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Elongation of the π-System of Phthalocyanines by Introduction of Thienyl Substituents at the Peripheral β Positions. Synthesis and Characterization

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1,4,8,11,15,18,22,25-Octabutoxyphthalocyanines ($(OBu)_8Pcs$) having eight 2-thienyl (**1**) and [2,2′-bithiophene]-5-yl (**2**) groups at β positions and their zinc(II) and cobalt(II) derivatives were prepared from 2-thienyl- (**3**) or [2,2′-bithiophene]-5-yl (**4**)-substituted phthalonitriles in moderate to good yields. The electronic absorption spectra of the Pcs showed red-shifted Q-bands relative to β-unsubstituted $(OBu)_8Pcs$. The longer substituent, the [2,2′-bithiophene]-5-yl group, is more effective than the 2-thienyl group in enlarging the π-conjugated system of the Pcs. The ring oxidation potential obtained by cyclic voltammetry shifted cathodically with increasing chain length, indicating destabilization of the HOMOs. Due to the shift of the Q-band, 2-thienyl- and [2,2′-bithiophene]-5-yl-substituted Pcs exhibit a remarkable color change from the original green color.

Introduction

Phthalocyanines (Pcs) are macrocyclic molecules whose π-electron system provides their unique photophysical, electronic, and electrical conducting properties.[1,2] Recently, the compounds have gained importance in optoelectronic industry, as exemplified by their potential use in electrophotography[3,4] and optical data storage materials.[5,6] In addition, their properties have been considered to have potential applications to photovoltaic cells,[7,8] gas-sensing materials,[9,10] and the photodynamic therapy (PDT) of cancer.[11,12] Undoubtedly, these properties are derived from the stability and delocalized electronic nature of the Pc ring systems. Most of the modern uses of Pcs are focused on the electronic properties of the π-electron system of the macrocycles. The diversity of the properties of Pcs has led us to develop extended Pc derivatives. One approach to extension of the π-system of the Pc ring is to benzoannulate the Pc molecules[13−15] and another is to substitute the rings with electron donors, thereby shifting the Q- and B-bands.[16,17] Furthermore, direct attachment of the Pc ring systems with other chromophores through π-conjugated bridges tends to alter the electronic structures.[18−21] In such cases, the Q-band of the Pcs undergoes a shift toward the near-infrared (NIR) direction, which has been attributed to the extension of the π-conjugation system, with concomitant splitting or broadening of the Q-band.

Much less effort has been focused on the preparation of the Pc systems having π-conjugated groups at β positions, such as with aromatic groups[22−25] or nonaromatic groups.[26,27] In preliminary studies by us,[28] the Q-band of a β-heteroaromatic-substituted Pc, 2,3,9,10,16,17,23,24-octa(2-thienyl)phthalocyanine, underwent a red shift of about 20 nm relative to those of tetra-*tert*-butylphthalocyanine. This phenomenon is considered to be a result of a strong interaction between the π-electrons

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of the Pc ring and the thiophene moieties. From these results, we noticed the reformation of the π-system of Pc by β-thienyl substitution which has the potential for synthetic flexibility compared to other methodologies. Oligothiophenes are a frequently investigated class of π-conjugated moieties due to their stability and the fact that their synthetic chemistry has been well-defined.[29] In addition, their structural planarity permits strong electronic conjugation within the structure. For these reasons, substitution of thienyl and bithienyl groups at the β positions of the Pc ring could result in the extension and refinement of the π-systems.

In this paper, we describe the preparation and electronic condition of β-octa(2-thienyl)- and ([2,2′-bithiophene]-5-yl)-1,4,8,11,15,18,22,25-octabutoxyphthalocyanines ((OBu)$_8$MPc, M = H_2, Zn, and Co). The electronic states of the Pcs are discussed by means of photophysical studies as well as by electrochemical studies. The (OR)$_8$Pcs generally are stable compounds that have an intense Q-band in the red to deep-red region.[17,30] This implies that they have potential to exhibit intense Q-absorption in the NIR region by the introduction of π-conjugated moieties to the Pc ring through a σ-bond and are useful in modern applications as a new class of Pcs.

Experimental Section

Dichloromethane (CH_2Cl_2) used for photophysical and electrochemical studies was predried by stirring with $CaCl_2$ and then distilled from P_2O_5. Toluene used for photophysical measurements was dried over P_2O_5 and distilled. *o*-Dichlorobenzene used in electrochemical studies was shaken with concentrated H_2SO_4, washed with water, predried with $CaCl_2$, and distilled from CaH_2 under reduced pressure. Pyridine used for photophysical studies was dried over KOH and distilled. *N,N*-Dimethylformamide (DMF) was dried over BaO and distilled under reduced pressure. These solvents were stored with molecular sieves 4A under dark and used as soon as possible. Tetrahydrofuran (THF) was distilled from $LiAlH_4$ and stored with sodium wire. *N,N*-Dimethylaminoethanol was dried over KOH and distilled prior to use. All other reagents and solvents were purchased and used without further treatment. In addition, we have synthesized 4-(2-thienyl)-3,6-dibutoxyphthalonitrile (4T(OBu)$_2$Phn) as a structural analogue of **3** and **4** from 4-bromo-3,6-dibutoxyphthalonitrile.[31] Silica gel (Fuji Silysia, BW-820MH), activated alumina (Wako, abt.200 mesh), and Bio Beads SX-3 (Bio-Rad) were used for column chromatography.

All spectroscopic measurements were performed at ambient temperature. Elemental analysis were carried out with a Perkin-Elmer 2400II-CHN. Proton and carbon-13 NMR spectra were measured with a Bruker AVANCE 400 spectrometer with TMS as a standard. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) spectra were obtained on a Perseptive Biosystems Voyager VE-Pro with a dithranol matrix. UV−Vis−NIR absorption spectra and emission spectra were taken on a Jasco V-570 spectrophotometer and a Jasco FP-750 spectrophotometer, respectively. Fluorescence quantum yields (Φ_f) of (OBu)$_8$Pcs were obtained using (OBu)$_8$ZnPc ($\Phi_f = 0.62$, in pyridine)[16] as a standard.[32]

Electrochemical measurements were carried out on an ALS MODEL 400S voltammetric analyzer. The cell consists of a platinum working electrode (BAS, 1.6 mm diameter), a platinum wire counter electrode, and a BAS RE-5 (Ag/AgNO$_3$) reference electrode. Typical experimental conditions: a 0.1 M solution of tetra-*n*-butylammonium hexafluorophosphate (Bu_4NPF_6, Aldrich) in CH_2Cl_2 or a 0.3 M tetra-*n*-butylammonium perchlorate (Bu_4NClO_4, Nakalai Tesque) in *o*-dichlorobenzene containing 1.0 mM of sample was purged with nitrogen for 20 min; then the voltammograms were recorded at ambient temperature under dark. Potential was referenced to Ag/Ag^+ in MeCN.

