HETEROCYCLES, Vol. 93, No. 2, 2016, pp. 762 - 769. © 2016 The Japan Institute of Heterocyclic Chemistry
Received, 31st August, 2015, Accepted, 20th October, 2015, Published online, 30th October, 2015
DOI: 10.3987/COM-15-S(T)32

UNSYMMETRICAL PHTHALOCYANINES WITH ONE TTF UNIT AND OCTYLTHIO OR OCTYLSULFONYL GROUPS: THEIR OPTICAL AND ELECTROCHEMICAL PROPERTIES

Takeshi Kimura,* Jasmin Kang, and Shidsuko Nakajo

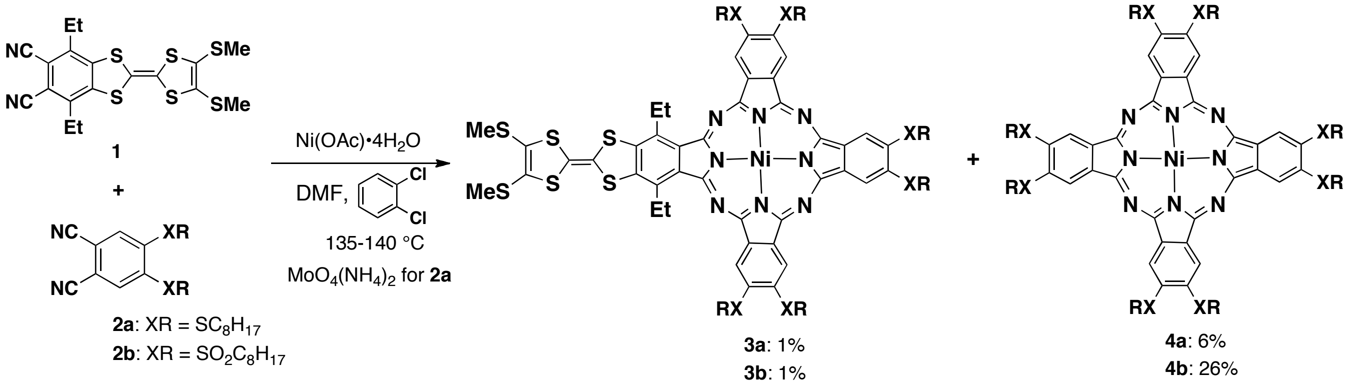
Center for Instrumental Analysis, Iwate University, Morioka 020-8551, Japan

Dedicated to Prof. Dr. Lutz F. Tietze on the occasion of his 75th birthday

Abstract – Unsymmetrical phthalocyanines fused with a TTF unit and six octylthio or six octylsulfonyl groups were prepared by the reaction of a mixture of phthalonitrile fused with a TTF unit and 4,5-di(octylthio)- or 4,5-di(octylsulfonyl)phthalonitrile. The optical and electrochemical properties of the products were determined by UV-vis absorption spectra, cyclic voltammetry, and ESR spectra.

Phthalocyanines (Pcs) have been utilized as catalysts in the petroleum industry, optical disks, allergen decomposers, and charge generating materials for photocopies, and have potential applications as semiconductors, optoelectronic devices, solar cells, and sensitizers for photodynamic therapy for cancer.[1] Therefore, there have been a great number of reports about Pcs and related compounds; for example, new Pc derivatives, fused with a variety of π-aromatic systems, have been synthesized to develop new functional materials.[1,2] It is known that unsymmetrical Pcs with suitable donor and acceptor groups show nonlinear optical properties different from symmetrically substituted derivatives.[1,3] Tetrathiafulvalene (TTF) is a strong electron donor and has been utilized as a building block of new functionalized molecular systems;[4] as related studies, it has been reported that TTF derivatives and Pcs were fused directly or bonded using some linkers and the products, obtained by the processes, could show electron transfer between the TTF unit and the Pc ring.[5-7] As one of the electron-withdrawing substituents, alkylsulfonyl groups have been introduced on Pc derivatives because it is convenient to adjust the electronic property and the solubility of the macrocycles.[2,8] In 2007, Kobayashi et al. reported Pc derivatives with C_{60} and butylsulfonyl groups; these products showed a multistep redox system and a lower energy shift of the Q band absorption.[9] Stimulated by these reports, we tried to prepare unsymmetrical Pcs with a TTF unit and octylsulfonyl groups as donor and acceptor groups.

