し，光誘起電子移動の研究を Guldi 教授（ドイツ，FAU）らとの共同研究で行った．その結果，電荷分離(CS)および電荷再結合(CR)速度が，対応する非架橋フェニレンビニレンで連結した系に比べてそれぞれ 6.5 倍，840 倍も加速されることを見出した．電荷再結合の顕著な加速は，半古典的マーカス理論に示される振電相互作用の発現によるものと考えられ，実験的に観測された例として注目されている．

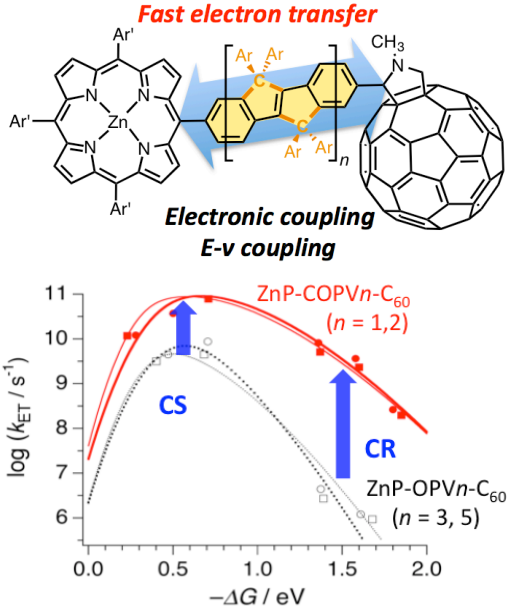

図 1　ポルフィリン–COPV–C_{60} 連結分子の構造と半古典的 Marcus プロット
1. (1)-4) *Nat. Chem.*, **6**, 899 (2014).

(2) 鉄触媒下の有機ホウ素による C–H 官能基化反応

鉄触媒による炭素–水素結合の，有機ホウ素化合物との直裁的な反応を実現した．すなわち，触媒量の鉄錯体とホスフィン配位子を用いることで，二座配位可能なアミドを配向基として有するアレーンおよびアルケンが様々な有機ホウ素化合物と反応し，高収率でクロッスカップリング体を与えることを見出した．この触媒系を用いることにより，ジエン，トリエン，スチレン類など，これまでパラジウムなどの貴金属を用いては達成できなかった様々な不飽和共役化合物の合成が可能になった．この反応の鍵は，二座配向基とジホスフィン配位子による鉄活性種の安定化および触媒量の亜鉛(II)を用いることで有機ホウ素中間体から鉄触媒へのトランスメタル化が温和な条件下で進行することである．

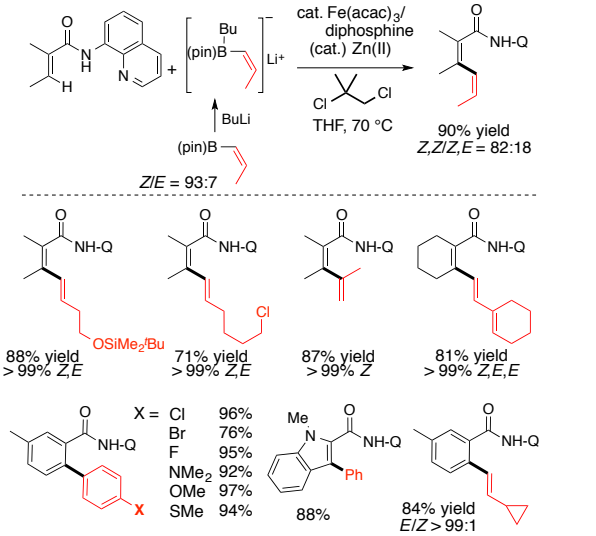

図 2　鉄触媒によるアミドと有機ホウ素化合物とのカップリング反応
1.(1)-2) *J. Am. Chem. Soc.*, **136**, 14349 (2014).