4,5-Dibromo3,6-dibutoxyphthalonitrile,[31] 2-(tri-*n*-buthyl)-stannylthiophene,[33] 2-(tri-*n*-butyl)stannyl-5,2′-bithiophene,[34] (OBu)$_8$ZnPc,[17] and (OBu)$_8$CoPc[35] were prepared according to the literature methods or their slight modification. We synthesized six types of new Pcs (**1, 2, 1-Zn, 1-Co, 2-Zn,** and **2-Co**) in this work (Scheme 1). All the synthesis of the Pcs was started from 4,5-dibromo-3,6-dibutoxyphthalonitrile.[31] The transformation of this compound into thiophene-substituted phthalonitriles involves palladium-catalyzed cross-coupling[29,34] between the starting material and the appropriate tri-*n*-butylstannane of the thiophene. The Pcs obtained in our study have high solubility ($>10^{-3}$ M) in common organic solvents such as CH_2Cl_2, THF, or toluene, but not in acetonitrile. The thiophene-substituted (OBu)$_8$Pcs, particularly the free-bases and zinc derivatives, are acid sensitive. It is advantageous to base-wash the glassware and the quartz cell prior to use for the Pcs.

3,6-Dibutoxy-4,5-di(2-thienyl)phthalonitrile (3). 4,5-Dibromo-3,6-dibutoxyphthalonitrile (1.0 g, 2.33 mmol) and 2-(tri-*n*-butyl)stannylthiophene (3.9 g, 10.0 mmol) were dissolved in 50 mL of dry DMF. The reaction mixture was added by catalytic amount (ca. 0.1 mol % for the substrates) of bis(triphenylphosphine)palladium(II) dichrolide, [Pd(II)(PPh$_3$)$_2$Cl$_2$], and then heated at 60−70 °C for 36 h under nitrogen atmosphere. The reaction mixture was concentrated in a vacuum and chromatographed on a silica gel column (*n*-hexane/CH_2Cl_2 = 1/1 v/v as an eluent) to give a light yellow solid. Recrystallization of the solid from ethanol gave 0.84 g (1.92 mmol; 83.4% yield) of **3** as a pale-yellow needle. TLC (SiO_2; *n*-hexane/CH_2Cl_2 = 1/1 v/v): $R_f = 0.75$. UV/Vis (CH_2Cl_2): λ_{max} ($\log \epsilon/M^{-1}\ cm^{-1}$) = 272 (4.17), 346 nm (4.08). ^1H NMR (400 MHz, $CDCl_3$, TMS): $\delta = 0.77-0.87$ (m, 6H, CH_3), 1.23−1.32 (m, 4H, CH_2), 1.52−1.59 (m, 4H, CH_2), 3.74−3.77 (m, 4H, OCH_2), 6.90−6.91 (m, 2H, 3-ArH), 6.95−6.97 (m, 2H, 4-ArH), 7.38−7.39 (m, 2H, 5-ArH). Elemental analysis calcd for $C_{24}H_{24}N_2O_2S_2$ (436.5): C, 66.02; H, 5.54; N, 6.42; O, 7.33; S, 14.61, found: C, 66.35; H, 5.50; N, 6.64. IR (KBr): $\nu = 2228$ cm^{-1} (m).

3,6-Dibutoxy-4-(2-thienyl)phthalonitrile, 4T(OBu)$_2$Phn. 4-Bromo-3,6-dibutoxyphthalonitrile[31] (0.4 g, 0.93 mmol) and 2-(tri-*n*-butyl)stannylthiophene (2.8 g, 7.2 mmol) were dissolved in 30 mL of dry DMF. A catalytic amount of [Pd(II)(PPh$_3$)$_2$Cl$_2$] was dissolved in the reaction mixture and then stirred at 60 °C for 48 h under nitrogen atmosphere. The reaction mixture was concentrated in a vacuum and passed through a silica gel column (*n*-hexane/CH_2Cl_2 = 1/1 v/v as an eluent) to give a light yellow solid. The solid material was purified by recrystallization from ethanol gave 0.34 g (0.89 mmol; 95.7% yield) of title compound as a pale-yellow needle. TLC (SiO_2; *n*-hexane/CH_2Cl_2 = 1/1 v/v): $R_f = 0.82$. UV/Vis (CH_2Cl_2): λ_{max} ($\log \epsilon/M^{-1}\ cm^{-1}$) = 318 (4.04), 362 nm (4.22). ^1H NMR (400 MHz, $CDCl_3$, TMS): $\delta = 0.89-1.05$ (m, 6H, CH_3), 1.44−1.59(m, 4H, CH_2), 1.78−1.89 (m, 4H, CH_2), 3.94−3.98 (t, 2H, OCH_2), 4.12−4.15 (t, 2H, OCH_2), 7.15−7.17 (q, 1H, 4-ArH), 7.34 (s, 1H, PhH), 7.51−7.53 (d, 1H, 3-ArH), 7.57−7.59 (d, 1H, 5-ArH). Elemental analysis calcd for $C_{20}H_{22}N_2O_2S$ (354.5): C, 67.77; H, 6.26; N, 7.90; O, 9.03; S, 9.05, found: C, 67.35; H, 6.30; N, 7.89. IR (KBr): $\nu = 2226$ cm^{-1} (m).

3,6-Dibutoxy-4,5-bis([2,2′-bithiophene]-5-yl)phthalonitrile (4). A mixture of 2-(tri-*n*-butyl)stannyl-5,2′-bithiophene (3.0 g, 6.59 mmol) and 4,5-dibromo-3,6-dibutoxyphthalonitrile

