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Preparation and Electrochemical Properties of 1,4,8,11,15,18,22,25-Octalkylphthalocyanines Containing Four Trithiole Rings

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1,4,8,11,15,18,22,25-Octalkyl-2,3;9,10;16,17;23,24-tetrakis(*o*-xylylenedithio)phthalocyanines **4a**–**d** (alkyl = ethyl, butyl, octyl, and dodecyl) were prepared in moderate yields by treatment of 3,6-dialkyl-4,5-(*o*-xylylenedithio)phthalonitriles **3a**–**d** with lithium in *n*-pentanol. Reductive removal of the four *o*-xylylene groups from **4b** and **4c** was performed with lithium/THF/ammonia, and the octathiolate anions generated were then treated with elemental sulfur to give the new phthalocyanines **6b** and **6c**, respectively, each containing four trithiole rings, after partial desulfurization and ring-contraction reactions of the corresponding phthalocyanines **5b** and **5c**. The structures of the phthalocyanines were determined by ^{1}H NMR spectroscopy and MALDI-TOF mass spectrometry. The absorptions of the Q-bands of **4a**–**d** were observed at $\lambda_{max} \approx 770$ nm in their UV/Vis spectra, while those of **4b**-Ni, **5b**, **5c**, and **6c** were found in a region, blue-shifted relative to **4a**–**d**. When the UV/Vis spectrum of **6c** was measured in concentrated sulfuric acid, the λ_{max} value of its Q-band was 887 nm (log ε = 4.5), which suggests that the positive charge generated on **6c** strongly affects the π-conjugation of the phthalocyanine skeleton. The ESR spectrum was observed as one broadening signal on treatment of **6c** with $SbCl_5$. The redox potentials of the phthalocyanines were determined by cyclic voltammetry.

Introduction

Phthalocyanines and related derivatives have been actively studied for a long time, much recent research having been focused on applications of these molecules in new functional materials.[1–11] These compounds have, for example, a variety of potential applications in many fields such as catalysts, optical disks, charge-generating materials, and sensitizers for photodynamic therapy. It is well known that the red-shifting of the wavelength of the Q-band is an important factor for application of phthalocyanines in functionalized materials. Optical properties are strongly affected by: (1) expansion of a π-system of phthalocyanine through fusion of several aromatic rings,[4b,5a,8j] (2) conjunction of two or more phthalocyanines with alkenyl or alkynyl groups,[2,6,8a] and (3) construction of dinuclear phthalocyanines.[3a,5b] To attach desired functionalities to phthalocyanines, the design and preparation of the molecules have been examined by: (1) introduction of several heteroatoms or crown ethers at the peripheries of the macrocycles,[9] (2) distortion of the molecular plane through steric congestion,[4] and (3) inclusion of several functional groups axially bonded to the central metal atom.[7a,10]

In contrast, from our ongoing studies of several cyclic oligosulfides,[12–14] we recently reported on the preparation of 5,6-dibromo-4,7-diethylbenzo[1,2,3]trichalcogenoles **1a** and **1a′** and their conversion into phthalocyanines [PcXBn] bearing eight benzylthio or benzylseleno substituents by four-step reactions (Scheme 1).[15] In addition, phthalocyanines [PcXSnBu] with four dichalcogenastannole rings were obtained in low yields through the removal of the benzyl groups by Birch reduction with lithium/THF/ammonia and subsequent functionalization of the octachalcogenate anions with dibutyltin dichloride. This suggested that the procedure could be useful for the preparation of new phthalocyanines with eight peripheral chalcogenated functional groups. However, to examine optical and electrochemical properties of debenzylated and modified phthalocyanines derived from PcXBn, it is essential to improve on the low solubilities of products lacking the dibutyldithiastannole ring. In addition, to develop a synthetic procedure for phthalocyanines with sulfur functional groups, a new protecting group for dithiolate anions is required, rather than the combination of the 2-cyanoethyl group and the benzyl group used in the previous study. In view of these

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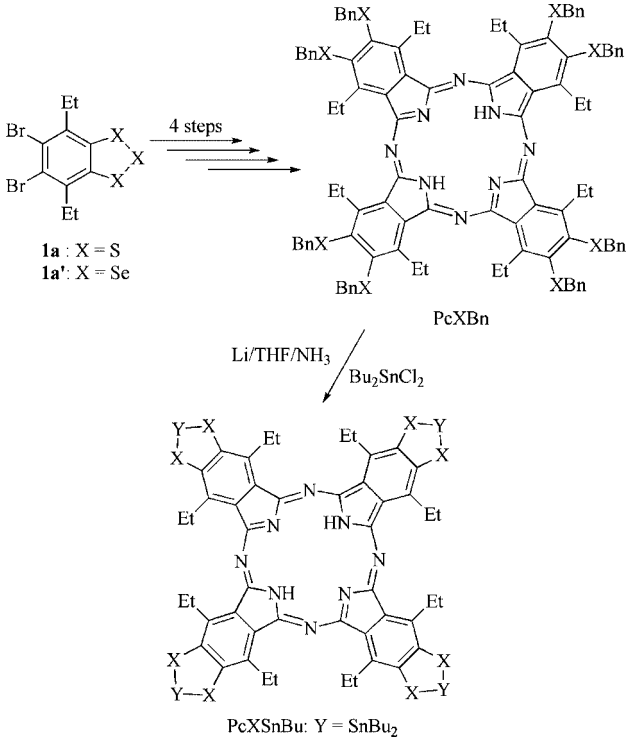
factors, we tried to introduce several kinds of long alkyl groups at the eight α-positions of phthalocyanine and to utilize the *o*-xylylene group as an alternative protecting group for the benzodithiolate. Furthermore, the optical and electrochemical properties of the unprecedented phthalocyanine with four five-membered oligosulfide rings were examined. This paper reports on the preparation of phthalocyanines, 1,4,8,11,15,18,22,25-octalkyl-2,3;9,10;16,17;23,24-tetrakis(*o*-xylylenedithio)phthalocyanines **4a**–**d** with eight peripheral sulfur atoms [alkyl = ethyl (Et), **4a**; *n*-butyl (Bu), **4b**; *n*-octyl (Oc), **4c**; *n*-dodecyl (Dd), **4d**], and a metal complex **4b**-Ni [alkyl = butyl, metal = Ni]. On treatment of **4b**, **4c**, and **4b**-Ni with lithium/THF/ammonia, reductive removal of four *o*-xylylene groups was achieved, and subsequent sulfurization and cyclization reactions of lithium octathiolate anions produced the phthalocyanines **5b**, **5c**, and **5b**-Ni, respectively, each containing one pentathiepin and three trithiole rings, together with related derivatives with higher molecular weights. Since **5b**, **5c**, and **5b**-Ni could not be isolated from these isomers, partial desulfurization and ring-contraction reactions of **5b** and **5c** with sodium borohydride were performed to give the new phthalocyanines **6b** and **6c**, respectively, each with four trithiole rings. The results of measuring the redox potentials by cyclic voltammetry and the absorption spectra by UV/Vis spectroscopy are also shown. The UV/Vis spectrum of **6c** measured in concentrated sulfuric acid was strongly affected by the generation of a positive charge on the trithiole rings, and the solution was ESR-active.

