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Preparation and Optical and Electrochemical Properties of Octaethylphthalocyanines Fused with Several Tetrathiafulvalene Units

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ABSTRACT: *3,6-Diethylphthalonitrile (**3**) with a tetrathiafulvalene (TTF) unit at 4,5-positions was prepared from 4,5-xylylenedithio-3,6-diethylphthalonitrile (**1a**) via elimination of the xylylene group, connection of a carbonyl group to benzenedithiolate generated, and condensation of 4,5-bis(methylthio)-1,3-dithiole-2-thione with benzo-1,3-dithiole-2-one (**2-O**) produced. A 1:1 mixture of phthalonitrile (**3**) and 4,5-bis(benzylthio)-3,6-diethylphthalonitrile (**1b**) was treated with lithium in n-hexanol at 120°C to produce hexakis (benzylthio)mono(tetrathiafulvaleno)phthalocyanine (**5**), tetrakis(benzylthio)bis(tetrathiafulvaleno)phthalocyanine (**6**), and bis(benzylthio)tris(tetrathiafulvaleno)phthalocyanine (**7**). The structures of **5**, **6**, and **7** were determined by ^1H NMR, FAB MS, MALDI-TOF MS (matrix assisted laser desorption ionization time-of-flight mass spectrometry), and UV–vis spectroscopy. Compound **6** is a mixture of trans and cis isomers (**6-trans** and **6-*cis***). The UV–vis spectrum of **5** measured in chloroform changed by addition of trifluoroacetic acid (TFA). The Q band absorption at λ_{max} = 755 nm (chloroform) decreased in intensity and resulted in a new absorption at λ_{max} = 740 nm (chloroform/TFA). The electrochemical properties of **5**, **6**, and **7** were determined by cyclic voltammetry using Ag/$AgNO_3$ as a reference electrode.* © 2011 Wiley Periodicals, Inc. Heteroatom Chem 22:605–611, 2011; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.20694

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INTRODUCTION

Phthalocyanines and related compounds have attracted considerable attention for their actual and potential applications in many fields including catalysis, new functional materials, and sensitizers for photodynamic therapy [1–3]. It is significant that Q-band absorption lies at the near infrared region to apply these molecules to new functional materials. Redshift of the Q-band absorption of phthalocyanines can be efficiently performed by attaching substituents at the α-positions of the macrocycles [4]. Introducing several heteroatoms in the benzene rings of phthalocyanine is also a procedure for improving its characteristics [5]. As a related study, we recently reported the preparation of octakis(benzylthio)phthalocyanine [**PcSBn**] and its selenium derivative [6]. Furthermore, tetrakis(trithiolo)phthalocyanines and double-decker phthalocyanine were prepared from tetrakis(*o*-xylylenedithio)phthalocyanines and octakis(methylthio)phthalocyaninato titanium (IV) oxide, respectively [7].

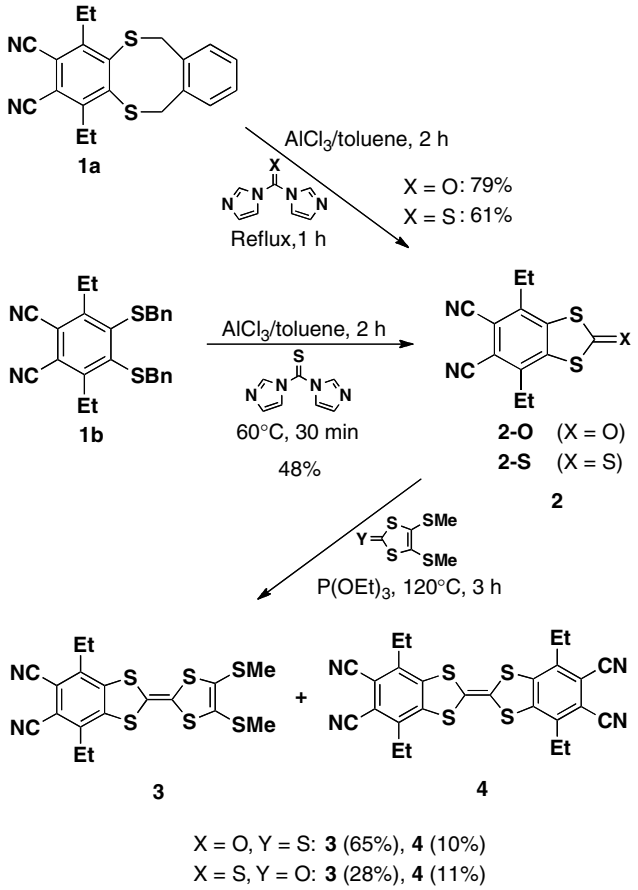
On the other hand, tetrathiafulvalene (TTF) has been known to be an excellent electron donor and has been applied to a variety of functional substances [8]. There are several reports that the TTF units are combined with phthalocyanines by means of connecting them through some linkers in the peripheral