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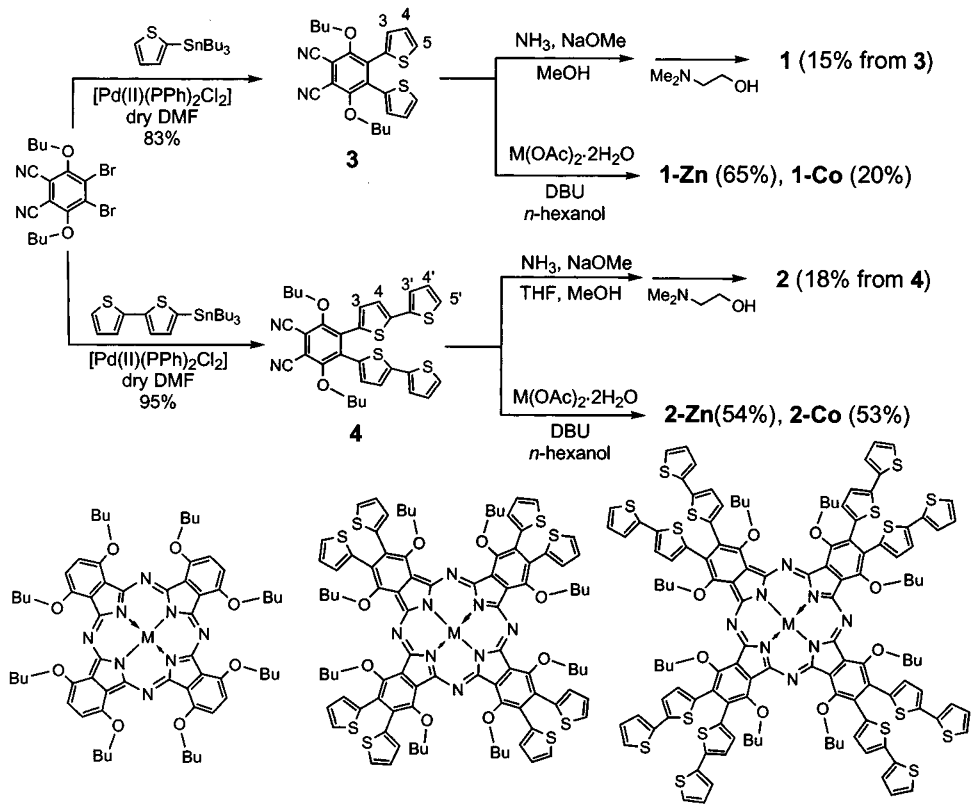
Scheme 1



(OBu)$_8$H$_2$Pc (M = 2H)
(OBu)$_8$ZnPc (M = Zn)
(OBu)$_8$CoPc (M = Co)

1 (M = 2H)
1-Zn (M = Zn)
1-Co (M = Co)

2 (M = 2H)
2-Zn (M = Zn)
2-Co (M = Co)

(1.0 g, 2.33 mmol) in 30 mL of dry DMF was added by the catalytic amount of [Pd(II)(PPh$_3$)$_2$Cl$_2$] and stirred at 60−70 °C for 56 h under nitrogen atmosphere. The reaction mixture was concentrated and chromatographed with a silica gel column (*n*-hexane/CHCl$_3$ = 3/1−1/1 v/v) afforded yellow solid. The solid was purified by recrystallization from 1-propanol/*n*-hexane gave 1.23 g (2.05 mmol; 87.9% yield) of **4** as a yellow scale. TLC (SiO$_2$; CHCl$_3$): $R_f = 0.65$. UV/Vis (CH$_2$Cl$_2$): λ_{max} (log ϵ/M^{-1} cm^{-1}) = 316 (4.48), 380 (4.29). ^{1}H NMR (400 MHz, CDCl$_3$, TMS): δ = 0.79−0.86 (m, 6H, CH$_3$), 1.30−1.39 (m, 4H), 1.59−1.66 (m, 4H), 3.83−3.86 (m, 4H), 6.84 (d, J = 3.52 Hz, 2H, 3-ArH), 6.99−7.02 (m, 2H, 3′-ArH), 7.04 (d, J = 3.50 Hz, 2H, 4-ArH), 7.13−7.15 (m, 2H, 4′-ArH), 7.22−7.24 (m, 2H, 5′-ArH). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$, TMS) δ = 14.0, 19.2, 32.3, 76.2, 110.4, 113.5, 123.8, 124.7, 125.5, 128.3, 131.7, 132.2, 136.3, 136.9, 141.2, 157.4. Elemental analysis calcd for $C_{32}H_{38}N_2O_2S_4$ (600.8): C, 63.97; H, 4.70; N, 4.66; O, 5.33; S, 21.35, found: C, 63.67; H, 4.78; N, 4.70. IR (KBr): ν = 2226 cm^{-1} (m).

1,4,8,11,15,18,22,25-Octabutoxy-2,3,9,10,16,17,23,24-octa-(2-thienyl)phthalocyanine (1). Compound **3** (0.2 g, 0.45 mmol) in 10 mL of absolute methanol was purged with NH$_3$ gas for 20 min. A catalytic amount of NaOMe was dissolved in the mixture and stirred at 50 °Cfor 6 h under NH$_3$ atmosphere. The mixture was poured into water. The precipitate formed, and 5,8-dibutoxy-6,7-di(2-thienyl)-1,3-dihydro-1,3-diiminoisoindole was filtered off and dried under vacuum. This material was used for the following reaction without further purification. 5,8-Dibutoxy-6,7-di(2-thienyl)-1,3-dihydro-1,3-di-iminoisoindole was suspended in freshly distilled *N*,*N*-dimethylaminoethanol (10 mL) under N$_2$ and heated at refluxed state for 48 h. After cooling to room temperature, the reaction mixture was diluted with excess methanol. The green precipitate formed was filtered off and chromatographed on activated alumina using CH$_2$Cl$_2$/*n*-hexane = 1/1 v/v ($R_f = 0.95$) and then SX-3 (CH$_2$Cl$_2$) to give **1** (29.5 mg, yield 15.0%) as a green powder. ^{1}H NMR (400 MHz, CDCl$_3$, TMS): δ = 0.52 (s, 2H, NH), 0.83−0.87 (m, 24H, CH$_3$), 1.21−1.30 (m, 16H, CH$_2$), 1.78−1.85 (m, 16H, CH$_2$), 4.74−4.78 (m, 16H, OCH$_2$), 7.06−7.09 (m, 8H, 4-ArH), 7.19−7.20 (m, 8H, 3-ArH), 7.44−7.45 (m, 8H, 5-ArH). MALDI-TOF-mass spectrum *m*/*z* calcd for ($C_{96}H_{98}N_8O_8S_8$) 1748.4, found 1749. Elemental analysis calcd for $C_{96}H_{98}N_8O_8S_8$: C, 65.95; H, 5.65; N, 6.41; O, 7.32; S, 14.67. found: C, 66.02; H, 5.82; N, 6.30. UV/Vis (in CH$_2$Cl$_2$): λ_{max} (log ϵ/M^{-1} cm^{-1}) = 778 (5.270), 684 (4.756), 338 nm (4.866).