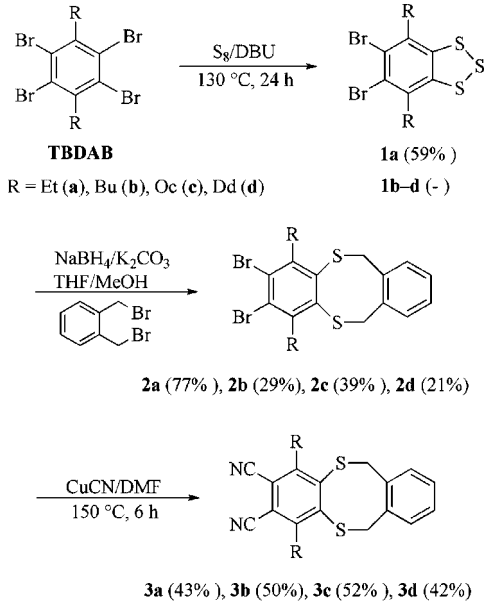


Scheme 1.

Results and Discussion

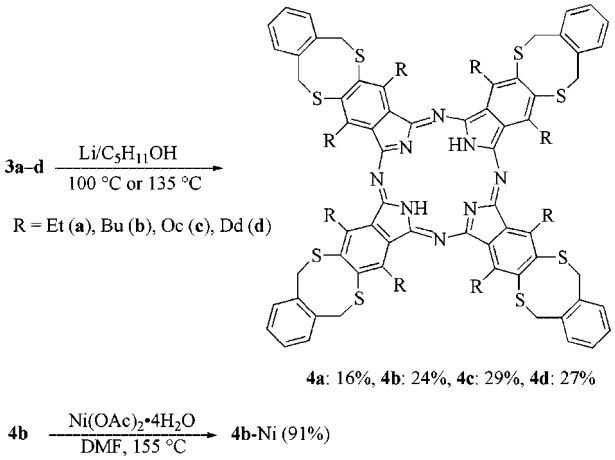
Preparation of Tetrakis(*o*-xylylenedithio)phthalocyanines

As a starting compound, **1a** was prepared by the procedure described in the previous paper (Scheme 2).[15] To improve the synthetic procedure for phthalonitrile, we tried to introduce the *o*-xylylene group on the sulfur atoms as a protecting group. Compound **1a** was treated with sodium borohydride and potassium carbonate in THF/methanol, and then with α,α′-dibromo-*o*-xylene to give 4,5-dibromo-3,6-diethyl-1,2-(*o*-xylylenedithio)benzene (**2a**) in 77% yield. The substitution of two bromo groups with nitrile groups was then performed by treatment of **2a** with copper(I) cyanide in DMF at 150 °C, the reaction giving 3,6-diethyl-4,5-(*o*-xylylenedithio)phthalonitrile (**3a**) in 43% yield.[16] By this procedure, the reaction pathway for the preparation of phthalonitriles was shortened in relation to the previous method. For the phthalonitrile cyclotetramerization reaction, **3a** was treated with lithium in *n*-pentanol at 135 °C for 1 h (Scheme 3). The solution immediately changed to dark green, finally giving a green suspension. The green precipitate was filtered off and was then purified by silica gel column chromatography to produce phthalocyanine **4a** in 16% yield.



Scheme 2.

The low solubilities of phthalocyanines are the result of their inherent tendency to agglomerate in solution. To provide phthalocyanines with sulfur functional groups and sufficient solubility by our original procedure as described above, we tried to introduce several kinds of long alkyl groups into its eight α-positions. Thus, 1,4-dialkylbenzenes (alkyl = Bu, Oc, and Dd) were prepared by cross-coupling between *p*-dichlorobenzene and several Grignard reagents (BuMgBr, OcMgBr, and DdMgBr) in diethyl ether in the presence of Ni(dppp)Cl_2 [dppp: 1,3-bis(diphenylphosphanyl)propane] as a catalyst [yields: alkyl = Bu (93%), Oc



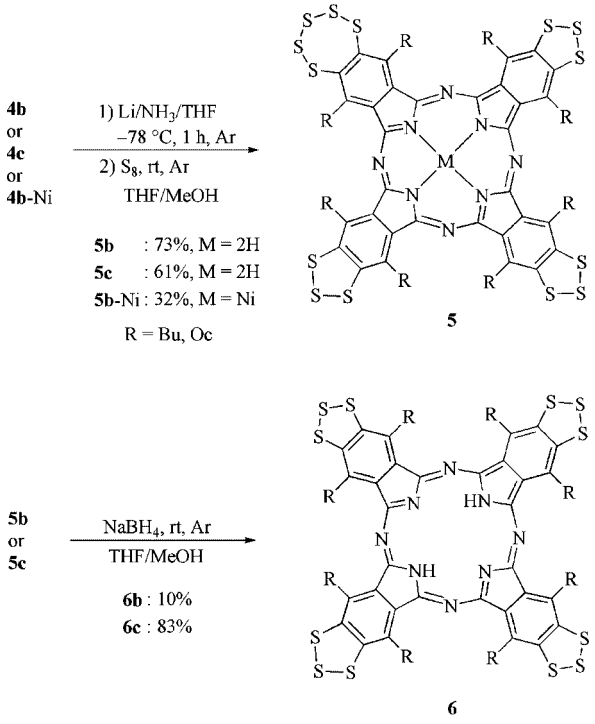
Scheme 3.