or axial directions [9]. In contrast, Becher reported that porphyrin and calixphyrin derivatives fused with one or four TTF units [10], whereas Decurtins prepared phthalocyanines with four TTF scaffolds [11]. Recently, unsymmetrically substituted phthalocyanine with one TTF part was reported [12]. To prepare phthalocyanine with eight alkyl groups at the α-positions and several TTF units at the β-positions, 3,6-diethylphthalonitrile (**3**) with the TTF skeleton at 4,5-positions was prepared and mixed with 4,5-bis(benzylthio)-3,6-diethylphthalonitrile (**1b**) in a 1:1 ratio and treated with lithium in *n*-hexanol. This paper reports the preparation, structure determination, and optical and electrochemical properties of unsymmetrically substituted phthalocyanines with eight ethyl groups at the α-positions and one through three TTF units at the β-positions.

RESULTS AND DISCUSSION

As starting compounds, 4,5-xylylenedithio-3,6-diethylphthalonitrile (**1a**) and 4,5-bis(benzylthio)-3,6-diethylphthalonitrile (**1b**) were prepared from 1,4-diethyltetrabromobenzene via several step reactions by the procedure reported previously [6,7]. Compound **1a** was treated with $AlCl_3$ in toluene at room temperature and then with carbonyldiimidazole or thiocarbonyldiimidazole at reflux temperature, which gave benzo-1,3-dithiole-2-one (**2-O**) and benzo-1,3-dithiole-2-thione (**2-S**) in 79% and 61% yields, respectively (Scheme 1). Similarly, **2-S** was prepared from **1b** in 48% yield on treatment with $AlCl_3$ and thiocarbonyldiimidazole. Compound **2-O** was further treated with 4,5-bis(methylthio)-1,3-dithiole-2-thione in triethylphosphite at 120°C for 4 h to produce phthalonitrile (**3**) with the TTF unit in 65% yield as red-orange crystals, whereas **2-S** gave **3** in 28% yield after the reaction with 4,5-bis(methylthio)-1,3-dithiole-2-one under similar reaction conditions. In these treatments, tetracyanodibenzotetrathiafulvalene (**4**) was produced by the self-condensation of **2-O** or **2-S** in 10% and 11% yields, respectively. The ^{1}H NMR spectrum of **4** can be measured in chloroform-*d* at room temperature, but the solubility of the compound is not high enough in the usual organic solvents.

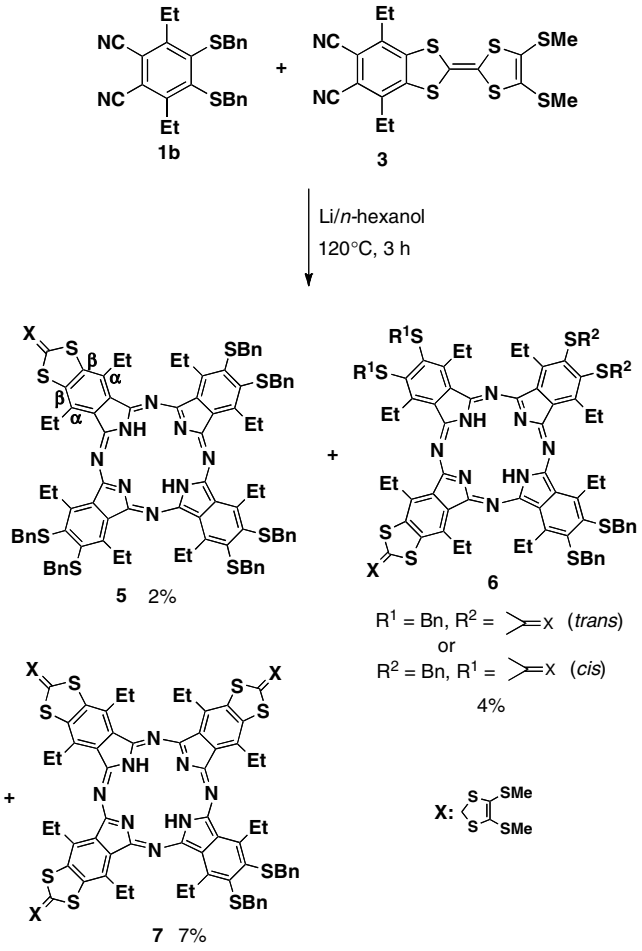
Although three approaches are known for preparing unsymmetrically substituted phthalocyanines [13–15], we used the statistical procedure. Compound **3** was mixed with **1b** in a 1:1 ratio and treated with lithium in *n*-hexanol at 120°C for 3 h (Scheme 2). The blue-green solid that precipitated in the solution was filtered, dried, and purified by silica gel and Bio-beads column chromatography, which gave