1,4,8,11,15,18,22,25-Octabutoxy-2,3,9,10,16,17,23,24-octa-([2,2′-bithiophene]-5-yl)phthalocyanine (2). Compound **4** (0.27 g, 0.45 mmol) was dissolved in minimum amount of dry THF at room temperature. This solution was added by 10 mL of absolute methanol and purged with NH$_3$ gas for 20 min. A catalytic amount of NaOMe was added to the mixture and stirred at 50 °C for 6 h under NH$_3$ bubbling. The reaction mixture was poured into water, and yellow precipitate formed, 5,8-dibutoxy-6,7-di([2,2′-bithiophene]-5-yl)-1,3-dihydro-1,3-di-iminoisoindole, which was isolated by filtration and dried under vacuum. The yellow intermediate was suspended in freshly distilled *N*,*N*-dimethylaminoethanol (10 mL) and refluxed for 48 h under N$_2$. The mixture was poured into excess methanol, and the precipitate formed was filtered off. This material was purified by column chromatography with activated alumina (toluene) and then SX-3 (CH$_2$Cl$_2$) to give **2** as a red powder (47.9 mg, 17.7%). ^{1}H NMR (400 MHz, CDCl$_3$, TMS): δ = 0.59 (s, 2H, NH), 0.85−0.89 (m, 24H, CH$_3$), 1.33−1.42 (m, 16H, CH$_2$), 1.85−1.98 (m, 16H, CH$_2$), 4.80−4.82 (m, 16H, OCH$_2$), 7.04−7.06 (m, 8H, 3′-ArH), 7.09 (d, J = 3.56 Hz, 8H, 3-ArH), 7.17 (d, J = 3.60 Hz, 8H, 4-ArH), 7.22−7.25 (m, 16H, 4′-ArH, 5′-ArH). MALDI-TOF-mass spectrum *m*/*z* calcd for ($C_{128}H_{114}N_8O_8S_{16}$) 2405.3, found 2404.9. Elemental analysis calcd for $C_{128}H_{114}N_8O_8S_{16}$: C, 63.91; H, 4.78; N, 4.66; O, 5.32; S, 21.33. found: C, 64.18; H, 4.81; N, 4.82. UV/Vis (in CH$_2$Cl$_2$): λ_{max} (log ϵ/M^{-1} cm^{-1}) = 794 (5.316), 705 (4.663), 493 (4.554).

General Procedure for the Preparation of 2-Thienyl- or ([2,2′-Bithiophene]-5-yl)-Substituted 1,4,8,11,15,18,22,-

25-Octabutoxyphthalocyaninato Complexes. A mixture of phthalonitrile (**3** or **4**, 0.9 mmol) and corresponding metal as chloride salt (0.23 mmol) in 2.5 mL of 1-hexanol was heated to 90 °C under N_2, and then 0.16 mL (1.08 mmol) of DBU was added. The reaction mixture was stirred at 100−120 °C for 18 h under N_2. After being cooled to room temperature, the reaction mixture was poured into excess methanol. The precipitate formed was filtered off and purified by column chromatography.

[1,4,8,11,15,18,22,25-Octabutoxy-2,3,9,10,16,17,23,24-octa(2-thienyl)phthalocyaninato]zinc(II) (1-Zn). 65% from **3**; yellow-green powder, purified using an activated alumina column (CH_2Cl_2/THF = 2/1 v/v) (R_f = 0.85) and SX-3 (CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$, TMS) δ = 0.83−0.87 (m, 24H, CH_3), 1.20−1.30 (m, 16H, CH_2), 1.78−1.85 (m, 16H, CH_2), 4.80−4.83 (m, 16H, OCH_2), 7.07−7.09 (m, 8H, 4-ArH), 7.19−7.20 (m, 8H, 3-ArH), 7.43−7.45 (m, 8H, 5-ArH). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, TMS) δ = 14.5, 19.6, 32.6, 77.0, 126.5, 127.1, 130.3, 131.0, 132.9, 138.8, 152.1, 152.8. MALDI-TOF-mass spectrum *m*/*z* calcd for ($C_{96}H_{96}N_8O_8S_8Zn$) 1811.76, found 1810. Elemental analysis calcd for $C_{96}H_{96}N_8O_8S_8Zn$: C, 63.64; H, 5.34; N, 6.18; O, 7.06; S, 14.16; Zn, 3.61. found: C, 63.73; H, 5.51; N, 6.15. UV/Vis (in CH_2Cl_2): λ_{max} (log ϵ/M^{-1} cm^{-1}) = 758 (5.42), 678 (4.73), 370 nm (4.78).

[1,4,8,11,15,18,22,25-Octabutoxy-2,3,9,10,16,17,23,24-octa(2-thienyl)phthalocyaninato] cobalt(II) (1-Co). 20% from **3**; yellow-green powder, purified using a silica gel column (CH_2Cl_2/*n*-hexane = 1/2 v/v) (R_f = 0.65) and SX-3 (CH_2Cl_2). MALDI-TOF-mass spectrum *m*/*z* calcd for ($C_{96}H_{96}N_8O_8S_8Co$) 1804.3, found 1805. Elemental analysis calcd for $C_{96}H_{96}N_8O_8S_8Co$: C, 63.87; H, 5.36; N, 6.21; O, 7.09; S, 14.21; Co, 3.26. found: C, 63.52; H, 5.17; N, 6.12. UV/Vis (in CH_2Cl_2): λ_{max} (log ϵ/M^{-1} cm^{-1}) = 746 (5.34), 670 (4.71), 304 nm (4.92).

[1,4,8,11,15,18,22,25-Octabutoxy-2,3,9,10,16,17,23,24-octa([2,2′-bithiophene]-5-yl) phthalocyaninato]zinc(II) (2-Zn). 54.0% from **4**; brown powder, purified using an almina column (CH_2Cl_2) (R_f = 0.98) and SX-3 (CH_2Cl_2). ^1H NMR (400 MHz, TMS) δ = 0.89−0.93 (m, 24H, CH_3), 1.33−1.38 (m, 16H, CH_2), 1.89−1.97 (m, 16H, CH_2), 4.86 (m, 16H, OCH_2), 7.04−7.06 (m, 8H, 3′-ArH), 7.09 (d, *J* = 3.60 Hz, 8H, 3-ArH), 7.17 (d, *J* = 3.80 Hz, 8H, 4-ArH), 7.22−7.25 (m, 16H, 4′-ArH, 5′-ArH). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, TMS) δ = 14.6, 19.9, 32.7, 76.9, 123.7, 124.5, 128.2, 131.1, 132.2, 137.8, 138.4, 139.1, 144.3, 148.2, 152.1, 152.9. MALDI-TOF-mass spectrum *m*/*z* calcd for ($C_{128}H_{112}N_8O_8S_{16}Zn$) 2468.75, found 2468. Elemental analysis calcd for $C_{128}H_{112}N_8O_8S_{16}Zn$: C, 62.27; H, 4.57; N, 4.54; O, 5.18; S, 20.78; Zn, 2.65. found: C, 62.35; H, 4.56; N, 4.61. UV/Vis (in CH_2Cl_2): λ_{max} (log ϵ/M^{-1} cm^{-1}) = 768 (5.48), 686 (4.85), 332 nm (5.20).

