

INORGANIC CHEMISTRY

Annual Research Highlights

(1) "Electronic properties of silicon surface-attached molecular wires"

Fabrication of nanoscaled architectures on substrate surfaces has gained increasing importance: 1 Examples in the early stage focused on self-assembled monolayers (SAMs) on metal electrodes, and recent works have begun to exploit self-assembled multilayers for the pursuit of more advanced functionalities. Linear and branched $\text{Fe}(\text{tpy})_2$ complex oligomer wires were quantitatively formed on hydrogen-terminated silicon wafers by means of hydrosilylation of ethynylterpyridine and following stepwise coordination reactions, and the redox property of surface-attached species and its photosensitivity can be controlled by the doping density of the silicon wafers.

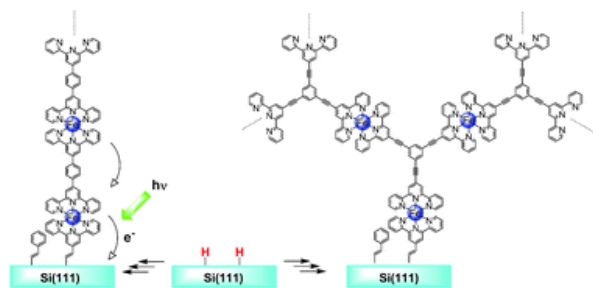


Fig. 1. Molecular wire prepared by stepwise complexation between iron ion and terpyridine moiety.

- 1.(1)-8) *Chem. Commun.*, **47**, 8644-8646 (2011)
 2-2) *Kobunshi*, **60**, 445-448 (2011)
 2-3) *Hyomenkagaku*, **32**, 641-646 (2011)

(2) Formation of Intensely Colored and Luminescent Quadrupolar Molecules Including a Missing Structural Isomer of Pechmann Dyes

Pechmann Dyes are expected to show the strong electron accepting ability in a donor-acceptor (D-A) connecting system because of their lactone skeletons and demonstrate particular photochemical properties derived from the D-A interaction. Here, we revealed acid-induced double lactonization in triarylamine-conjugated dimethyl diethynylfumarate, *E*-1, which opens up a new synthetic route to Pechmann Dyes-contraining donor-acceptor-donor (D-A-D) shaped molecules. This one-pot reaction affords three molecules (*P*₅₅-1, *P*₆₆-1 and *P*₅₆-1); the single crystal X-ray structural analysis clarified that *P*₅₅-1 and *P*₆₆-1 have known 5,5- and 6,6-membered ring structures, especially, *P*₅₆-1 possesses a novel 5,6-membered fused-ring structure (one of the missing Pechmann dye isomers), respectively (Fig. 2). These three lactonized molecules are intensely colored and brightly luminescent in visible

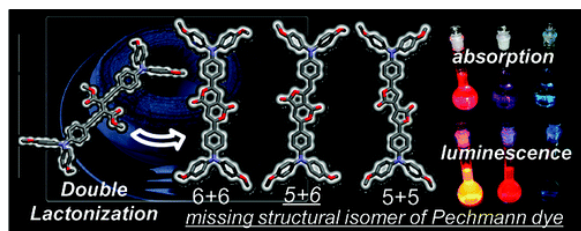


Fig. 2. Double Lactonization in *E*-1 and the Three Resultant Triarylamine-Appended Pechmann Dyes.

and NIR regions originated in the strong D-A interaction. In addition, we also revealed that an organic field effect transistor device fabricated with *P*₆₆-1 functions as a p-type semiconductor.

- 1.(1)-6) *J. Am. Chem. Soc.*, **133**, 14518-14521 (2011)

(3) "Construction and Properties of Pyrylium Cation Species"

The donor-acceptor-donor (D-A-D) conjugated molecules

1,4-bis(diarylaminophenylethynyl)anthraquinone (1,4-Am₂Aq) and 1,4-bis(ferrocenylethynyl)anthraquinone (1,4-Fc₂Aq), undergo a double proton cyclization reaction with bis(trifluoromethanesulfone) imide acid (TFSIH) to yield 1,4-bis(diarylaminophenyl or ferrocenyl) dipyrylium salts [1,4-R₂PyL₂](TFSI)₂ (R = Am or Fc) with novel planar pentacyclic structures similar to the aromatic benzo[e]pyrene-type skeleton (Fig. 3). [1,4-Am₂PyL₂](TFSI)₂ could be reduced to give the neutral molecule [1,4-Am₂PyL₂], which is stable and maintains the benzo[e]pyrene-type skeleton. To the best of our knowledge, this is the first oxygen-atom-containing polycyclic aromatic hydrocarbon with 22 (4n+2) π -electrons. The obtained condensed-ring benzo[e]pyrene-type skeleton compounds show physical and chemical properties that are significantly different from those of [1,5-Am₂PyL₂]₂, which has a perylene-type skeleton.

