

Annual Research Highlights

(1) “Surface-junction effects on electron transfer between bis(terpyridine)iron complex and semiconductor electrode”

Four types of bis(terpyridine)iron complexes (Si-A^xFeL, x = 1-4) were prepared on hydrogen-terminated silicon(111) surfaces by the stepwise coordination method (Fig. 1). The electron transfer rate constant values of Si-A²FeL and Si-A⁴FeL whose structures include the phenylene spacer were greater than non-phenylene spacer systems, Si-A¹FeL and Si-A³FeL, in spite of their longer distance between the iron center and the electrode. According to DFT calculations of model molecules, the phenylene spacer makes the small energy difference between HOMO level and HOMO-3 spreading from iron atom to silicon atom. These orbitals may contribute the redox reaction and the electron transfer respectively. Therefore, this small energy difference may enhance the electronic coupling between these molecular orbitals, and accelerate their electron transfer rate.

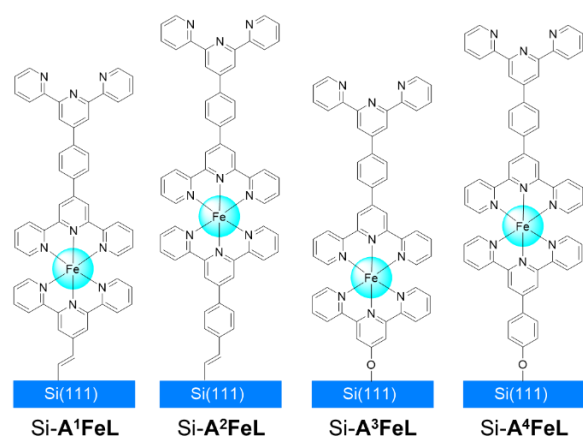


Fig. 1 Chemical structures of Si-A^xFeL (x = 1–4) on Si(111).

1.(1)-14) *Chem. Eur. J.* **20**, 2761-2764 (2014)

(2) “Fabrication of Dense and Multi-Layered Films of the Nickel Bis(dithiolene) Nanosheet By Means of the Langmuir–Schäfer Method”

We have immobilized densely multilayer nickel bis(dithiolene) nanosheet on substrates via the Langmuir-Schäfer method using a Langmuir-Blodgett (LB) apparatus. We first observed π -A isotherm of the nanosheet with various amounts of benzenehexathiol. Each sample showed increasing surface pressure with decreasing trough area, indicating compression of the nickel bis(dithiolene) nanosheet and two samples made with more BHT showed collapse of the nanosheet.

The density of the nanosheet was estimated by AFM. The samples were transferred to HOPG substrates at several surface pressure, and their density increased with trough area decreasing which indicated possibility of densely nanosheet fabrication.

Furthermore, we checked vis-NIR spectra of the

nanosheet with iterative deposition onto transparent ITO substrates. In this case, absorption of the nanosheet increased linearly with the number of deposition times, suggesting successful of multi-layer nanosheet fabrication.

1.(1)-15) *Chem. Lett.*, **43**, 252-253 (2014)

(3) “Luminescence of an open-shell (3,5-dichloro-4-pyridyl)bis(2,4,6-trichlorophenyl)methyl radical”

While most known luminescent molecules are in the closed-shell ground state, luminescent open-shell radicals have attracted interest recently. However, the number of reports of the luminescent radical is limited so far. Tris(2,4,6-trichlorophenyl)methyl radical (TTM) is known as a rare example of a luminescent radical; however, it decomposes rapidly under photoirradiation to yield non-fluorescent products.

We have synthesized a novel luminescent stable radical (3,5-dichloro-4-pyridyl)bis(2,4,6-trichlorophenyl)methyl radical (PyBTM). It displayed fluorescence under various conditions. The absolute photoluminescence quantum yield (ϕ) of 3% was obtained in chloroform. The PyBTM molecules dispersed in a poly(methyl methacrylate) film showed luminescence with $\phi = 0.26$ at room temperature. PyBTM was luminescent with excellent quantum yield ($\phi = 81\%$) in EPA (diethyl ether : isopentane : ethanol = 5 : 5 : 2 v/v) at 77 K. The photostability of PyBTM was evaluated and compared with that of TTM. When acetone solutions of PyBTM and TTM were irradiated at $\lambda = 370$ nm, the decay of the fluorescence intensity of PyBTM was 115 times smaller than that of TTM.

