

Preparation, Structure Determination, and Electrochemical Properties of Bis{[1,4,8,11,15,18,22,25-octaethyl-2,3,9,10,16,17,23,24-octakis(methylthio)-phthalocyaninato]titanium(IV)} Benzene-1,2,4,5-tetrathiolate

Takeshi Kimura,^{*,[a]} Jun Kumasaka,^[a] and Toshiharu Namao^[a]

Keywords: Phthalocyanines / Titanium / S ligands / Double-decker molecules

4,5-Bis(methylthio)phthalonitrile **2** was prepared from 2,3,5,6-tetrabromodiethylbenzene in four steps. Tetramerization and cyclization of phthalonitrile **2** with lithium *n*-pentoxide at 115 °C produced octaethyl-octakis(methylthio)phthalocyanine (**3**). A titanium atom was introduced into the phthalocyanine **3** by treatment with titanium(IV) tetrabutoxide in DMF at 130 °C to give the corresponding metal complex **3-TiO**. Linking of two molecules of the phthalocyanine **3-TiO** with benzene-1,2,4,5-tetrathiol (**BTT**) produced a double-decker-type compound, bis{[octaethyl-octakis(methylthio)phthalocyaninato]titanium(IV)} benzenetetrathiolate (**6**), in which the two phthalocyanines are con-

nected axially through four titanium–sulfur coordination bonds. Double-decker derivative **7** was also obtained by a similar treatment of (tetra-*tert*-butylphthalocyaninato)titanium(IV) oxide with **BTT**. The structures of **6** and **7** were determined by NMR, IR, UV/Vis spectroscopy and FAB mass spectrometry. Both phthalocyanine skeletons of **6** have symmetrical structures, as shown by the ¹H and ¹³C NMR spectra. The electrochemical properties of **6** were examined by cyclic voltammetry with Ag/AgNO₃ as the reference electrode.

(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2008)

Introduction

Tetraazaporphyrins, phthalocyanines, and related compounds have a variety of actual and potential applications in many fields, for example, as dyes, pigments, catalysts, new functional materials, and sensitizers for photodynamic therapy.^[1–4] Among the large number of these derivatives, phthalocyanines that connect one or two axially coordinating groups on the central metal atom or that have a double-decker structure have attracted much attention because such molecules may be applied to electrochromic displays, field-effect transistors, nonlinear optical materials, and dye-sensitized solar cells.^[1,5,6] Recently, Hanack and co-workers reported (phthalocyaninato)titanium(IV) complexes as compounds that have axially coordinating groups linked through titanium–oxygen or titanium–sulfur bonds,^[7] and Kobayashi and co-workers have prepared a mutually perpendicular phthalocyanine pentamer and related derivatives.^[8] These products were prepared by the ligand-exchange reaction of (tetra-*tert*-butylphthalocyaninato)titanium(IV) oxide (**tBuPcTiO**) with *o*-catechol derivatives, *o*-benzenedithiol, tetrahydroxy-*p*-benzoquinone, and octahydroxyphthalocyanine. The compound constructed by the reaction of **tBuPcTiO** with tetrahydroxy-*p*-benzoquinone in a 2:1 ratio is an unsymmetric double-decker-type molecule. As a result of our continuing study of several cyclic oligosulfides,^[9] we recently reported the preparation and the elec-

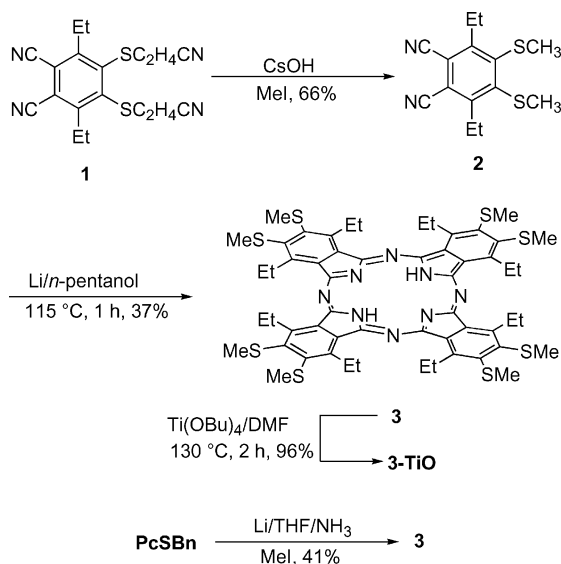
trochemical and optical properties of octakis(benzylthio)-phthalocyanine (**PcSBn**), tetrakis(*o*-xylylenedithio)phthalocyanines (**PcSXyl**), and related derivatives.^[10] In relation to the application of phthalocyanine to new functional materials, it is significant that a Q-band absorption lies in the near-infrared region of the UV/Vis absorption spectrum. The Q-bands of **PcSBn** and **PcSXyl** are observed at around 760 nm, which is a longer wavelength than that of unsubstituted phthalocyanine. To fabricate a double-decker-type phthalocyanine with a symmetric structure and titanium–sulfur bonds, octaethyl-octakis(methylthio)phthalocyaninatotitanium(IV) oxide (**3-TiO**) was prepared from diethylbenzene in seven steps and treated with benzene-1,2,4,5-tetrathiol (**BTT**). A double-decker compound consisting of **tBuPcTiO** and **BTT** was also constructed. This paper reports the preparation, structure determination, and the electrochemical and optical properties of the double-decker-type phthalocyanines connected through four titanium–sulfur bonds.