This paper reports the preparation of unsymmetrical phthalocyanines fused with one TTF unit and octylthio or octylsulfonyl groups and their optical and electrochemical properties.



Scheme 1

As a starting compound for unsymmetrical Pcs with one TTF unit, 4,7-diethyl-5,6-dicyano-2-(4’,5’-bis(methylthio)-1’,3’-dithiole-2’-ylidene)benzo[*d*]-1,3- dithiole (**1**) was synthesized from 1,4-diethylbenzene *via* six step reactions.[7a] In addition, 3,6-di(octylthio)phthalonitrile (**2a**) and 3,6-di(octylsulfonyl)phthalonitrile (**2b**) were prepared according to a method reported previously.[3a] It is generally expected that the sulfonyl group of **2b** is readily substituted under a basic cyclization reaction condition. To construct an unsymmetrically substituted tetraazaporphyrin skeleton, phthalonitriles **1** and **2b** were mixed in a 1 : 3 ratio and the mixture was treated with $Ni(OAc)_2$•$4H_2O$ in 1,2-dichlorobenzene/DMF (4 : 1) at 135 °C to give Ni(II) mono-TTF-Pc derivative **3b** (1%) and Ni(II) *β*-octa(octylsulfonyl)-phthalocyaninato (**4b**) (26%) together with a recovery of **1** (75%) (Scheme 1).[8] Apparently, the reactivity of **1** should be lower than that of **2b** under the reaction condition. In the reaction mixture, a trace amount of di-TTF derivatives may exist; the products could be observed as very minor signals in the ^{1}H NMR spectrum. However, we could not isolate these isomers by column chromatography using silica gel and Biobeads. The reaction of **1** and **2b** in a 1 : 1 ratio under the similar condition gave **3b** in 2% yield. By the reaction of **1** and **2a**, Ni(II) mono-TTF-Pc derivative **3a** and Ni(II) *β*-octa(octhylthio)phthalocyaninato (**4a**) were obtained in 1% and 6% yields, respectively;[8] the recovery of **1** was 81% in the reaction. It seemed that the reactivity of **2a** was lower than that of **2b**; therefore, the reaction of **1** and **2a** needed a longer reaction time (140 °C, 48 h) and a small amount of a catalyst $[MoO_4(NH_4)_2]$. On the other hand, since the polarity and the molecular size of **3a** and **3b** would be similar to **4a** and **4b**, respectively, column chromatography was repeatedly performed to separate the products.

In the ^{1}H NMR spectra of **3a** and **3b** measured at 323 K, one singlet peak was observed for the methylthio group of the TTF unit (**3a**: 2.59 ppm; **3b**: 2.46 ppm) and three broadened aromatic signals appeared at 7.96, 8.42, and 8.48 ppm for **3a** and 9.83, 10.14, and 10.18 ppm for **3b**. Three signals of SCH$_2$ protons of **3a** were found as two broadened signals and one broadened triplet at 3.13, 3.36, and 3.42 ppm and those of SO$_2$CH$_2$ protons of **3b** came out as three broadened triplet at 3.99, 4.09, and 4.12 ppm. In addition, while the CH$_2$ signal of the ethyl groups appeared as one broadened signal at 3.76 ppm for **3b**, that of **3a** would be overlaid with the SCH$_2$ signals. Fast atom bombardment mass spectrometry (FAB-MS) experiments showed the corresponding molecular ion peak: **3a**: (matrix: 2-nitrophenyl octyl ether) *m/z* = 1759.6001 [MH$^+$]; **3b**: (matrix: *m*-nitrobenzyl alcohol) *m/z* = 1950.5 [M$^+$]. The IR spectrum of **3b** showed two signals for the sulfonyl group at 1306 and 1141 cm^{-1}.