(96%), and Dd (83%)].[17] Friedel–Crafts-type treatment of the 1,4-dialkylbenzenes with 4 equiv. of bromine in dichloromethane in the presence of Fe powder as a catalyst gave 1,4-dialkyl-2,3,5,6-tetrabromobenzenes [TBDABs; alkyl = Bu (82%), Oc (51%), and Dd (86%)]. These reactions were performed under dark conditions. The three types of TBDAB obtained were then treated with elemental sulfur in DBU at 130 °C for 24 h to produce 4,7-dialkyl-5,6-dibromobenzo[1,2,3]trithiole derivatives **1b**–**d**, respectively (Scheme 2). The structures of **1b**–**d** were determined by ^{1}H NMR spectroscopy and mass spectrometry[18] and attempts were made to purify **1b**–**d** by column chromatography and recrystallization. Unlike **1a**, however, the substances could not be completely separated from small amounts of elemental sulfur, since their solubilities were greater than that of **1a**; therefore, **1b**–**d** were used for the next reaction without further purification. Introduction of the *o*-xylylene group into **1b**–**d** was performed by a procedure similar to that described above, to produce **2b**–**d** as colorless crystals in 29, 39, and 21% yields, respectively.[19] Treatment of **2b**–**d** with copper(I) cyanide under argon in DMF at 150 °C for 6 h produced phthalonitrile derivatives **3b**–**d** as yellow to orange crystals in 50, 52, and 42% yields, respectively, after purification by silica gel column chromatography.

Phthalocyanines **4b**–**d** containing long alkyl groups were also prepared from **3b**–**d** by a procedure similar to that described above, in 24, 29, and 27% yields, respectively (Scheme 3).[20] Compounds **4b**–**d** are blue-green powders and more soluble than **4a** in conventional organic solvents such as chloroform, dichloromethane, and hexane. The structures of **4a**–**d** were determined by ^{1}H NMR and UV/Vis spectroscopy and by MALDI-TOF mass spectrometry. As a prominent property, the ^{1}H NMR spectra of **4a**–**d** measured in [D]chloroform all showed large downfield shifts of the signals for the methylene groups linked to the α-positions of the phthalocyanine skeleton, and the methylene groups of **4b**–**d** were observed as broadening signals. To prepare a metal complex of phthalocyanine without proton alternation between four nitrogen atoms, **4b** was further treated with nickel(II) acetate in DMF at 155 °C for 0.5 h to produce a (phthalocyaninato)nickel(II) complex (**4b**-Ni) in 91% yield. The structure of **4b**-Ni was determined by ^{1}H NMR and MALDI-TOF MS. It seems that the solubility of **4b**-Ni is lower than that of **4b**.

Deprotection and Functionalization of 4b, 4c, and 4b-Ni

There are some pioneering reports regarding the functionalization of porphyrazine derivatives by way of S–C bond cleavage of the benzylthio groups in Birch reductions.[21] In contrast, peripheral modification of phthalocyanines through the S–C bond cleavage of thioethers is rare.[15] Deprotection and subsequent functionalization of **4b**, **4c**, and **4b**-Ni was thus tried. Typically, the four *o*-xylylene groups of **4c** were removed under argon by treatment with lithium metal in THF/liquid ammonia at –78 °C for 1 h (Scheme 4). The phthalocyanine with eight lithium thiolate groups, a reddish-brown solid, was very sensitive to air. After evaporation of the ammonia, deoxygenated methanol was slowly added to produce a clear light-brown solution, to which ammonium chloride was added, and a THF solution of elemental sulfur was then added dropwise by syringe. The color of the solution gradually changed from reddish-brown to dark green, and the solution was stirred at room temperature for 20 h. After usual treatment, the product was separated by silica gel column chromatography to produce the phthalocyanine **5c** with four oligosulfide rings (61%).



Scheme 4.

To determine the structure of the product, its MALDI-TOF MS was measured and the molecular ion of **5c** was observed at m/z = 1851.803 as $[M + H]^+$ (Figure 1a), implying that **5c** contained one pentathiepin ring and three

trithiole rings on the phthalocyanine skeleton. On the other hand, since a weak signal corresponding to a species with a molecular weight higher than that of **5c**, [(*M* + H of **5c**) + 64]$^+$, was observed in the spectrum, a small amount of phthalocyanine with two pentathiepin and two trithiole rings may also be contained in the product. The ^{1}H NMR spectrum showed **5c** to have an unsymmetrical structure, and the chemical shifts of the protons on the eight methylene groups bonded at the α-positions were observed at $\delta \approx$ 4.25–5.09 ppm. The signals are broad and complex. From these results it was concluded that the major product obtained in this reaction was the phthalocyanine **5c**, but containing analogues of higher molecular weight as minor products. Although small, dark brown, needle-like crystals were obtained by recrystallization from methanol/chloroform, they were not suitable for X-ray crystallographic analysis. On similar treatment of **4b** and **4b**-Ni with lithium/THF/ammonia and with elemental sulfur, **5b** and **5b**-Ni were obtained in 73 and 32% yields, respectively. The ^{1}H NMR spectra for **5b** and **5b**-Ni each show a pattern similar to that of **5c** regarding the signal of the methylene groups bonded with the α-positions. The structures of **5b** and **5b**-Ni were determined by MALDI-TOF MS, the weak signals corresponding to the products with higher molecular weights being observed in both spectra.

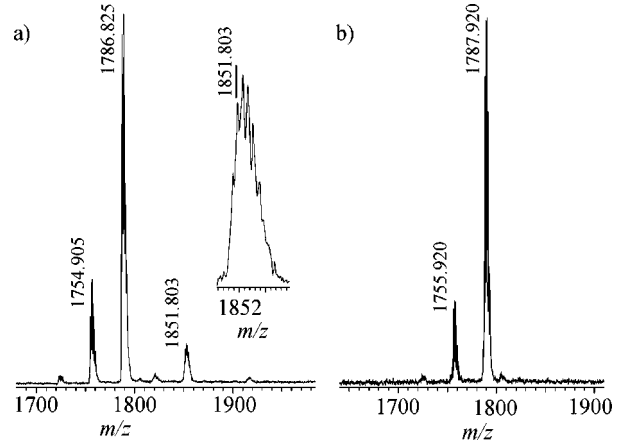


Figure 1. MALDI-TOF MS of a) **5c** and b) **6c**.

