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PREPARATION AND ELECTROCHEMICAL PROPERTIES OF PHTHALOCYANINATO TITANIUM(IV) AND PORPHYRINATO TITANIUM(IV) BENZENEDICHALCOGENOLATES

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This paper is dedicated to Prof. Dr. Albert Eschenmoser on the occasion of his 85th birthday.

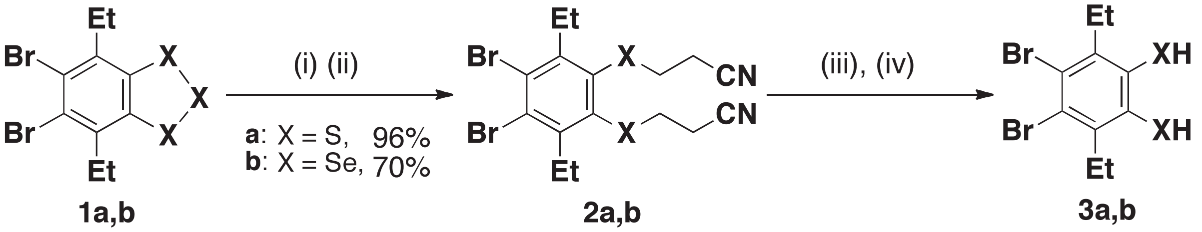
Abstract – The reaction of phthalocyaninato titanium(IV) oxides with benzenedithiol or benzenediselenol produced the corresponding complexes with titanium-sulfur or titanium-selenium bonds. Tetraphenylporphyrinato titanium (IV) benzenedichalcogenolates were obtained by the similar procedure. Their optical and electrochemical properties were determined by UV-vis spectroscopy and cyclic voltammetry.

INTRODUCTION

Phthalocyanines (Pcs) and porphyrins have attracted much attention because of their potential applications in electrochromic displays, field-effect transistors, nonlinear optical materials, and dye-sensitized solar cells.[1-3] The optical and electrochemical characteristics of these compounds could be based on their large and flat π-conjugated ring systems. The structures of the complexes depend on the central metal atom and its oxidation state and ligands. It was reported that phthalocyaninato titanium (IV) complexes could have two ligands in one face of the Pc-plane.[4] As related compounds with bidentate ligands, Hanack reported phthalocyaninato titanium(IV) complexes with titanium-oxygen or titanium-sulfur bonds,[5] while Kobayashi synthesized a mutually perpendicular phthalocyanine pentamer and related derivatives.[6] In addition, we reported a double-decker phthalocyanine complex linked with four titanium-sulfur bonds.[7,8] Alternatively, porphyrinato titanium(IV) complexes with titanium-oxygen or titanium-sulfur bonds were described.[9] To construct new types of phthalocyanine and porphyrin complexes with an axial ligand connected by titanium-sulfur or titanium-selenium bonds, octa-*n*-butoxyphthalocyaninato titanium(IV) oxide (**4**), tetra-*t*-butylphthalocyaninato titanium(IV) oxide (**5**),[5b] octamethylthiophthalocyaninato titanium(IV) oxide (**6**), and tetraphenylporphyrinato titanium(IV) oxide (**10**) were reacted with 3,6-diethyl-4,5-dibromobenzene-1,2-dithiol (**3a**) or 3,6-diethyl-4,5-dibromobenzene-1,2-diselenol (**3b**). This paper reports the preparation and electrochemical properties of octabutoxyphthalocyaninato titanium(IV) benzenedithiolate (**7a**) and related compounds.