[1,4,8,11,15,18,22,25-Octabutoxy-2,3,9,10,16,17,23,24-octa([2,2′-bithiophene]-5-yl)phthalocyaninato]cobalt(II) (2-Co). 52.8% from **4**; green-black powder, purified using a silica gel column (CH_2Cl_2) (R_f = 0.95) and Bio Beads SX-3 (CH_2Cl_2). MALDI-TOF-mass spectrum *m*/*z* calcd for ($C_{128}H_{112}N_8O_8S_{16}Co$) 2462.30, found 2462. Elemental analysis calcd for $C_{128}H_{112}N_8O_8S_{16}Co$: C, 62.44; H, 4.58; N, 4.55; O, 5.20; S, 20.84; Co, 2.39. found: C, 62.58; H, 4.45; N, 4.50. UV/Vis (in CH_2Cl_2): λ_{max} (log ϵ/M^{-1} cm^{-1}) = 762 (5.43), 680 (4.71), 304 nm (4.92).

Results and Discussion

From CPK modeling of compounds **3** and **4**, each of thiophene moieties in the phthalonitrile derivatives is in very close proximity with a neighboring thiophene moiety. The proton NMR observation of compounds **3** and **4** supports this explanation. In the proton NMR spectrum of 4-(2-thienyl)-3,6-dibutoxyphthalonitrile (4T$(OBu)_2$Phn, Figure 1A), the asymmetric analogue of **3** and **4**, the heteroaromatic resonance of the 3-, 4-, and 5-positions were observed at 7.533−7.518, 7.173−7.151, and 7.587−7.575 ppm, respectively. Each of the resonance of the 3- and 5-positions was observed as a pair of doublet signals with the same intensity, while the resonance of the 4-position was observed as a quasi-triplet or multiplet. On the other hand, the heteroaromatic resonant peaks of compound **3** and **4** underwent upfield shifting relative to 4T$(OBu)_2$Phn (Figure 1B and 1D). In both cases, these shifting are most firmly observed in the resonance of the 3-positions. From these results, the significant shifting is attributed to the shielding effect caused by the close proximity of the thiophene moieties. Given the interesting NMR behavior of the precursors, we also examined the NMR studies for the Pcs under the same conditions. The proton NMR spectra of **1-Zn** and **2-Zn** were also well resolved and showed downfield shifts due to the intense ring current of the Pc nucleus (Figure 1C and 1E). For both **1-Zn** and **2-Zn**, the downfield shifting was most firmly observed for the eight protons at the 3-positions. On the other hand, the downfield shifting of the outer side thiophene rings, the 3′-, 4′-, and 5′-positions, in **2-Zn** was relatively small compared with those of the inner side protons. This observation also supports the above explanation of the proton NMR. Due to the high solubility and rigid structures, the carbon-13 NMR spectra of **1-Zn** and **2-Zn** were well resolved and showed 12 carbon signals for **1-Zn** and 16 carbon signals for **2-Zn**, respectively.

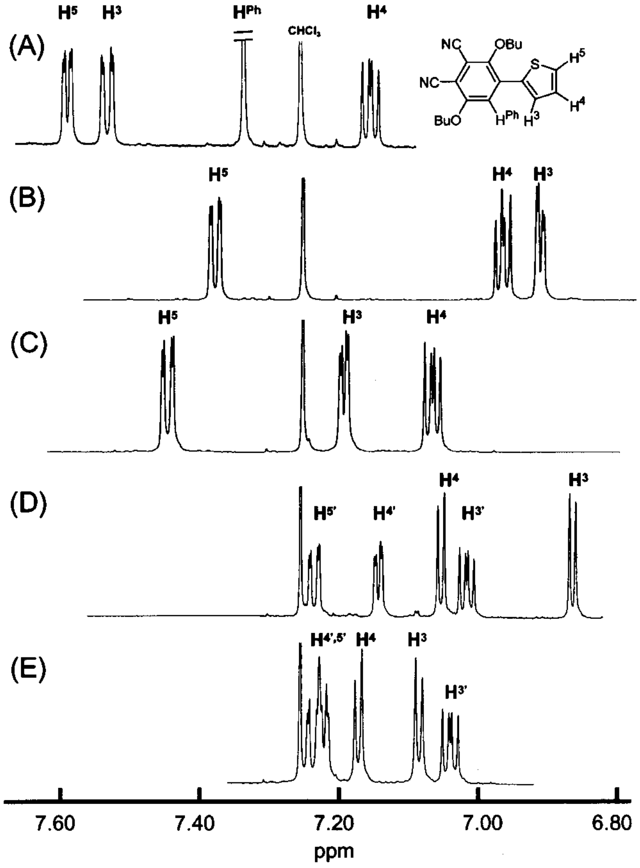


Figure 1. Partial ^1H NMR spectra of (A) 4T$(OBu)_2$Phn, (B) **3**, (C) **1-Zn**, (D) **4**, and (E) **2-Zn**, respectively, in $CDCl_3$ (400 MHz) at room temperature. Inset in (A) shows structural formula of 4T$(OBu)_2$Phn.

Table 1 summarizes the photophysical data of $(OBu)_8$-MPcs and their thiophene-substituted analogues. The absorption spectra of $(OR)_8H_2Pc$ have intense Q-bands with a $Q_{(0,0)}$ maxima at 755−760 nm with a small vibronic satellite at 734 nm, and the molar extinction coefficient (ϵ) of the $Q_{(0,0)}$ band was reported for 135000−138000 M^{-1}

Table 1. Photophysical Data for Phthalocyanines

compd	wavelength, nm $Q_{(0-0)}$ (log ϵ, M^{-1} cm^{-1}), fwmh, cm^{-1}	 λ_F (Stokes shift, nm)[a]	Φ_f [b]
$(OBu)_8H_2Pc$	758 (5.13)[f], 1055.8[g]	778 (20)[h]	0.58[i]
1[c]	778 (5.27), 954,5	808 (30)	0.81
2[c]	794 (5.31), 932.0	818 (24)	0.49
$(OBu)_8ZnPc$[d]	744 (5.12), 327.0	769 (25)	0.74
1-Zn[d]	758 (5.42), 307.8	778 (19)	0.69
2-Zn[d]	768 (5.52), 287.7	794 (26)	0.60
$(OBu)_8CoPc$[e]	730 (4.88), 689.5	-	-
1-Co[e]	746 (5.34), 659.3	-	-
2-Co[e]	762 (5.43), 572.6	-	-

[a] $\lambda_{EX} = 355$ nm. [b] Obtained using $(OBu)_8ZnPc$ in pyridine ($\Phi_f = 0.62$)[16] as a standard. [c] In toluene. [d] In CH_2Cl_2 containing 0.5 vol % pyridine. [e] In CH_2Cl_2. [f] In toluene. From ref 17. [g] In ethanol. Taken from: Kaneko, Y.; Arai, T.; Sakuragi, H.; Tokumaru, K.; Pac, C. *J. Photochem. Photobiol. A: Chem.* **1996**, *97*, 155−162. [h] In benzene. From ref 30. [i] In THF. From ref 16.