SCHEME 1

hexakis(benzylthio)mono(tetrathiafulvaleno)phthalocyanine (**5**) in 2% yield together with tetrakis(benzylthio)bis(tetrathiafulvaleno)phthalocyanine (**6**) and bis(benzylthio)tris(tetrathiafulvaleno) phthalocyanine (**7**) in 4% and 7% yields, respectively. In this reaction, tetrakis(tetrathiafulvaleno)phthalocyanine was not obtained. In the ^{1}H NMR spectrum, **5** shows two broadened and complex triplet signals for the eight methyl groups in a 1:3 integral ratio, two broadened signals for the eight methylene groups in a 1:3 integral ratio, one singlet peak for the six benzylthio groups, and one singlet peak for the two methylthio groups, implying that **5** has one TTF unit and six benzylthio groups on the peripheral positions.

If unsymmetrically substituted phthalocyanine consists of two different types of benzopyrrole components (A) and (B) in a 1:1 ratio, the product is a mixture of the ABAB (trans) isomer and the AABB (cis) isomer, which cannot be isolated from each other [13]. Since **6** has two TTF units on the macrocycle, it should consist of two isomers, 2,3,16,17-tetrakis(benzylthio) bis(tetrathiafulvaleno)phthalocyanine (**6-*trans***) and



SCHEME 2

2,3,9,10-tetrakis(benzylthio)bis(tetrathia-fulvaleno) phthalocyanine (**6-*cis***). It is expected that **6-*trans*** shows one singlet peak for the four methylthio groups and one singlet peak for the four benzylthio groups in the spectrum, whereas two singlet signals in a 1:1 integral ratio for the four methylthio groups and two singlet signals for the four benzylthio groups appear in the spectrum of **6-*cis***. Compound **6** showed two broadened signals for the eight methylene groups in a 1:1 integral ratio, and two complex signals for the eight methyl groups in the ^{1}H NMR spectrum. In addition, two singlet peaks with different heights were observed for the four methylthio groups, in which one signal could overlay two types of the methylthio groups, suggesting that **6** contains two isomers **6-*trans*** and **6-*cis***. These isomers cannot be separated by silica gel and Bio-beads column chromatography.

When the ^{1}H NMR of **7** was measured in chloroform-*d* at 25°C, broadened and unclear signals were observed in the spectrum. Measuring the spectrum of **7** at 50°C showed two broadened triplet signals for the eight methyl groups in a 3:1 integral ratio, two broadened signals for the eight methylene groups in a 3:1 integral ratio, one singlet peak for the two benzylthio groups, and one singlet peak for the six methylthio groups. The results suggest that **7** has three TTF units and two benzylthio groups on the peripheral positions and possesses aggregative properties in solution at room temperature. The structures of **5** and **6** were finally determined with MALDI-TOF MS (matrix assisted laser desorption ionization time-of-flight mass spectrometry): m/z = 1740.59 [M^+] for **5** and m/z = 1765.14 [M^+] for **6**. Compound **7** showed the molecular ion peak at 1788.1 [MH^+] by FAB MS measurement.