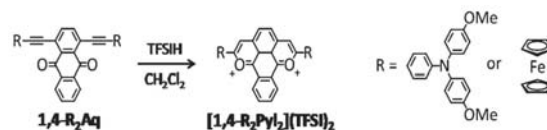


Fig. 3. Construction of Pyrylium Cation Species

- 1.(1)-3) *Chem. Lett.*, **40**, 1456-1458 (2011)
 1.(1)-4) *Chem. Eur. J.*, **17**, 14010-14019 (2011)
 1.(1)-15) *Chem. Commun.*, **47**, 2330-2332 (2011)
 2.-1) *Chem. Lett.*, **40**, 1316-1326 (2011)

研究ハイライト

(1) シリコン電極表面に固定した分子ワイヤの電子機能

本研究では従来の金電極に代わり、水素終端化シリコンを用いてビステルピリジン鉄錯体ワイヤの構築を行った。半導体を用いることにより金属電極とは異なる電気化学特性が観測されることが期待される。

逐次の錯形成反応を用いて、シリコン表面上に多層ワイヤを構築し、サイクリックボルタンメトリー(CV)測定から表面上のビステルピリジン錯体の被覆量を見積ると、定量的にワイヤが伸長していることが示された。また、X線光電子分光法および原子間力顕微鏡による測定からも、ワイヤが構築されていることが支持された。ドーパ量の異なるシリコン電極を用いてCV測定を行ったところ、低ドーパの電極においては光照射の有無に応じて酸化還元特性が変化する様子が観測された。

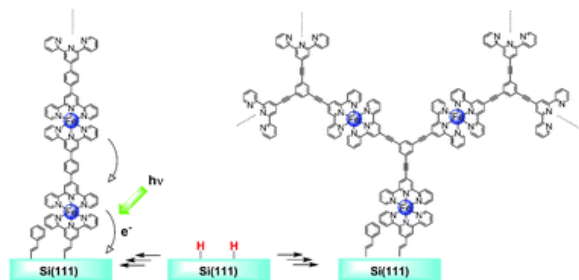


図1. テルピリジン基を逐次積層させた分子ワイヤ

1.(1)-8) *Chem. Commun.*, **47**, 8644-8646 (2011)

2-2) *高分子*, **60**, 445-448 (2011)

2-3) *表面科学*, **32**, 641-646 (2011)

(2) ペックマン色素の未知構造異性体を含む、強発光、強吸収を示す四重極子型分子群の創製

ペックマン色素群は電子供与(ドナー)、電子受容(アクセプター)連結系において、そのラクトン環骨格に由来する強い電子受容性を示し、ドナー・アクセプター(D-A)相互作用がもたらす特徴的な光化学物性を示すことが期待される。今回、我々はジエチルフルマル酸ジメチルとトリアリールアミンを共役させた化合物 **E-1** の酸性条件下二重ラクトン環化反応が、ペックマン色素群の骨格を有するドナー・アクセプター・ドナー(D-A-D)型分子群の新規合成法であることを見出した。この反応により

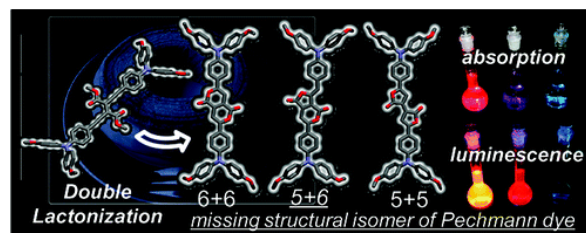


図2. 分子内二重環化反応を利用したピラノピランジオン骨格の合成

三種の分子を一度に得、単結晶 X 線構造解析の結果より、各々がペックマン色素骨格 (**P₅₅**) とその既知構造異性体骨格 (6,6-membered ring) を有する **P₅₅-1** と **P₆₆-1**、そして未知構造異性体骨格 (5,6-membered fused-ring structure) を有する **P₅₆-1** である事が示された(図2)。これら三種の環化分子は強い D-A 相互作用に由来する可視から近赤外領域における強吸収、強発光を示す。加えて、我々は **P₆₆-1** を原料として作製された OFET が p 型の半導体特性を示す事も明らかとした。