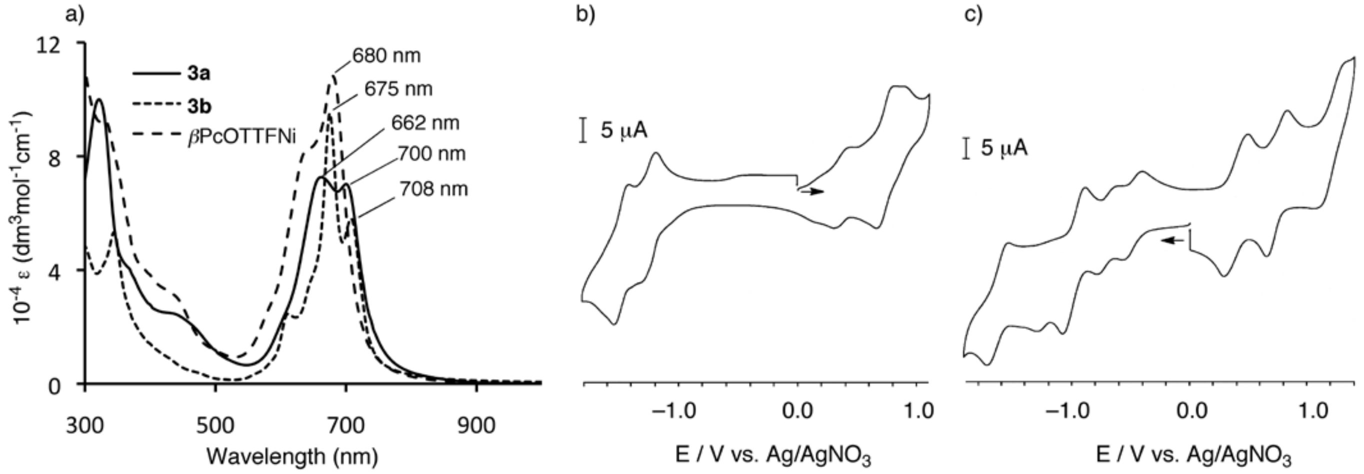


Figure 1. a) UV-vis spectra of **3a**, **3b**, and *β*PcOTTFNi measured in chloroform and cyclic voltammograms of b) **3a** and c) **3b**.

Table 1. Oxidation and reduction potentials of phthalocyanines

Compound	E$_{1/2}$ [V]							
	5th redn	4th redn	3rd redn	2nd redn	1st redn	1st oxid	2nd oxid	3rd oxid
3a		-	-	−1.48	−1.25[a]	0.38[a]	0.75	
3b	−1.60	−1.16[a]	–0.97	–0.70	–0.48	0.42	0.75	1.22
4a		-	-	−1.52[a]	−1.28[a]	0.41[a]	0.78[a]	-
4b	−1.81	−1.47	–0.93	–0.52	–0.37	1.23	-	-
*α*PcOTTF	-	-	-	−1.52	−1.18	0.34[a]	0.69[a]	-
*β*PcOTTF	-	-	−1.47[a]	−1.27[a]	–0.78[a]	0.41[a]	0.72[a]	-
*β*PcOTTFNi	-	-	-	−1.36[b]	–0.98[a]	0.39[a]	0.73[a]	-

[a]Quasi-reversible, [b]irreversible.

In the UV-vis spectrum, the split Q-band absorption of *β*-octylthio derivative **3a** was observed at 662 and 700 nm (Figure 1a). *β*-Octylsulfonyl derivative **3b** also showed the split Q band absorption at 675 nm and 708 nm. In contrast, symmetrically substituted Pcs **4a** and **4b** showed the Q band absorption at 703 nm and 675 nm, respectively. While *β*-hexa(octyloxy)Pc with one TTF unit [*β*PcOTTF] showed the Q band absorption as split peaks at 680.5 nm and 704.5 nm, its nickel complex *β*PcOTTFNi showed the absorption as a broadened signal at 679.5 nm.[7b] The UV-vis spectrum of **3b** is similar to that of metal free *β*PcOTTF.

