

PHYSICAL ORGANIC CHEMISTRY

Annual Research Highlights

(1) "Rigid Planar COPV for Dye-sensitized Solar Cells"

We have recently developed carbon-bridged *p*-phenylenevinylenes (COPVs) possessing rigid planar π -electron framework, and found unique photophysical and electronic properties as well as their high light, heat, and redox stabilities. Taking advantage of these properties, we applied COPVs to dye-sensitized solar cells and found improved power conversion efficiencies of up to 7.54%, which was higher than the unbridged counterpart (ca. 5%). We attribute this high efficiency to the rigidity of COPV and the bulky substituent on the bridging carbon atoms, which may help improve open-circuit voltage and fill factor, respectively.

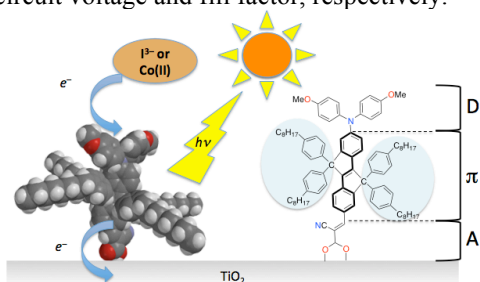


Fig. 1 Schematic picture of the COPV dye on the TiO₂ surface
1. (1)-15) *Chem. Commun.*, **49**, 582 (2013).

(2) "Iron-Catalyzed *ortho*-Allylation of Amides"

We developed the first iron-catalyzed directed reaction of a C–H bond with an electrophile. Thus, an amide possessing a bidentate directing group was *ortho*-allylated with allyl phenyl ether in the presence of an iron/diphosphine catalyst and an organozinc base. The key to the success of this reaction was the stabilization of a putative iron intermediate by the bidentate directing group and diphosphine ligand.

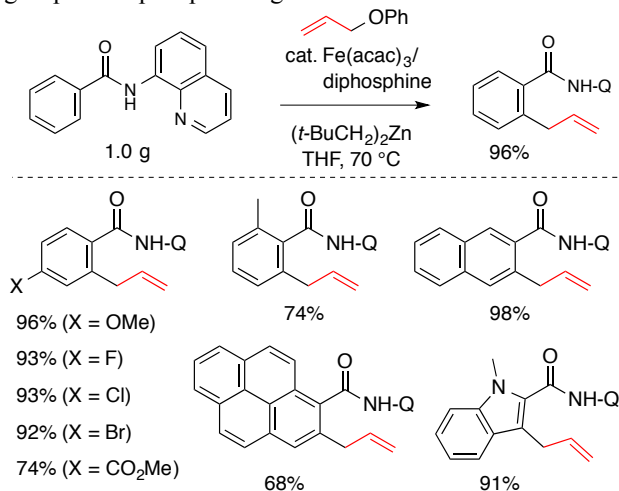


Fig. 2 Iron-catalyzed allylation of benzamides with allyl phenyl ether via directed C–H bond activation.

1. (1)-1) *J. Am. Chem. Soc.*, **135**, 17755 (2013).

(3) "1-Aryl-4-Silylmethyl[60]fullerenes for Organic Solar Cells"

We found that the addition of aryl group and silylmethyl group into the C₆₀ fullerene improved the material properties for the organic solar cells. Especially, the addition of thienyl group was effectively increased the LUMO level, which is beneficial for improving the open circuit voltage. Moreover, the addition resulted in the formation of tightly packed-crystal structure with the short distance of C₆₀ core that facilitate to increase the electron mobility, and hence improved short circuit current density as well as overall performance.

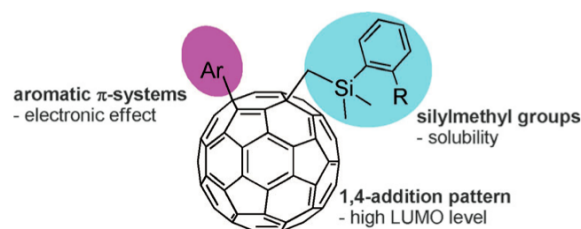


Fig. 3 Molecular design of fullerene derivative.
1. (1)-13) *Chem. Asian J.*, **8**, 121 (2013).