1.(1)-6) *J. Am. Chem. Soc.*, **133**, 14518-14521 (2011)

(3) ピリリウムカチオン化学種の創製と物性

フェロセン (Fc) またはトリアリールアミン (Am) とアントラキノンを結ぶドナー-アクセプター-ドナー (D-A-D) 共役分子 **1,4-R₂Aq** (R = Fc, Am) が、トリフルオロメタンスルホンイミドとの反応により、ベンゾ[e]ピレンと同様の6員環が5つ縮環した新規平面分子 **[1,4-R₂Py₂](TFSI)₂** を与えることを見出した(図3)。また **[1,4-Am₂Py₂](TFSI)₂** を還元することで、ベンゾ[e]ピレン骨格を有する中性分子 **[1,4-Am₂Py₂]** が得られた。この分子は酸素原子を骨格内に有する 22p 電子系多環芳香族炭化水素の初めての例である。ベンゾ[e]ピレン骨格を有する **[1,4-Am₂Py₂]** とペリレン骨格を有する **[1,5-Am₂Py₂]** は構造異性体であるが、両者の物理および化学特性は大きく異なっていることが明らかになった。

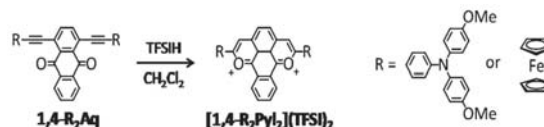


図3. ピリリウムカチオン化学種の創製

1.(1)-3) *Chem. Lett.*, **40**, 1456-1458 (2011)

1.(1)-4) *Chem. Eur. J.*, **17**, 14010-14019 (2011)

1.(1)-15) *Chem. Commun.*, **47**, 2330-2332 (2011)

2.-1) *Chem. Lett.*, **40**, 1316-1326 (2011)