Since the obtained phthalocyanines **5b**, **5c**, and **5b**-Ni could not be purified sufficiently, the desulfurization and ring-contraction reactions of **5c** were performed with sodium borohydride in THF/methanol under argon. In this reaction, a new type of phthalocyanine containing four trithiole rings (**6c**) was first obtained in 83% yield (Scheme 4). Compound **6c** is soluble in chloroform, dichloromethane, and hexane, while it is insoluble in methanol and acetonitrile. In the ^{1}H NMR spectrum of **6c**, the signal for the eight methylene groups connected at the α-positions is a simple and slightly broadening triplet (δ = 4.43 ppm), suggesting that the molecule has a symmetric structure on the NMR timescale. The molecular weight of **6c** was determined by MALDI-TOF MS to be *m*/*z* = 1787.920 [*M* + H]$^+$ (Figure 1b), revealing that **6c** is clearly the phthalocyanine derivative with four peripheral trithiole rings. No species with higher molecular weight could be observed in the spectrum. Compound **5b** was similarly treated with sodium borohydride to give **6b** in 10% yield. The solubility of **6b** is lower than that of **6c**. It would be expected that a desulfurized intermediate generated from **5b** would tend to aggregate more readily in solution than that generated from **5c**. Low solubility and an aggregative property of the butyl derivative may be the cause of the low yield of **6b**. In the ^{1}H NMR spectrum of **6b**, the signal for the methylene groups at the α-positions was observed at δ = 4.46 ppm. The molecular weight of **6b** was also determined by MALDI-TOF MS.

Optical and Electrochemical Properties

The absorption wavelengths and molar extinction coefficients of the phthalocyanines were then determined by UV/Vis spectroscopy (Table 1). Although the absorptions of the Q-bands of unsubstituted phthalocyanines have been observed at ca. 680 nm, it has been reported that phthalocyanines with functional groups at their α-positions show large red shifts in their absorptions.[6c] As shown in Table 1, all the phthalocyanines show large red shifts in their Q-bands relative to unsubstituted phthalocyanines. Absorption by the metal-free phthalocyanines **4b**–**d** was observed at ca. 770 nm, while that of **4a** was observed in a region, blue-shifted relative to **4a**–**d**, suggesting that **4a** tends to aggregate in solution more readily than **4b**–**d**. In the cases of **5b** and **5c**, the absorption wavelengths of the Q-bands are shorter than those of the corresponding metal-free *o*-xylylenedithio derivatives, which is presumably related to the difference in strain energy between the trithiole ring (or the pentathiepin ring) and the dithiocin ring. The spectra of the metalated phthalocyanines **4b**-Ni and **5b**-Ni showed the Q-band absorptions at more blue-shifted positions. From these results it is inferred that the red shifts of the Q-bands of all the obtained phthalocyanines are more strongly affected by the alkyl groups in the α-positions than by the sulfur functional groups in the β-positions.

Table 1. UV/Vis spectra and redox potentials of phthalocyanines.

Compounds	UV/Vis[a]	$E_{1/2}$ [V]			
	λ_{max} nm (log ε)	2nd oxid	1st oxid	1st redn	2nd redn
4a	760 (5.2)	0.73	0.54	–0.92	–1.22
4b	772 (5.2)	0.61	0.43	–1.01	–1.29
4c	772 (5.1)	0.69	0.48	–0.98	–1.24
4d	774 (5.2)	0.68	0.50	–0.96	–1.21
4b-Ni	745 (5.4)	1.01	0.49	–1.11	–1.45
5b	766 (5.16)	–	–	–	–
5c	768 (5.13)	–	–	–	–
5b-Ni	740 (5.12)	–	–	–	–
6c	768 (5.11) 887 (4.5)[b]	0.82	0.56	–1.04[c]	–
PcXBn (X = S)	755 (5.1)	0.72	0.49	–1.02	–1.31

[a] UV/Vis spectra were measured in $CHCl_3$. [b] Measured in concentrated sulfuric acid. Redox potentials were measured in CH_2Cl_2 (vs. $Ag/AgNO_3$). [c] Quasi-reversible. The reference electrode was prepared from 0.01 M $AgNO_3$ and 0.1 M nBu$_4$NClO$_4$ in CH_3CN.

It has been reported that benzo-annulated five-membered heterocycles such as benzo[1,2-*d*:4,5-*d*′]bis[1,2,3]trithiole derivatives produce the corresponding radical cations or dications on oxidation with concentrated sulfuric acid or $SbCl_5$.[14,22] To examine the generation of a radical cation or a dication, **6c** was dissolved in concentrated sulfuric acid and the UV/Vis spectrum of the solution was measured as a preliminary experiment (Figure 2).[23] The absorption measured in chloroform was observed at λ_{max} = 768 nm while that measured in concentrated sulfuric acid was at λ_{max} = 887 nm. The result suggests that the radical cation or dication of **6c** generated in concentrated sulfuric acid and the positive charge generated on **6c** strongly affect the π-conjugation of the phthalocyanine skeleton, through conformation change of the trithiole rings, to induce the large red shift of the Q-band ($\Delta\lambda_{max}$ = 119 nm).[9a,11] It appeared that the solubility of **6c** in concentrated sulfuric acid was low and **6c** slowly decomposed in the solution. Although a concentrated [D_2]sulfuric acid solution of **6c** was examined by NMR spectroscopy, no signals for the dication were observed in the spectrum. In contrast, when the solution of **6c** was measured by ESR, two signals – g = 2.015 and g = 2.003 – were observed in the spectrum. If a radical cation or a dication is generated in concentrated sulfuric acid, corresponding sulfoxides or disproportionation products are obtained after the solution is treated with ice/water.[14,23] On treatment of the sulfuric acid solution with ice/water, **6c** was recovered together with a decomposed product that had no phthalocyanine skeleton and could be separated from **6c** by column chromatography. When the decomposed product was dissolved in concentrated sulfuric acid, an ESR signal was observed at g = 2.015. It was thus expected that, since the former signal was caused with the decomposed product, the latter signal should be derived from positively charged **6c**. To obtain further information about the radical cation and the dication, a solution of **6c**, dissolved in chloroform, was treated with an excess of $SbCl_5$, dissolved in dichloromethane.[24,25] The absorption in the UV/Vis spectrum measured in chloroform changed immediately on addition of the $SbCl_5$ solution and the Q-band was observed at λ_{max} = 908 nm. An ESR signal of the solution was observed at g = 2.002 as one broadening signal (Figure 2c). The species generated in the solution was stable for several hours, but slowly decomposed at room temperature and the solution finally became colorless. Interestingly, when PcXBn (X = S) was treated with $SbCl_5$, the phthalocyanine skeleton immediately decomposed in the solution. These results implied that: (1) the radical cation of **6c** is generated by oxidation with concentrated sulfuric acid or $SbCl_5$, (2) the radical cation gradually decomposed via the dication in both solutions, and (3) the trithiole rings on phthalocyanine can stabilize a positive charge relative to the benzylthio groups.

