

PHYSICAL ORGANIC CHEMISTRY

Annual Research Highlights

(1) “Stable Materials that Exhibit Near-Infrared Light Absorption and Emission”

Near-infrared absorbing and emitting dyes are expected to be useful in various fields, such as organic solar cells, chemotherapy, and *in-vivo* deep tissue imaging. We have succeeded in developing stable near-infrared absorptive and emitting compounds **TQ** (Fig 1). **TQ** can be depicted using two resonance structures: a cumulated *p*-quinodimethane form and open-shell biradical forms. Thus, **TQ** appears to be unstable but it is actually very stable in solid state for more than one year. This stability may result from the effect of the cross-linking carbon atoms shown in blue color in the figure and the terminal cyano groups (CN). Measurement of the photophysical properties of **TQ** revealed that the compound exhibits the longest wavelength absorption maximum at a wavelength of 1,100 nm in the near-infrared region and the emission maximum at a wavelength of 1,179 nm. It has also been revealed that the optical absorption and emission of **TQ** change in the visible region when the compound is chemically or electrically reduced. These near-infrared absorption and emission characteristics and the switching phenomenon of optical properties upon redox will be utilized in various fields.

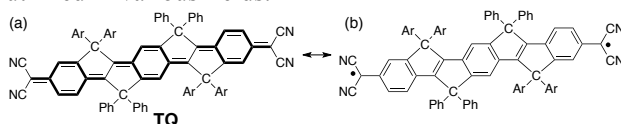


Fig. 1 Resonance Structures of NIR-absorbing/emitting dye **TQ**

1.(1)-20) *J. Am. Chem. Soc.*, **133**, 16342 (2011).

(2) “Iron-Catalyzed C–C Bond Formation via C–H Activation under Mild Conditions”

Similar to crude oil, our society is facing a crisis of chemical elements’ supply, which has led to our proposal for a national policy of “element strategy”. Iron has been receiving much attention for catalysis because it is ubiquitous, inexpensive and non-toxic. Moreover, organoiron species show very high reactivity and unique selectivities. We showed that under oxidative iron catalysis, a Grignard reagent can arylate the C–H bond of an alkene possessing a directing group at 0 °C within 5 minutes (Fig. 2a). We could control the stereoselectivity of the reaction by simply changing the solvent. We also showed that an alkyne can be annulated with a biphenyl donor in the presence of an iron catalyst and an oxidant to produce a variety of disubstituted phenanthrenes at room temperature (Fig. 2b). This reaction proceeds through mild C–H activation to generate an unprecedented biphenylferracycle. These reactions will find applications for the synthesis of stereodefined polysubstituted alkenes and for the creation of fused aromatic compounds under mild conditions using sustainable iron catalysis.

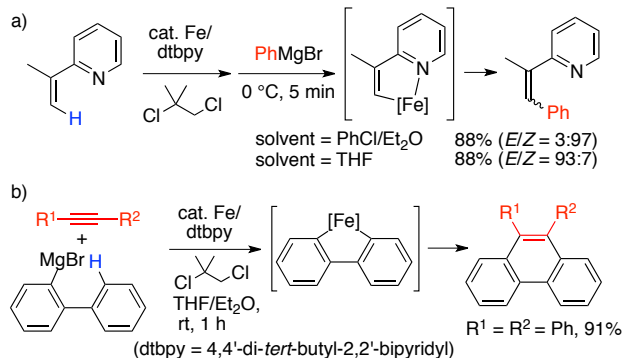


Fig. 2 Iron-catalyzed C–H functionalization under mild conditions: a) Stereospecific arylation of alkenes; b) [4+2] Annulation to produce disubstituted phenanthrenes.

1.(1)-10) *J. Am. Chem. Soc.*, **133**, 7672 (2011).

1.(1)-5) *J. Am. Chem. Soc.*, **133**, 6557-6559 (2011).

(3) “Functional Fullerenes at Interface”

Chemically-modified fullerenes self-assemble in solution and on solid surfaces to produce new functional heterointerfaces. We have demonstrated that nonpolar/polar/nonpolar fullerene amphiphiles form bilayer vesicles in water and provide a hydrophobic environment at the interface with aqueous phase (Fig. 3a). The vesicles are very robust and maintain their spherical shape on a solid substrate. Self-assembled monolayer (SAM) of functional fullerenes on an inorganic electrode also showed unique properties. For example, the work function of indium-tin oxide (ITO) can be tuned by using umbrella-shaped fullerene derivatives, through the effect of their molecular dipoles (Fig. 3b). We also developed a device that generates bidirectional photocurrent upon irradiation with different wavelength of light, by making SAM of two fullerene molecules on ITO.