Results and Discussion

4,5-Bis[(2-cyanoethyl)thio]-3,6-diethylphthalonitrile (**1**) was prepared according to a method described previously.^[10a] Compound **1** was treated with cesium hydroxide and then methyl iodide in THF/methanol at room temperature to produce 3,6-diethyl-4,5-bis(methylthio)phthalonitrile (**2**) in 66% yield (Scheme 1). Two ethyl groups on the benzene ring positioned next to the two sulfur atoms are required

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

to prepare compound **1** from 1,4-diethylbenzene by way of diethyl-1,2,3-benzotrithiole as a precursor. It is expected that electron-donating functional groups at the α -positions of phthalocyanine cause the Q-band to shift to a longer wavelength,^[11] and phthalocyanine with methylthio groups simplifies the structure of the double-decker molecule compared with the benzylthio and xylylenedithio derivatives.^[10a,10b] Tetramerization and cyclization of phthalonitrile **2** upon treatment with lithium in *n*-pentanol at 115 °C for 1 h gave a green solid, which was filtered, dried, and purified by silica gel column chromatography to produce octaethyl-octakis(methylthio)phthalocyanine (**3**) in 37% yield. Although the ethyl and methylthio groups on the macrocycle are unobtrusive substituents, phthalocyanine **3** is soluble in chloroform and THF. In the ¹H NMR spectrum, compound **3** shows one triplet and one broadened quartet for the ethyl groups at δ = 1.66 and 4.89 ppm, respectively, and one singlet peak for the methylthio groups at δ = 2.75 ppm. The signal of the two protons on the central pyrrole nitrogen atoms could not be observed in the spectrum because of proton alternation. A UV/Vis absorption spectrum showed that the Q-band absorption of **3** (λ_{max} = 750 nm, $\log \epsilon$ = 5.06) lies close to that of **PcSBn** (λ_{max} = 755 nm, $\log \epsilon$ = 5.1). The structure of **3** was determined by fast atom bombardment mass spectrometry (FAB-MS), which showed the molecular ion peak ($[M]^+$) at m/z = 1106.35.



Scheme 1. Preparation of the phthalocyanines.

Removal of the benzyl groups from **PcSBn** by Birch reduction may be utilized to prepare a new phthalocyanine with eight sulfur functional groups at the β -positions.^[10,12] Thus, **PcSBn** was treated with lithium metal in THF/liquid ammonia under argon at –70 °C for 1 h. The solution was gradually warmed to –33 °C and then to room temperature. After evaporation of the ammonia, methyl iodide was slowly added, and the solution was stirred for 20 h to pro-

duce a dark-green precipitate. The product was separated by silica gel column chromatography to give phthalocyanine **3** in 41% yield.

It is essential that phthalocyanine must have an appropriate metal atom in the central cavity in order to bind a bidentate ligand in an axial fashion. Compound **3** was treated with titanium(IV) tetrabutoxide in DMF at 130 °C under argon for 2 h. After workup, a green solid was obtained and purified by column chromatography on silica gel to produce [octaethyl-octakis(methylthio)phthalocyaninato]titanium(IV) oxide (**3-TiO**) in 96% yield. In contrast, the reaction of **2** with urea, a few drops of DBU, and titanium(IV) tetrabutoxide in *n*-pentanol at 155 °C under argon, which is a procedure used for the preparation of (phthalocyaninato)-titanium(IV) oxide,^[7] gave no product. In the ¹H NMR spectrum of compound **3-TiO**, one triplet and one double quartet signal for the ethyl groups were observed together with one singlet peak for the methylthio groups (δ = 1.74, 2.78, 4.94, and 5.02 ppm). The signals appeared at a slightly lower field than did those of **3**. The ¹³C NMR spectrum of **3-TiO** showed three signals for the ethyl and the methylthio groups (δ = 16.8, 22.3, and 25.2 ppm) and four aromatic signals for the phthalocyanine core (δ = 134.0, 146.8, 147.1, and 151.8 ppm), which suggests that the compound has a symmetric structure.^[13] In the UV/Vis spectrum, the Q-band of **3-TiO** (λ_{max} = 760 nm, $\log \epsilon$ = 5.15) was observed at a lower energy and with a narrower bandwidth than that of **3** (Figure 1). It seems that the metallation of phthalocyanine with titanium(IV) oxide shifts the Q-band absorption to a longer wavelength compared with that of the metal-free molecule. To determine the structure, the FAB mass spectrum of **3-TiO** was recorded and the molecular ion peak ($[M]^+$) observed at m/z = 1168.3. In contrast, **tBuPcTiO** was prepared by treatment of *tert*-butylphthalonitrile with titanium(IV) tetrabutoxide by using a literature procedure.^[7]

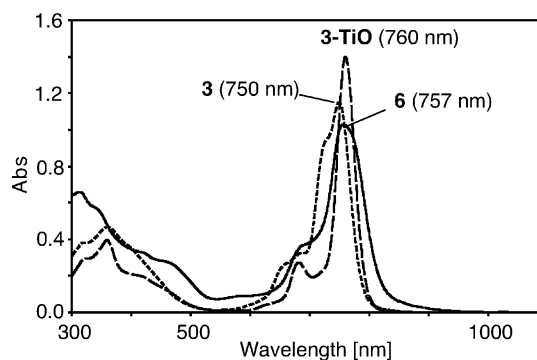
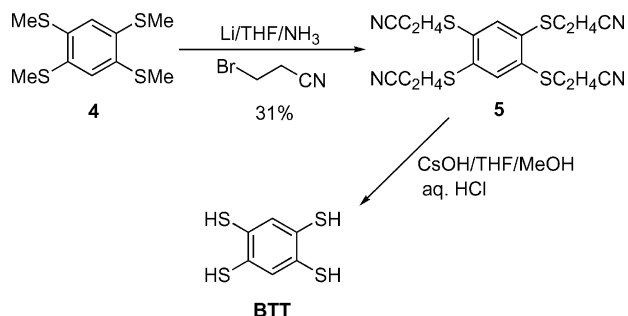


