HETEROCYCLES, Vol. 99, No. 2, 2019, pp. 1355 - 1360. © 2019 The Japan Institute of Heterocyclic Chemistry
Received, 10th September, 2018, Accepted, 11th October, 2018, Published online, 17th December, 2018
DOI: 10.3987/COM-18-S(F)67

PREPARATION AND OPTICAL AND ELECTROCHEMICAL PROPERTIES OF PHTHALOCYANINE WITH FOUR BIS(CARBOMETHOXY)TETRATHIAFULVALENE UNITS

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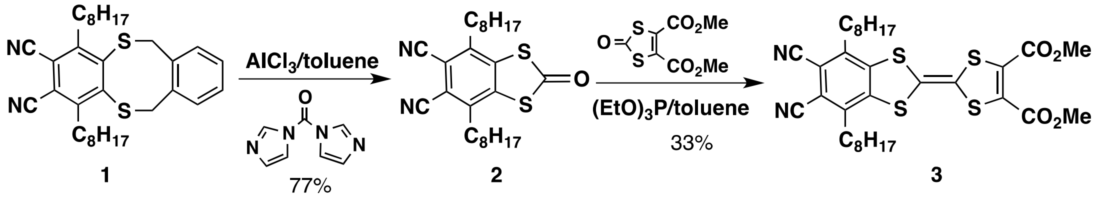
Dedicated to Professor Tohru Fukuyama on the celebration of his 70th birthday

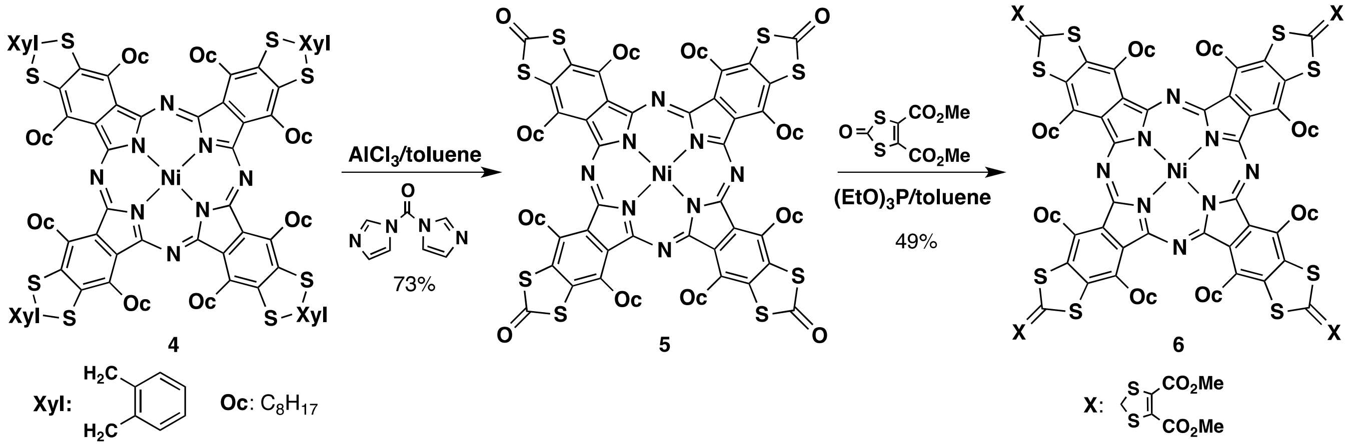
Abstract – *α*-Octaoctylphthalocyaninato Ni(II) with four bis(carbomethoxy)tetrathiafulvalene units was prepared from *β*-tetrakis(*o*-xylylenedithio)-*α*-octaoctylphthalocyaninato Ni(II) *via* C-S bond cleavage, carbonylation, and condensation with 4,5-bis(carbomethoxy)-1,3-dithiol-2-one. The structure of the product was determined by NMR and MALDI-TOF-MS and the electrochemical and optical properties were examined by cyclic voltammetry, UV-vis spectra, and ESR spectrum.