(3) 電子顕微鏡による単一炭化水素鎖の配座解析

水島三一郎らによる 1,2-ジクロロエタンのゴーシュ配座の発見以来，有機分子の立体配座解析は集団としての分子の時間および空間平均の観察に基づいて行われてきた．我々は，高分解能透過電子顕微鏡を用いて個々の炭化水素鎖に対する炭素-炭素結合レベルでの構造解析が可能であることを実証した．アルキル基およびパーフルオロアルキル基を結合したフラーレン分子をカーボンナノチューブに内包し 82 個の分子に対して統計解析を行った結果，CF_2-CF_2 結合の方が CH_2-CH_2 結合よりも *anti* 配座が優勢であることが示された．本手法では配座変換の実時間観察も可能であり，有機分子の静的構造および動的挙動を研究する新しい実験手法として期待される．

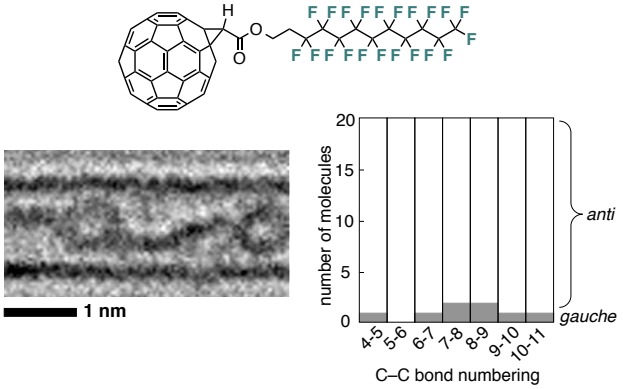

図 3　パーフルオロアルキルフラーレン分子の透過電子顕微鏡像，および各炭素-炭素結合の *anti*/*gauche* 比．
1.(1)-21) *J. Am. Chem. Soc.*, **136**, 466-473 (2014).