RESULT AND DISCUSSION

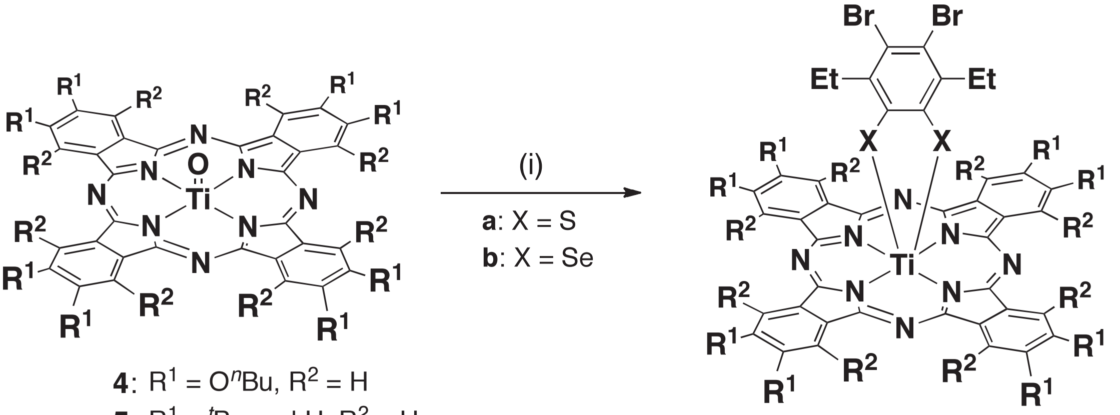
1,2-Bis(2-cyanoethylchalcogeno)-4,5-dibromo-3,6-diethylbenzenes (**2a**,**b**) were prepared from 5,6-dibromo-4,7-diethylbenzo[1,2,3]trichalcogenoles (**1a**,**b**) in 96% and 70% yields, respectively, upon treatment with $NaBH_4$ and then 2-cyanoethyl bromide (Scheme 1).[8] To generate benzenedithiol (**3a**) as a bidentate sulfur ligand, **2a** was reacted with cesium hydroxide in THF/MeOH under Ar (Scheme 1). The reaction mixture was acidified with concentrated hydrochloric acid to give **3a**. Benzenediselenol (**3b**) could be generated from **2b** by the similar procedure.



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

The prepared solution of **3a** was transferred to a reactor containing **4**, and the reaction mixture was stirred at room temperature for 24 h (Scheme 2). After workup and purification with silica gel column chromatography and Bio-beads column chromatography, phthalocyanine (**7a**) with benzenedithiolate as the axial ligand was obtained in 67% yield. Compound (**6**) was prepared from the corresponding metal-free derivative on treatment with titanium(IV) tetrabutoxide by the procedure reported previously.[7] The treatment of **6** with **3a** produced phthalocyanine (**9a**) in 51% yield. Tetra-*t*-butyl derivative (**8a**) was also prepared from **5** by the similar process in 58% yield.

In the ^{1}H NMR spectrum of **7a**, the signals of the butoxy groups appeared at $\delta = 1.20$ (t), 1.81 (sext), 2.18 (quint), 4.63 (dt), and 4.67 (dt) ppm. These chemical shifts are located at a slightly upper field compared with those of **4**: δ = 1.25 (t), 1.86 (sext), 2.21 (quint), 4.64 (dt), and 4.68 (dt) ppm. Signals for the ethyl group of benzenedithiolate were observed at δ = -0.02 (t) and 1.48 (bq) ppm, which are a higher magnetic field than those of **2a**: δ = 1.29 (t) and 3.28 (q) ppm. These results could indicate that the benzene ring lies on the phthalocyanine plane and is strongly affected in the magnetic shielding range of the macrocycle. The ^{13}C NMR spectrum of **7a** showed four signals for the phthalocyanine skeleton, six signals for the ethyl and butoxy groups, and three signals for the coordinating benzene ring. Apparently, the phthalocyanine skeleton of **7a** is a C4v symmetric structure in the NMR time scale at 25 °C, although benzenedithiolate coordinates to the central titanium atom.