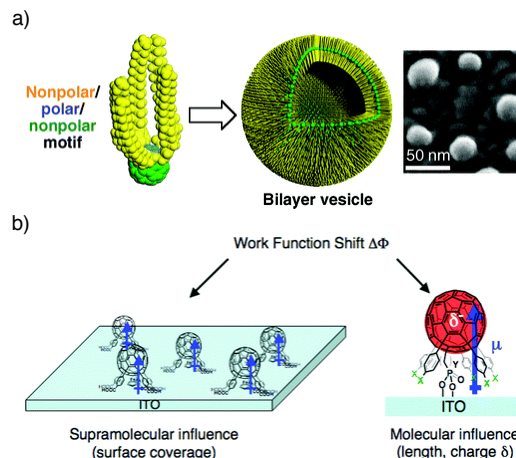


Fig. 3 (a) Formation of bilayer vesicles from nonpolar/polar/nonpolar fullerene amphiphiles. (b) Control of the work function of an electrode with self-assembled monolayer of umbrella-shaped fullerene derivatives.

1.(1)-4) *J. Am. Chem. Soc.*, **133**, 6364 (2011).

1.(1)-13) *J. Am. Chem. Soc.*, **133**, 9932 (2011).

1.(1)-21) *J. Am. Chem. Soc.*, **133**, 16997 (2011).

物理有機化学研究室

研究ハイライト

(1) 近赤外吸収・発光をもつ安定ピラジカル化合物

近赤外吸収・発光色素は、有機太陽電池などのエネルギー変換材料や、化学療法、生体内の深部組織のイメージングなどの生体材料など、多様な応用が期待されている。我々は炭素架橋オリゴフェニレンピニレン化合物 (COPV, 図 1) をプラットフォームに用いることで、安定な近赤外吸収・発光性化合物を開発することに成功した。

化合物 (以下 **TQ** と略す) は、図 1 a に示すような *p*-キノジメタンと呼ばれる不安定なユニットが 3 つ連結した極限構造と、図 1 b に示すような開殻系とよばれる一般に不安定な極限構造の重ね合わせの状態をもっている。このような不安定そうな構造をもつにもかかわらず、実際には **TQ** は非常に安定であり、固体状態であれば空气中で 1 年以上も変化しない。これは、図中青で示した架橋炭素原子と末端シアノ基 (CN) の安定化効果によるものである。光物性測定から、**TQ** は近赤外領域の 1,100 nm に最長吸収極大と 1,179 nm に発光極大を示すことを見いだした。さらに、**TQ** は化学的または電気的な還元により、吸収と発光が可視領域に変化することも見いだした。このような近赤外吸収・発光特性や酸化還元による光物性のスイッチング現象を利用した多方面への応用が期待される。

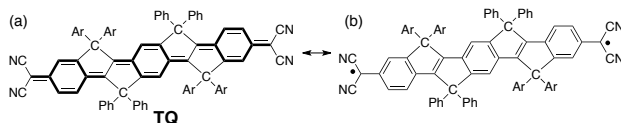


図 1 近赤外吸収・発光性化合物 **TQ** の共鳴構造

1.(1)-20) *J. Am. Chem. Soc.*, **133**, 16342 (2011).

(2) 温和な条件下での炭素-水素結合活性化を経た鉄触媒炭素-炭素結合生成反応の開発

鉄は地殻中に最も豊富に存在する遷移金属元素であり、また安価かつ無毒であることから、次世代の環境調和型有機合成および我々が提案した「元素戦略」に最も適切な元素として注目を集めている。我々は鉄触媒を用いた、グリニヤール試薬と配向基を有するオレフィン炭素-水素結合の酸化的アリール化反応が 0°C において 5 分で完結することを見出した。本反応の立体選択性は溶媒により容易に制御できる (図 2a)。さらに我々は鉄触媒と酸化剤を用いたピフェニルグリニヤール試薬とアルカンによる様々な置換基を有する二置換フェナントレン合成法を開発した。本反応の中間体として、室温という非常に温和な条件下炭素-水素結合活性化を経て生成する前例のないピフェニルフェラサイクルの存在が示唆されている。

