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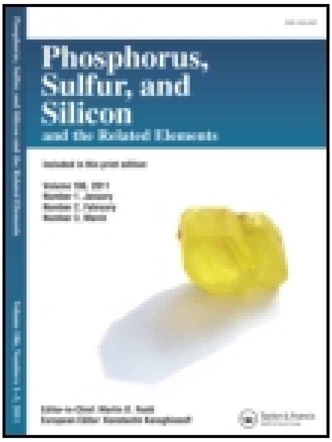

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Preparation of Octakis (methylthio)octaethylphthalocyaninato Titanium (IV) Benzenedichalcogenolates

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PREPARATION OF OCTAKIS (METHYLTHIO)OCTAETHYLPHTHALOCYANINATO TITANIUM (IV) BENZENEDICHALCOGENOLATES

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Octakis(methylthio)octaethylphthalocyaninato titanium (IV) oxide (PcSMeTiO) was prepared from octakis(methylthio)octaethylphthalocyanine (PcSMe) upon treatment with titanium (IV) tetrabutoxide in DMF at 130°C. The reaction of PcSMeTiO with benzenedithiol or benzenediselenol produced octakis(methylthio)octaethylphthalocyaninato titanium (IV) benzenedichalcogenolates (4a,b) bearing titanium–sulfur or titanium–selenium bonds.

Keywords Phthalocyanine; S ligand; Se ligand; titanium

INTRODUCTION

Tetraazaporphyrins and related compounds have a variety of actual and potential applications in many fields such as dyes, pigments, catalysts, new functional materials, and sensitizers for photodynamic therapy.[1,2] Among the great number of tetraazaporphyrins, phthalocyanines connecting one or two axial coordinating groups on the central metal atom have attracted much attention because the molecules could be applied to electrochromic displays, field-effect transistors, nonlinear optical materials, and dye-sensitized solar cells.[3] Recently, Hanack and colleagues reported phthalocyaninato titanium (IV) complexes as compounds that have axial coordinating groups connected with titanium–oxygen or titanium–sulfur bonds,[4] while Kobayashi and colleagues synthesized a mutually perpendicular phthalocyanine pentamer and related derivatives.[5] These products were prepared by the ligand exchange reaction of tetra-*t*-butylphthalocyaninato titanium (IV) oxide with *o*-catechols, *o*-benzenedithiol, tetrahydroxy-*p*-benzoquinone, and octahydroxyphthalocyanine. In contrast, we reported the double-decker phthalocyanine, which was obtained by the reaction of two molecules of octakis(methylthio)octaethylphthalocyaninato titanium (IV) oxide (PcSMeTiO) with benzene-1,2,4,5-tetrathiol.[6] To construct a new type of phthalocyanines with an axial ligand, PcSMeTiO was reacted with 3,6-diethyl-4,5-dibromobenzene-1,2-dithiol (**3a**) or 3,6-diethyl-4,5-dibromobenzene-1,2-diselenol (**3b**). This article reports the preparation

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Dedicated to Professor Naomichi Furukawa on the occasion of his 70th birthday.

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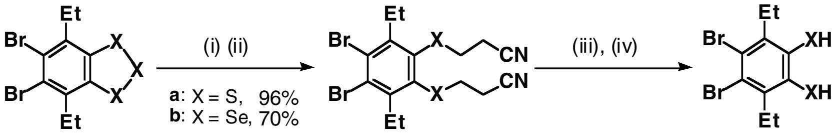
and electrochemical property of octakis(methylthio)octaethylphthalocyaninato titanium (IV) diethyldibromobenzenedichalcogenolates (**4a**,**b**).