1. 原著論文

(1) Refereed Journals

1) Ferromagnetic Ordering in Superatomic Solids, C.-H. Lee, L. Liu, C. Bejger, A. Turkiewicz, T. Goko, C. J. Arguello, B. A. Frandsen, S. C Cheung, T. Medina, T. J. S. Munsie, R. D'Ortenzio, G. M. Luke, T. Besara, R. A. Lalancette, T. Siegrist, P. W. Stephens, A. C. Crowther, L. E. Brus, Y. Matsuo, E. Nakamura, Y. J. Uemura, P. Kim, C. Nuckolls, M. L. Steigerwald, X. Roy, *J. Am. Chem. Soc.*, **136**, 16926-16931 (2014).
2) Iron-catalyzed C(sp^2)–H Bond Functionalization with Organoboron Compounds, R. Shang, L. Ilies, S. Asako, and E. Nakamura, *J. Am. Chem. Soc.*, **136**, 14349-14352 (2014).
3) Hydrogen/deuterium isotope effect of the host material on the lifetime of organic light-emitting diodes, H. Tsuji, C. Mitsui, E. Nakamura, *Chem. Commun.*, **50**, 14870–14872 (2014).
4) Electron transfer through rigid organic molecular wires enhanced by electronic and electron–vibration coupling, J. Sukegawa, C. Schubert, X. Zhu, H. Tsuji, D. M. Guldi, E. Nakamura, *Nat. Chem.*, **6**, 899–905 (2014).
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6) Iron-Catalyzed Directed Alkylation of Aromatic and Olefinic Carboxamides with Primary and Secondary Alkyl Tosylates, Mesylates, and Halides, L. Ilies, T. Matsubara, S. Ichikawa, S. Asako, E. Nakamura, *J. Am. Chem. Soc.*, **136**, 13126-13129 (2014).
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8) siRNA Delivery Targeting to the Lung via Agglutination-Induced Accumulation and Clearance of Cationic Tetraamino Fullerene, K. Minami, K. Okamoto, K. Doi, K. Harano, E. Noiri, E. Nakamura, *Sci. Rep.*, **4**, 4916 (2014).
9) *ortho*-Allylation of 1-Arylpyrazoles with Allyl Phenyl Ether *via* Iron-Catalyzed C-H Bond Activation under Mild Conditions, S. Asako, J. Norinder, L. Ilies, N. Yoshikai, E. Nakamura, *Adv. Synth. Catal.*, **356**, 1481-1485 (2014).
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11) Formation of a Polycrystalline Film of Donor Material on PEDOT:PSS Buffer Induced by Crystal Nucleation, K. Harano, S. Okada, S. Furukawa, H. Tanaka, E. Nakamura, *J. Polym. Sci. Part B: Polym. Phys.*, **52**, 833-841 (2014).
12) Photo-cross-linking of Exterior of Fullerene Bilayer that Prevents Vesicle Aggregation, K. Harano, A. Narita, E. Nakamura, *Chem. Lett.*, **43**, 877-879 (2014).
13) Mobility of Long-Lived Fullerene Radical in Solid State and Nonlinear Temperature Dependence, Y. Abe, H. Tanaka, Y. Guo, Y. Matsuo, E. Nakamura, *J. Am. Chem. Soc.*, **136**, 3366-3369 (2014).
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15) Synthesis of Polysubstituted Enynes via Iron-Catalyzed Carbomagnesiation of Conjugated Diynes, L. Ilies, T. Yoshida, E. Nakamura, *Synlett*, **25**, 527-530 (2014).
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17) Large Electronic Coupling in a Homoconjugated Donor-Acceptor System Involving Carbon-Bridged Oligo-*p*-Phenylenevinylene and Triazine, J. Sukegawa, H. Tsuji, E. Nakamura, *Chem. Lett.*, **43**, 699-701 (2014).
18) Synthesis of Triphosphatruxene via Sextuple Aromatic Nucleophilic Substitution and Simple Isolation of Stereoisomers, T. Kojima, S. Furukawa, H. Tsuji, E. Nakamura, *Chem. Lett.*, **43**, 676-677 (2014).
19) Unraveling Organocuprate Complexity: Fundamental Insights into Intrinsic Group Transfer Selectivity in Alkylation Reactions, N. J. Rijs, N. Yoshikai, E. Nakamura, R. A. J. O'Hair, *J. Org. Chem.*, **79**, 1320-1334 (2014).

20) Synthesis of Anthranilic Acid Derivatives through Iron-Catalyzed Ortho Amination of Aromatic Carboxamides with *N*-Chloroamines, T. Matsubara, S. Asako, L. Ilies, E. Nakamura, *J. Am. Chem. Soc.*, **136**, 646-649 (2014).
21) Conformational Analysis of Single Perfluoroalkyl Chains by Single-Molecule Real-Time Transmission Electron Microscopic Imaging, K. Harano, S. Takenaga, S. Okada, Y. Niimi, N. Yoshikai, H. Isobe, K. Suenaga, H. Kataura, M. Koshino, E. Nakamura, *J. Am. Chem. Soc.*, **136**, 466-473 (2014).
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(2) その他

2. 総説・解説

1) Synthetic Strategy for Multisubstituted Fused Furan Compounds Using Main-Group Metal Reagents, H. Tsuji, L. Ilies, E. Nakamura, *Synlett,* **25**, 2099–2110 (2014).
2) Iron-Catalyzed Cross-Coupling Reactions, E. Nakamura, T. Hatakeyama, S. Ito, K. Ishizuka, L. Ilies, M. Nakamura, *Organic Reactions*, **83**, 3-209 (2014).

3. 著書

1) 鉄化合物を触媒とする有機合成化学，イリエシュ　ラウレアン，中村栄一,「鉄の事典」，朝倉書店 2014年; pp 234–241.
2) Iron-Catalyzed Cross-Coupling Reactions, L. Ilies, E. Nakamura, in *The Chemistry of Organoiron Compounds*, Eds.: I. Marek and Z. Rappoport, pp 539–567, John Wiley&Sons, Ltd.: Chichester, UK (2014).