The electrochemical properties of the phthalocyanines were then determined by cyclic voltammetry with Ag/$AgNO_3$ as a reference electrode. In the previous paper, the metal-free phthalocyanine PcXBn (X = S) showed a multiredox system.[15] As shown in Table 1, two reversible oxidation potentials ($E_{1/2}$ = 0.48 and 0.69 V) and two reversible reduction potentials ($E_{1/2}$ = –0.98 and –1.24 V) were observed for **4c**. The voltammograms of **4c** and PcXBn (X = S) resemble each other. Similar results were found in the cases of **4a**, **4b**, **4d**, and **4b**-Ni. On the other hand, two reversible oxidation potentials ($E_{1/2}$ = 0.56 and 0.82 V) and one quasi-reversible reduction potential ($E_{1/2}$ = –0.96 V) were found in the case of **6c** (see Supporting Information). The obtained oxidation potentials of the phthalocyanines are similar to those of PcXBn (X = S), which should imply that the peripheral *o*-xylylenedithio groups or trithiole rings could not strongly affect the oxidation potentials of the phthalocyanines because the functional groups have no strong interaction between their lone pairs and the π-electrons in the phthalocyanine skeleton. Although the potential difference between **4c** and **6c** is small, it should originate from the difference of strain energy between the trithiole ring and the dithiocin ring. In contrast, the first reduction potential of **6c** was observed at $E_{1/2}$ = –0.96 V while the second one did not appear clearly, which suggests that the reduction potential of **6c** is affected by S–S bond cleavage of the trithiole ring.

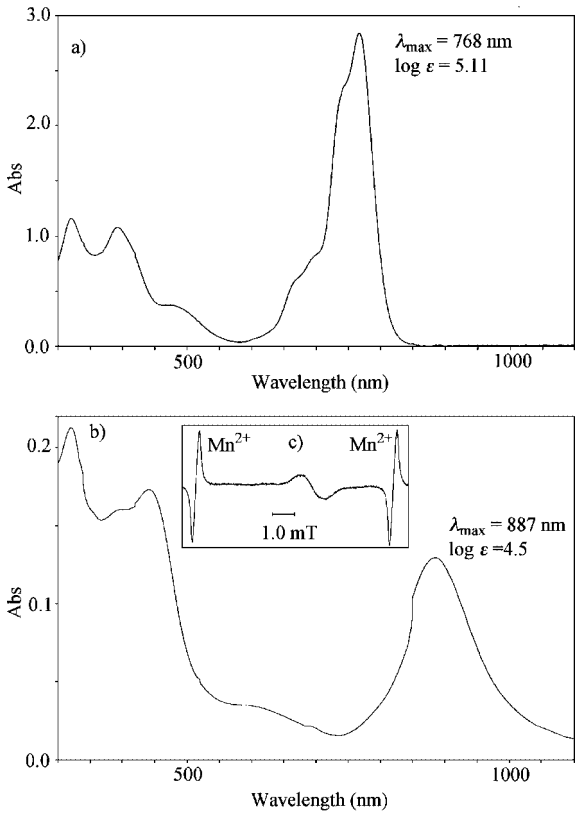


Figure 2. UV/Vis and ESR spectra of **6c**: a) UV/Vis spectrum measured in $CHCl_3$, b) UV/Vis spectrum measured in H_2SO_4, c) ESR spectrum measured in $CHCl_3$ after oxidation with $SbCl_5/CH_2Cl_2$ (inset).

Conclusion

Phthalocyanines **6b** and **6c** with four trithiole rings have been obtained for the first time by way of the preparation

and the functionalization of phthalocyanines **4a**–**d**. The absorptions of the Q-bands of **4a**–**d** were observed at $\lambda_{max} \approx$ 770 nm in their UV/Vis spectra, while those of **4b**-Ni, **5b**, **5c**, **5b**-Ni, and **6c** were found in a region blue-shifted relative to **4a**–**d**. In contrast, the UV/Vis spectrum of **6c**, measured in concentrated sulfuric acid, shows a large red shift in its Q-band, suggesting that: (1) the radical cation and the dication of **6c** were generated in the solution, (2) the positive charge strongly affects the π-electrons of phthalocyanine, and (3) the trithiole rings of **6c** have a greater ability to stabilize the positive charge than the benzylthio groups of PcXBn (X = S). It is expected that the conformation change of the trithiole rings from the neutral envelope structure to the positively charged planar structure gives rise to expansion of the π-conjugation system of the phthalocyanine skeleton of **6c** and a large red shift of the Q-band.

Experimental Section

General: The NMR spectra were measured with a Bruker AC 400 spectrometer at 25 °C. The IR spectra were recorded with a JASCO FT-7300 spectrometer. The mass spectra were obtained with a Hitachi M-2000 mass spectrometer and a JEOL JMS-700 mass spectrometer. MALDI-TOF (matrix-assisted laser desorption ionization time-of-flight) mass spectrometry was performed with a PerSeptive Biosystems Voyager RP-DE mass spectrometer and a Bruker BIFLEX (III) mass spectrometer. The UV/Vis spectra were measured with a JASCO V-570 spectrometer. ESR spectra were obtained with a JEOL JES-SA100 spectrometer. For measurement of oxidation potential, a Hokuto Denko Co. Model HAB-151 apparatus was used. The elemental analyses were performed with a Yanako MT5 analyzer.

Oxidation Potentials: All measurements were performed by cyclic voltammetry, with Ag/0.01 M $AgNO_3$ as a reference electrode, Pt wire as a counter electrode, and glassy carbon as a working electrode. nBu$_4$NClO$_4$ (0.1 M) was used as an electrolyte and CH_2Cl_2 was used as a solvent. The scan rate was 200 mV s^{-1} for all measurements. The reference electrode was prepared from 0.01 M $AgNO_3$ and 0.1 M nBu$_4$NClO$_4$ in CH_3CN.