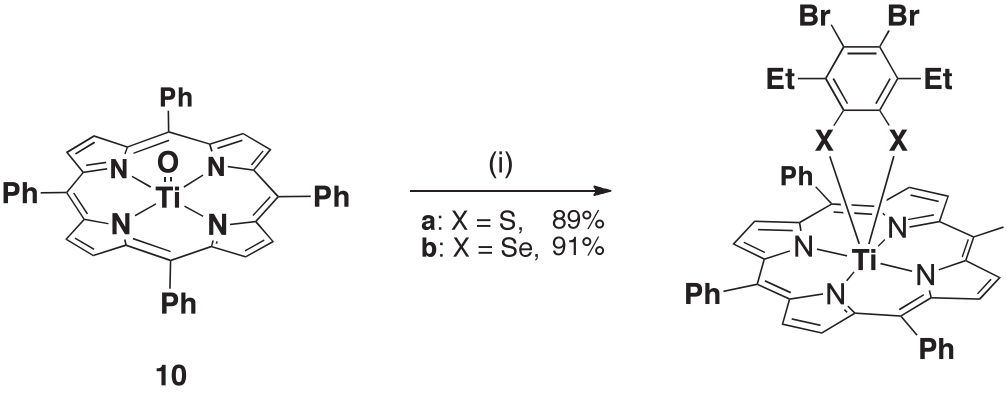
4: R^1 = O^{n}Bu, R^2 = H
5: R^1 = ^{t}Bu and H, R^2 = H
6: R^1 = SMe, R^2 = Et

7a: R^1 = O^{n}Bu, R^2 = H (67%)
8a: R^1 = ^{t}Bu and H, R^2 = H (58%)
9a: R^1 = SMe, R^2 = Et (51%)
9b: R^1 = SMe, R^2 = Et (33%)

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

Compound (**9a**) showed the signals for the ethyl and methylthio groups of the phthalocyanine core at δ = 1.60 (t), 2.72 (s), and 4.68-5.00 (m) ppm in the ^{1}H NMR spectrum. The signals for the ethyl group of benzenedithiolate were observed at δ = 0.23 (t) and 1.81 (q) ppm. The ^{13}C NMR spectrum showed twelve signals for the compound, suggesting that **9a** has also a C4v symmetric structure in the NMR time scale. The FABMS spectra of **7a** and **9a** exhibited the corresponding molecular ion peaks at m/z = 1488.4187 [M$^+$] for **7a** and m/z = 1504.13 [M$^+$] for **9a**.

A similar treatment of **6** with **3b** produced phthalocyanine (**9b**) with benzenediselenolate in 33% yield. The ^{1}H NMR and ^{13}C NMR spectra of **9b** were similar to those of **9a**, while the signals for the ethyl group of **9b** were observed at a slightly lower magnetic field than were those of **9a**. This result could be related to the difference of the bond distance between the titanium-sulfur and titanium-selenium bonds. The ^{77}Se NMR spectrum showed the signal at δ = 448.5 ppm, which is an extremely higher magnetic field than that of the bis(cyclopentadienyl)benzodiselenatitanole derivatives.[10] The FABMS spectrum of **9b** exhibited the molecular ion peak at m/z = 1600.13 [M^+].



10

11a,b

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

The solution of benzenedithiol was then added to **10** and the reaction gave **11a** with benzenedithiolate as the axial ligand in 89% yield (Scheme 3). Compound (**11a**) seems more unstable than **7a**. A similar treatment of **10** with **3b** produced **11b** with benzenediselenolate in 91% yield. In the ^{1}H NMR spectrum, **11a** showed the signals of the phenyl groups and the porphyrin core at δ = 7.74-7.85 (m, Ph), 8.16 (m, Ph), 8.25 (m, Ph), and 9.05 (s, β) ppm. These chemical shifts are situated at a slightly upper field compared with those of **10**. The signals for the ethyl group of **11a** were observed at δ = 0.20 (t) and 1.64 (q) ppm. The ^{13}C NMR spectrum of **11a** showed fourteen signals because two ortho and two meta carbon atoms of the phenyl group are unsymmetric, respectively. Although the ^{1}H and ^{13}C NMR of **11b** are similar to those of **11a**, the signals for the ethyl group were observed at δ = 0.27 (t) and 1.80 (q) ppm in ^{1}H NMR. The FABMS spectrum of **11a** showed the corresponding molecular ion peak at m/z = 1012.0384 [M^+], while that of **11b** exhibited the molecular ion peak at m/z = 1108.0 [MH^+].