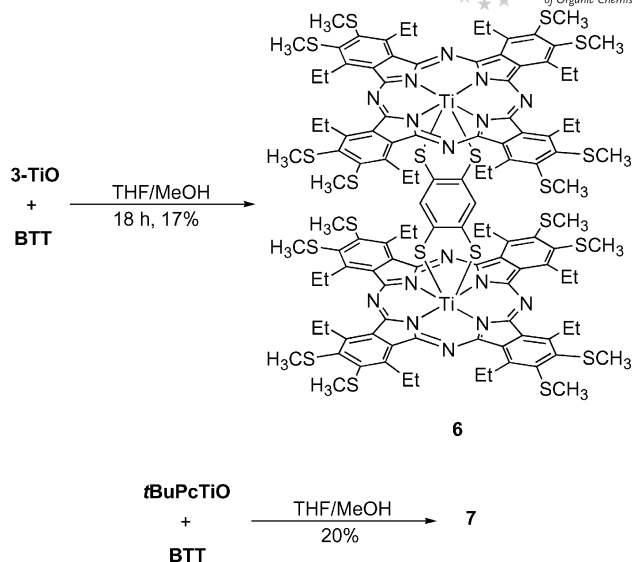
Figure 1. UV/Vis spectra of phthalocyanines **3**, **3-TiO**, and **6** (c = 1.00×10^{-5} mol/L).

The construction of the double-decker-type compound with titanium–sulfur bonds from two molecules of (phthalocyaninato)titanium(IV) oxide required **BTT** as a link molecule. Wudl and co-workers have reported an excellent procedure for the preparation of **BTT**.^[14,15] 1,2,4,5-Tetrakis(methylthio)benzene (**4**) was prepared from 1,2,4,5-tetrachlorobenzene according to the reported procedure.^[14] The

carbon–sulfur bond cleavage was achieved by the reaction of **4** with lithium in THF/liquid ammonia, and the product was purified by column chromatography. However, the **BTT** obtained was easily oxidized in air to give an insoluble colorless solid. Therefore, the tetrathiol groups of **BTT** were protected: Compound **4** was treated with lithium in THF/liquid ammonia according to the procedure described above, and the generated benzenetetrathiolate was subsequently treated with 3-bromopropionitrile in THF/methanol at room temperature. 1,2,4,5-Tetrakis(2-cyanoethylthio)benzene (**5**) was obtained according to this procedure in 31% yield (Scheme 2). Compound **5** was purified more readily than **BTT**. The four thiol groups of **BTT** can be generated from **5** in the reaction mixture before use in the complexation reaction with **3-TiO** and *t*BuPcTiO by treatment with cesium hydroxide in THF/methanol under argon at room temperature for 3 h. The reaction mixture was acidified with concentrated hydrochloric acid. The prepared solution was transferred by syringe under argon to a reactor containing **3-TiO**, and the reaction mixture was stirred for 18 h. In the reaction, the oxygen atom on the titanium atom was gradually exchanged with benzenetetrathiolate. After workup, the green product was purified by column chromatography on silica gel and then on Bio-beads to produce bis{[octaethyl-octakis(methylthio)phthalocyaninato]titanium(IV)} benzenetetrathiolate (**6**) in 17% yield (Scheme 3). According to a similar treatment of *t*BuPcTiO with **BTT** as described above, bis{[tetra-*tert*-butylphthalocyaninato]titanium(IV)} benzenetetrathiolate (**7**) was obtained in 20% yield. Compounds **6** and **7** are stable in air.

Scheme 2. Preparation of **BTT**.

The structures of **6** and **7** were examined by NMR spectroscopy. In the ^1H NMR spectrum of **6**, the signals of the ethyl and methylthio groups connected to the phthalocyanine core show clear up-field shifts compared with those of **3** and **3-TiO** ($\delta = 1.40, 2.61$, and 4.64 ppm), and the methylene proton was observed as one broadened signal, which suggests that the two phthalocyanines exist in a C_4 -symmetric structure on the NMR timescale. The signal arising from the central benzene ring of the benzenetetrathiolate was observed at $\delta = 3.79$ ppm as one singlet peak, which shows that the benzene ring lies between the two phthalocyanine planes and is strongly influenced by the magnetic shielding of the macrocycle. According to Hanack et al. the chemical



Scheme 3. Construction of the double-decker molecules.

shift of the aromatic *ortho* protons of benzenedithiolate connected axially to (tetra-*tert*-butylphthalocyaninato)titanium(IV) appeared at $\delta \approx 5.9$ ppm.^[7b]

The ^1H NMR spectrum of **7** shows similar signals to that of *t*BuPcTiO, and the aromatic protons of the benzenetetrathiolate were observed at $\delta \approx 3.60$ – 3.62 ppm. When the ^{13}C NMR spectrum of **6** was recorded, the four signals corresponding to the phthalocyanine skeleton and the three signals arising from the ethyl and methylthio groups appeared at $\delta = 16.4, 22.1, 25.1, 132.7, 146.5(0), 146.5(4)$, and 151.0 ppm, which are similar chemical shifts to those of **3-TiO**. The signals arising from the aromatic carbon atoms of benzenetetrathiolate were observed at $\delta = 117.3$ and 146.3 ppm and are different to the corresponding signals of **5** ($\delta = 134.3, 136.2$ ppm).