Research on phthalocyanines (Pcs) has been done to develop new functional materials or photocatalysts for electrochromic displays, field-effect transistors, solar cells, photodynamic therapy of cancer and so on.[1,2] Pcs and related compounds can be prepared through the tetramerization reaction of phthalonitrile derivatives modified in electrochemical and/or optical properties.[1,2] Functional group transformation on the Pc core is one of the methods to prepare π-expanded macrocycles.[3] In a related study, we reported that the removal of the benzyl and *o*-xylylene groups can be performed on the Pc core *via* the C-S bond cleavage, which can be applied to the construction of the tetrathiafulvalene (TTF) unit and the dithiaphosphole ring.[4,5] It is important that the Q band absorption of *α*-alkylated Pcs is observed at the lower energy field than that of *β*-alkylated ones.[6] Recently, we prepared *α*-octaoctylPcs fused with four TTF units [PcTTF4(SMe)8] and [PcTTF4(EDT)4] bearing eight methylthio and four ethylenedithio (EDT) groups as electron donating substituents on the TTF edges, respectively.[4] While porphyrins and Pcs fused with the TTF units were reported by several research groups,[7,8] tetraazaporphyrins with four TTF units which have eight carboalkoxy groups as electron acceptors, were reported by Yin et al.[9] To prepare *α*-substituted Pcs fused with the TTF units substituted with carbomethoxy groups, we tried a tetramerization reaction of the corresponding phthalonitriles and a functional exchange reaction on the Pc core. In this paper, we report the preparation, structure determination, and optical and electrochemical properties of octaoctylPc Ni(II) (**6**) fused with four bis(carbomethoxy)TTF units *via* 1) C-S bond cleavage of β-tetrakis(*o*-xylylenedithio)-α-octaoctylphthalocyaninato Ni(II) (**4**), 2) carbonylation of octathiolates with carbonyldiimidazole, and 3) condensation of resulted 1,3-dithiol-2-one rings with 4,5-bis(carbomethoxy)-1,3-dithiol-2-one.



Scheme 1

4,5-(*o*-Xylylenedithio)-3,6-dioctylphthalonitrile (**1**) was prepared and treated with toluene in the presence of aluminum chloride under argon for 1 h to generate the corresponding dithiolates. Carbonyldiimidazole was added to the reaction mixture and the solution was stirred at 100 °C for 3 h to produce 3,6-dioctylphthalonitrile **2** fused with a 1,3-dithiol-2-one ring in 77% yield (Scheme 1).[4] To construct a TTF unit, compound **2** was reacted with 4,5-bis(carbomethoxy)-1,3-dithiol-2-one in toluene and triethylphosphite at 100 °C for 1 h. The reaction produced 4,7-octyl-5,6-dicyano-2-(4',5'-bis(carbomethoxy)-1',3'-dithiol-2'-ylidene)benzo[*d*]-1,3-dithiol (**3**) in 33% yield. Then, we attempted to prepare Pc fused with four TTF units. Thus, compound **3** was treated with lithium alkoxide in 1-hexanol at 120 °C for 1 h. However, the reaction produced a complex mixture; we could not obtain the cyclized compound and **3** was not recovered at all. Furthermore, the cyclization reaction of **3** in the presence of DBU in 1-hexanol at 120 °C for 3 h gave also complex mixture.



Scheme 2

Next, we tried to exchange functional groups at the *β*-positions of the Pc core. It was reported that the peripheral modification could be performed by Birch reduction according to Hoffman's method.[10] Meanwhile, we utilized the C-S bond cleavage of *o*-xylylenedithio groups using toluene in the presence of aluminum chloride under argon. Since metallated Pcs showed better yield than free-base during the C-S bond cleavage reaction, we used compound **4** as a substrate (Scheme 2).[5] After addition of aluminum chloride, toluene solution of **4** was changed from a greenish color to reddish brown under argon, and then carbonyldiimidazole was added to the reaction mixture. The solution was stirred at 105 °C for 1 h to produce Pc **5** fused with four 1,3-dithiol-2-one rings in 73% yield, after purification with column chromatography with silica gel and bio-beads. Then, a mixture of compound **5** and 4,5-bis(carbomethoxy)-1,3-dithiol-2-one was dissolved in toluene and triethylphosphite under argon and the solution was stirred at 120 °C for 1 h. After purification, Pc **6** fused with four bis(carbomethoxy)TTF units was obtained in 49% yield. The structure of **6** was determined by NMR, IR, and MALDI-TOF-MS. In the ^{1}H NMR spectrum of **6**, the signal of the xylylene groups disappeared and we found a new signal of methyl protons of carbomethoxy groups at 3.91 ppm. MALDI-TOF-MS showed the corresponding molecular ion peaks at $m/z = 2637.9$ [M^+].