UV–Visible Absorption Spectroscopy

The absorption wavelengths and molar extinction coefficients of **5**, **6**, and **7** were determined by UV–vis spectroscopy (Fig. 1 and Table 1). It is expected that the shape of absorption of the Q band is different between the symmetric phthalocyanine and the unsymmetric one and between the phthalocyanines with the AABB (cis) form and the ABAB (trans) form [16]. Interestingly although both **5** and **7** have an unsymmetrical structure, their absorption wavelengths, shapes, and molar extinction coefficients are similar to those of symmetric phthalocyanine, **PcSBn** (λ_{max} = 755.0 nm, log ε = 5.1); **5** (λ_{max} = 755.0 nm, log ε = 5.10); **7** (λ_{max} = 757.0 nm, log ε = 5.14). The absorption of phthalocyanine (**6**), which would be a mixture of cis and trans isomers is also similar to that of **PcSBn**; **6** (λ_{max} = 756.0 nm, log ε = 5.12). These results might suggest that since all the phthalocyanines obtained have eight sulfur atoms at the β-positions although the functional groups linked to the sulfur atoms are different, such as the

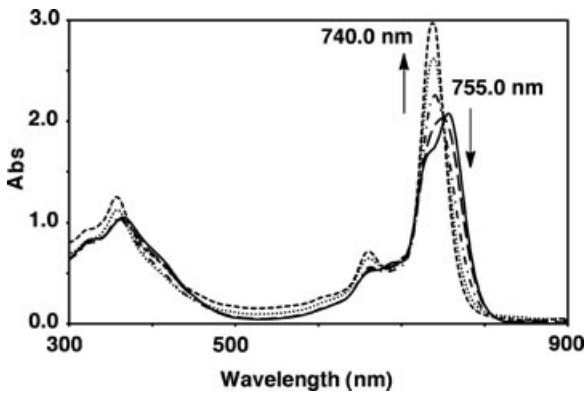


FIGURE 1 UV–vis spectra for phthalocyanine (**5**) titrated with TFA ($CHCl_3$).

TABLE 1 UV–vis Spectra and Redox Potentials of Phthalocyanines

		$E_{1/2}$(V)			
Compound	*UV–vis λ_{max} (nm) (log ε)*	*Second Reduction*	*First Reduction*	*First Oxidation*	*Second Oxidation*
5	755.0 (5.10)	−1.39	−1.04	0.41	1.36 (E_p)
6	756.0 (5.12)	−1.30	−1.03	0.38	0.77
7	757.0 (5.14)	−1.05	−0.79	0.38	0.73
PcSBn	755 (5.1)	−1.31	−1.02	0.49	0.72
3	–	–	–	0.55	0.96

UV–vis spectra were measured in $CHCl_3$; redox potentials were measured in CH_2Cl_2 (vs. $Ag/AgNO_3$).

TTF unit and the benzyl group, the π-electronic system on the central phthalocyanine core is not strongly affected by the difference of the outer functional groups. The electronic effect of the TTF unit on phthalocyanine through the sulfur atoms might be similar to that of the benzyl group in the neutral forms. On the other hand, it was reported that splitting of the Q band absorption of metal-free phthalocyanines decreases with increasing wavelength of the absorption [4b]. Since the Q bands of **5**, **6**, **7**, and **PcSBn** are shifted lower energy than that of unsubstituted phthalocyanines, they should contain several splitting absorption in their broadened Q bands.

It has been previously reported that phthalocyanines and related compounds can be protonated with acids to produce cationic species, which change the absorption in the UV–vis spectra [16,17]. When the UV–vis spectra of **5** (1.0×10^5 mol/L) were measured in the absence and presence of trifluoroacetic acid (TFA) (0–200 equiv) to examine the effect of acid concentration, the absorption in the spectra gradually changed (Fig. 1). Finally **5** was treated with 1×10^2 mol/L of TFA in chloroform, which generated cationic species in the solution. The major absorption band at $\lambda_{max} = 755$ nm gradually decreased in intensity and resulted in a new band at $\lambda_{max} = 740$ nm.