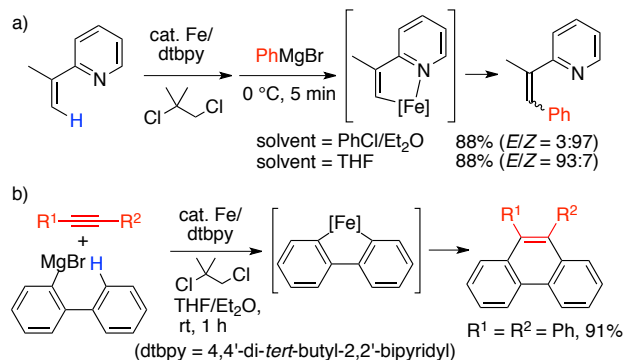


図 2 鉄触媒による温和な条件下における炭素-水素結合官能基化

1.(1)-10) *J. Am. Chem. Soc.*, **133**, 7672 (2011).

1.(1)-5) *J. Am. Chem. Soc.*, **133**, 6557-6559 (2011).

(3) 化学修飾フラーレンが生み出す機能性界面

適切な化学修飾を施したフラーレンは溶液中や固体表面で自己組織化し、新たな界面機能を生み出す。我々は疎水-親水-疎水の三元型構造をもった両親媒性フラーレンが水中で自発的に集合して二重膜ベシクルを形成し、従来の分子膜ではみられない「水相に呈示された疎水性表面」という特殊な界面環境を生み出すことを明らかにした (図 3a)。これらのベシクルは安定で固体表面上でも形状を保つことが出来る。一方、無機電極表面にアンブレラ型フラーレンの単分子膜を作製することで、分子が持つ双極子の効果によりマクロな性質である仕事関数や接触角の制御が可能になった (図 3b)。また、二種類のフラーレン分子から電極上に単分子膜を作製することで、異なる波長の光に応答して光電流の発生方向を制御可能な光電変換素子を作製することにも成功した

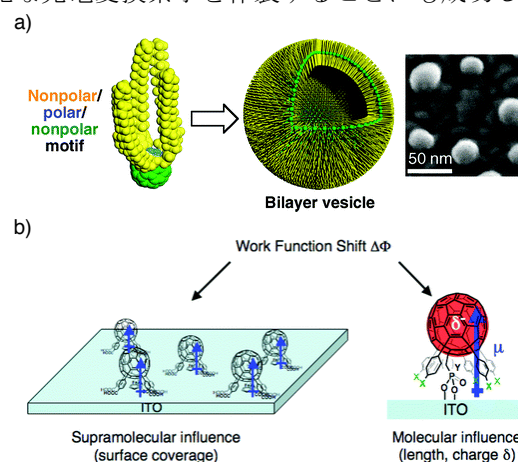


図 3 (a)三元型フラーレン両親媒性分子の自己組織化による二重膜ベシクル形成 (b)アンブレラ型フラーレンの透明電極表面への配列化による仕事関数制御

1.(1)-4) *J. Am. Chem. Soc.*, **133**, 6364 (2011).

1.(1)-13) *J. Am. Chem. Soc.*, **133**, 9932 (2011).

1.(1)-21) *J. Am. Chem. Soc.*, **133**, 16997 (2011).