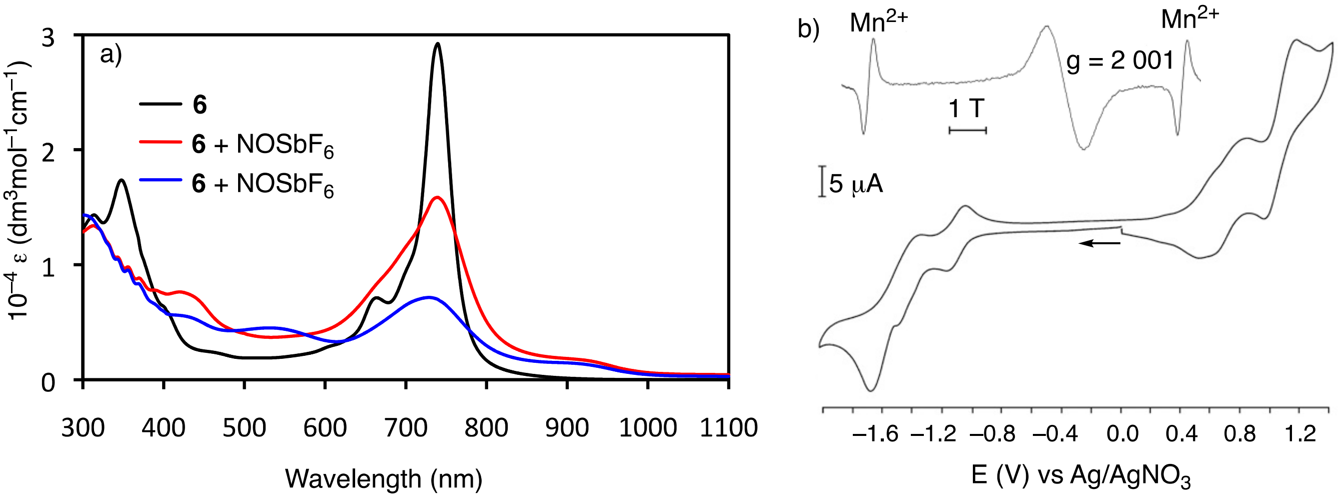


Figure 1. a) UV-vis spectra of **6** and **6** + $NOSbF_6$ [red line (after several minutes) and blue line (after 30 min)] measured in $CHCl_3$, b) ESR spectrum of **6** + $NOSbF_6$ ($CHCl_3$) and cyclic voltammogram of **6** using $Ag/AgNO_3$ as a reference electrode.

While compound **6** shows the Q band absorption at $\lambda_{max} = 739$ nm in the UV-vis spectrum measured in chloroform (Figure 1a), there was no emission in the fluorescence spectrum measurement. The redox potentials of **6** were determined by cyclic voltammetry; scan rate: 200 mV/s (Table 1). In the voltammogram, two quasi-reversible couples for oxidation ($E_{1/2}$ = 0.70 and 1.11 V) and two reversible couples and one peak potential for reduction ($E_{1/2}$ = –1.68, –1.47 and –1.11 V) could be observed (Figure

1b), which showed anode-shift compared with those of PcTTF4(SMe)8 and PcTTF4(EDT)4 bearing eight methylthio or four ethylenedithio (EDT) groups instead of eight carbomethoxyl groups of **6** (Table 1). When *β*-hexa(octylthio)phthalocyaninato Ni(II) fused with one bis(methylthio)TTF unit [1st oxidation potential, $E_{1/2}$ = 0.38 V (quasi-reversible)] was treated with tetrafluorotetracyanoquinodimethane (F4-TCNQ) as an electron acceptor, we could observe new absorption at 865 nm in the UV-vis spectrum and the solution showed a broadened ESR signal (g = 2.0056).[11] In the UV-vis spectrum of **6** in the presence of excess amount of F4-TCNQ in chloroform, the Q band absorption did not changed at all. On the other hand, when a one-electron-oxidazing reagent, nitrosonium hexafluoroantimonate, was added to the chloroform solution, the absorption at 739 nm immediately decreased and a new absorption appeared at the longer wavelength at around 900 nm (Figure 1a). When the concentrated solution of **6** + $NOSbF_6$ in chloroform was measured by ESR at room temperature, one strong broadened signal was found at g = 2.001 in the spectrum (Figure 2). The chloroform solution of PcTTF4(EDT)4 showed one broadened signal at g = 2.0072 in the presence of iodine and the TTF radical cation reported by Wudl showed the signal at g = 2.008 in the ESR spectrum; therefore, the g value of the electron transfer complex $\mathbf{6}^{\bullet +}$ was slightly lower than those of PcTTF4(EDT)4 and TTF.[12]

Table 1. Redox potentials of phthalocyanines

Compound	$E_{1/2}$ [V]					E_{1oxid}–E_{1redn} [V]	λ_{max}[c] [nm]	ΔE_{calcd} [eV]
	3rd redn	2nd redn	1st redn	1st oxid	2nd oxid			
6	–1.68[b]	–1.47	–1.11	0.70[a]	1.11	1.81	739	1.68
PcTTF4(SMe)8		–1.48	–1.19	0.42[a]	0.83	1.61	741	1.67
PcTTF4(EDT)4		–1.53	–1.18	0.30[a]	0.55	1.48	741	1.67

[a]Quasi-reversible, [b]irreversible, [c]Q-band absorption, ΔE_{calcd} was calculated using λ_{max}.