Electrochemical Properties

To determine the electrochemical properties of **5**, **6**, and **7**, their redox potentials were measured by cyclic voltammetry using $Ag/AgNO_3$ as a reference electrode (solvent: CH_2Cl_2, scan rate: 200 mV/s). As shown in Fig. 2, compound **7** showed two reversible oxidation potentials ($E_{1/2} = 0.38$ and 0.73 V) and two reversible reduction potentials ($E_{1/2} = -0.79$ and -1.05 V). In the voltammogram of **5**, one reversible and one irreversible oxidation potential ($E_{1/2} = 0.41$ V and $E_p = 1.36$ V) and two reversible reduction potentials ($E_{1/2} = -1.04$ and -1.39 V) were observed. Compound **6** shows two reversible oxidation potentials ($E_{1/2} = 0.38$ and 0.77 V) and two reversible reduction potentials ($E_{1/2} = -1.03$ and -1.30 V). The first oxidation potentials of **5**, **6**, and **7** are lower than that of **PcSBn**. Compound **3** exhibited two reversible oxidation potentials at $E_{1/2} = 0.55$ and 0.96 V.

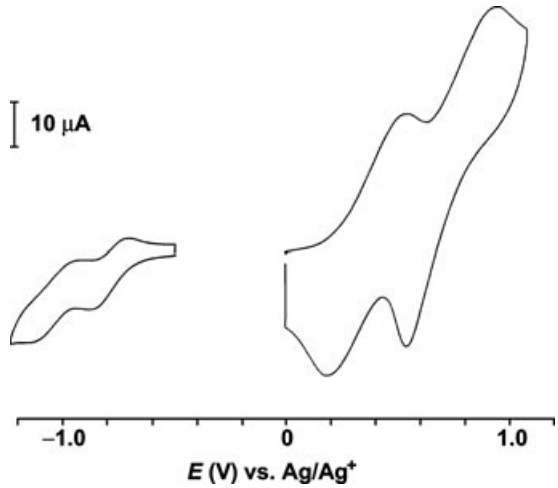


FIGURE 2 Cyclic voltammogram of **7**.

CONCLUSION

3,6-Diethylphthalonitrile (**3**) was mixed with **1b** in the 1:1 ratio and treated with lithium in *n*-hexanol to produce corresponding unsymmetrically substituted phthalocyanines **5**, **6**, and **7** with one through three TTF units, respectively. The UV–vis spectra of these products show similar absorption wavelengths, shapes, and molar extinction coefficients to those of **PcSBn**, suggesting that the π-electronic systems of these phthalocyanines are not strongly affected by the outer functional groups at the β-position under neutral conditions. The major absorption band of the cationic species of **5** generated in chloroform/TFA shifted to shorter wavelengths by ca. 15 nm from that of **5** measured in chloroform. It is expected that the proton alternation on the central

four nitrogen atoms disappears by protonation with TFA in the solution, which changes the Q-band of **5**. The electrochemical properties of **5**, **6**, and **7** were determined by cyclic voltammetry.

EXPERIMENTAL

General

NMR spectra were measured with Bruker AC-400 and Avance 500 spectrometers. The mass spectra were obtained using a JEOL JMS-700 mass spectrometer. MALDI-TOF MS was examined with a Bruker BIFLEX (III) mass spectrometer. UV–vis spectra were measured with a JASCO Ubest-30 spectrometer. A Hokuto Denko Company model HAB-151 apparatus was used to measure the redox potentials. Bio-beads (S-X1) for column chromatography were purchased from Nippon Bio-Rad Laboratories.

Redox Potentials

All measurements were performed by cyclic voltammetry, using $Ag/AgNO_3$ (0.01 mol/L) as a reference electrode. A solution of 0.1 mol/L n-Bu_4NClO_4 in CH_2Cl_2 was used as an electrolyte.

*Xylylenedithio-3,6-diethylphthalonitrile (**1a**) and 4,5-Bis(benzylthio)-3,6-diethylphthalonitrile (**1b**)*

Compounds **1a** and **1b** were prepared from 1,4-diethylbenzene by a method described previously [6,7].

*4,7-Diethyl-5,6-dicyanobenzo-1,3-dithiole-2-thione (**2-S**)*

Method A. A mixture of **1a** (365.3.0 mg, 1.04 mmol) and $AlCl_3$ (570 mg, 4.3 mmol) in toluene (10 mL) was stirred at room temperature for 2 h under Ar. To the solution, thiocarbonyldiimidazole (454 mg, 2.55 mmol) was added and the mixture was stirred at reflux temperature for 1 h. The solution was cooled to room temperature, and aqueous HCl solution was added. The product was extracted with toluene and purified with column chromatography (n-hexane/$CHCl_3$) to produce **2-S** in 61% yield (185.1 mg): yellow crystals; mp 150–151°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.34 (t, $J = 7.6$ Hz, 6H, CH_3), 2.92 (q, $J = 7.6$ Hz, 4H, CH_2Ar); ^{13}C NMR (101 MHz, $CDCl_3$) δ 13.1, 28.7, 113.9, 114.2, 140.4, 145.8, 206.9; HRMS (EI): calcd. for $C_{13}H_{10}N_2S_3$, 290.0006; found, 290.0002 (M^+).