5,6-Dibromo-4,7-diethylbenzo[1,2,3]trithiole (1a): Compound **1a** was prepared from 2,3,5,6-tetrabromo-1,4-diethylbenzene by the method described in the previous paper.[15]

4,5-Dibromo-3,6-diethyl-1,2-(*o*-xylylenedithio)benzene (2a). Procedure A: $NaBH_4$ (44.8 mg, 1.18 mmol) was added slowly to a solution of **1a** (0.138 g, 0.357 mmol, in 40 mL of THF and 10 mL of MeOH), and the solution was stirred for 30 min. After addition of K_2CO_3 (50.7 mg, 0.367 mmol), α,α′-dibromo-*o*-xylene (0.108 g, 0.407 mmol) was added, and the solution was stirred at room temperature for 24 h. After conventional workup, the solution was extracted with $CHCl_3$ and the solvent was evaporated. The residue was purified by column chromatography (Wakogel C-300HG, *n*-hexane/$CHCl_3$ = 20:1) to produce **2a** in 77% yield (0.127 g). **Procedure B:** 2,3,5,6-Tetrabromo-1,4-diethylbenzene (6.75 g, 15.0 mmol) and elemental sulfur (4.81 g, 150 mmol) were placed in a glass reactor, and DBU (60 mL) was added. The solution was stirred at 130 °C for 24 h and then at room temperature for 12 h. The solution was treated with aqueous H_2SO_4 solution and extracted with $CHCl_3$. After distillation of the solvent, the reaction mixture was separated by column chromatography (Wakogel C-300HG, *n*-hexane) to produce **1a** (2.60 g) as crude product; elemental sulfur was filtered off after recrystallization from diethyl ether. $NaBH_4$ (1.03 g, 27.7 mmol) was then added slowly to a solution of the product (in 120 mL of THF and 30 mL of methanol), and the solution was stirred for 30 min. After addition of K_2CO_3 (0.940 g, 6.8 mmol), α,α′-dibromo-*o*-xylene (1.79 g, 6.80 mmol) was added, and the solution was stirred at room temperature for 24 h. After conventional workup, the solution was extracted with $CHCl_3$ and the solvent was evaporated. The residue was purified by column chromatography (Wakogel C-300HG, *n*-hexane/$CHCl_3$ = 15:1) to produce **2a** (1.73 g, 25% yield from 2,3,5,6-tetrabromo-1,4-diethylbenzene); colorless crystals, m.p. 144 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.11 (t, J = 7.4 Hz, 6 H), 3.13 (q, J = 7.4 Hz, 4 H), 4.41 (s, 4 H), 6.86–7.14 (m, 4 H) ppm. MS: m/z = 458 $[M]^+$. $C_{18}H_{18}Br_2S_2$ (458.28): calcd. C 47.18. H 3.96; found C 47.17, H 4.00.

3,6-Dibutyl-4,5-dibromo-1,2-(*o*-xylylenedithio)benzene (2b): Compound **2b** was obtained in 29% yield by similar treatment of 1,4-dibutyl-2,3,5,6-tetrabromobenzene; colorless crystals, m.p. 143 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.98 (t, J = 7.0 Hz, 6 H), 1.37–1.53 (m, 8 H), 3.01–3.13 (m, 4 H), 4.41 (s, 4 H), 6.96–7.04 (m, 4 H) ppm. MS: m/z = 514 $[M]^+$. $C_{22}H_{26}Br_2S_2$ (514.38): calcd. C 51.37, H 5.09; found C 51.68, H 5.12.

4,5-Dibromo-3,6-dioctyl-1,2-(*o*-xylylenedithio)benzene (2c): Compound **2c** was obtained in 39% yield by similar treatment of 2,3,5,6-tetrabromo-1,4-dioctylbenzene; colorless crystals, m.p. 85 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (t, J = 6.8 Hz, 6 H), 1.20–1.53 (m, 24 H), 3.00–3.10 (m, 4 H), 4.40 (s, 4 H), 6.92–7.04 (m, 4 H) ppm. MS: m/z = 626 $[M]^+$. $C_{30}H_{42}Br_2S_2$ (626.59): calcd. C 57.50, H 6.76; found C 57.54, H 6.72.

4,5-Dibromo-3,6-didodecyl-1,2-(*o*-xylylenedithio)benzene (2d): Compound **2d** was obtained in 21% yield by similar treatment of 2,3,5,6-tetrabromo-1,4-didodecylbenzene; colorless crystals, m.p. 61 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.9 Hz, 6 H), 1.15–1.51 (m, 40 H), 3.00–3.09 (m, 4 H), 4.40 (s, 4 H), 6.93–7.04 (m, 4 H) ppm. MS: m/z = 738 $[M]^+$. $C_{38}H_{58}Br_2S_2$ (738.81): calcd. C 61.78, H 7.91; found C 61.61, 7.89.

3,6-Diethyl-4,5-(*o*-xylylenedithio)phthalonitrile (3a): Compound **2a** (917 mg, 2.00 mmol) and CuCN (448 mg, 5.00 mmol) were placed in a glass reactor, DMF (10 mL) was added under Ar, and the solution was stirred at 155 °C for 6 h. After the reactor had been cooled, $FeCl_3 \cdot 6H_2O$ (1.35 g, 5.00 mmol) and a trace amount of aqueous HCl were added, and the solution was stirred at 70 °C for 15 min. After the reactor had been cooled and the addition of ice/water, the product was extracted with $CHCl_3$ and the solvent was evaporated. The residue was purified by column chromatography (Wakogel C-300HG, *n*-hexane/$CHCl_3$ = 1:1) to produce **3a** in 40% yield (278 mg); yellow crystals, m.p. 203 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.20 (t, J = 7.5 Hz, 6 H), 3.05 (q, J = 7.5 Hz, 4 H), 4.52 (s, 4 H), 6.96–7.02 (m, 2 H), 7.03–7.08 (m, 2 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 14.5, 28.2, 38.1, 114.8, 114.9, 128.4, 129.8, 134.3, 146.4, 151.3 ppm. IR (KBr): $\tilde{\nu}$ = 2227 (CN) cm^{-1}. MS: m/z = 350 $[M]^+$. $C_{20}H_{18}N_2S_2$ (350.50): calcd. C 68.53, H 5.18, N 7.99; found C 68.19, H 5.31, N 7.88.