In conclusion, we prepared *α*-substituted phthalocyanines fused with four bis(carbomethoxy)TTF units. The oxidation and reduction potentials of **6** show anode-shift compared with those of PcTTF4(SMe)8 and PcTTF4(EDT)4. The electron transfer complex generated from compound **6** and $NOSbF_6$ in chloroform has a radical cationic character, and the charge generated on the TTF unit can delocalize to the π-aromatic system of the central phthalocyanine core.

EXPERIMENTAL

General

NMR spectra were measured with a Bruker AVANCE-500 spectrometer. Mass spectra were obtained using a JEOL JMS-700 mass spectrometer and a Shimadzu Biotech Axima Confidence mass spectrometer. UV-vis spectra were recorded with a JASCO Ubest V-570 spectrometer. A Hokuto Denko Co. Model HAB-151 apparatus was applied to measurements of redox potentials. ESR spectrum was measured by JEOL JES-FA100 ESR spectrometer. Bio-beads (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. 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.

4,5-(*o*-Xylylenedithio)-3,6-diocylphthalonitrile (1), 4,7-dioctyl-5,6-dicyanobenzo-1,3-dithiol-2-one- (2), tetrakis(*o*-xylylenedithio)octaoctylphthalocyanine nickel(II) (4), and tetrakis(4,7-dioctyl-2-one-benzo-1,3-dithiolo[5,6-*b*: 5',6'-*g*: 5",6"-*l*: 5''',6'''-*q*])porphyrazinato nickel(II) (5)

Compounds **1**, **2**, **4**, and **5** were prepared by a method reported previously.[4c]

4,7-Dioctyl-5,6-dicyano-2-(4',5'-bis(carbomethoxy)-1',3'-dithiol-2'-ylidene)benzo[*d*]-1,3-dithiol (3)

Compound **2** (350.0 mg, 0.8 mmol) and 4,5-bis(carbomethoxy)-1,3-dithiol-2-one (300 mg, 1.2 mmol) were dissolved in toluene (1.0 mL)/triethyl phosphite (1.5 mL) and the mixture was stirred at 100 °C for 1 h. The solution was cooled to room temperature and MeOH and brine were added. A precipitate was filtered and the residue was dissolved in $CHCl_3$. The solution was dried and the solvent was evaporated. The solid product was purified with column chromatography (Wakogel C-300HG, $CHCl_3$) to produce **3** in 33% yield (182 mg); ^1H NMR (500 MHz, $CDCl_3$) δ 0.88 (t, J = 7.0 Hz, 6H, CH_3), 1.22 - 1.37 (m, 16H, CH_2), 1.37-1.44 (m, 4H, CH_2), 1.62 (quint, J = 8.0 Hz, 4H, CH_2), 2.76 (t, J = 8.0 Hz, 4H, CH_2), 3.86 (s, 6H, CH_3); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 14.0, 22.6, 28.3, 29.0, 29.1, 29.4, 31.7, 35.5, 53.5, 107.3, 112.6, 113.7, 114.5, 131.7, 138.6, 143.3, 159.4; IR (KBr) 2925, 2854, 2230, 1716, 1278 cm^{-1}; HRMS (FAB): calcd for $C_{32}H_{40}N_2O_4S_4$, 644.1871; found, 644.1871 (M^+).

Preparation of tetrakis(4,7-dioctyl-2-(4',5'-(carbomethoxy)-1',3'-dithiol-2'ylidene)bonzo-1,3-dithiolo[5,6-*b*: 5',6'-*g*: 5",6"-*l*: 5''',6'''-*q*])porphyrazinato nickel(II) (6)

Phthalocyanine (**5**) (97 mg, 0.05 mmol) and 4,5-bis(carbomethoxy)-1,3-dithiol-2-one (133 mg, 0.53 mmol) were placed in a glass reactor, and toluene (4 mL) and triethyl phosphite (3 mL) were added under Ar. The solution was stirred at 120 °C for 1 h. After cooling the reactor, MeOH and water were added to the reaction mixture. The green precipitate was filtered and the residue was dissolved in $CHCl_3$. After evaporation, the product was purified by column chromatography (Wakogel C-300HG and Bio-beads

SX-1, $CHCl_3$) to give **6** in 49% yield (69.0 mg); **6**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.66-0.81 (br, 24H,CH_3), 1.01-1.21 (m, 48H, CH_2), 1.41-1.53 (m, 16H, CH_2), 1.74-1.98 (m, 16H, CH_2), 3.91 (s, 24H, CH_3), 4.10-4.35 (m, 16H, CH_2); IR (KBr) 2923, 2852, 2360, 1732, 1666, 1259, 1096, 1026 cm^{-1}; MALDI-TOF-MS (*m*/*z*) 2637.9 [M^+].

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