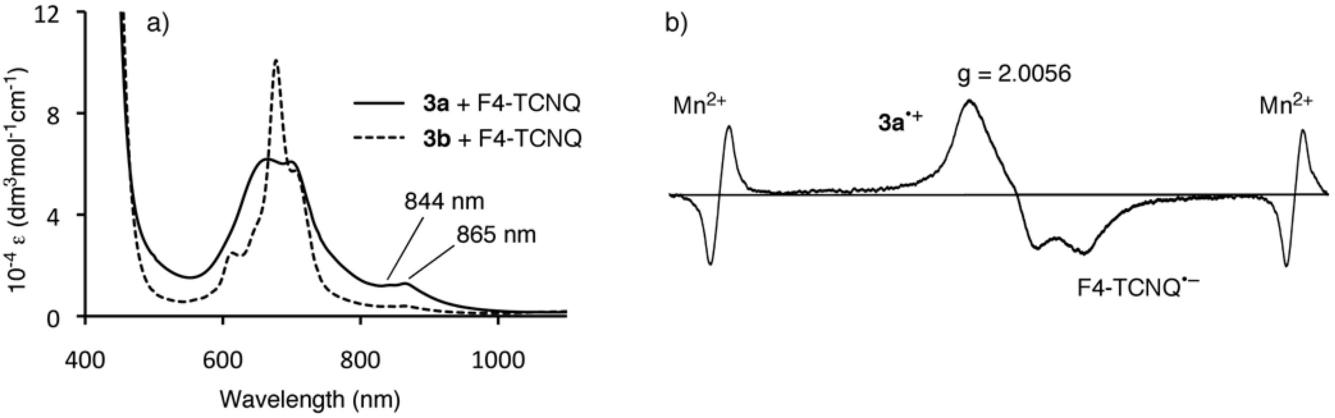


Figure 2. a) UV-vis spectra of **3a** + F4-TCNQ and **3b** + F4-TCNQ measured in chloroform and b) ESR spectrum of **3a** + F4-TCNQ.

The redox potentials of **3a**, **3b**, **4a**, and **4b** were determined by cyclic voltammetry; scan rate: 200 mV/s (Table 1). While the cyclic voltammogram of **3b** showed three reversible couples for oxidation ($E_{1/2}$ = 0.42, 0.75, and 1.22 V), quasi-reversible and reversible five couples were observed for reduction ($E_{1/2}$ = –1.60, –1.16, –0.97, –0.70, and –0.48 V) (Figure 1c). In the voltammogram of **4b**, we could observe one reversible couple for oxidation and five reversible couples for reduction. Apparently, the first two oxidation couples of **3b** could be generated from the TTF unit and the first reduction potential of **3b** is slightly higher than that of **4b**. Although the 4th reduction couple of **3b** is not clear, it may be a quasi-reversible couple. Therefore, **3b** could have an eight-step-redox system between –1.8 V and 1.4 V. In the voltammogram of **3a**, we could observe two quasi-reversible couples for oxidation ($E_{1/2}$ = 0.38 and 0.75 V) and quasi-reversible and reversible couples for reduction ($E_{1/2}$ = –1.48 and –1.25 V) (Figure 1b). The voltammgram of **4a** showed two quasi-reversible couples for oxidation and overlaid quasi-reversible couples for reduction. While the difference of the first reduction potential of **3a** and **3b** is large, that of their first oxidation potential is small; the effect of the sulfonyl group of **3b** could be estimated as about 0.8 V for the first reduction potential. In addition, the first reduction potential of **3a** is higher than that of *β*PcOTTFNi and the first oxidation potential of **3a** is similar to that of *β*PcOTTFNi.

Since the oxidation couples of **3b** more clearly appear in the voltammogram than do that of **3a**, it is expected that the aggregative property of **3b** is weaker than that of **3a** in the solution.