3,6-Dibutyl-4,5-(*o*-xylylenedithio)phthalonitrile (3b): Compound **3b** was obtained in 50% yield (0.822 g) on treatment of **2b** (2.068 g, 4.02 mmol) with CuCN (0.896 g, 10.0 mmol) in DMF (20 mL) under Ar at 155 °C for 6 h; yellow crystals, m.p. 130 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.98 (t, J = 7.5 Hz, 6 H), 1.39–1.56 (m, 8 H), 2.96–3.04 (m, 4 H), 4.51 (s, 4 H), 6.96–7.02 (m, 2 H), 7.03–7.08 (m, 2 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 13.8, 22.8, 32.4, 34.7, 38.0, 115.0, 115.1, 128.4, 129.8, 134.4, 146.5, 150.0 ppm. IR (KBr): $\tilde{\nu}$ = 2227 (CN) cm^{-1}. MS: m/z = 406 $[M]^+$. $C_{24}H_{26}N_2S_2$

(406.61): calcd. C 70.89, H 6.45, N 6.89; found C 70.64, H 6.38, N 6.81.

3,6-Dioctyl-4,5-(*o*-xylylenedithio)phthalonitrile (3c): Compound **3c** was obtained in 52% yield (1.08 g) on treatment of **2c** (2.507 g, 4.20 mmol) with CuCN (0.8996 g, 10.04 mmol) in DMF (15 mL) under Ar at 155 °C for 6 h; orange crystals, m.p. 90 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89 (t, J = 7.0 Hz, 6 H), 1.18–1.47 (m, 24 H), 2.88–2.94 (m, 4 H), 4.23 (s, 4 H), 7.03–7.06 (m, 2 H), 7.18–7.22 (m, 2 H) ppm. IR (KBr): $\tilde{\nu}$ = 2226 (CN) cm^{-1}. MS: m/z = 518 $[M]^+$. $C_{32}H_{42}N_2S_2$ (518.82): calcd. C 74.08, H 8.16, N 5.40; found C 74.09, H 8.32, N 5.30.

3,6-Didodecyl-4,5-(*o*-xylylenedithio)phthalonitrile (3d): Compound **3d** was obtained in 42% yield (0.537 g) on treatment of **2d** (1.478 g, 2.00 mmol) with CuCN (0.448 g, 5.00 mmol) in DMF (10 mL) under Ar at 155 °C for 6 h; yellow crystals, m.p. 77 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, J = 7.0 Hz, 6 H), 1.19–1.53 (m, 40 H), 2.95–3.03 (m, 4 H), 4.50 (s, 4 H), 6.96–7.02 (m, 2 H), 7.03–7.09 (m, 2 H) ppm. IR (KBr): $\tilde{\nu}$ = 2227 (CN) cm^{-1}. MS: m/z = 630 $[M]^+$. $C_{40}H_{58}N_2S_2$ (631.03): calcd. C 76.13, H 9.26, N 4.44; found C 75.96, H 9.22, N 4.39.

1,4,8,11,15,18,22,25-Octaethyl-2,3;9,10;16,17;23,24-tetrakis(*o*-xylylenedithio)phthalocyanine (4a): Lithium (35 mg, 5.04 mmol) was placed in a glass reactor, *n*-pentanol (2 mL) was added under argon, and the solution was stirred at 100 °C for several minutes. After the lithium had dissolved, **3a** (350.5 mg, 1.00 mmol) was added, and the solution was stirred at 135 °C for 1 h. After cooling of the reactor and addition of MeOH containing HCl, the green precipitate was filtered. The residue was purified by column chromatography (Wakogel C-300HG, *n*-hexane/$CHCl_3$ = 1:1) to produce **4a** in 16% yield (56.5 mg); green powder, m.p. 225 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.45–1.54 (m, 24 H), 4.41–4.63 (m, 16 H), 4.63–4.76 (m, 16 H), 6.65–6.81 (m, 8 H), 6.93–7.10 (m, 8 H) ppm. UV/Vis ($CHCl_3$): λ_{max} (log ε) = 760 (5.2) nm. MALDI-TOF MS: m/z = 1402.63 $[M]^+$.

1,4,8,11,15,18,22,25-Octabutyl-2,3;9,10;16,17;23,24-tetrakis(*o*-xylylenedithio)phthalocyanine (4b): Compound **4b** was obtained in 24% yield (96.8 mg) on treatment of **3b** (407 mg, 1,00 mmol) with lithium (34.7 mg, 5.00 mmol) in *n*-pentanol (2 mL) under argon at 100 °C for 1 h; green powder, m.p. > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.82–1.05 (m, 24 H), 1.40–1.75 (m, 32 H), 4.54–4.80 (m, 32 H), 6.75–6.92 (m, 8 H), 7.02–7.15 (m, 8 H) ppm. UV/Vis ($CHCl_3$): λ_{max} (log ε) = 772 (5.2) nm. MALDI-TOF MS: m/z = 1626.86 $[M]^+$.

1,4,8,11,15,18,22,25-Octaoctyl-2,3;9,10;16,17;23,24-tetrakis(*o*-xylylenedithio)phthalocyanine (4c): Compound **4c** was obtained in 29% yield (151 mg) on treatment of **3c** (520.5 mg, 1.0 mmol) with lithium (34.1 mg, 4.92 mmol) in *n*-pentanol (2 mL)under argon at 100 °C for 1 h; green powder, m.p. 105 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.60–0.99 (m, 24 H), 1.04–1.79 (m, 94 H), 4.47–4.85 (m, 32 H), 6.73–6.91 (m, 8 H), 6.99–7.17 (m, 8 H) ppm. UV/Vis ($CHCl_3$): λ_{max} (log ε) = 752 (5.1) nm. MALDI-TOF MS: m/z = 2075.39 $[M]^+$.