(4) "Chemical Modification of Fullerene Bilayer Vesicles"

We succeeded in controlling properties of bilayer vesicles made of water-soluble pentasubstituted fullerene amphiphiles through covalent and noncovalent chemical modification. For instance, we introduced protein ligands on an alkynylated fullerene vesicle through click reaction and then avidin to form protein-coated vesicles. The ligand-decorated vesicle was found to be an efficient carrier for water-soluble anticancer drugs *in vitro*. The bilayer vesicle also binds hydrophobic molecules primarily in the interior of the fullerene bilayer, as illustrated by the complete quenching of the fluorescent dye. We also demonstrated that photocrosslinking of the fullerene bilayer dramatically changes water permeability of the membrane.

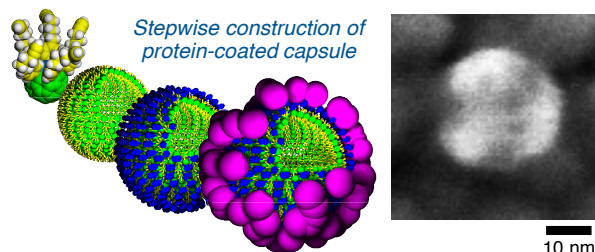


Fig. 4 High-resolution SEM image of a protein-coated fullerene bilayer vesicle.

1. (1)-10) *Chem. Commun.*, **49**, 3525 (2013).

1. (1)-5) *Chem. Lett.*, **42**, 1176 (2013).

1. (1)-4) *Chem. Commun.*, **49**, 7629 (2013).

物理有機化学研究室

研究ハイライト

(1) 炭素架橋 μ -フェニレンビニレン (COPV) の色素増感太陽電池への応用

我々が独自に開発した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 は強い光吸収等の興味深い光物性と高い安定性を有する。この特徴を活かして、色素増感太陽電池へと応用したところ、光電変換効率 (PCS) 7.54% を達成した。対応するフェニレンビニレン誘導体を用いた色素の PCE (5% 程度) と比較して、顕著な効率の向上が見られた。強固な COPV 骨格と架橋炭素上の置換基のかさ高さによって、開放電圧と曲線因子 (FF) が改善されたものと考えられる。

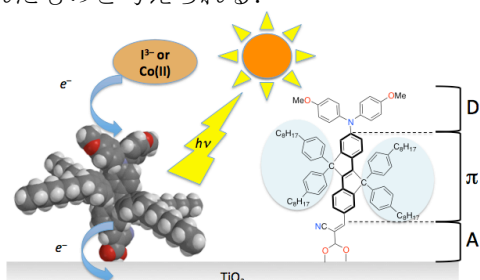


図 1 炭素架橋フェニレンビニレン (COPV) を用いた色素増感太陽電池の模式図

1. (1)-15) *Chem. Commun.*, **49**, 582 (2013).

(2) 鉄触媒を用いたアリルフェニルエーテルによる芳香族炭素-水素結合の直接アリル化反応

鉄触媒による炭素-水素結合の、求電子剤との直裁的な反応を実現できた。すなわち、触媒量の鉄錯体とホスフィン配位子、アリル化剤としてアリルフェニルエーテル、塩基として有機亜鉛試薬を用いた条件下において、二座配位可能なアミドを配向基として有した芳香環のオルト位炭素-水素結合が直接アリル化されることを見出した。本反応の有機鉄中間体の、配向基と配位子による安定化により達成されたものである。

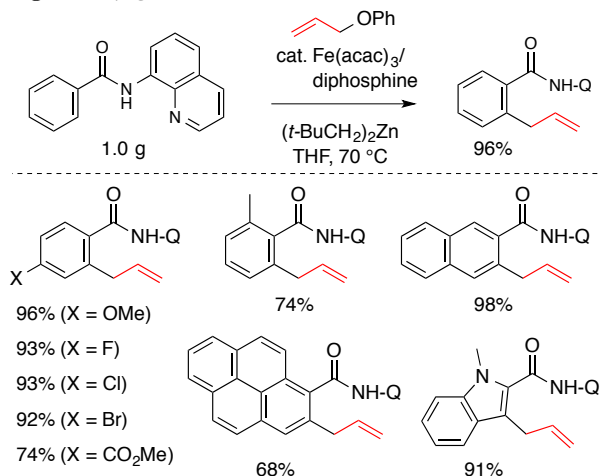


図 2 鉄触媒による芳香族アミドの直接アリル化反応

1. (1)-1) *J. Am. Chem. Soc.*, **135**, 17755 (2013).