RESULTS AND DISCUSSION

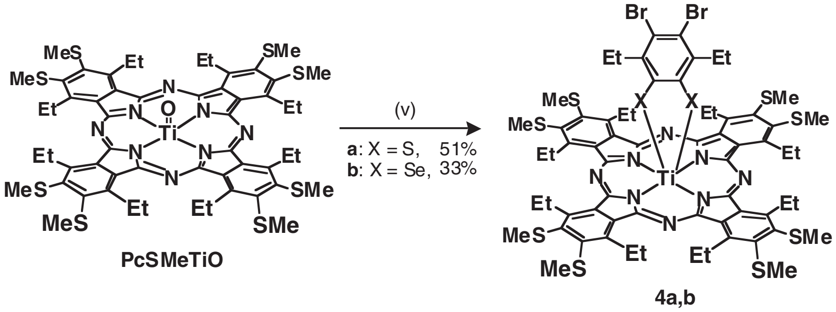
5,6-Dibromo-4,7-diethylbenzotrichalcogenoles (**1a**,**b**) were converted into 1,2-bis(2-cyanoethylchalcogeno)-4,5-dibromo-3,6-diethylbenzenes (**2a**,**b**) in 96% and 70% yields, respectively, upon treatment with $NaBH_4$ and then 2-cyanoethyl bromide (Scheme 1).[7]



1a,b **2a,b** **3a,b**

Scheme 1 (i) $NaBH_4$, K_2CO_3, THF/MeOH; (ii) $BrCH_2CH_2CN$; (iii) CsOH, THF/MeOH; (iv) HCl

The treatment of octakis(methylthio)octaethylphthalocyanine (PcSMe) with titanium (IV) tetrabutoxide by the procedure reported previously produced PcSMeTiO.[6] To prepare benzenedithiol (**3a**) as a bidentate sulfur ligand, **2a** was reacted with CsOH in THF/MeOH under Ar (Scheme 1).[8,9] The reaction mixture was acidified with concentrated HCl to generate **3a**. The prepared solution was transferred to the reactor containing PcSMeTiO, and the reaction mixture was stirred for 24 h (Scheme 2). After workup and purification with silica gel column chromatography and Bio-beads column chromatography, phthalocyanine (**4a**) with benzenedithiolate as the axial ligand was obtained in 51% yield.



PcSMeTiO

4a,b

Scheme 2 (v) **3a** or **3b**, THF/MeOH.

In the ^{1}H NMR spectrum, **4a** showed the signals of the ethyl and methylthio groups connected to the phthalocyanine core at $\delta = 1.60$ (t), 2.72 (s), and 4.68–5.00 (m) ppm. These chemical shifts are slightly upper field compared with those of PcSMeTiO: $\delta = 1.74$ (t), 2.78 (s), 4.94 and 5.02 (dq) ppm. The signals for the ethyl group of benzenedithiolate were observed at $\delta = 0.23$ (t) and 1.81 (q) ppm, which are higher magnetic field than those of **2a**: $\delta = 1.29$ (t) and 3.28 (q) ppm. These results could show that the benzene ring lies on the phthalocyanine plane and is strongly affected in the magnetic shielding range of the macrocycle. When ^{13}C NMR of **4a** was measured, the four signals for the phthalocyanine skeleton, the five signals for the ethyl and the methylthio groups, and three signals for the coordinating benzene ring appeared in the following spectrum: $\delta = 11.5$, 16.4, 22.7, 25.4, 30.0, 124.9, 132.9, 136.4, 146.7, 146.8, 147.9, 151.4 ppm. Since the signals for PcSMeTiO were observed at $\delta = 16.8$, 22.3, 25.2, 134.0, 146.8, 147.1, 151.8 ppm, the signals for **4a** at 11.5, 30.0, 124.9, 136.4, 147.9 ppm might be the carbon of benzenedithiolate. It appears that the phthalocyanine skeleton of **4a** is a C4 symmetric structure in the NMR time scale at 25°C, though benzenedithiolate coordinates to the central titanium atom. Furthermore, the FABMS spectrum of **4a** showed the corresponding molecular ion peak at m/z = 1504.13 [M^+].

The similar treatment of PcSMeTiO with **3b** produced phthalocyanine (**4b**) with benzenediselenolate in 33% yield. The ^{1}H NMR and ^{13}C NMR spectra of **4b** were similar to those of **4a**. The ^{77}Se NMR spectrum showed the signal at $\delta = 448.5$ ppm, which is a much higher magnetic field than that of the bis(cyclopentadienyl)benzodiselenatitanole derivatives.[10] The FABMS spectrum of **4b** exhibited the molecular ion peak at m/z = 1600.13 [M^+].