Method B. A mixture of **1b** (428.0 mg, 1.00 mmol) and $AlCl_3$ (550 mg, 4.00 mmol) in toluene (10 mL) was stirred at room temperature for 2 h under Ar. To the solution, thiocarbonyldiimidazole (360 mg, 2.00 mmol) was added and the solution was stirred for 30 min. The reaction mixture was cooled to 0°C, and aqueous HCl solution was added after evaporation of toluene. The product was extracted with CH_2Cl_2, and purified with column chromatography (n-hexane/$CHCl_3$) to produce **2-S** in 40% yield (110 mg).

*4,7-Diethyl-5,6-dicyanobenzo-1,3-dithiole-2-one (**2-O**)*

A mixture of **1a** (350 mg, 1.00 mmol) and $AlCl_3$ (568 mg, 4.3 mmol) in toluene (18 mL) was stirred at room temperature for 2 h under Ar. To the solution, carbonyldiimidazole (407 mg, 2.5 mmol) was added and the mixture was stirred at reflux temperature for 1 h. The solution was cooled to room temperature, and aqueous HCl solution was added. The product was extracted with toluene and purified with column chromatography (n-hexane/$CHCl_3$) to produce **2-O** in 79% yield (215.2 mg): colorless crystals mp 171–171.5°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.33 (t, $J = 7.6$ Hz, 6H, CH_3), 2.96 (q, $J = 7.6$ Hz, 4H, CH_2Ar); ^{13}C NMR (101 MHz, $CDCl_3$) δ 13.0, 29.3, 113.6, 114.0, 138.4, 141.5, 185.3; HRMS (EI): calcd. for $C_{13}H_{10}N_2OS_2$, 274.0235; found, 274.0242 (M^+).

*4,7-Diethyl-5,6-dicyano-2-(4′,5′-bis(methylthio)-1′,3′-dithiole-2′-ylidene)benzo[d]-1,3-dithiole (**3**)*

Method A. Compound **2-O** (200 mg, 0.73 mmol) and 4,5-bis(methylthio)-1,3-dithiole-2-thione (332 mg, 1.47 mmol) were dissolved in triethylphosphite (5 mL), and the mixture was stirred at 120°C for 4 h. The solution was cooled to room temperature, and MeOH and brine were added. The precipitate formed was filtered. The residue was purified with column chromatography (n-hexane/$CHCl_3$) to produce **3** in 65% yield (214.5 mg) together with 4,4′,7,7′-tetraethyl-5,5′,6,6′-tetracyano-2,2′-bis(benzo-1,3-dithiole-2-ylidene) (**4**) in 10% yield (33.5 mg); **3**: red crystals; mp 224.5–225.5°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.29 (t, $J = 7.6$ Hz, 6H, CH_3), 2.45 (s, 6H, SCH_3), 2.82 (q, $J = 7.6$ Hz, 4H, CH_2Ar); ^{13}C NMR (101 MHz, $CDCl_3$) δ 12.7, 19.2, 28.9, 105.8, 113.3, 114.5, 115.4, 127.6, 139.6, 143.6; HRMS (EI): calcd. for $C_{18}H_{16}N_2S_6$, 451.9638; found, 451.9643 (M^+); **4**: yellow powder; mp. >300°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.31 (t, $J = 7.6$ Hz, 12H, CH_3), 2.85 (q, $J = 7.6$ Hz, 8H,

CH_2Ar); HRMS (EI): calcd. for $C_{26}H_{20}N_4S_4$, 516.0571; found, 516.0575 (M^+).