1. 原著論文

(1) Refereed Journals

- 1) Y. Itoh, B. Kim, R. I. Gearba, N. J. Tremblay, R. Pindak, Y. Matsuo, E. Nakamura, and C. Nuckolls, "Simple Formation of C₆₀ and C₆₀-Ferrocene Conjugated Monolayers Anchored onto Silicon Oxide with Five Carboxylic Acids and Their Transistor Applications", *Chem. Mater.*, **23**, 970-975 (2011).
- 2) Q. Chen, L. Ilies, and E. Nakamura, "Cobalt-Catalyzed *ortho*-Alkylation of Secondary Benzamide with Alkyl Chloride through Directed C–H Bond Activation", *J. Am. Chem. Soc.*, **133**, 428-429 (2011).
- 3) L. Ilies, Q. Chen, X. Zeng, and E. Nakamura, "Cobalt-Catalyzed Chemoselective Insertion of Alkene into the Ortho C–H Bond of Benzamide", *J. Am. Chem. Soc.*, **133**, 5221-5223 (2011).
- 4) T. Homma, K. Harano, H. Isobe, and E. Nakamura, "Preparation and Properties of Vesicles Made of Nonpolar/Polar/Nonpolar Fullerene Amphiphiles", *J. Am. Chem. Soc.*, **133**, 6364-6370 (2011).
- 5) A. Matsumoto, L. Ilies, and E. Nakamura, "Phenanthrene Synthesis by Iron-Catalyzed [4 + 2] Benzannulation between Alkyne and Biaryl or 2-Alkenylphenyl Grignard Reagent", *J. Am. Chem. Soc.*, **133**, 6557-6559 (2011).
- 6) H. Tsuji, K. Yamagata, Y. Ueda, and E. Nakamura, "Indium-Catalyzed Synthesis of Furans and Pyrroles via Cyclization of α -Propargyl- β -keto Esters", *Synlett*, **7**, 1015-1017 (2011).
- 7) M. Maruyama, J.-D. Guo, S. Nagase, E. Nakamura, and Y. Matsuo, "Isolation of Planar Four-Membered Aromatic Systems by Using Confined Spaces of Cobalt Pentaaryl[60]fullerene Complexes", *J. Am. Chem. Soc.*, **133**, 6890-6893 (2011).
- 8) Y. Matsuo, Y. Zhang, I. Soga, Y. Sato, and E. Nakamura, "Synthesis of 1,4-Diaryl[60]fullerenes by Bis-Hydroarylation of C₆₀ and their Use in Solution-Processable", Thin-Film Organic Photovoltaic Cells, *Tetrahedron Lett.*, **52**, 2240-2242 (2011)
- 9) H. Tsuji, G. M. O. Favier, C. Mitsui, S. Lee, D. Hashizume, and E. Nakamura, "Mechanochromic and Color-change Properties of 2,6-Di(2-pyridyl)benzo[1,2-*b*:4,5-*b'*]difuran in the Solid and Solution", *Chem. Lett.*, **40**, 576-578 (2011).
- 10) L. Ilies, S. Asako, and E. Nakamura, "Iron-Catalyzed Stereospecific Activation of Olefinic C-H Bonds with Grignard Reagent for Synthesis of Substituted Olefins", *J. Am. Chem. Soc.*, **133**, 7672-7675 (2011).
- 11) H. Tsuji, C. Mitsui, Y. Sato, E. Nakamura, "Modular Synthesis and Photophysical and Electrochemical Properties of 2,3,5,6-Tetraaryl-Substituted Benzo[1,2-*b*:5,4-*b'*]difurans", *Heteroatom Chem.*, **22**, 316-324 (2011).
- 12) Y. Zhang, Y. Matsuo, C.-Z. Li, H. Tanaka, and E. Nakamura, "A Scalable Synthesis of Methano[60]fullerene and Congeners by the Oxidative Cyclopropanation Reaction of Silylmethylfullerene", *J. Am. Chem. Soc.*, **133**, 8086-8089 (2011).
- 13) Y. Matsuo, T. Ichiki, and E. Nakamura, "Molecular Photoelectric Switch Using a Mixed SAM of Organic [60]Fullerene and [70]Fullerene Doped with a Single Iron Atom", *J. Am. Chem. Soc.*, **133**, 9932-9937 (2011).
- 14) Q. Chen, L. Ilies, N. Yoshikai, and E. Nakamura, "Cobalt-Catalyzed Coupling of Alkyl Grignard Reagent with Benzamide and 2-Phenylpyridine Derivatives through Directed C-H Bond Activation under Air", *Org. Lett.*, **13**, 3232-3234 (2011).
- 15) H. Tsuji, Y. Yokoi, Y. Sato, H. Tanaka, and E. Nakamura, "Bis-Cinnolines as n-Type Semiconducting Material with High Electron Mobility and Thermal Stability and their Application in Organic Photovoltaic Cells", *Chem. Asian J.*, **6**, 2005-2008 (2011).
- 16) C. Mitsui, H. Tanaka, H. Tsuji, and E. Nakamura, "Bis(carbazolyl)benzodifuran has a High Triplet Energy Level for Application in Blue Phosphorescent OLED", *Chem. Asian J.*, **6**, 2296-2300 (2011).
- 17) E. Nakamura, M. Koshino, T. Saito, Y. Niimi, K. Suenaga, and Y. Matsuo, "Electron Microscopic Imaging of a Single Group 8 Metal Atom Catalyzing C-C Bond Reorganization of Fullerenes", *J. Am. Chem. Soc.*, **133**, 14151-14153 (2011).
- 18) C.-Z. Li, S.-C. Chien, H.-L. Yip, C.-C. Chueh, F.-C. Chen, Y. Matsuo, E. Nakamura, and A. K.-Y. Jen, "Facile Synthesis of a 56 π -electron 1,2-Dihydromethano-[60]PCBM and its Application for Thermally Stable Polymer Solar