1. 原著論文

(1) Refereed Journals

- 1) M. P. Yutkin, M. S. Zavakhina, A. V. Virovets, D. N. Dybtsev, V. P. Fedin, T. Kusamoto, H. Nishihara, "Synthesis, structure and magnetic behavior of new 1D metal-organic coordination polymer with Fe₃O₄ core.", *Inorg. Chim. Acta*, **365**, 513-516 (2011).
- 2) Y. Yamamoto, M. Miyachi, Y. Yamanoi, A. Minoda, S. Maekawa, S. Oshima, Y. Kobori, H. Nishihara, "Synthesis of Vanadium-Doped Palladium Nanoparticles for Hydrogen Storage Materials", *J. Nanopart. Res.*, **13**, 6333-6338 (2011).
- 3) K. P. Rao, M. Kondo, R. Sakamoto, T. Kusamoto, S. Kume, H. Nishihara, "Protonation-Induced Cyclization of 1,8-Bis(diarylethynyl)anthraquinones: Monopyrylium Salt Formation and Intensification of Donor-Acceptor Interaction", *Chem. Lett.*, **40**, 1456-1458 (2011).
- 4) K. P. Rao, M. Kondo, R. Sakamoto, T. Kusamoto, M. Nishikawa, S. Kume, M. Nihei, H. Oshio, H. Nishihara, "Benzo[e]pyrene Skeleton Dipyrilium Dication with a Strong Donor-Acceptor-Donor Interaction, and Its Two-Electron Reduced Molecule", *Chem. Eur. J.*, **17**, 14010-14019 (2011).
- 5) S. Muratsugu, K. Sodeyama, F. Kitamura, S. Tsukada, M. Tada, S. Tsuneyuki, H. Nishihara, "Normal and inverted redox potentials and structural changes tuned by medium effects in [M₂Mo(η⁵-C₅Me₅)₂(S₂C₆H₄)₂(CO)₂] (M: Co, Rh)", *Chem. Sci.*, **2**, 1960-1968 (2011).
- 6) M. Hayashi, F. Toshimitsu, R. Sakamoto, H. Nishihara, "Double Lactonization in Triarylamine-Conjugated Dimethyl Diethynylfumarate: Formation of Intensely Colored and Luminescent Quadrupolar Molecules Including a Missing Structural Isomer of Pechmann Dyes", *J. Am. Chem. Soc.*, **133**, 14518-14521 (2011).
- 7) K. Namiki, M. Murata, S. Kume, H. Nishihara, "Synthesis of photo-switchable 3-FcAB-modified polymer particles", *New J. Chem.*, **35**, 2146-2152 (2011).
- 8) H. Maeda, R. Sakamoto, Y. Nishimori, J. Sendo, F. Toshimitsu, Y. Yamanoi, H. Nishihara, "Bottom-up fabrication of redox-active metal complex oligomer wires on an H-terminated Si(111) surface", *Chem. Commun.*, **47**, 8644-8646 (2011).
- 9) T. Kambe, S. Tsukada, R. Sakamoto, H. Nishihara, "Expanding Family of π-Conjugated Trinuclear Dithiolenes: The Cases of Group 8 (RuII) and 10 (NiII and PtII) Metals", *Inorg. Chem.*, **50**, 6856-6858 (2011).
- 10) K. Uchida, Y. Yamanoi, T. Yonezawa, H. Nishihara, "Reversible On/Off Conductance Switching of Single Diarylethene Immobilized on a Silicon Surface", *J. Am. Chem. Soc.*, **133**, 9239-9241 (2011).
- 11) I. Nakamura, Y. Yamanoi, T. Imaoka, K. Yamamoto, H. Nishihara, "A Uniform Bimetallic Rhodium/Iron Nanoparticle Catalyst for the Hydrogenation of Olefins and Nitroarenes", *Angew. Chem. Int. Ed.*, **50**, 5830-5833 (2011).
- 12) H. Kondo, Y. Yamanoi, H. Nishihara, "Preferential carbene insertion into Ge-H vs. other heavier group 14 hydrides via samarium carbenoids", *Chem. Commun.*, **47**, 6671-6673 (2011).
- 13) Y. Hasegawa, K. Takahashi, S. Kume, H. Nishihara, "Complete solid state photoisomerization of bis(dipyrazolylstyrylpyridine)iron(II) to change magnetic properties", *Chem. Commun.*, **47**, 6846-6848 (2011).
- 14) S. Umeki, S. Kume, H. Nishihara, "Switching of Molecular Insertion in a Cyclic Molecule via Photo- and Thermal Isomerization", *Inorg. Chem.*, **50**, 4925-4933 (2011).
- 15) K. P. Rao, T. Kusamoto, R. Sakamoto, Y. Yamamoto, S. Kume, M. Nihei, H. Oshio, H. Nishihara, "Platinadithiolene-conjugated pyrylium salt with strong intramolecular donor-acceptor interaction", *Chem. Commun.*, **47**, 2330-2332 (2011).
- 16) S. Kume, H. Nishihara, "Synchronized motion and electron transfer of a redox-active rotor", *Dalton Trans.*, **40**, 2299-2305 (2011).
- 17) Y. Shishino, T. Yonezawa, S. Udagawa, K. Hase, H. Nishihara, "Preparation of Optical Resins Containing Dispersed Gold Nanoparticles by the Matrix Sputtering Method", *Angew. Chem. Int. Ed.*, **50**, 703-705 (2011).

18) S. Kume, H. Nishihara, "Tuning-up and driving a redox-active rotor", *Chem. Commun.*, **47**, 415-417 (2011).

2. 総説・解説

- 1) R. Sakamoto, K. P. Rao, H. Nishihara, "Arylethynylanthraquinone and Bis(arylethynyl)anthraquinone: Strong Donor-Acceptor Interaction and Proton-induced Cyclization to Form Perylium and Diperylium Salts", *Chem. Lett.*, **40**, 1316-1326 (2011) (Highlight Review).
- 2) 西原 寛、"π 共役高分子錯体の界面配位プログラミング", *高分子*, **60**, 445-448 (2011).
- 3) 前田 啓明, 坂本 良太, 西原 寛, "錯体分子ワイヤの電気化学評価とその長距離電子移動能", *表面科学*, **32**, 641-646 (2011).

3. 著書

なし

4. その他

なし