The absorption wavelength and molar extinction coefficient of phthalocyanine **6** were determined by UV/Vis spectroscopy (Figure 1). The Q-band absorption of phthalocyanine **6** was observed at $\lambda_{\text{max}} = 757$ nm ($\log \epsilon = 5.05$). It can be observed that the absorption of **6** has a slightly blue-shifted wavelength (3 nm), decreased intensity, and broadened bandwidth compared with that of **3-TiO**, which could originate from the double-decker structure of **6**. Thus, it is expected that the two phthalocyanines in the molecule interact electronically with each other in the excited state on measuring the spectrum. In the UV/Vis spectrum of **7**, one slightly broadened Q-band was observed at a slightly shorter wavelength than that of *t*BuPcTiO. To determine the structure, FAB mass spectra of **6** and **7** were recorded, which showed molecular ion peaks ($[\text{M}]^+$) at $m/z = 2508.50$ for **6** and $m/z = 1770.60$ for **7**. These results imply that compounds **6** and **7** consist of two phthalocyanines and a benzenetetrathiolate. In the IR spectrum, the signal observed at 972 cm^{-1} for the Ti=O bond of *t*BuPcTiO faded away in the spectrum of **7**.^[7,16] The signal at 977 cm^{-1} in the spectrum of **3-TiO** also disappeared in the spectrum of **6** with four strong signals observed at around 1050 cm^{-1} .

The electrochemical properties of phthalocyanines **3**, **3-TiO**, and **6** were examined by cyclic voltammetry using Ag/AgNO₃ as the reference electrode (solvent: CH₂Cl₂; scan rate: 200 mV/s). The cyclic voltammogram of **3** contains two reversible oxidations ($E_{1/2} = 0.52$ and 0.91 V) and two reversible reduction potentials ($E_{1/2} = -1.08$ and -1.41 V), which are slightly lower reduction potentials and higher oxidation potentials than those of **PcSBn** (Table 1). In the case of **3-TiO**, there is one reversible and one irreversible oxidation potential ($E_{1/2} = 0.68$ V and $E_p = 1.13$ V, respectively) and two reversible reduction potentials ($E_{1/2} = -0.80$ and -1.14 V). It appears that the oxidation potential of the titanium complex **3-TiO** is slightly higher than that of **3**. As shown in Figure 2, one quasi-reversible oxidation potential ($E_{1/2} = 0.70$ V) and two reversible reduction potentials ($E_{1/2} = -0.86$ and -1.14 V) were observed for **6**. However, the compound clearly did not show a peak potential for a second oxidation. It seems that the first oxidation potential for **6** is an overlay of two slightly different potentials. The two different potentials may be related to an electronic interaction between the two phthalocyanines through the central benzene ring under the oxidation conditions. The first oxidation potential of **6** is slightly higher than those of **3** and **PcSBn**, whereas the reduction and first oxidation potentials are similar to those of **3-TiO**. The differences in potential (ΔE) between the first oxidation and the first reduction were calculated to estimate the HOMO–LUMO gaps of **3**, **3-TiO**, and **6**, and are $\Delta E = 1.60$, 1.48 , and 1.56 V, respectively. It appears that the HOMO–LUMO gap of **6** is lower than that of **3** and higher than that of **3-TiO**. The order of the HOMO–LUMO gaps of **3**, **3-TiO**, and **6** are in accord with the wavelengths of the Q band absorption.

Table 1. Redox potentials (vs. Ag/AgNO₃).

Compound	$E_{1/2}$ [V]				$\Delta E^{[a]}$ [V]
	2nd reduction	1st reduction	1st oxidation	2nd oxidation	
3	−1.41	−1.08	0.52	0.91	1.60
3-TiO	−1.14	−0.80	0.68	1.13 ^[b]	1.48
6	−1.14	−0.86	0.70 ^[c]	–	1.56
PcSBn	−1.32	−1.03	0.49	0.72	1.52

[a] ΔE is the difference between the first oxidation potential and the first reduction potential. [b] Irreversible oxidation potential (E_p). [c] Quasi-reversible oxidation potential.

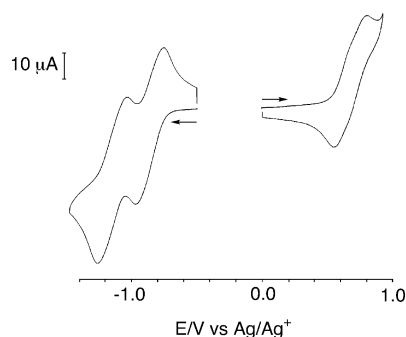


Figure 2. Cyclic voltammograms of **6**.

Conclusions

Phthalocyanine **3** was prepared by tetramerization and cyclization of **2** and subsequent treatment with titanium(IV) tetrabutoxide, and then **BTT** produced double-decker phthalocyanine **6**. Double-decker derivative **7** was obtained by a similar treatment of *tert*-butylphthalonitrile. As compounds **6** and **7** did not decompose in air, the four titanium–sulfur bonds in the product are stable. In the ¹H NMR spectrum of **6**, the proton signal arising from the central benzene ring was observed at an extremely high field compared with that of usual aromatic compounds, which suggests that the aromatic protons are strongly shielded in the magnetic field of the phthalocyanines. As there are three signals in the ¹H NMR spectrum and seven signals in the ¹³C NMR spectrum for the phthalocyanines in compound **6**, both phthalocyanines are C₄-symmetric structures, which suggests that the phthalocyanine rings can rotate around the axial axis. The UV/Vis spectrum of **6** showed decreased absorption and a broader bandwidth than those of the corresponding titanium oxides. Furthermore, the first oxidation potential of **6** was observed as one quasi-reversible oxidation potential. The results suggest that the two phthalocyanines of **6** electronically interact with each other through the central benzenetetra-thiolate moiety in photochemically excited and electrically oxidized states.