Cells”, *Chem. Commun.*, 10082-10084 (2011).

- 19) N. Yoshikai, S. Asako, T. Yamakawa, L. Ilies, and E. Nakamura, “Iron-Catalyzed C-H Bond Activation for the ortho-Arylation of Aryl Pyridines and Imines with Grignard Reagents”, *Chem. Asian J.*, **6**, 3059-3065 (2011).
- 20) X. Zhu, H. Tsuji, K. Nakabayashi, S. Ohkoshi, and E. Nakamura, “Air- and Heat-Stable Planar Tri-p-quinodimethane with Distinct Biradical Characteristics”, *J. Am. Chem. Soc.*, **133**, 16342-16345 (2011).
- 21) S. Lacher, M. Matsuo, and E. Nakamura, “Molecular and Supramolecular Control of the Work Function of an Inorganic Electrode with Self-Assembled Monolayer of Umbrella-Shaped Fullerene Derivatives”, *J. Am. Chem. Soc.*, **133**, 16997-17004 (2011).
- 22) X. Zeng, L. Ilies, and E. Nakamura, “Synthesis of Functionalized 1H-Indenes via Copper-Catalyzed Arylative Cyclization of Arylalkynes with Aromatic Sulfonyl Chlorides”, *J. Am. Chem. Soc.*, **133**, 17638-17640 (2011).
- 23) Y. Nakamura, L. Ilies, and E. Nakamura, “Iron-Catalyzed Oxidative Monoarylation of Primary Amines with Organozinc Reagents”, *Org. Lett.*, **13**, 5998-6001 (2011).
- 24) Y. Zhang, Y. Matsuo, E. Nakamura, Regiocontrolled Synthesis of 1,2-Di(organo)fullerenes via Copper-Assisted 1,4-Aryl Migration from Silicon to Carbon, *Org. Lett.*, **13**, 6058-6061 (2011).
- 25) C.-Z. Li, Y. Matsuo, and E. Nakamura, “Regioselective Synthesis of Tetra(aryl)-Mono(silylmethyl)[60]fullerenes and Derivatization to Methanofullerene Compound”, *Tetrahedron*, **67**, 9944-9949 (2011).
- 26) P. A. Ulmann, H. Tanaka, Y. Matsuo, Z. Xiao, I. Soga, and E. Nakamura, “Electric Field Dependent Photocurrent Generation in a Thin-Film Organic Photovoltaic Device with a [70]fullerene-Benzodifuranone Dyad”, *Phys. Chem. Chem. Phys.*, **13**, 21045-21049 (2011).
- 27) N. Obata, Y. Sato, E. Nakamura, and Y. Matsuo, “Small-molecule-based organic photovoltaic devices covering visible and near-infrared absorption through phase transition of titanylphthalocyanine induced by solvent exposure”, *Jpn. J. Appl. Phys.*, **50**, 121603 (2011).

(2) その他

2. 総説・解説

- 1) Managing the Scarcity of Chemical Elements, E. Nakamura, K. Sato, *Nat. Mater.*, **10**, 158-161 (2011).
- 2) One Hundred Years since the Discovery of the "Umami" Taste from Seaweed Broth by Kikunae Ikeda, who Transcended his Time, E. Nakamura, *Chem. Asian J.*, **6**, 1659-1663 (2011).

3. その他

- 1) 日経産業新聞 (2011年8月23日) 「鉄原子1個の触媒作用 東大が動画撮影成功」
- 2) 日刊工業新聞Newsウェブ21 (2011年8月23日) 「鉄の触媒作用を直接観察-白金の燃料電池研究応用」