In the UV-vis spectra of **7a** and **8a** measured in chloroform, the Q band absorptions were observed at λ_{max} = 702 nm (ε = 120000) for **7a** and λ_{max} = 698 nm (ε = 110000) for **8a** (Figure 1). These absorptions were wider bandwidths compared with that of **4** (λ_{max} = 702 nm, ε = 220000) and **5** (λ_{max} = 701 nm, ε = 150000), respectively. Compounds (**9a**) and (**9b**) showed the Q band absorptions at λ_{max} = 764 (ε = 110000) and λ_{max} = 766 nm (ε = 62000), respectively, which were wider bandwidths and slightly longer wavelengths than that of **6** (λ_{max} = 760 nm, ε = 140000). The absorption of the selenium derivative was observed at a slightly red-shifted region compared with the sulfur derivative. In contrast, **11a** and **11b** exhibited two split Soret band absorptions at λ_{max} = 399 nm (ε = 66000) and 432 nm (ε = 110000) for **11a** and λ_{max} = 396 nm (ε = 74000) and 427 nm (ε = 78000) for **11b**, although the Soret band absorption of **10** was observed at $\lambda_{\max} = 424$ nm (log ε = 330000).

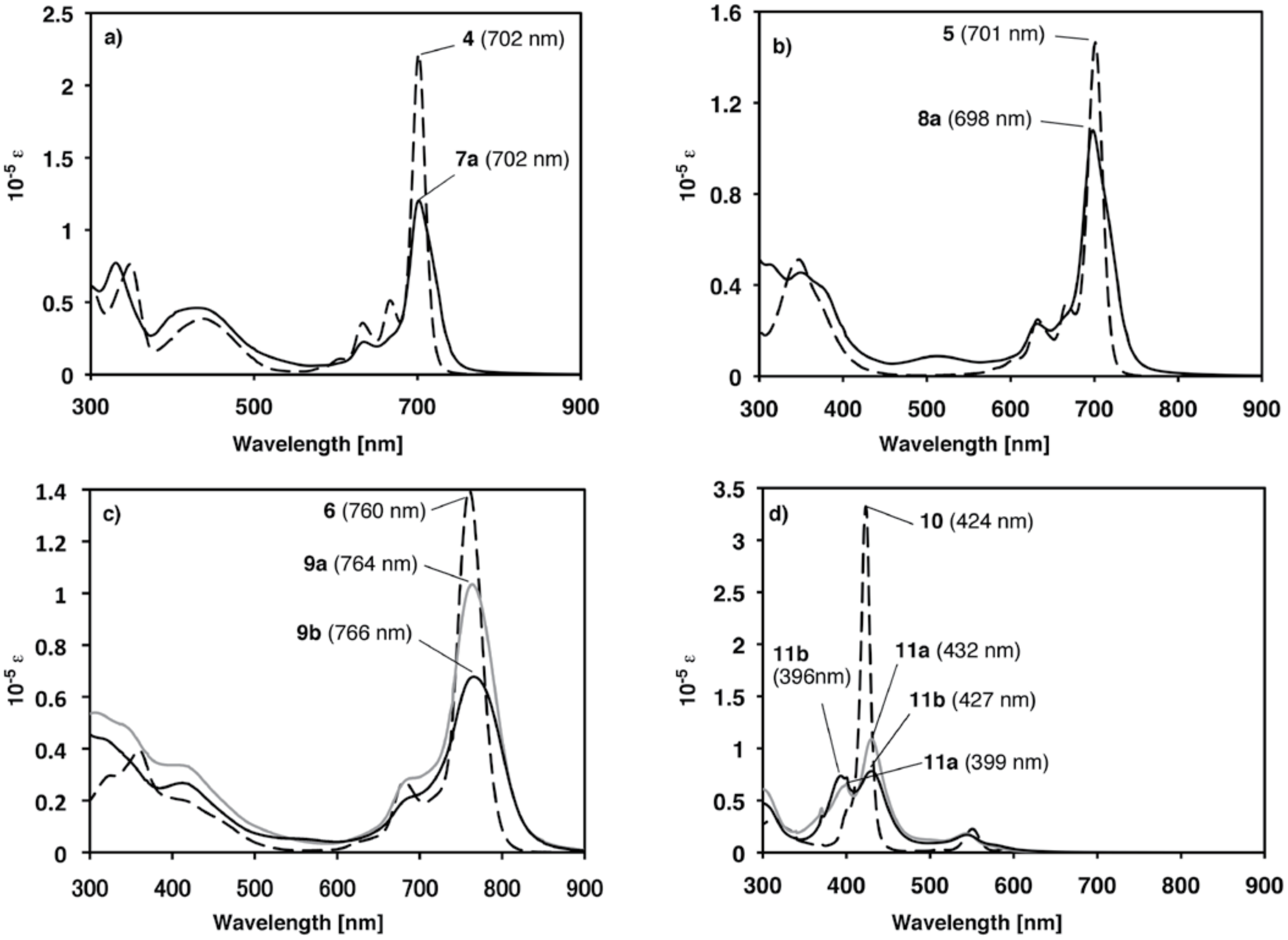


Figure 1. UV-vis spectra measured in $CHCl_3$: a) **4** and **7a**, b) **5** and **8a**, c) **6**, **9a**, and **9b**, and d) **10**, **11a**, and **11b**