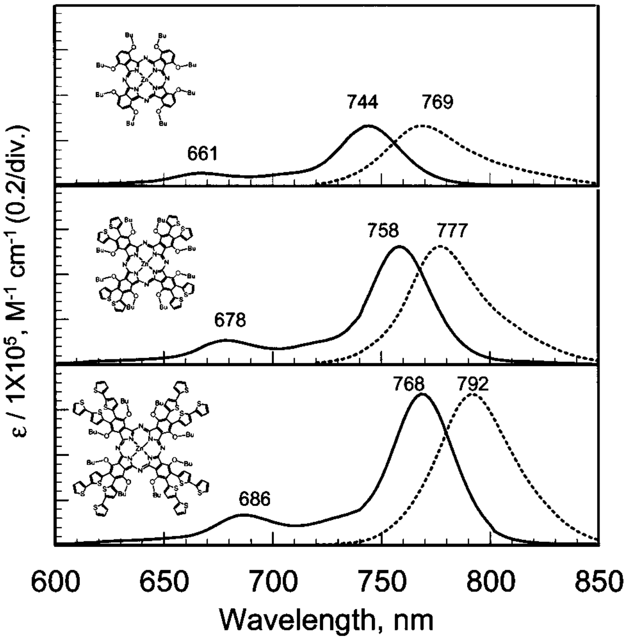


Figure 2. Vis-NIR absorption (solid line) and emission (dashed line, $\lambda_{ex} = 355$ nm) spectra of $(OBu)_8ZnPc$ (top), **1-Zn** (middle), and **2-Zn** (bottom), respectively, in CH_2Cl_2 containing 0.5 vol % pyridine. The emission intensities are normalized at the absorption intensity and do not reflect actual emission intensity.

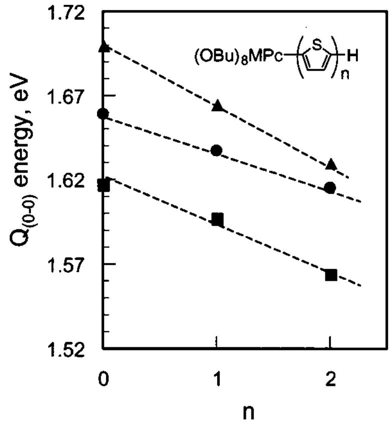


Figure 3. Relation between the substituent length (*n*) and the $Q_{(0-0)}$ absorption energy of the free-base in toluene (M = 2H, ■), zinc derivatives in CH_2Cl_2 containing 0.5 vol % pyridine (M = Zn, ●), and cobalt derivatives in CH_2Cl_2 (M = Co, ▲), respectively.

cm^{-1} in toluene[17] and benzene.[30] On the other hand, the β-(2-thienyl)-substituted analogue **1** exhibits a red-shifted $Q_{(0,0)}$ band at 778 nm with the ϵ of 187000 M^{-1} cm^{-1} in the same media. The two Q-band feature of bare $(OR)_8H_2Pc$, a $Q_{(0-0)}$ band and a vibronic satellite, is retained, and this Q-band shifting is attributed to the electronic interaction between the Pc ring and 2-thienyl groups. The red-shifting of the Q-absorption of Pcs often causes broadening of the band,[18,19] while our system maintained the well-defined absorption structure of the $(OR)_8H_2Pcs$. This spectroscopic behavior is observed not only in the absorption but also in the emission spectra. The emission band of **1** which mirrors the Q-absorption also underwent a red-shift about 20 nm relative to the $(OR)_8H_2Pc$. These results suggested that the introduction of 2-thienyl groups to β positions of the $(OR)_8H_2Pc$ ring prolongs the π-system and preserves the sharpness of the spectra. Furthermore, [2,2′-bithiophene]-5-yl-substituted **2** displays an intense Q-band at 794 and fluorescence at 818 nm, respectively. Interestingly, the $Q_{(0-0)}$ band of **1** and **2** with a D_{2h} space group does not clearly split into $Q_{x(0-0)}$ and $Q_{y(0-0)}$ compared with β-unsubstituted species, and similar to that of the metal complexes. The full width of the half-maximum (fwhm) value of the $Q_{(0-0)}$ band of the free-bases implies that symmetrical β-substitution lowers the D_2 nature of the free-base and intensifies the D_4-like nature of the ring system. This effect is seen to a larger extent in the longer substituent system. Besides the free-bases, we undertook spectroscopic consideration of zinc Pcs, a class of Pc for which spectral assignments are the most firmly established.[16,30] As is observed in bare $(OBu)_8ZnPcs$, both **1-Zn** and **2-Zn** also exhibited a relatively small absorption band near 820 nm in addition to the intense Q-band at 758−770 nm in pure CH_2Cl_2. This longer wavelength component disappears upon the addition of a very small amount, less than 1.0 vol %, of pyridine to the solvent.[30] Thus we have carried out the photophysical measurements of the $(OBu)_8ZnPcs$ in CH_2Cl_2 containing 0.5 vol % pyridine. The thiophene-substituted $(OBu)_8ZnPcs$, **1-Zn** and **2-Zn**, exhibited a sharper Q-band compared with those of the corresponding free-base and cobalt derivative. The spectral events upon thiophene substitution to the $(OBu)_8ZnPc$ nucleus were similar to the observation in the free-base system. Figure 2 shows a comparison of the Q-absorption and emission of three types of zinc phthalocyanines with different substituent lengths. The Q-absorption energy of $(OBu)_8ZnPc$ is decreased by eight 2-thienyl substitutions to about 179.4 cm^{-1}, or 0.022 eV, and by eight [2,2′-bithiophene]-5-yl substitutions to about 356.9 cm^{-1}, or 0.035 eV, respectively. The Q-absorption of the Pcs corresponds to a transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO).[16,38] Therefore, the red shift can be explained by a decrease of the HOMO−LUMO energy gap. Figure 3 shows the relation between the substituent length and the $Q_{(0-0)}$ energy of the $(OBu)_8$-