1,4,8,11,15,18,22,25-Octadodecyl-2,3;9,10;16,17;23,24-tetrakis(*o*-xylylenedithio)phthalocyanine (4d): Compound **4d** was obtained in 27% yield (173.1 mg) on treatment of **3c** (634 mg, 1.0 mmol) with lithium (35 mg, 5.0 mmol) in *n*-pentanol (2 mL) under argon at 100 °C for 1 h; green solid, m.p. 82–83 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.60–0.99 (m, 24 H), 1.04–1.79 (m, 94 H), 4.47–4.85 (m, 32 H), 6.73–6.91 (m, 8 H), 6.99–7.17 (m, 8 H) ppm. UV/Vis ($CHCl_3$): λ_{max} (log ε) = 774 (5.2) nm. MALDI-TOF MS: m/z = 2523.13 $[M]^+$.

[1,4,8,11,15,18,22,25-Octabutyl-2,3;9,10;16,17;23,24-tetrakis(*o*-xylylenedithio)phthalocyaninato]nickel(II) (4b-Ni): Compound **4b** (325.6 mg, 0.20 mmol) and $Ni(OAc)_2 \cdot 4H_2O$ (504.1 mg, 2.03 mmol) were placed in a glass reactor, and DMF (20 mL) was added under argon. After the solution had been stirred at 155 °C for 30 min, it was cooled to room temperature and poured into ice/water. The green precipitate was then filtered off and the residue washed with water and MeOH. After drying, the product was purified by column chromatography (Wakogel C-300HG, *n*-hexane/$CHCl_3$ = 1:1) and recrystallization to produce **4b**-Ni in 91% yield (306.7 mg); green powder m.p. > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.85–1.09 (m, 24 H), 1.38–1.82 (m, 32 H), 4.34–4.82 (m, 32 H), 6.75–6.96 (m, 8 H), 7.02–7.15 (m, 8 H) ppm. UV/Vis ($CHCl_3$): λ_{max} (log ε) = 745 (5.4) nm. MALDI-TOF MS: m/z = 1682.92 $[M]^+$.

Deprotection of 4c and Cyclization of Lithium Octathiolate with S_8: Compound **4c** (104.4 mg, 0.05 mmol) and lithium (30.5 mg, 4.39 mmol) were placed in a glass reactor. THF (5 mL) was added under argon, and the solution was cooled to –78 °C. NH_3 (30 mL) was introduced into the reactor and condensed. The solution was stirred at this temperature for 1 h and gradually warmed to room temperature. The NH_3 gas was evaporated under an N_2 gas stream. After the evaporation of NH_3, deaerated MeOH (20 mL) was added to the reddish-brown solid, and NH_4Cl (272.6 mg, 5.10 mmol) was added to the solution. S_8 (160.5 mg, 5.0 mmol) in THF (15 mL) was added dropwise by syringe, and the solution was stirred at room temperature. for 20 h. The solution was then concentrated and the product was dissolved in $CHCl_3$. After filtration and concentration, the product was separated by column chromatography (Wakogel C-300HG, *n*-hexane) to produce **5c** in 61% yield (57.1 mg); brownish-green needles, m.p. 226.5–227.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.69–0.85 (m, 24 H), 1.04–2.36 (m, 64 H), 1.42–1.60 (m, 16 H), 1.64–1.95 (m, 16 H), 4.25–5.09 (m, 16 H) ppm. UV/Vis ($CHCl_3$): λ_{max} (log ε) = 768 (5.13) nm. MALDI-TOF MS: m/z = 1851.803 $[M + H]^+$.

Deprotection of 4b and Cyclization of Lithium Octathiolate with S_8: Compound **4b** (88.9 mg, 0.055 mmol) was similarly treated as described above [lithium (31.6 mg, 4.55 mmol) in THF/NH_3, NH_4Cl (281.0 mg, 5.35 mmol) and S_8 (162.6 mg, 5.1 mmol)] to produce **5b** in 73% yield (56.2 mg); brownish-green powder, m.p. > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.68–0.85 (m, 24 H), 1.34–1.47 (m, 16 H), 1.56–1.79 (m, 16 H), 4.14–5.00 (m, 16 H) ppm. UV/Vis ($CHCl_3$): λ_{max} (log ε) = 766 (5.16) nm. MALDI-TOF MS: m/z = 1402.595 $[M]^+$.

Deprotection of 4b-Ni and Cyclization of Lithium Octathiolate with S_8: Compound **4b**-Ni (89.8 mg, 0.053 mmol) was similarly treated as described above [lithium (31.3 mg, 4.51 mmol) in THF/NH_3, NH_4Cl (274.7 mg, 4.63 mmol) and S_8 (164.5 mg, 5.1 mmol)] to produce **5b**-Ni in 32% yield (25.0 mg); brownish-green powder, m.p. 288–290 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.67–0.88 (m, 24 H), 1.29–1.48 (m, 16 H), 1.54–1.79 (m, 16 H), 4.11–4.91 (m, 16 H) ppm. UV/Vis ($CHCl_3$): λ_{max} (log ε) = 740 (5.12) nm. MALDI-TOF MS: m/z = 1458.210 $[M]^+$.

Desulfurization of 5c with $NaBH_4$: Compound **6c** (56.7 mg, 0.031 mmol) and $NaBH_4$ (1.17 mg, 0.031 mmol) were placed in a glass reactor, and THF (5 mL) and MeOH (2 mL) were added under argon. The solution was stirred for 1 h and then quenched with water. The solution was extracted with $CHCl_3$. After concentration, the product was separated by column chromatography (Wakogel C-300HG, *n*-hexane) to produce **6c** in 83% yield (45.4 mg); brownish-green powder, m.p. 226–227 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.76 (t, J = 6.4 Hz, 24 H), 1.07–1.22 (m, 48 H), 1.22–1.32 (m, 16 H), 1.45–1.55 (m, 16 H), 1.84 (quint, J = 7.0 Hz, 16 H), 4.43 (t,

J = 7.0 Hz, 16 H) ppm. UV/Vis ($CHCl_3$): λ_{max} (log ε) = 768 (5.11) nm. MALDI-TOF MS: m/z = 1787.920 [M + H]$^+$.

Desulfurization of 5b with $NaBH_4$: Compound **5b** (15.3 mg, 0.11 mmol) was similarly treated with $NaBH_4$ (0.5 mg, 0.13 mmol) to produce **6b** in 10% yield (1.5 mg); brownish-green powder, m.p. > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, J = 7.3 Hz, 24 H), 1.46–1.58 (m, 16 H), 1.86 (quint, J = 7.7 Hz, 16 H), 4.46 (t, J = 7.6 Hz, 16 H) ppm. MALDI-TOF MS: m/z = 1339.218 [M + H]$^+$.

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