The electrochemical properties of **7a**, **8a**, **9a**, **9b**, **11a**, and **11b** were examined by cyclic voltammetry using $Ag/AgNO_3$ as a reference electrode (measured in dichloromethane, scan rate: 200 mV/s). The results are summarized in Table 1. The redox potentials of **7a** were observed at $E_{1/2} = –1.82$, –1.34, and –1.03 V for the reduction and $E_{1/2} = 0.59$ V for the oxidation (Figure 2). Compound (**8a**) showed three reversible couples for reduction potentials ($E_{1/2} = –1.84$, –1.27, and –0.89 V) and one quasi-reversible ($E_{1/2} = 0.82$ V) and one reversible couples ($E_{1/2} = 1.15$ V) for oxidation potentials. The cyclic voltammogram of **9a** contained an irreversible oxidation ($E_p = 0.87$ V) and three quasi-reversible reduction potentials ($E_{1/2} = –1.73$, –1.06, and –0.76 V). Compound (**9b**) exhibited an irreversible oxidation potential at $E_p = 0.85$ V and three quasi-reversible reduction potentials at $E_{1/2} = –1.78$, –1.04, and –0.75 V. The oxidation potential of **11a** was found at $E_{1/2} = 1.04$ V (reversible) and $E_p = 1.37$ V (irreversible), while one reversible couple ($E_{1/2} = –1.30$ V) was observed for the reduction potential.

Compound (**11b**) showed one irreversible oxidation peak (Ep = 0.96 V) and one reversible and one irreversible reduction peak ($E_{1/2}$ = –1.29 V and E_p = –1.05 V). It appeared that the first oxidation and the first reduction potential of **7a**, **9a**, **9b**, **11a**, and **11b** show slight anode shifts compared with those of the corresponding titanium oxides.