(3) 有機太陽電池に適したアクセプターフラレンの分子設計

[60] フラレンにアリール基とシリルメチル基を一つずつ付加することで、有機薄膜太陽電池のアクセプターに最適な光電子物性が得られる事を明らかにした。特に、電子供与性の 2-チエニル基を導入したフラレンは LUMO 位が増加し、かつフラレンコアが密にパッキングした結晶構造をもつことから開放端電圧および電子移動度の向上に効果的であり、従来の高性能フラレン誘導体に匹敵する材料となる事が期待される。

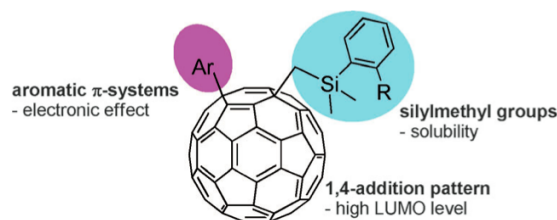


図 3 新型フラレン誘導体の分子設計

1. (1)-13) *Chem. Asian J.*, **8**, 121 (2013).

(4) フラレン二重膜の化学修飾と機能制御

水溶性五重付加型フラレンから形成される二重膜ベシクルへの共有結合および超分子的な化学修飾により、膜および集合体としての性質の制御を実現した。一例として、クリック反応によるベシクル表面のリガンド導入を介してタンパク質を結合させることに成功し、修飾されたベシクルが細胞への水溶性薬剤の輸送に有効な担体となることが示された。一方でフラレン二重膜は疎水性分子に対して優れた取り込み能を示し、取りこんだ分子とフラレンとの間に電子的な相互作用があることも見いだした。その他、光照射でフラレン同士をクロスリンクし二重膜に対する水透過性を制御することにも成功した。

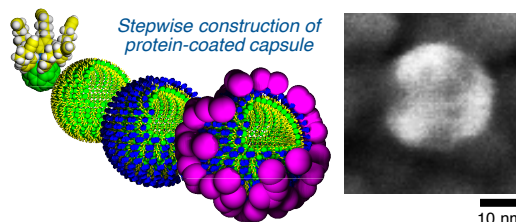


図 4 タンパク質 (アビジン) が結合したフラレン二重膜ベシクルの高分解能走査電子顕微鏡像

1. (1)-10) *Chem. Commun.*, **49**, 3525 (2013).

1. (1)-5) *Chem. Lett.*, **42**, 1176 (2013).

1. (1)-4) *Chem. Commun.*, **49**, 7629 (2013).