In a previous paper, when α-hexa(octyloxy)Pc fused with one TTF unit [αPcOTTF] was treated with iodine, we could observe that the Q band absorption shifted to the lower energy field in the UV-vis spectra (from 771 nm to 863 nm) and the solution showed a broadened ESR signal (g = 2.0076).[7c] Based on these results, **3a** and **3b** were treated with iodine in chloroform. However, the UV-vis spectra did not change at all except for the absorption of added iodine. Therefore, we used tetrafluoro-tetracyanoquinodimethane (F4-TCNQ) as an electron acceptor instead of iodine.[10] On measurement of the UV-vis spectrum of **3a** in the presence of excess amounts of F4-TCNQ, the Q band absorption was changed in the spectrum. The intensity of the absorption of **3a** slightly decreased (665 and 699 nm) and the broadened and new red shifted absorption (844 and 865 nm) appeared in the spectrum (Figure 2a). The absorption spectrum did not change after 48 h. It is expected that compound **3a** and F4-TCNQ produced an electron transfer complex and the complex and unreacted **3a** are in equilibrium in the solution. In contrast, although **3b** seemed to produce an electron transfer complex under the similar condition, the concentration of the complex was apparently lower than that of **3a** (Figure 2a). On the other hand, when the solution of the complex, produced from **3a** and F4-TCNQ, was measured by ESR at room temperature after concentration, one strong broadened signal was found at g = 2.0056 (Figure 2b). However, the signal was overlaid with the signal of the radical anion of F4-TCNQ (g = 2.0025); hence, the signal of **3a** was observed as an unsymmetrical shape in the spectrum.[10] In contrast, compound **3b** showed a faint signal together with a weak signal of F4-TCNQ$^{\bullet-}$. The g value of the electron transfer complex **3a**$^{\bullet+}$ could be related to the radical cation of TTF,[11] which suggests that the electron transfer complex has a radical cationic character based on the TTF unit.

In conclusion, we prepared unsymmetrical phthalocyanines fused with one TTF unit and six octylthio or six octylsulfonyl groups by the reaction of the mixture of phthalonitrile fused with the TTF unit and 4,5-di(octylthio)- or 4,5-di(octylsulfonyl)phthalonitrile. Compound **3b** showed the eight-step-redox system, though **3a** showed the quasi-reversible four step one. Although compounds **3a** and **3b** were not oxidized with iodine, they produced radical cationic complexes by the reaction with F4-TCNQ in chloroform. While the electron transfer complex generated from **3a** has radical cationic character, the complex of **3b** showed the faint signals.

EXPERIMENTAL

General

NMR spectra were measured with a Bruker AVANCE-500 spectrometer. Mass spectra were obtained using a JEOL JMS-700 mass spectrometer. UV-vis spectra were recorded with a JASCO Ubest V-570 spectrometer. IR spectrum was obtained employing a JASCO FT/IR-4200 spectrometer. ESR spectra were measured by JEOL JES-FA100 spectrometer. A Hokuto Denko Co. Model HAB-151 apparatus was applied to measurements of redox potentials. Biobeads (SX-1) for column chromatography was purchased from Nippon Bio-Rad Laboratories. All measurements for redox potentials were performed by cyclic voltammetry, using Ag/$AgNO_3$ (0.01 mol/L) as a reference electrode, glassy carbon as a working electrode, and Pt wire as a counter electrode (scan rate: 200 mV/s). A solution of *n*-Bu_4NClO_4 in CH_2Cl_2 (0.1 mol/L) was used as an electrolyte. The oxidation potential of ferrocene was observed at $E_{1/2}$ = 0.09 V by the apparatus without any correction.

Preparation of phthalocyanine 3a.

To a mixture of **1** (113.0 mg, 0.25 mmol), **2a** (313.9 mg, 0.75 mmol), $Ni(OAc)_2$•$4H_2O$ (62.9 mg, 0.25 mmol), and $MoO_4(NH_4)_2$ (18 mg, 0.09 mmol), 1,2-dichlorobenzene (2 mL) and DMF (0.5 mL) were added under argon and the mixture was stirred at 140 °C for 48 h. The solution was cooled to room temperature, and MeOH and suitable amount of H_2O were added to the solution. The blue-green precipitate was filtered and the residue was dissolved in $CHCl_3$. The solution was dried and evaporated and the product was purified with repeated column chromatography (silica gel, hexane/$CHCl_3$ and Biobeads, $CHCl_3$) to produce **3a** in 1% yield (3.4 mg) together with **4a** (6% yield, 18.1 mg); **3a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.79-1.00 (m, 18H, CH_3), 1.16-1.63 (m, 48H CH_3 and CH_2), 1.66-1.82 (m, 12H, CH_2), 1.93-2.12 (m, 12H, CH_2), 2.59 (s, 6H, SCH_3), 3.13 (brs, 4H, SCH_2), 3.28-3.47 (m, 12H, CH_2 and SCH_2), 3.42 (brt, *J* = 7.3 Hz, 4H, OCH_2), 7.96 (brs, 2H, ArH), 8.42 (brs, 2H, ArH), 8.48 (brs, 2H, ArH); UV-Vis ($CHCl_3$), λ_{max} nm (ε): 322 (98400), 662 (71500), 700 (69100); HR-FAB-MS (matrix: 2-nitrophenyl octyl ether): calcd for $C_{90}H_{125}N_8NiS_{12}$ = 1759.6029; found *m/z* = 1759.6001 (MH^+).