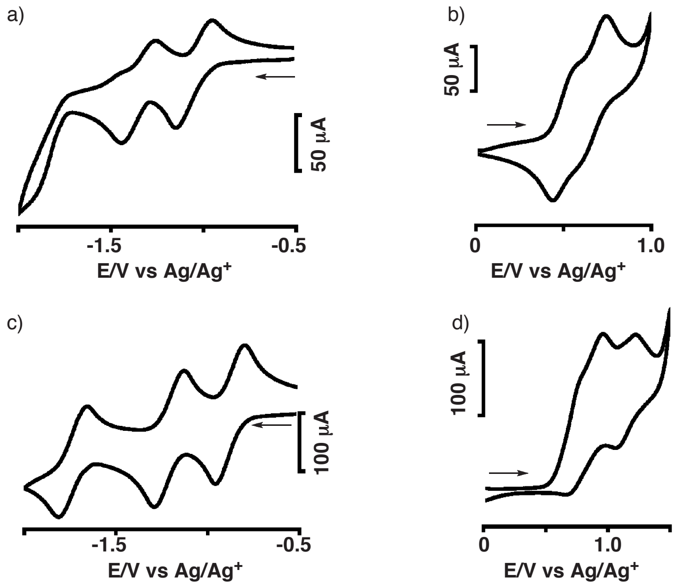


Figure 2. Cyclic voltammograms of **7a** and **8a**: a) reduction of **7a**, b) oxidation of **7a**, c) reduction of **8a**, d) oxidation of **8a**

Table 1. Redox potentials (vs. $Ag/AgNO_3$).

Compounds	$E_{1/2}$ [V]							ΔE (V)
	5th reduction	4th reduction	3rd reduction	2nd reduction	1st reduction	1st oxidation	2nd oxidation	
4		–1.54	–1.39	–1.20	–1.12	0.44^a	0.95^a	1.56
7a			–1.82	–1.34	–1.03	0.59^a		1.62
5	–1.73	–1.50	–1.32	–1.09	–0.92	0.85^b	1.23^b	1.77
8a			–1.84	–1.27	–0.89	0.82^a	1.15	1.71
6				–1.14	–0.80	0.68	1.13^b	1.48
9a			–1.73^a	–1.06^a	–0.76^a	0.87^b		1.63
9b			–1.78^a	–1.04^a	–0.75^a	0.85^b		1.60
10				–1.64	–1.55^b	0.91	1.15	2.46
11a					–1.30	1.04	1.37^b	2.34
11b				–1.29	–1.05^b	0.96^b		2.01

^{a}Quasi reversible; ^{b}irreversible (Ep /V). ΔE is the difference between the first oxidation and the first reduction potential.

CONCLUSION

The reactions of phthalocyaninato titanium(IV) oxides (**4**), (**5**), and (**6**) and tetraphenylporphyrinato titanium(IV) oxide (**10**) with benzenedithiol or benzenediselenol produced corresponding complexes with titanium-sulfur or titanium-selenium bonds. Compounds (**7a**), (**9a**), (**9b**), (**11a**), and (**11b**) showed the C4v symmetric structure in the NMR time scale. Their optical and electrochemical properties were determined by UV-vis spectroscopy and cyclic voltammetry.

EXPERIMENTAL

General

NMR spectra were measured with a Bruker AVANCE-500 III spectrometer and a Bruker AC400 spectrometer at 25 °C. For measurements of the NMR spectra, tetramethylsilane (^{1}H and ^{13}C) and dimethyl selenide (^{77}Se) were used as reference compounds. 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. Bio-beads (SX-1) for column chromatography was 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: 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**), and (**5**) were prepared using a method described previously.[8]

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. H_2O was added 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; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 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, $CDCl_3$) δ = 14.3, 18.7, 26.2, 36.2, 118.3, 130.3, 137.7, 149.5 ppm; ^{77}Se NMR (76 MHz, $CDCl_3$) δ = 325.2 ppm; IR (KBr) 2244 cm^{-1} (CN); 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**) (287.5 mg, 0.62 mmol) and CsOH (955.5 mg, 6.37 mmol) were placed in a glass reactor under Ar. THF (4 mL) and MeOH (4 mL) were added to the reactor and the solution was stirred for 2 h. HCl (0.6 mL) in MeOH (2.0 mL) was added to the solution to generate the corresponding dithiol (**3a**).