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MPcs. The degree of the Q-energy lowering upon the thienyl substitution is in inverse proportion to the number of aromatic rings in a substituent. This implies that the substituents smoothly decrease the HOMO−LUMO gap by π-elongation in this region. The fwhm value of the $Q_{(0-0)}$ band of each ZnPc is maintained at the range of 287−327 cm^{-1}. This fwhm value clearly suggests conservation of the Q-band sharpness before and after substitution. In addition, the substitution of thiophene moieties to the Pc ring system tends to intensify the ϵ value of the Q-band, and [2,2′-bithiophene]-5-yl groups are more effective than the 2-thienyl groups. This hyperchromic effect also supports the π-system enlargement in the Pcs.[14] In this case, spectral changes such as splitting or broadening of the Q-band were not detected. This indicates that the introduction of thiophene moieties did not affect the D_{4h} symmetry of the Pcs. The Φ_f values of the free-bases and zinc Pcs were obtained using $(OBu)_8ZnPc$[16] as a Φ_f known standard, because $(OBu)_8Pcs$ exhibit their fluorescence at the NIR region. The Φ_f values of the $(OBu)_8Pcs$ decreased as the π-system was elongated. This implies that Φ_f values become smaller as the HOMO−LUMO energy gap decreases. However, the magnitude of the Q-band shift was relatively small; the spectroscopic events observed in the Pcs were similar to those in benzoannulated Pcs such as naphthalocyanines and anthracocyanines.[13−15]

The large Q-band shift of our Pcs was accompanied with visible color change relative to bare $(OBu)_8MPcs$. The original green color of $(OR)_8Pcs$ originates from their Q-absorption in the deep-red region. The Q-bands of thiophene-substituted Pcs, particularly [2,2′-bithiophene]-5-yl-substituted Pcs, penetrate into the NIR region, and hence the color of the solution changes from the $(OBu)_8$ MPc's green to brown (**2-Zn**) to red (**2**). Because of high stability and strong NIR absorbing nature, the β-thienyl-substituted $(OR)_8Pcs$ have potential for new applications as NIR-absorbing dyes.[36]

To examine the electronic states of thiophene-substituted Pcs, we undertook electrochemical studies by means of cyclic voltammetry (CV). As described by other groups, the HOMO−LUMO energy gap of the Pc ring systems is estimated from the difference between the first oxidation and the first reduction potential obtained from the electrochemical studies,[20,37−39] and this principle is applicable to the Pcs having a main group atom(s) as a central ion(s). The electrochemical studies for the $(OR)_8ZnPcs$[40,41] and $(OR)_8CoPcs$[42,43] have been reported by several groups. Figure 4A shows a preliminary CV experiment using the β-unsubstituted $(OBu)_8ZnPc$ in 0.3 M Bu_4NClO_4 in *o*-dichlorobenzene under dark conditions. Above the potential of +1000 mV, the complex shows an irreversible wave and decomposes immediately. Thus, we examined the CV studies below +900 mV. The voltammogram under this condition was characterized by an oxidation couple around +240 mV and a reduction couple around −1525 mV, respectively. From these potentials, the HOMO−LUMO gap of $(OBu)_8ZnPc$ was calculated at 1765 mV. This value is similar to the value reported for Pc derivatives.[39,41] Because of the anodic shift for reduction and the cathodic shift for oxidation, the HOMO−LUMO gap of the thiophene-substituted Pc decreases as the π-conjugation increases. The HOMO−LUMO gaps obtained from the thiophene-substituted ZnPcs were calculated at 1555 mV for **1-Zn** and at 1570 mV for **2-Zn**, respectively. The results of the CV experiments of $(OBu)_8ZnPc$, **1-Zn,** and **2-Zn** are summarized in Table 2. The eight 2-thienyl-substituted $(OBu)_8ZnPc$, **1-Zn**, and the [2,2′-bithiophene]-5-yl substituted $(OBu)_8ZnPc$, **2-Zn**, showed a quasi-reversible first oxidation peak at 180 and 220 mV, respectively. In addition, both of the thiophene-substituted Pcs showed the second oxidation around +670 mV. On the other hand, these complexes were reduced at more positive potentials than the control experiment with $(OBu)_8ZnPc$. A similar observation, a decrease of the HOMO−LUMO gap, was reported for the Pcs by others who attributed these results to π-elongation of the extended Pcs.[20]

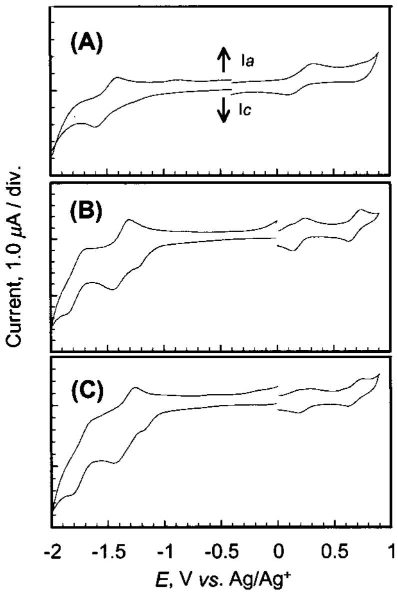

Figure 4. Cyclic voltammograms of (A) $(OBu)_8ZnPc$, (B) **1-Zn**, and (C) **2-Zn** in 0.3 M NBu_4ClO_4 in *o*-dichlorobenzene. Conditions: [Pc] = 1.0 mM, scan rate = 50 mV s^{-1}.

Table 2. Electrochemical Data for Phthalocyanines

	potential, mV vs. Ag/Ag$^+$ in MeCN (ΔE)[a]			
compd	$E_{1/2}$ (red2)	$E_{1/2}$ (red1)	$E_{1/2}$ (ox1)	$E_{1/2}$ (ox2)
$(OBu)_8ZnPc$[b]		−1525 (150)	240 (221)	675 (90)
1-Zn[b]		−1375 (130)	180 (80)	668 (120)
2-Zn[b]		−1350 (140)	220 (80)	850[d]
$(OBu)_8CoPc$[c]	−1705 (190)	−455 (90)	530 (120)	718 (150)
1-Co[c]	−1640 (110)	−604 (243)	352 (107)	710 (119)
2-Co[c]		−562 (130)	350 (103)	

[a] $\Delta E = |E_{p,c} - E_{p,a}|$. [b] Recorded with 0.3 M Bu_4NClO_4 as an electrolyte in *o*-dichlorobenzene with a scan rate of 50 mV s^{-1}. [c] Recorded with 0.1 M Bu_4NPF_6 as an electrolyte in CH_2Cl_2 with a scan rate of 50 mV s^{-1}. [d] Irreversible wave.