Experimental Section

General: NMR spectra were measured with a Bruker AC-400 spectrometer. Mass spectra were obtained with a JEOL JMS-700 mass spectrometer. UV/Vis spectra were recorded with a JASCO Ubest V-570 spectrometer. A JASCO FT/IR-4200 spectrometer was employed to record IR spectra. A Hokuto Denko Co. Model HAB-151 apparatus was used to measure the oxidation potentials. Bio-beads (SX-1) for column chromatography were purchased from Nippon Bio-Rad Laboratories.

Oxidation Potentials: All measurements were performed by cyclic voltammetry using Ag/AgNO₃ (0.01 mol/L) as a reference electrode (scan rate: 200 mV/s). A solution of *n*Bu₄NClO₄ in CH₂Cl₂ (0.1 mol/L) was used as the electrolyte. The oxidation potential of ferrocene was observed at $E_{1/2} = 0.09$ V with the apparatus without any correction.

4,5-Bis[(2-cyanoethyl)thio]-3,6-diethylphthalonitrile (1): Compound **1** was prepared from 1,4-diethylbenzene according to a method described previously.^[10a]

3,6-Diethyl-4,5-bis(methylthio)phthalonitrile (2): Compound **1** (0.522 g, 1.48 mmol) in THF (20 mL)/MeOH (20 mL) was treated with CsOH·H₂O (0.98 g, 6.60 mmol) at room temperature. Methyl iodide (0.5 mL, 8.0 mmol) was then added, and the solution was stirred at room temperature for 12 h. After acidification and evaporation of the solvent, the product was extracted with CHCl₃. The solvent was evaporated, and the residue was purified by column chromatography (Wakogel C-300HG, *n*-hexane/CHCl₃ = 1:1 and then CHCl₃) to produce **2** in 66% yield (0.250 g); yellow crystals; m.p. 150.5–151.0 °C. ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 1.29 (t, ⁴J_{H,H} = 7.5 Hz, 6 H, CH₃), 2.51 (s, 6 H, SCH₃), 3.23 (q, ⁴J_{H,H} = 7.5 Hz, 4 H, CH₂Ar) ppm. ¹³C NMR (101 MHz, CDCl₃, 25 °C): δ = 15.5, 21.0, 28.8, 115.0, 116.0, 149.6, 152.0 ppm. HRMS (EI): calcd. for C₁₄H₁₆N₂S₂ [M]⁺ 276.0755; found 276.0756.

1,4,8,11,15,18,22,25-Octaethyl-2,3,9,10,16,17,23,24-octakis(methylthio)phthalocyanine (3): Lithium (40 mg, 5.7 mmol) was placed in a glass reactor, and *n*-pentanol (2 mL) was added under Ar. The solution was stirred at 115 °C for several minutes. Compound **2** (190 mg, 0.688 mmol) was added to the solution, which was then stirred at 115 °C for 1 h. Then the reactor was cooled, aqueous HCl and MeOH were added, and a green precipitate was filtered off. The residue was purified by column chromatography (Wakogel C-300HG, *n*-hexane/CHCl₃ = 1:1, and Bio-beads, CHCl₃) to produce **3** in 37% yield (70 mg); dark-green crystals; m.p. >300 °C. ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 1.66 (t, ⁴J_{H,H} = 7.4 Hz, 24 H, CH₃), 2.75 (s, 24 H, SCH₃), 4.89 (br. q, ⁴J_{H,H} = 7.4 Hz, 16 H, CH₂) ppm. UV (CHCl₃): λ_{max} = 750 nm (log ε = 5.06). MS (FAB): *m/z* = 1106.35 [M]⁺. **PcS₂Sn** (120 mg, 0.07 mmol) and lithium (42 mg, 6.1 mmol) were placed in a glass reactor, and THF (5 mL) was added under Ar. Then the solution was cooled to –70 °C, and NH₃ (30 mL) was introduced into the reactor and condensed. The solution was stirred at this temperature for 1 h and gradually warmed to –33 °C. NH₃ was evaporated in a stream of N₂ gas. After the evaporation of NH₃ was complete, THF (5 mL) and MeOH (10 mL) were added to the blue-green solid. NH₄Cl (370 mg, 6.9 mmol) and MeI (0.4 mL, 6.4 mmol) were added, and the solution was stirred at room temperature for 20 h. Aqueous HCl and MeOH were added to the solution, and a green precipitate was filtered off. The residue was purified by column chromatography (Wakogel C-300HG, *n*-hexane/CHCl₃ = 1:1) to produce **3** in 41% yield (31.6 mg).