Octa-*n*-butoxyphthalocyaninato titanium(IV) benzenedithiolate (7a)

The solution of **3a**, prepared as described above, was transferred by a syringe to the reactor containing **4** (195.7 mg, 0.17 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, $CHCl_3$) and (Bio-beads, $CHCl_3$) to produce **7a** in 67% yield (168.7 mg); Green powder; ^{1}H NMR (500 MHz, $CDCl_3$) δ = -0.02 (t, J = 6.4 Hz, 6H, CH_3), 1.20 (t, J = 7.4 Hz, 24H, CH_3), 1.48 (br-q, J = 6.4 Hz, CH_2), 1.81 (sext, J = 7.4 Hz, 16H, CH_2), 2.18 (quint, J = 7.4 Hz, 16H, CH_2), 4.64 (dt, J = 8.0, 7.4 Hz, 8H, CH_2), 4.68 (dt, J = 8.0, 7.4 Hz, 8H, CH_2), 8.77 (bs, 8H, Ar-H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 11.4, 14.1, 19.6, 29.7, 31.6, 69.5, 105.4, 124.3, 130.7, 135.5, 148.5, 150.8, 153.0; HRFAB MS: calcd for $C_{74}H_{90}Br_2N_8O_8S_2Ti$ = 1488.4169, found: m/z = 1488.4187 (M^+).

Tetra-*t*-butylphthalocyaninato titanium(IV) benzenedithiolate (8a)

58%; Green powder; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 0.01-0.17 (m, 6H, CH_3), 1.50-1.67 (m, 4H, CH_2), 1.77-1.93 (m, 36H, *t*-Bu), 8.35-8.43 (m, 4H, Ar-H), 9.32-9.62 (m, 8H, Ar-H); HRFAB MS: calcd for $C_{58}H_{58}{}^{79}Br_2N_8O_8S_2{}^{46}Ti$ = 1134.2119, found: m/z = 1134.2086 (M^+).

Octakis(methylthio)octaethylphthalocyaninato titanium(IV) benzenedithiolate (9a)

51%; Dark green powder; mp > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.23 (t, J = 7.2 Hz, 6H, CH_3), 1.60 (t, J = 7.2 Hz, 24H, CH_3), 1.81 (q, J = 7.2 Hz, 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 ($CHCl_3$) λ_{max}= 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) benzenediselenolate (9b)

33%; Dark green powder: mp 225 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 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, $CDCl_3$) δ = 448.5 ppm; FAB MS (m/z) 1600.13 [M^+].

Tetraphenylporphyrinato titanium(IV) benzenedithiolate (11a)

89%; Black green powder: ^{1}H NMR (400 MHz $CDCl_3$) δ = 0.20 (t, J = 7.4 Hz, 6H, CH_3), 1.64 (q, J = 7.4

Hz, 4H, CH_2), 7.74-7.85 (m, 12H, *m,p*-PhH), 8.16 (m, 4H, *o*-PhH), 8.25 (m, 4H, *o*-PhH), 9.05 (s, 8H, β); ^{13}C NMR (126 MHz $CDCl_3$) δ = 11.4, 29.6, 123.7, 125.5, 127.1, 127.2, 128.3, 132.6, 133.1, 134.7, 141.2, 148.8, 150.3; HRFAB MS: Calcd for $C_{54}H_{38}Br_2N_4S_2{}^{48}Ti$ = 1012.0384. Found: m/z = 1012.0384 (M^+); Anal. Calcd for $C_{54}H_{38}Br_2N_4S_2Ti$: C, 63.92; H, 3.77; N, 5.52%. Found: C, 63.46; H, 4.02; N, 5.15%.

Tetraphenylporphyrinato titanium(IV) benzenediselenolate (11b)

91%; Black green powder: ^{1}H NMR (400 MHz $CDCl_3$) δ = 0.27 (t, *J* = 7.3 Hz, 6H, CH_3), 1.80 (q, *J* = 7.3 Hz, 4H, CH_2), 7.44-7.86 (m, 12H, *m,p*-PhH), 8.15 (d, *J* = 6.72 Hz, 4H, *o*-PhH), 8.29 (d, *J* = 6.72 Hz, 4H, *o*-PhH), 9.05 (s, 8H, β); ^{13}C NMR (126 MHz $CDCl_3$) δ = 11.6, 29.7, 124.2, 125.4, 127.1, 127.2, 128.3, 132.6, 133.0, 134.8, 138.0, 141.1, 149.3, 150.3; FABMS m/z = 1108.0 [MH^+].

