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Article

Preparation and Electrochemical and Optical Properties of Unsymmetrically Substituted Phthalocyanines with One or Two Trithiole Rings and Related Symmetric Derivatives

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4,5-Bis(benzylthio)-3,6-diethylphthalonitrile (**1**) was mixed with 4-*t*-butylphthalonitrile and then treated with lithium alkoxide in *n*-hexanol to produce the corresponding unsymmetrically substituted phthalocyanines (**2**) and (**3**) with two or four benzylthio groups, respectively. Treatment of phthalocyanine (**2**) with nickel(II) acetate yielded the corresponding metal complex **2-Ni**. Two benzyl groups of **2** and **2-Ni** were removed with lithium/THF/ammonia at −78 °C under argon, and the dithiolate anions generated were then reacted with elemental sulfur to give monotrithiolophthalocyanines (**5**) and (**5-Ni**). A similar treatment of **3** produced bistrithiolophthalocyanine (**6**). Tetrakistrithiolophthalocyanine (**7-Ni**) was prepared by complexation of phthalocyanine (**4**) with nickel(II) acetate, followed by a Birch reduction of the resulting nickel(II) complex (**4-Ni**), and then sulfurization and cyclization of the octathiolate anions that were generated. The structures of the phthalocyanines were determined by ^{1}H NMR and matrix-assisted laser desorption ionization time-of-flight mass spectrometry. The optical and electrochemical properties of the phthalocyanines were examined by UV–vis absorption spectroscopy and cyclic voltammetry. Treatment of **5**, **5-Ni**, **6**, **7**, and **7-Ni** with trifluoroacetic acid in chloroform generated positively charged species, which were characterized by UV–vis and/or NMR spectroscopy.

Introduction

Phthalocyanines and related compounds have attracted considerable interest because of their actual or potential applications in numerous fields including use in catalysis, new functional materials, and as sensitizers for photodynamic therapy.[1,2] A wide variety of functionalized phthalocyanines have been synthesized previously, and their electrochemical, physicochemical and optical properties have been assessed.[3,4] One of the most important properties of phthalocyanines in the context of functional materials is a bathochromic shift of the Q-band absorption. Preventing aggregation is also a significant consideration. Phthalocyanines and related derivatives have been modified by various procedures to introduce new functionalities by distorting the molecular plane through steric congestion,[4] peripherally expanding the π-conjugation system,[5,7] and axially connecting two functional groups to the central metal atom.[6] These processes can be used to

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enhance the suitability of the optical and electrochemical properties of phthalocyanine for specific applications. Introducing heteroatoms as substituents at the peripheral positions or in fused ring systems can also be an efficient method for synthesizing phthalocyanine derivatives.[3d,4c,7] In a related study, we recently reported the preparation and functionalization of 2,3,9,10,16,17,23,24-octakis(benzylthio)phthalocyanine [**PcSBn**] and the corresponding selenium derivatives.[8] Tetrakistrithiolophthalocyanines were prepared through treatment of tetrakis(*o*-xylylenedithio)phthalocyanines with lithium/THF (tetrahydrofuran)/ammonia and elemental sulfur.[9] While this procedure can obviously be used to functionalize phthalocyanine in all four peripheral directions, we are primarily interested in modifying the phthalocyanine structure in only one or two directions to obtain a new functionality in the field of nonlinear optical materials.[1a,b,10] In this paper we report the preparation and structural determination of unsymmetrically substituted mono and bistrithiolophthalocyanines together with their optical and electrochemical properties. The UV–vis and/or NMR spectroscopy studies of the generation of cationic species upon treatment of phthalocyanines with TFA (trifluoroacetyl) are also described.

Experimental Section

General Information. NMR spectra were measured with a Bruker AC-400 spectrometer and a JEOL JNM-ECX600 spectrometer. The mass spectra were obtained using a JEOL JMS-700 mass spectrometer. MALDI-TOF MS (matrix assisted laser desorption ionization time-of-flight mass spectrometry) were examined with a Bruker BIFLEX (III) mass spectrometer. UV–vis spectra were measured with a JASCO Ubest-30 spectrometer. A Hokuto Denko Co. model HAB-151 apparatus was used to measure of oxidation potentials.

Oxidation Potentials. All measurements were performed by cyclic voltammetry, using Ag/0.01 M $AgNO_3$ as a reference electrode. A solution of 0.1 M n-Bu_4NClO_4 in CH_2Cl_2 was used as an electrolyte. A scan rate of 200 mV/s was used for all measurement.