[1,4,8,11,15,18,22,25-Octaethyl-2,3,9,10,16,17,23,24-octakis(methylthio)phthalocyaninato]titanium(IV) Oxide (3-TiO): Compound **3** (130.5 mg, 0.118 mmol) was placed in a glass reactor, and Ti(OBu)₄ (1.0 mL, 2.942 mmol) and DMF (10 mL) were added under Ar. Then the solution was stirred at 130 °C for 2 h, cooled to room temperature, and poured into brine. Then the green precipitate was filtered. After drying, the product was purified by column chromatography (Wakogel C-300HG, *n*-hexane/CHCl₃ = 1:1 and then CHCl₃) to produce **3-TiO** in 96% yield (131.9 mg); dark-green powder; m.p. >300 °C. ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 1.74 (t, ⁴J_{H,H} = 7.3 Hz, 24 H, CH₃), 2.78 (s, 24 H, SCH₃), 4.94 (dq, ³J_{H,H} = 12.2 Hz, ⁴J_{H,H} = 7.3 Hz, 8 H, CH₂), 5.02 (dq, ³J_{H,H} = 12.2 Hz, ⁴J_{H,H} = 7.3 Hz, 8 H, CH₂) ppm. ¹³C NMR (101 MHz, CDCl₃, 25 °C): δ = 16.8, 22.3, 25.2, 134.0, 146.8, 147.1, 151.8 ppm. UV/Vis (CHCl₃): λ_{max} = 760 nm (log ε = 5.15). IR (KBr): ν̄ = 2950, 2917, 2861, 1655, 1300, 1244, 1180, 1094, 1074, 1052, 977, 794 cm^{–1}. MS (FAB): *m/z* = 1168.3 [M]⁺. C₅₆H₆₄N₈OS₈Ti (1168.24): C 57.51, H 5.52, N 9.58; found C 54.43, H 5.30, N 8.74.

1,2,4,5-Tetrakis[(2-cyanoethyl)thio]benzene (5): 1,2,4,5-Tetrakis(methylthio)benzene (**4**) (682 mg, 2.6 mmol) and lithium (359 mg, 50 mmol) were placed in a glass reactor. THF (5 mL) was added under Ar, and the solution was cooled to –78 °C. NH₃ (about 30 mL) was introduced into the reactor and condensed. The solution was stirred at this temperature for 2 h and gradually warmed to room temperature. NH₃ was evaporated under a stream of N₂ gas. After the evaporation of NH₃, deaerated MeOH (10 mL) and THF (10 mL) were added to the residue, and NH₄Cl (3984 mg, 74.5 mmol) was added to the solution. 3-Bromopropionitrile (1.5 mL, 18 mmol) was added dropwise from a syringe, and the solution was stirred at room temperature for 12 h. The solvent was then evaporated, and the product was dissolved in CHCl₃/MeOH = 1:1. The solution was washed with water and dried. After evaporation the product was separated by column chromatography (Wakogel C-300HG, CHCl₃/MeOH = 1:1) to produce **5** in 31% yield (337 mg); colorless crystals; m.p. 115.1–115.6 °C. ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 2.70 (t, ⁴J_{H,H} = 6.8 Hz, 8 H, CH₂),

3.21 (t, ⁴J_{H,H} = 6.8 Hz, 8 H, CH₂), 7.50 (s, 2 H, ArH) ppm. ¹³C NMR (101 MHz, CDCl₃, 25 °C): δ = 18.4, 29.2, 117.8, 134.3, 136.2 ppm. HRMS (EI): calcd. for C₁₈H₁₈S₄ [M]⁺ 418.0414; found 418.0408.

Bis{[1,4,8,11,15,18,22,25-Octaethyl-2,3,9,10,16,17,23,24-octakis(methylthio)phthalocyaninato]titanium(IV)} Benzene-1,2,4,5-tetrathiolate (6): Compound **5** (24.1 mg, 0.058 mmol) and CsOH·H₂O (400 mg, 2.4 mmol) were placed in a glass reactor under Ar. THF (5 mL) and MeOH (5 mL) were added to the reactor, and the solution was stirred for 3 h. Concentrated HCl (0.4 mL) was added, and the solution was transferred by syringe under Ar to a reactor containing **3-TiO** (99.6 mg, 0.085 mmol) and THF (3 mL). The solution was stirred for 18 h, and the solvent was evaporated. The residue was purified by column chromatography (Wakogel C-300HG, *n*-hexane/CHCl₃ = 1:1, and Bio-beads, CHCl₃) to produce **6** in 17% yield (18.6 mg); dark-green powder, m.p. >300 °C. ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 1.40 (t, ⁴J_{H,H} = 7.3 Hz, 48 H, CH₃), 2.61 (s, 48 H, SCH₃), 3.79 (s, 2 H, ArH), 4.64 (br., 32 H, CH₂) ppm. ¹³C NMR (101 MHz, CDCl₃, 25 °C): δ = 16.4, 22.1, 25.1, 117.3, 132.7, 146.3, 146.5(0), 146.5(4), 151.0 ppm. UV/Vis (CHCl₃): λ_{max} = 757 nm (log ε = 5.05). IR (KBr): ν̄ = 2962, 2917, 2850, 1733, 1455, 1340, 1298, 1262, 1217, 1181, 1094, 1051, 968, 941, 801 cm^{–1}. MS (FAB): *m/z* = 2506.50 [M]⁺. C₁₁₈H₁₃₀N₁₆S₂₀Ti₂ (2506.40): C 56.48, H 5.22, N 8.93; found C 57.57, H 5.71, N 8.16.