REFERENCES

1. *'The Porphyrin Handbook'*, Vols. 15-20, ed. by K. M. Kadish, K. M. Smith, and R. Guilard, Academic Press, San Diego, 2003; *'Phthalocyanines: Properties and Applications'*, Vols. 1-4, ed. by C. C. Leznoff and A. B. P. Lever, VCH, New York, 1989-1996.
2. D. Wöhrle, O. Suvorova, R. Gerdes, O. Bartels, L. Lapok, N. Baziakina, S. Makarov, and A. Slodek, *J. Porphyrins Phthalocyanines*, 2004, **8**, 1020; b) G. de la Torre, P. Vázquez, F. Agulló-López, and T. Torres, *Chem. Rev.*, 2004, **104**, 3723; c) G. de la Torre, C. G. Claessens, and T. Torres, *Chem. Commun.*, 2007, 2000.
3. A. Morandeira, I. López-Duarte, M. V. Martínez-Díaz, B. O'Regan, C. Shuttle, N. A. Haji-Zainulabidin, T. Torres, E. Palomares, and J. R. Durrant, *J. Am. Chem. Soc.*, 2007, **129**, 9250; b) L. Matín-Gomis, K. Ohkubo, F. Fernández-Lázaro, S. Fukuzumi, and Á. Sastre-Santos, *Org. Lett.*, 2007, **9**, 3441; c) B. C. O'Regan, I. López-Duarte, M. V. Martínez-Díaz, A. Forneli, J. Albero, A. Moranderia, E. Palomares, T. Torres, and J. R. Durrant, *J. Am. Chem. Soc.*, 2008, **130**, 2906.
4. V. L. Goedken, G. Dessy, C. Ercolani, V. Fares, and L. Gastaldi, *Inorg. Chem.*, 1985, **24**, 991.
5. M. Barthel and M. Hanack, *J. Porphyrins Phthalocyanines*, 2000, **4**, 635; b) M. Barthel, D. Dini, S. Vagin, and M. Hanack, *Eur. J. Org. Chem.*, 2002, 3756.
6. N. Kobayashi and A. Muranaka, *Chem. Commun.*, 2000, 1855; b) A. Muranaka, M. Okuda, N. Kobayashi, K. Somers, and A. Ceulemans, *J. Am. Chem. Soc.*, 2004, **126**, 4596; c) A. Muranaka, K. Yoshida, T. Shoji, N. Moriichi, S. Masumoto, T. Kanda, Y. Ohtake, and N. Kobayashi, *Org. Lett.*, 2006, **8**, 2447; A. Muranaka, K. Yoshida, Y. Akagi, H. Naka, M. Uchiyama, Y. Kondo, N. Kobayashi, *Tetrahedron Lett.*, 2008, **49**, 5084.
7. T. Kimura, J. Kumasaka, and T. Namauo, *Eur J. Org. Chem.*, 2008, 5079.

8. T. Kimura, A. Yomogita, T. Matsutani, T. Suzuki, I. Tanaka, Y. Kawai, Y. Takaguchi, T. Wakahara, and T. Akasaka, *J. Org. Chem.*, 2004, **69**, 4716; b) T. Kimura, N. Kanota, K. Matsui, I. Tanaka, T. Tsuboi, Y. Takaguchi, A. Yomogita, T. Wakahara, S. Kuwahara, F. Nagatsugi, and T. Akasaka, *Inorg. Chem.*, 2008, **47**, 3577.

9. Deronzier and J. M. Latour, *Nou. J. Chim.*, 1984, **8**, 393.

10. N. Nagahora, S. Ogawa, S. Yoshimura, Y. Kawai, and R. Sato, *Bull. Chem. Soc. Jpn.*, 2003, **76**, 1043.