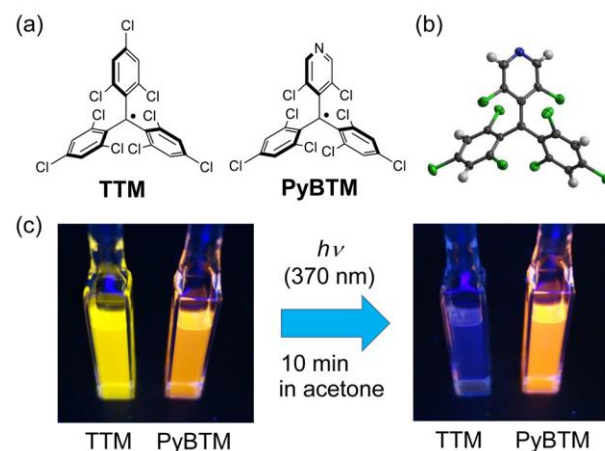


Fig. 2 (a) Structures of TTM and PyBTM. (b) Molecular structure of crystalline PyBTM with thermal ellipsoids at the 50% level. (c) Photographs of TTM (left cuvette) and PyBTM (right cuvette) solutions in acetone recorded before and after irradiation with UV light at $\lambda = 370$ nm for 10 minutes.

1.(1)-5) *Angew. Chem. Int. Ed.*, **53**, 11845-11848 (2014).

1.(1)-6) *Chem. Lett.*, **43**, 1037-1039 (2014).

1.(1)-13) *Inorg. Chem.*, **53**, 2831-2840 (2014).

研究ハイライト

(1) 錯体—半導体電極ジャンクションが電子移動速度定数に与える影響

水素終端化シリコン(111)表面に図1に示す4種類の異なる架橋構造を持ったビス(テルピリジン)鉄錯体(Si-A^xFeL, x = 1-4)を逐次的錯形成法で構築し、その錯体—電極間の電子移動速度定数を算出した。フェニレン構造を有する表面固定用配位子を用いたSi-A²FeLとSi-A⁴FeLが電極—錯体間の距離が遠いにも関わらず、大きな電子移動速度定数を示した。モデル構造のDFT計算から、フェニレン構造の導入により、電子輸送に寄与する鉄中心からケイ素原子まで広がった共役系をもつHOMO-3と、酸化還元反応に関わるHOMOのエネルギー準位差が小さくなったことが示された。これにより両軌道間の相互作用が大きくなったことが、電子移動速度を高めた要因と考えられる。

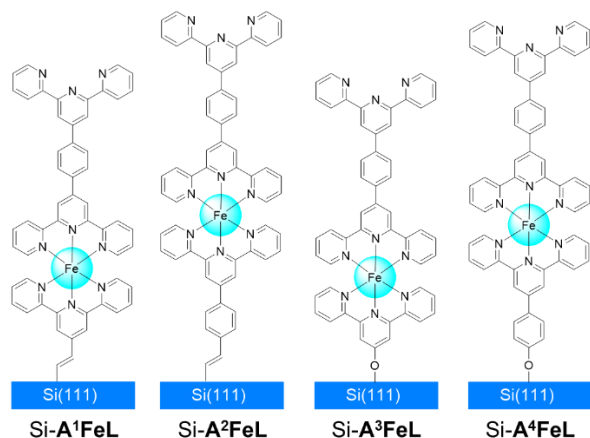


図1 作製したSi-A^xFeL (x = 1-4) の構造

1.(1)-14) *Chem. Eur. J.* **20**, 2761-2764 (2014)

(2) LS法を用いた密で多層のニッケルビスジチオレンナノシートの構築

LB膜作成装置を用いて、当研究室にて合成されたニッケルビスジチオレンナノシートの高密度集積化を行った。表面圧とトラフ面積の関係を表すπ-Aカーブの観測により、表面圧の上昇からナノシートの集積を見出し、さらにより高密度のナノシートにおいては集積の限界によるナノシートの崩壊を見出した。続いて原子間力顕微鏡AFMによって各トラフ面積におけるナノシートの被覆面積を観測したところ、トラフ面積が小さくなるに従い被覆量が増大することが分かり、ナノシートの集積化が可能であることを示した。さらに等しい表面圧の下でITO基板に対してナノシートの転写を繰り返し行った。それぞれの可視近赤外吸光の測定から転写されたナノシート