Preparation of phthalocyanine 3b.

To a mixture of **1** (227.4 mg, 0.5 mmol), **2** (723.8 mg, 1.5 mmol), and $Ni(OAc)_2$•$4H_2O$ (125.1 mg, 0.5 mmol), 1,2-dichlorobenzene (2 mL) and DMF (0.5 mL) were added under argon and the mixture was stirred at 135 °C for 18 h. The solution was cooled to room temperature and MeOH and suitable amount of H_2O were added to the solution. The blue-green precipitate was filtered and the residue was dissolved in $CHCl_3$. The solution was dried and evaporated and the product was purified with repeated column chromatography (silica gel, $CHCl_3$ and Biobeads, $CHCl_3$) to produce **3b** in 1% yield (7.6 mg) together with **4b** (26% yield, 194.5 mg); **3b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.78 (t, *J* = 6.7 Hz, 6H, CH_3), 0.85 (t, *J* = 6.8 Hz, 6H, CH_3), 0.87 (t, *J* = 6.9 Hz, 6H, CH_3), 1.15-1.64 (m, 62H, CH_3 and CH_2), 1.69 (br. quint, *J* = 7.2 Hz, 4H, CH_2), 1.99 (br. quint, *J* = 7.3 Hz, 4H, CH_2), 2.16 (br. quint, *J* = 7.5 Hz, 4H, CH_2), 2.20 (br. quint, *J* = 7.2 Hz, 4H, CH_2), 2.46 (s, 6H, SCH_3), 3.76 (br. s, 4H, CH_2), 3.99 (br. t, J = 7.3 Hz, 4H, SO_2CH_2), 4.09 (br. t, J = 7.5 Hz, 4H, SO_2CH_2), 4.12 (br. t, J = 7.2 Hz, 4H, SO_2CH_2), 9.83 (br. s, 2H, ArH), 10.14 (br. s, 2H, ArH), 10.18 (br. s, 2H, ArH); IR (KBr) 1306, 1141 cm^{-1} (SO_2); UV-Vis ($CHCl_3$), λ_{max} nm (ε): 345 (53200), 612 (24600), 675 (95000), 708 (58100); FAB-MS (matrix: *m*-nitrobenzylalcohol) *m/z* = 1950.5 (M^+).

ACKNOWLEDGMENT

This work was supported by a Special Grant from Iwate University.

REFERENCES AND NOTES

1 a) V. N. Nemykin and E. A. Luk'yanets, in *Handbook* of *Porphyrin Science*, Vol. 3, ed. by K. M. Kadish, K. M. Smith, and R. Guilard, World Scientific, Singapore, 2010, 1; b) T. Fukuda and N. Kobayashi, in *Handbook* of *Porphyrin Science*, Vol. 9, ed. by K. M. Kadish, K. M. Smith, and R. Guilard, World Scientific, Singapore, 2010, pp. 1-644; c) K. M. Kadish, K. M. Smith, and R. Guilard, *The Porphyrin Handbook*, Vols. 15-20, Academic Press, San Diego, 2003; J. Mack and N. Kobayashi, *Chem. Rev.*, 2011, **111**, 281; T. Kimura, *Heterocycles*, 2013, **87**, 245.