(Tetra-*tert*-butylphthalocyaninato)titanium(IV) Oxide (tBuPcTiO): *tert*-Butylphthalonitrile (1.038 g, 5.672 mmol), urea (188 mg, 3.133 mmol), and 8 drops of DBU were placed in a glass reactor under Ar. Ti(OBu)₄ (0.8 mL, 2.354 mmol) and *n*-pentanol (10 mL) were added to the reactor, and the solution was stirred at 155 °C for 7 h. After cooling to room temperature, MeOH (400 mL) and water (100 mL) were added, and the solution was filtered. The residue was purified by column chromatography (Wakogel C-300HG, *n*-hexane/CHCl₃ = 1:1 and then CHCl₃) to produce **tBuPcTiO** in 31% yield (360 mg); dark-blue powder. ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 1.85–1.92 (m, 36 H, CH₃), 8.37–8.43 (m, 4 H, ArH), 9.40–9.64 (m, 8 H, ArH) ppm. UV/Vis (CHCl₃): λ_{max} = 702, 666, 637, 604 nm.^[7]

Bis[(tetra-*tert*-butylphthalocyaninato)titanium(IV)] Benzene-1,2,4,5-tetrathiolate (7): Compound **5** (28 mg, 0.067 mmol) and CsOH·H₂O (554 mg, 3.70 mmol) were placed in a glass reactor under Ar. Compound **7** was obtained in 20% yield (26.9 mg) according to the procedure described above; dark-blue powder; m.p. >300 °C. ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 1.67–1.72 (s, 36 H, CH₃), 3.60–3.62 (m, 2 H, ArH), 8.18–8.22 (m, 4 H, ArH), 9.22–9.43 (m, 8 H, ArH) ppm. UV/Vis (CHCl₃): λ_{max} = 697 nm. IR (KBr): ν̄ = 2959, 2363, 1612, 1483, 1395, 1364, 1326, 1256, 1150, 1073, 927, 829, 803, 754 cm^{–1}. MS (FAB): *m/z* = 1770.60 [M]⁺. C₁₀₂H₉₈N₁₆S₄Ti₂ (1770.60): C 69.14, H 5.57, N 12.65; found C 68.15, H 5.97, N 11.75.

- [1] a) K. M. Kadish, K. M. Smith, R. Guilard, *The Porphyrin Handbook*, Academic Press, San Diego, **2003**, vols. 15–20; b) C. C. Leznoff, A. B. P. Lever, *Phthalocyanines: Properties and Applications*, VCH, New York, **1989–1996**, vols. 1–4.
- [2] a) D. Wöhrle, O. Suvorova, R. Gerdes, O. Bartels, L. Lapok, N. Baziakina, S. Makarov, A. Slodek, *J. Porphyrins Phthalocyanines* **2004**, *8*, 1020–1041; b) G. de la Torre, P. Vázquez, F. Agulló-López, T. Torres, *Chem. Rev.* **2004**, *104*, 3723–3750; c) G. de la Torre, C. G. Claessens, T. Torres, *Chem. Commun.* **2007**, 2000–2015.
- [3] a) T. Fukuda, S. Masuda, N. Kobayashi, *J. Am. Chem. Soc.* **2007**, *129*, 5472–5479; b) L. Martín-Gomis, K. Ohkubo, F. Fernández-Lázaro, S. Fukuzumi, Á. Sastere-Santos, *Org. Lett.*