の吸光度の直線的な増加を見ることができ、ナノシートの積層化を達成した。

1.(1)-15) *Chem. Lett.* **43**, 252-253 (2014)

(3) 開殻(3,5-ジクロロ-4-ピリジル)ビス(2,4,6-トリクロロフェニル)メチルラジカルの発光

ほとんどの発光分子は閉殻の基底状態を持つが、近年開殻の発光ラジカルが注目を集めてきている。しかし、現状発光ラジカルの報告数は限られている。トリス(2,4,6-トリクロロフェニル)メチルラジカル(TTM)は珍しい発光ラジカルの一例であるが、光照射下で非蛍光性の生成物に速やかに分解してしまう。当研究室では新たな発光安定ラジカル(3,5-ジクロロ-4-ピリジル)ビス(2,4,6-トリクロロフェニル)メチルラジカルを合成し、様々な条件下で蛍光を示すことを見出した。クロロホルム溶液中での絶対発光量子収率(φ)は3%であった。PyBTMをポリメタクリル酸メチルポリマー中に分散させたところ室温でφ = 26%を示した。また、PyBTMはEPA混合溶媒(ジエチルエーテル : イソペンタン : エタノール = 5 : 5 : 2 v/v)中77 Kでφ = 81%の非常に高い量子収率を示した。PyBTMの光安定性を評価し、TTMと比較した。PyBTMとTTMのアセトン溶液をλ = 370 nmで光照射したところPyBTMの蛍光強度の減衰はTTMより115倍も小さいことがわかった。

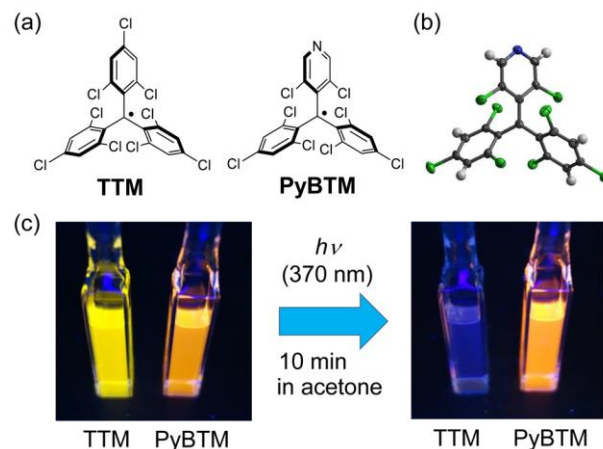


図2 (a)TTMとPyBTMの構造。(b)PyBTMのX線結晶構造解析結果。(c)紫外光(λ = 370 nm, 10分)照射前後のTTM(左セル)とPyBTM(右セル)の写真。

1.(1)-5) *Angew. Chem. Int. Ed.*, **53**, 11845-11848 (2014)

1.(1)-6) *Chem. Lett.*, **43**, 1037-1039 (2014).

1.(1)-13) *Inorg. Chem.*, **53**, 2831-2840 (2014).