In the UV-vis spectra measured in $CHCl_3$, the Q band absorptions of **4a** and **4b** were observed at $\lambda_{max} = 763.5$ and 765.5 nm, respectively, which were wider bandwidth and slightly longer wavelengths than that of PcSMeTiO ($\lambda_{max} = 760$ nm). The bandwidth of the Q band absorption of the free-base phthalocyanine, PcSMe, is more enlarged than that of PcSMeTiO because of the proton alternation between the central pyrrolic nitrogen atoms. Although the phthalocyanine skeleton of **4a** and **4b** is the C4 symmetry, the coordination of benzenedichalcogenolate to the central titanium atom in the axial direction could have made the symmetry of the π-electronic system decrease from C4 to C2, which resulted in the broadening of the Q band absorption of **4a** and **4b** compared with that of PcSMeTiO.

The electrochemical properties of **4a** and **4b** were examined by cyclic voltammetry using Ag/$AgNO_3$ as a reference electrode (measured in CH_2Cl_2, scan rate: 100 mV/s). The cyclic voltammogram of **4a** contained one irreversible oxidation (Ep = 0.87 V) and three quasi-reversible reduction potentials ($E_{1/2}$ = –1.73, –1.06, and –0.76 V). Compound (**4b**) showed the irreversible oxidation potential at Ep = 0.85 V while the quasi-reversible reduction potentials were observed at $E_{1/2}$ = –1.78, –1.04, and –0.75 V. As shown in Table I, it appeared that the oxidation and reduction potentials of **4a** and **4b** are higher than those of PcSMe and PcSMeTiO.

Table I Redox potentials (vs. Ag/$AgNO_3$)

	E1/2 [V]					
Compounds	3rd reduction	2nd reduction	1st reduction	1st oxidation	2nd oxidation	ΔE (V)
PcSMe[a]	—	–1.41	–1.08	0.52	0.91	1.60
PcSMeTiO[a]	—	–1.14	–0.80	0.68	1.13[c]	1.48
4a[b]	–1.73[d]	–1.06[d]	–0.76[d]	0.87[c]	—	1.63
4b[b]	–1.78[d]	–1.04[d]	–0.75[d]	0.85[c]	—	1.60

[a] Scan rate: 200 mV/s.
[b] Scan rate: 100 mV/s.
[c] Irreversible (Ep /V).
[d] Quasi reversible.
ΔE is the difference between the first oxidation potential and the first reduction potential.

EXPERIMENTAL

NMR spectra were measured with a Bruker AC-400 spectrometer at 25°C. Mass spectra were obtained using a JEOL JMS-700 mass spectrometer. UV-vis spectra were recorded with a JASCO Ubest V-570 spectrometer. A Hokuto Denko Co. Model HAB-151 apparatus was employed for measuring oxidation potentials. Elemental analysis was performed using a Yanako MT-5 analyzer. 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/$AgNO_3$ (0.01 mol/l) as a reference electrode (scan rate: 100 mV/s or 200 mV/s). A solution of n-Bu_4NClO_4 in CH_2Cl_2 (0.1 mol/l) was used as an electrolyte. The oxidation potential of ferrocene was observed at $E_{1/2} = 0.09$ V by the apparatus without any correction.

Materials

Compounds (**1a**), (**1b**), (**2a**), PcSMe, and PcSMeTiO were prepared using a method described previously.[6,7]

1,2-Bis(2-cyanoethylseleno)-4,5-dibromodiethylbenzene (2b)