Method B. Compound **2-S** (200 mg, 0.73 mmol) and 4,5-bis(methylthio)-1,3-dithiole-2-one (332 mg, 1.47 mmol) were dissolved in triethylphosphite (5 mL), and the mixture was stirred at 120°C for 4 h. The solution was cooled to room temperature, and MeOH and brine were added. The precipitate formed was filtered. The residue was purified with column chromatography (*n*-hexane/$CHCl_3$) to produce **3** in 28% yield (77.4 mg) together with 4,4′,7,7′-tetraethyl-5,5′,6,6′-tetracyano-2,2′-bis(benzo-1,3-dithiole-2-ylidene) (**4**) in 11% yield (29.8 mg).

*Preparation of 1,4,8,11,15,18,22,25-Octaethyl-2,3,9,10,16,17-hexakis(benzylthio)-23,24-[4′,5′-bis (methylthio)tetrathiafulvaleno]phthalocyanine (**5**), Octaethyltetrakis(benzylthio)bis[4′,5′-bis (methylthio)tetrathiafulvaleno]phthalocyanine (**6**), and 1,4,8,11,15,18,22,25-Octaethyl-23,24-bis(benzylthio)-2,3,9,10,16,17-tris[4′,5′-bis (methylthio)tetrathiafulvaleno]-phthalocyanine (**7**)*

Lithium (36 mg, 5.2 mmol) was placed in a glass reactor, and *n*-hexanol (1.5 mL) was added under Ar. The solution was stirred at 120°C for several minutes. A mixture of **3** (117 mg, 0.26 mmol) and **1a** (111 mg, 0.26 mmol) was added, and the solution was stirred at 120°C for 3 h. After cooling to room temperature, a MeOH solution of HCl was added and the resulting blue-green precipitate was filtered. The residue was purified by column chromatography (Wakogel C-400HG, *n*-hexane/$CHCl_3$) to produce **5** in 2% yield (7.9 mg) together with **6** (9.5 mg, 4%) and **7** (11.2 mg, 7%). It should be noted that **6** may be a mixture of 1,4,8,11,15,18,22,25-octaethyl-16,17,23,24-tetrakis(benzylthio)-2,3,9,10-bis[4′,5′-bis(methylthio)tetrathiafulvaleno]-phthalocyanine (**6-*cis***) and 1,4,8,11,15,18,22,25-octaethyl-9,10,23,24-tetrakis(benzylthio)-2,3,16,17-bis[4′,5′-bis(methylthio)tetrathiafulvaleno]phthalocyanine (**6-*trans***). However, these isomers could not be isolated from each other; **5**: dark green powder; mp 105–105.5°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ1.42–1.60 (m, 18H, CH_3), 1.64 (t, $J = 7.4$ Hz, 6H, CH_3), 2.46 (s, 6H, SCH_3), 4.24–4.32 (m, 4H, CH_2Ar), 4.45 (s, 12H, SCH_2Ar), 4.53–4.71 (m, 12H, CH_2Ar), 7,12–7.17 (m, 6H, Ar), 7.17–7.24 (m, 12H, Ar), 7.29–7.36 (m, 12H, Ar); UV–vis ($CHCl_3$) λ_{max} nm (log ε) 755 (5.10); MALDI-TOF-MS *m*/*z* 1740.59 (M^+); **6**: dark green powder; mp. 107–107.5°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.44–1.72 (m, 24H, CH_3), 2.47 and 2.48 (s, 12H, SCH_3), 4.23–4.33 (m, 8H, CH_2Ar), 4.45(9) and 4.46(4) (s, 8H, SCH_2Ar), 4.57–4.70 (m, 8H, CH_2Ar), 7,13–7.19 (m, 4H, Ar), 7.19–7.24 (m, 8H, Ar), 7.29–7.37 (m, 8H, Ar); UV–vis ($CHCl_3$) λ_{max} nm (log ε) 756 (5.12); MALDI-TOF-MS *m*/*z* 1766.44 (M^+); **7**: dark green powder; mp. 110–111°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.54 (t, $J = 7.4$ Hz, 6H, CH_3), 1.58–1.76 (m, 18H, CH_3), 2.50 (s, 18H, SCH_3), 4.15–4.36 (m, 12H, CH_2Ar), 4.47 (s, 4H, SCH_2Ar), 4.62–4.78 (m, 4H, CH_2Ar), 7,11–7.37 (m, 10H, Ar); UV–vis ($CHCl_3$) λ_{max} nm (log ε) 757 (5.14); FABMS *m*/*z* 1788.1 (MH^+).

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