1. 原著論文

(1) Refereed Journals

- 1) Iron-Catalyzed *Ortho*-Allylation of Aromatic Carboxamides with Allyl Ethers, S. Asako, L. Ilies, E. Nakamura, *J. Am. Chem. Soc.*, **135**, 17755-17757 (2013).
- 2) Addition of Dihydromethano Group to Fullerenes to Improve the Performance of Bulk Heterojunction Organic Solar Cells, Y. Matsuo, J. Kawai, H. Inada, T. Nakagawa, H. Ota, S. Otsubo, E. Nakamura, *Adv. Mater.*, **25**, 6266-6269 (2013).
- 3) Selective Synthesis of Co₈S₁₅ Cluster in Bowl-Shaped Template of the Pentaaryl[60]fullerene Ligand, M. Maruyama, K. Imoto, M. König, D. M. Guldi, S. Ohkoshi, E. Nakamura, Y. Matsuo, *J. Am. Chem. Soc.*, **135**, 10914-10917 (2013).
- 4) Binding of Aromatic Molecules in the Fullerene-Rich Interior of a Fullerene Bilayer Vesicle in Water, K. Harano, R. M. Gorgoll, E. Nakamura, *Chem. Commun.*, **49**, 7629-7631 (2013).
- 5) Photocrosslinking of Fullerene Vesicles that Prevents Phase Transition and Decreases Water Permeation, K. Harano, A. Narita, E. Nakamura, *Chem. Lett.*, **42**, 1176-1178 (2013).
- 6) Magnetic Properties of Decamethyl Fullerenes: Radical Spin Interactions in Chemically Functionalized Fullerenes, H. Nitta, Y. Matsuo, E. Nakamura, S. Okada, *Appl. Phys. Express*, **6**, 045102 (2013).
- 7) Regioselective [2 + 2] Cycloaddition of a Fullerene Dimer with an Alkyne Triggered by Thermolysis of an Interfullerene C-C Bond, Z. Xiao, Y. Matsuo, M. Maruyama, E. Nakamura, *Org. Lett.*, **15**, 2176-2178 (2013).
- 8) β -Arylation of Carboxamides via Iron-Catalyzed C(sp³)-H Bond Activation, R. Shang, L. Ilies, A. Matsumoto, E. Nakamura, *J. Am. Chem. Soc.*, **135**, 6030-6032 (2013).
- 9) Polymer Janus Particles Containing Block-Copolymer Stabilized Magnetic Nanoparticles, H. Yabu, M. Kanahara, M. Shimomura, T. Arita, K. Harano, E. Nakamura, T. Higuchi, H. Jinnai, *ACS Appl. Mater. Interfaces*, **5**, 3262-3266 (2013).
- 10) Protein-Coated Nanocapsules via Multilevel Surface Modification. Controlled Preparation and Microscopic Analysis at Nanometer Resolution, K. Harano, K. Minami, E. Noiri, K. Okamoto, E. Nakamura, *Chem. Commun.*, **49**, 3525-3527 (2013).
- 11) Synthesis of Benzotriofuran and Benzotripyrrole Derivatives and Molecular Orientations on the Surface and in the Solid State, H. Tsuji, G. Cantagrel, Y. Ueda, T. Chen, L.-J. Wan, E. Nakamura, *Chem. Asian J.*, **8**, 2377-2382 (2013).
- 12) Reactivity of a Metastable Cobalt(III) Trisulfide Complex: Multiple C-H Functionalization of p-Xylene and Disulfides to Afford Photofunctional Cobalt Complexes, M. Maruyama, M. König, D. M. Guldi, E. Nakamura, Y. Matsuo, *Angew. Chem. Int. Ed.*, **52**, 3015-3018 (2013).
- 13) 1-Aryl-4-Silylmethyl[60]fullerenes: Synthesis, Properties, and Photovoltaic Performance, Y. Matsuo, H. Oyama, I. Soga, T. Okamoto, H. Tanaka, A. Saeki, S. Seki, E. Nakamura, *Chem. Asian J.*, **8**, 121-128 (2013).
- 14) Iron-Catalyzed Allylic Arylation of Olefins via C(sp³)-H Activation under Mild Conditions, M. Sekine, L. Ilies, E. Nakamura, *Org. Lett.*, **15**, 714-717 (2013).
- 15) New Sensitizers for Dye-sensitized Solar Cells Featuring a Carbon-bridged Phenylenevinylene, X. Zhu, H. Tsuji, A. Yella, A.-S. Chauvin, M. Grätzel, E. Nakamura, *Chem. Commun.*, **49**, 582-584 (2013).
- 16) Photostability of a Dyad of Magnesium Porphyrin and Fullerene and its Application to Photocurrent Conversion, T. Ichiki, Y. Matsuo, E. Nakamura, *Chem. Commun.*, **49**, 279-281 (2013).

(2) その他

2. 総説・解説

- 1) Movies of Molecular Motions and Reactions: The Single-Molecule, Real-Time Transmission Electron Microscope Imaging Technique, E. Nakamura, *Angew. Chem. Int. Ed.*, **52**, 236-252 (2013).
- 2) 原野幸治, 中村栄一, π 電子研究の歴史と将来展望(分担執筆), 未来材料を創出する π 電子系の化学(CSJ カレントレビュー12), 化学同人, 20-24 (2013).