To a solution of **1b** (1.604 g, 3 mmol) and K_2CO_3 (831 mg, 6 mmol) in THF (20 ml)/MeOH (10 ml), $NaBH_4$ (347 mg, 9.1 mmol) was added under Ar, and the solution was stirred for 30 min. 3-Bromopropionitrile (0.97 ml, 12 mmol) was added to the solution. After stirring for 6 h and acidification with HCl, the solvent was evaporated, and the product was extracted with $CHCl_3$. The solvent was evaporated, and the residue was purified by column chromatography (Wakogel C-400, n-hexane:$CHCl_3$ = 1:1) to produce **2b** in 70% yield (1.182 g); colorless crystals; mp 83–86°C; ^1H NMR (400 MHz, $CDCl_3$) $\delta = 1.18$ (t, $J = 7.4$ Hz, 6H), 2.71 (t, $J = 7.2$ Hz, 4H), 3.20 (t, $J = 7.2$ Hz, 4H), 3.43 (q, $J = 7.4$ Hz, 4H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) $\delta = 14.3$, 18.7, 26.2, 36.2, 118.3, 130.3, 137.7, 149.5 ppm; ^{77}Se NMR (76 MHz, $CDCl_3$) $\delta = 325.2$ ppm; HRMS Calcd for $C_{16}H_{18}{}^{79}Br_2N_2{}^{80}Se_2$, 555.8167. Found ($m/z$) 555.8167 ($M^+$).

Generation of 3,6-Diethyl-4,5-dibromobenzene-1,2-dithiol (3a)

Compound (**2a**) (156.5 mg, 0.342 mmol) and CsOH (517.6 mg, 3.45 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 2 h. Concentrated HCl (0.29 mL) was added to the solution to generate the corresponding dithiol (**3a**).

Generation of 3,6-Diethyl-4,5-dibromobenzene-1,2-diselenol (3b)

Compound (**2b**) (98.4 mg, 0.177 mmol) and CsOH (263.8 mg, 1.76 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 2 h. Concentrated HCl (0.14 mL) in methanol (6.9 mL) was added to the solution to generate the corresponding diselenol (**3b**).

Octakis(methylthio)octaethylphthalocyaninato Titanium (IV) Benzenedithiolate (4a)

The solution of **3a**, prepared as described above, was transferred by syringe to the reactor containing PcSMeTiO (97.4 mg, 0.0845 mmol) under Ar. The solution was stirred for 24 h, and the solvent was evaporated. The residue was purified by column chromatography (Wakogel C-300HG, *n*-hexane:$CHCl_3$ = 1:1 and $CHCl_3$) and (Bio-beads, $CHCl_3$) to produce **4a** in 51% yield (65.2 mg); dark green powder, mp > 300°C; ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 0.23$ (t, $J = 7.2$ Hz, 6H, CH_3), 1.60 (t, $J = 7.2$ Hz, 24H, CH_3), 1.81 (q, 4H, CH_2), 2.72 (s, 24H, SCH_3), 4.68–5.00 (m, 16H, CH_2) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ = 11.5, 16.4, 22.7, 25.4, 30.0, 124.9, 132.9, 136.4, 146.7, 146.8, 147.9, 151.4 ppm; UV-vis ($CHCl_3$) λmax = 763.5 nm; FAB MS (m/z) 1504.13 [M^+]; Anal. Calcd for $C_{66}H_{74}Br_2N_8S_{10}Ti$: C, 52.58; H, 4.95; N, 7.43. Found: C, 52.36; H, 5.09; N, 6.53.

Octakis(methylthio)octaethylphthalocyaninato Titanium (IV) Benzenediselenoolate (4b)

Compound (**4b**) was prepared in 33% yield by the procedure as described above; dark green powder, mp 225°C; ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 0.29$ (t, $J = 7.4$ Hz, 6H, CH_3), 1.59 (t, $J = 7.2$ Hz, 24H, CH_3), 1.93 (q, 4H, CH_2), 2.74 (s, 24H, SCH_3), 4.60–4.99 (m, 16H, CH_2) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ = 11.7, 16.4, 22.7, 25.4, 29.7, 125.2, 132.9, 139.5, 146.6, 146.8, 148.5, 151.2 ppm; ^{77}Se NMR (76 MHz, $CDCl_3$) $\delta = 448.5$ ppm; UV-vis ($CHCl_3$) $\lambda_{max} = 765.5$ nm; FAB MS (m/z) 1600.13 [M^+].

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