2 a) M. Abel, S. Clair, O. Ourdjini, M. Mossoyan, and L. Porte, *J. Am. Chem. Soc.*, 2011, **133**, 1203; b) X. Ding, L. Chen, Y. Honsho, X. Feng, O. Saengsawang, J. Guo, A. Saeki, S. Seki, S. Irle, S. Nagase, V. Parasuk, and D. Jiang, *J. Am. Chem. Soc.*, 2011, **133**, 14510; c) T. Honda, T. Kojima, N. Kobayashi, and S. Fukuzumi, *Angew. Chem. Int. Ed.*, 2011, **50**, 2725; d) N. Kobayashi, T. Furuyama, and K. Satoh, *J. Am. Chem. Soc.*, 2011, **133**, 19642.

3 a) B. del Rey, U. Keller, T. Torres, G. Rojo, F. Agulló-López, S. Nonell, C. Martí, S. Brasselet, I. Ledoux, and J. Zyss, *J. Am. Chem. Soc.*, 1998, **120**, 12808; b) E. M. Maya, C. García, E. M. García-Frutos, P. Vázquez, and T. Torres, *J. Org. Chem.*, 2000, **65**, 2733.

4 J. L. Segura and N. Martín, *Angew. Chem. Int. Ed.*, 2001, **40**, 1372; J. O. Jeppesen and J. Becher, *Eur. J. Org. Chem.*, 2003, 3245; M. Iyoda, M. Hasegawa, and Y. Miyake, *Chem. Rev.*, 2004, **104**, 5085; N. Martín, L. Sánchez, M. Á. Herranz, B. Illescas, and D. M. Guldi, *Acc. Chem. Res.*, 2007, **40**, 1015.

5 C. Loosli, C. Jia, S.-X. Liu, M. Haas, M. Dias, E. Levillain, A. Neels, G. Labat, A. Hauser, and S. Decurtins, *J. Org. Chem.*, 2005, **70**, 4988; C. A. Donders, S.-X. Liu, C. Loosli, L. Sanguinet, A. Neels, and S. Decurtins, *Tetrahedron*, 2006, **62**, 3543.

6 a) T. Kimura, D. Watanabe, and T. Namauo, *Heteroat. Chem.*, 2011, **22**, 605; b) T. Kimura, N. Takahashi, T. Tajima, and Y. Takaguchi, *Heterocycles*, 2012, **84**, 333; c) T. Kimura, N. Takahashi,

T. Tajima, and Y. Takaguchi, *Heterocycles*, 2012, **86**, 679; d) T. Kimura, *Heterocycless*, 2014, **88**, 207.

7 a) M. A. Blower, M. R. Bryce, and W. Devonport, *Adv. Mater.*, 1996, 63; b) M. J. Cook, G. Cooke, and A. Jafari-Fini, *Chem. Commun.*, 1996, 1924; c) C. Farren, C. A. Christensen, S. FitzGerald, M. R. Bryce, and A. Beeby, *J. Org. Chem.*, 2002, **67**, 9130; d) J. Sly, P. Kasák, E. Gomar-Nadal, C. Rovira, L. Górriz, P. Thordarson, D. B. Amabilino, A. E. Rowan, and R. J. M. Nolte, *Chem. Commun.*, 2005, 1255.

8 M. Nicolau, B. del Rey, T. Torres, C. Mingotaud, P. Delhaes, M. J. Cook, and S. C. Thorpe, *Synth. Metal.,* 1999, **102**, 1462.

9 a) T. Fukuda, S. Masuda, and N. Kobayashi, *J. Am. Chem. Soc.*, 2007, **129**, 5472; b) T. Fukuda, S. Masuda, N. Hashimoto, and N. Kobayashi, *Inorg. Chem.*, 2008, **47**, 2576.

10 a) T. Akutagawa, K. Kakiuchi, T. Hasegawa, T. Nakamura, C. A. Christensen, and J. Becher, *Langmuir*, 2004, **20**, 4187; b) R. Hou, C. Jiang, and B. Yin, *Heterocycles*, 2010, **81**, 717.

11 F. Wudl, G. M. Smith, and E. J. Hufnagel, *J. Chem. Soc., Chem. Commun.*, 1970, 1453