1. 原著論文

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- 3) S. Muratsugu and H. Nishihara, “ π -Conjugation modification of photochromic and redox-active dimethyldihydropyrene by phenyl and ethynyl-terpyridines and Ru(bis-terpyridine) complexes”, *New J. Chem.*, **38**, 6114-6124 (2014).
- 4) T. Kambe, R. Sakamoto, T. Kusamoto, T. Pal, N. Fukui, T. Shimojima, Z. Wang, T. Hirahara, K. Ishizaka, S. Hasegawa, F. Liu and H. Nishihara, “Redox Control and High Conductivity of Nickel Bis(dithiolene) Complex π -Nanosheet: A Potential Organic Two-Dimensional Topological Insulator”, *J. Am. Chem. Soc.*, **136**, 14357-14360 (2014).
- 5) Y. Hattori, T. Kusamoto and H. Nishihara, “Luminescence, Stability, and Proton Response of an Open-Shell (3,5-Dichloro-4-pyridyl)bis(2,4,6-trichlorophenyl)methyl Radical”, *Angew. Chem. Int. Ed.*, **53**, 11845-11848 (2014).
- 6) Y. Hattori, M. Nishikawa, T. Kusamoto, S. Kume and H. Nishihara, “Steric Interference on the Redox-Conjugated Pyrimidine Ring Rotation of Mono- and Di-nuclear Copper Complexes with (4-Methyl-2-pyrimidinyl)imine Ligands”, *Chem. Lett.*, **43**, 1037-1039 (2014).
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- 8) M. Tsuchiya, R. Sakamoto, S. Kusaka, Y. Kitagawa, M. Okumura and H. Nishihara, “Asymmetric dinuclear bis(dipyrrinato)zinc(II) complexes: Broad absorption and unidirectional quantitative exciton transmission”, *Chem. Commun.*, **50**, 5881-5883 (2014).
- 9) H. Inubushi, Y. Hattori, Y. Yamanoi and H. Nishihara, “Structures and Optical Properties of Tris(trimethylsilyl)silylated Oligothiophene Derivatives”, *J. Org. Chem.*, **79**, 2974-2979 (2014).
- 10) M. Kishida, T. Kusamoto and H. Nishihara, “Photoelectric Signal Conversion by Combination of Electron-Transfer Chain Catalytic Isomerization and Photoisomerization on Benzodimethyldihydropyrenes”, *J. Am. Chem. Soc.*, **136**, 4809-4812 (2014).
- 11) S. Kusaka, R. Sakamoto and H. Nishihara, “Luminescent Heteroleptic Tris(dipyrrinato)indium(III) complexes”, *Inorg. Chem.*, **53**, 3275-3277 (2014).
- 12) Y. Rao, T. Kusamoto, R. Sakamoto, H. Nishihara and S. Wang, “Reactivity and Electronic Properties of a Ferrocene Molecule Bearing an N,C-chelate BMes₂ Unit”, *Organometallics*, **33**, 1787-1793 (2014).
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- 14) H. Maeda, R. Sakamoto and H. Nishihara, “Surface Junction Effects on Interfacial Electron Transfer Between Bis(terpyridine)iron(II) and Hydrogen-Terminated Silicon(111) Electrode”, *Chem. Eur. J.*, **20**, 2761-2764 (2014).
- 15) K. Hoshiko, T. Kambe, R. Sakamoto, K. Takada and H. Nishihara, “Fabrication of Dense and Multi-Layered Films of the Nickel Bis(dithiolene) Nanosheet By Means of the Langmuir-Schaefer Method”, *Chem. Lett.*, **43**,

252-253 (2014).

- 16) M. Miyachi, Y. Yamanoi, K. Nakazato and H. Nishihara, "Bio-inspired photoresponse of porphyrin-attached gold nanoparticles on a field-effect transistor", *BBA - Bioenerg.*, **1837**, 1567-1571 (2014).
- 17) Y. Yamamoto, M. Miyachi, Y. Yamanoi, A. Minoda, S. Maekawa, S. Oshima, Y. Kobori and H. Nishihara, "Synthesis and Hydrogen Storage Properties of Palladium Nanoparticle-Organic Frameworks", *J. Inorg. Organomet. Polym. Mater.*, **24**, 208-213 (2014).

(2) その他

- 1) 坂本良太, 永山達大, 西原 寛「機能性「ボトムアップ型」ナノシート」, 化学工業, **65**, 944-948 (2014).
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2. 総説・解説

- 1) H. Nishihara, "Coordination Programming-A Concept for the Creation of Multifunctional Molecular Systems", *Chem. Lett.* 2014, **43**, 388-395 (2014).

3. 著書

- 1) M. Nishikawa, "Photofunctionalization of Molecular Switch Based on Pyrimidine Ring Rotation in Copper Complexes" (Springer, Japan, 2014).

4. その他

- 1) 西原 寛, 坂本良太, 高田健司, 獅野裕一 「エレクトロクロミックシート及びその製造方法」平成26年4月15日, 日本, 特願2014-84072
- 2) 西原 寛, 坂本良太, 星子 健, 八木俊樹, 永山達大, 獅野裕一 「光電変換特性を有するジピリン金属錯体シート及びその製造方法」平成26年4月15日, 日本, 特願2014-84073