- 2007, 9, 3441–3444; c) P. Y. Reddy, L. Giribabu, C. Lyness, H. J. Snaith, C. Vijaykumar, M. Chandrasekharam, M. Lakshmi-kantam, J.-H. Yum, K. Kalyanasundaram, M. Grätzel, M. K. Nazeeruddin, *Angew. Chem. Int. Ed.* **2007**, 46, 373–376.
- [4] a) P. A. Stuzhin, E. M. Bauer, C. Ercolani, *Inorg. Chem.* **1998**, 37, 1533–1539; b) A. E. Pullen, C. Faulmann, P. Cassoux, *Eur. J. Inorg. Chem.* **1999**, 269–276; c) M. T. M. Choi, P. P. S. Li, D. K. P. Ng, *Tetrahedron* **2000**, 56, 3881–3887; d) A. de la Escosura, M. V. Martínez-Díaz, P. Thordarson, A. E. Rowan, R. J. M. Nolte, T. Torres, *J. Am. Chem. Soc.* **2003**, 125, 12300–12308; e) F. Mitzel, S. FitzGerald, A. Beeby, R. Faust, *Chem. Eur. J.* **2003**, 9, 1233–1241; f) W. J. Youngblood, *J. Org. Chem.* **2006**, 71, 3345–3356.
- [5] a) J. Li, D. Gryko, R. B. Dabke, J. R. Diers, D. F. Bocian, W. G. Kuhr, J. S. Lindsey, *J. Org. Chem.* **2000**, 65, 7379–7390; b) V. H. F. Armand, J. P. Bourgoïn, S. Palacin, *Langmuir* **2001**, 17, 1928–1935; c) J. Jiang, Y. Bian, F. Furuya, W. Liu, M. T. M. Choi, N. Kobayashi, H.-W. Li, Q. Yang, T. C. W. Mak, D. K. P. Ng, *Chem. Eur. J.* **2001**, 7, 5059–5069; d) Y. Chen, L. R. Subramanian, M. Fujitsuka, O. Ito, S. O’Flaherty, W. J. Blau, T. Schneider, D. Dini, M. Hanack, *Chem. Eur. J.* **2002**, 8, 4248–4254; e) Y. Chen, M. Barthel, M. Seiler, L. R. Subramanian, H. Bertagnolli, M. Hanack, *Angew. Chem. Int. Ed.* **2002**, 41, 3239–3242; f) K. Hatsusaka, M. Kimura, K. Ohta, *Bull. Chem. Soc. Jpn.* **2003**, 76, 781–787; g) N. Ishikawa, M. Sugita, T. Ishikawa, S. Koshihara, Y. Kaizu, *J. Am. Chem. Soc.* **2003**, 125, 8694–8695; h) A. Muranaka, Y. Matsumoto, M. Uchiyama, J. Jiang, Y. Bian, A. Ceulemans, N. Kobayashi, *Inorg. Chem.* **2005**, 44, 3818–3826; i) A. N. Cammidge, G. Berber, I. Chambrier, P. W. Hough, M. J. Cook, *Tetrahedron* **2005**, 61, 4067–4074.
- [6] a) M. Brewis, G. J. Clarkson, V. Goddard, M. Helliwell, A. M. Holder, N. B. McKeown, *Angew. Chem. Int. Ed.* **1998**, 37, 1092–1094; b) M. Brewis, G. J. Clarkson, M. Helliwell, A. M. Holder, N. B. McKeown, *Chem. Eur. J.* **2000**, 6, 4630–4636; c) C. Farren, C. A. Christensen, S. FritzGerald, M. R. Bryce, A. Beeby, *J. Org. Chem.* **2002**, 67, 9130–9139; d) M. Brewis, M. Helliwell, N. B. McKeown, *Tetrahedron* **2003**, 59, 3863–3872; e) A. Morandeira, I. López-Duarte, M. V. Martínez-Díaz, B. O’Regan, C. Shuttle, N. A. Haji-Zainulabidin, T. Torres, E. Palomares, J. R. Durrant, *J. Am. Chem. Soc.* **2007**, 129, 9250–9251; f) L. Matin-Gomis, K. Ohkubo, F. Fernández-Lázaro, S. Fukuzumi, Á. Sastre-Santos, *Org. Lett.* **2007**, 9, 3441–3444; g) B. C. O’Regan, I. López-Duarte, M. V. Martínez-Díaz, A. Forneli, J. Albero, A. Morandieria, E. Palomares, T. Torres, J. R. Durrant, *J. Am. Chem. Soc.* **2008**, 130, 2906–2907.
- [7] a) M. Barthel, M. Hanack, *J. Porphyrins Phthalocyanines* **2000**, 4, 635–638; b) M. Barthel, D. Dini, S. Vagin, M. Hanack, *Eur. J. Org. Chem.* **2002**, 3756–3762.
- [8] a) N. Kobayashi, A. Muranaka, *Chem. Commun.* **2000**, 1855–1856; b) A. Muranaka, M. Okuda, N. Kobayashi, K. Somers, A. Ceulemans, *J. Am. Chem. Soc.* **2004**, 126, 4596–4604; c) A. Muranaka, K. Yoshida, T. Shoji, N. Moriichi, S. Masumoto, T. Kanda, Y. Ohtake, N. Kobayashi, *Org. Lett.* **2006**, 8, 2447–2450.
- [9] T. Kimura, S. Ogawa, R. Sato, *Mini.-Rev. Org. Chem.* **2007**, 4, 15–29.
- [10] a) T. Kimura, A. Yomogita, T. Matsutani, T. Suzuki, I. Tanaka, Y. Kawai, Y. Takaguchi, T. Wakahara, T. Akasaka, *J. Org. Chem.* **2004**, 69, 4716–4723; b) T. Kimura, T. Suzuki, Y. Takaguchi, A. Yomogita, T. Wakahara, T. Akasaka, *Eur. J. Org. Chem.* **2006**, 1262–1270; c) T. Kimura, N. Kanota, K. Matsui, I. Tanaka, T. Tsuboi, Y. Takaguchi, A. Yomogita, T. Wakahara, S. Kuwahara, F. Nagatsugi, T. Akasaka, *Inorg. Chem.* **2008**, 47, 3577–3583.
- [11] M. J. Cook, M. J. Heeney, *Chem. Commun.* **2000**, 969–970; N. Kobayashi, H. Ogata, N. Nonaka, E. A. Luk’yanets, *Chem. Eur. J.* **2003**, 9, 5123–5134.
- [12] a) C. S. Velázquez, W. E. Broderick, M. Sabat, A. G. M. Barrett, B. M. Hoffman, *J. Am. Chem. Soc.* **1990**, 112, 7408–7410; b) C. S. Velázquez, G. A. Fox, W. E. Broderick, K. A. Anderson, O. P. Anderson, A. G. M. Barrett, B. M. Hoffman, *J. Am. Chem. Soc.* **1992**, 114, 7416–7424.
- [13] It has been reported that the tautomerization of inner protons affects the signals of ^1H and ^{13}C NMR spectra: a) R. J. Abraham, G. E. Hawkes, K. M. Smith, *Tetrahedron Lett.* **1974**, 15, 1483–1486; b) R. J. Abraham, G. E. Hawkes, M. F. Hudson, K. M. Smith, *J. Chem. Soc. Perkin Trans. 2* **1975**, 204–211; c) M. J. Cook, S. J. Cracknell, G. R. Moore, M. J. Osborne, D. J. Williamson, *Magn. Reson. Chem.* **1991**, 29, 1053–1060.
- [14] C. W. Dirk, S. D. Cox, D. E. Wellman, F. Wudl, *J. Org. Chem.* **1985**, 50, 2395–2397.
- [15] a) L. Testaferri, M. Tingoli, M. Tiecco, *J. Org. Chem.* **1980**, 45, 4376–4380; b) F. Maiolo, L. Testaferri, M. Tiecco, M. Tingoli, *J. Org. Chem.* **1981**, 46, 3070–3073.
- [16] V. L. Goedken, G. Dessy, C. Ercolani, V. Fares, L. Gastaldi, *Inorg. Chem.* **1985**, 24, 991–995.

Received: May 23, 2008

Published Online: September 16, 2008