The redox potentials and reaction paths of CoPcs are well studied and known to be affected by the nature of the solvents.[39,44] The first oxidation and second reduction

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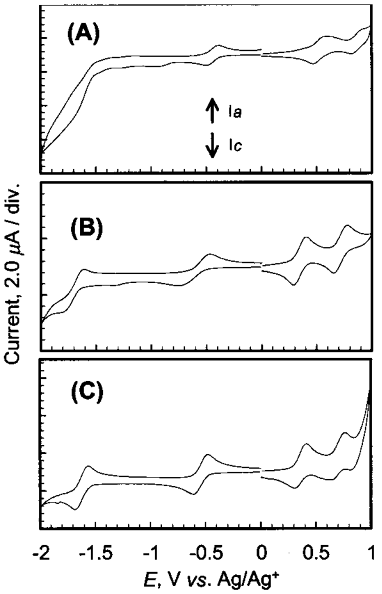

Figure 5. Cyclic voltammograms of (A) $(OBu)_8CoPc$, (B) **1-Co**, and (C) **2-Co** in CH_2Cl_2 containing 0.1 M NBu_4PF_6. Conditions: [Pc] = 1.0 mM, scan rate = 50 mV s^{-1}.

peaks of CoPcs generally have been assigned to the ligand oxidation and the ligand reduction potential, respectively, in nondonating media.[39] These potentials are generally situated within potential ranges between −2000 and +1000 mV,[20] and this permits the electrochemical consideration of $(OBu)_8Pcs$ from $E_{1/2}$(ox1) and $E_{1/2}$(red2) values in Table 2. In addition, the electrochemical process of the CoPcs generally contains cobaltous-centered reactions.[20,44] Because the redox center of this process is enveloped by the Pc ring, this potential is influenced by the electron-accepting/donating nature of the Pc ring. A preliminary CV experiment of bare $(OBu)_8CoPc$ was carried out in CH_2Cl_2 containing 0.1 M Bu_4NPF_6 between +900 and −2000 mV. Under these conditions, $(OBu)_8CoPc$ exhibits three redox couples at +530, +850, and −455 mV, respectively, but lacks the second reduction couple which is present in a normal CoPc system (Figure 5A).[39,44] The second oxidation, $E_{1/2}$(ox2), and first reduction, $E_{1/2}$(red1), couples under these conditions are assigned to the cobaltous-centered processes Co(II)/Co(III) and Co(I)/Co(II), respectively.[39] To evaluate the electrochemical stability of the thiophene-substituted CoPcs, we have carried out the continuous potential sweeping of **1-Co** and **2-Co** under the same condition. The electrochemical results obtained from the cobalt complexes are summarized in Table 2. The CV trace of both **1-Co** and **2-Co** did not suffer any potential shift and change on the trace shape, indicating an electrochemical stability of the Pc derivatives under these conditions (Figure 5B and 5C). The cobalt complexes **1-Co** and **2-Co** display a two-oxidation and two-reduction couple in this region. Each of the oxidation couples underwent a large cathodic shift relative to bare $(OBu)_8CoPc$. This implies the enhancement of the electron-donating nature with increasing conjugation length. However, the difference between the **1** and **2** system was not clearly detected; this result is in agreement with the zinc derivatives. In addition, **1-Co** and **2-Co** systems clearly exhibit the second reduction couple at −1705 and −1640 mV, respectively. Since bare $(OBu)_8CoPc$ lacks the second reduction peak, we only noticed the difference between **1-Co** and **2-Co**, but the difference was too small to make a comparison. As described above, the second reduction wave of CoPcs is assigned to the reduction peak of the Pc ligand to form Co(I)Pc(3−).[39] A remarkable trend obtained from the CV of $(OBu)_8CoPcs$ is enhancement of the electron-donating nature of $(OBu)_8CoPcs$ by thiophene-substitution, and this also suggests the destabilization of the HOMOs in the thiophene-substituted Pcs.

From the electrochemical results, the HOMO−LUMO gap of the $(OBu)_8ZnPcs$ is narrowed about 190 mV by the introduction of thiophene moieties. However, the redox processes of $(OBu)_8Pcs$ have a slightly irreversible nature; decrease of the HOMO−LUMO gap upon thiophene substitution is mainly ascribed to the destabilized nature of the HOMOs.

Conclusions

The synthesis of eight 2-thienyl- and ([2,2′-bithiophene]-5-yl)-substituted Pcs has been achieved starting from readily available 4,5-dibromo-3,6-dibutoxyphthalonitrile.[31] The 2-thienyl-substituted $(OBu)_8Pc$ derivatives exhibit a red-shifted Q-band, but the spectral shape is little influenced. Substitution of eight ([2,2′-bithiophene]-5-yl) groups to the $(OBu)_8Pc$ nucleus further shifts the Q-absorption to the NIR region, but the spectral features are still retained. Interestingly, the addition of thiophene moieties to the nucleus strongly intensifies the ϵ values, and the longer substituent, ([2,2′-bithiophene]-5-yl), is more effective than the 2-thienyl group. The sufficient Q-band shift from the deep red to the NIR region by thiophene-substitution implies the decrease of the HOMO−LUMO gap by π-elongation. The CV observations of the Pcs showed that the decrease of the HOMO−LUMO gap was mainly attributed to the destabilized nature of their HOMOs and that the influence of the substituent length on the CV is small. Furthermore, the Pcs obtained are a stable group of compounds that can be made by a reliable synthetic procedure in good yields. These results demonstrate a further diversity in the effects on the Pc ring system by β-substitution and enable potential application of the thiophene-substituted Pcs as attractive NIR-absorbing dyes or superior photosensitizers having an intense and tunable absorption band in the far red/NIR region.[36]

Acknowledgment. This work was partially supported by a Grant-in-Aid for COE Research “Advanced Fiber/Textiles Science and Technology” from the Ministry of Education, Culture, Sports, Science and Technology of Japan (No. 10CE2003).

Supporting Information Available: UV−Vis−NIR absorption (**1**, **2**, **1-Zn**, **1-Co**, **2-Zn**, and **2-Co**) and fluorescence spectra (**1**, **2**, **1-Zn**, and **2-Zn**) of the new Pcs. This material is available free of charge via the Internet at http://pubs.acs.org.

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