4,5-Bis(benzylthio)-3,6-diethylphthalonitrile (1). Compound **1** was prepared from 1,4-diethyltetrabromobenzene using a method described previously.[8]

Preparation of 2,3-Bis(benzylthio)-1,4-diethyl-tri(*t*butyl)phthalocyanine (2) and Tetrakis(benzylthio)-tetraethyl-di(*t*-butyl)-phthalocyanine (3). Lithium (17.4 mg, 2.5 mmol) was placed in a glass reactor, *n*-hexanol (2 mL) was added under Ar, and the solution was stirred at 100 °C for several minutes. A mixture of 4,5-bis(benzylthio)-3,6-diethylpthalonitrile (214.3 mg, 0.5 mmol) and *t*-butylphthalonitrile (276.0 mg, 1.5 mmol) was added, and the solution was stirred at 100 °C for 2 h. After cooling to room temperature, a MeOH solution of HCl was added, and the resulting blue−green precipitate was filtered. The residue was purified by column chromatography (Wakogel C-300HG, *n*-hexane/$CHCl_3$ = 1:1) to produce **2** in 23% yield (89.8 mg) together with **3** (55.2 mg, 9%), tetra(*t*-butyl)phthalocyanine (187.7 mg, 68%), and **PcSBn** (trace); **2**, blue−green powder; mp 116 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 1.66–2.07 (m, 33H), 4.32–4.71 (m, 8H), 7.15–9.38 (m, 19H); MALDI-TOFMS (*m/z*) 982.719 (M^+); **3**, blue−green powder; mp 114 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 1.49–2.08 (m, 30H), 2.45–5.16 (m, 16H), 7.14–9.49 (m, 26H); MALDI-TOFMS (*m/z*) 1227.94 (MH^+). It should be noted that compound **3** may, in fact, be a mixture of 2,3,16,17-tetrakis(benzylthio)-1,4,15,18-tetraethyl-di(*t*-butyl)phthalocyanine (**3a**) and 2,3,9,10-tetrakis(benzylthio)-1,4,8,11-tetraethyl-di(*t*-butyl)phthalocyanine (**3b**). However, these isomers could not be resolved.

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Preparation of 2,3-Bis(benzylthio)-1,4-diethyl-tri(*t*-butyl)-phthalocyaninato Nickel(II) (2-Ni). Phthalocyanine (**2**) (98.2 mg, 0.09 mmol) and Ni(OAc)$_2$·4H$_2$O (248.4 mg, 0.99 mmol) were placed in a glass reactor, and dimethylformamide (DMF, 20 mL) was added under Ar. The solution was stirred at 155 °C for 0.5 h. After cooling to room temperature, the reaction mixture was poured into 200 mL of water. The blue−green precipitate was filtered and washed with MeOH. The residue was purified by column chromatography (Wakogel C-300HG, *n*-hexane/CHCl$_3$ = 1:1) to give **2-Ni** in 65% yield (67.6 mg); blue−green powder; mp 155 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.33–1.97 (m, 33H), 3.95–4.88 (m, 8H), 7.25–9.18 (m, 19H); MALDI-TOFMS (*m*/*z*) 1038.512 (M$^+$).

Preparation of Monotrithiolophthalocyanine (5). Compound **2** (49.1 mg, 0.05 mmol) and lithium (27.3 mg, 3.93 mmol) were placed in a glass reactor, and THF (3 mL) was added under Ar. After the solution was cooled to −78 °C, NH$_3$ (30 mL) was introduced into the reactor and condensed. The solution was stirred for 3 h at this temperature and gradually warmed to room temperature. NH$_3$ was evaporated in a stream of N$_2$ gas. After the evaporation of NH$_3$ was complete, THF (20 mL) and MeOH (20 mL) were added to the blue−green solid. NH$_4$Cl (267.0 mg, 4.9 mmol) and S$_8$ (129.1 mg, 5 mmol) were added, and the solution was stirred for 6 h at room temperature. The product was extracted with CHCl$_3$. The solvent was evaporated, and the product was separated by column chromatography (Wakogel C-300HG, *n*-hexane). Phthalocyanine (**5**) was obtained in 30% yield (12.3 mg); ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.00–2.08 (m, 33H), 3.42–4.47 (m, 4H), 7.96–9.42 (m, 16H); MALDI-TOFMS (*m*/*z*) 832.345 (M$^+$).

Preparation of Monotrithiolophthalocyaninato Nickel(II) (5-Ni). Compound **2-Ni** (51.9 mg, 0.05 mmol) and lithium (26.7 mg, 3.93 mmol) were placed in a glass reactor, and THF (3 mL) was added under Ar. The solution was treated in the manner described above to give **5-Ni** in 96% yield (42.9 mg); blue−green powder; mp 262 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ = 1.22–2.08 (m, 33H), 3.10–4.40 (m, 4H), 7.85–9.24 (m, 9H); MALDI-TOFMS (*m*/*z*) 888.277 (M$^+$).

Preparation of Bistrithiolophthalocyanine (6). Compound **3** (59.8 mg, 0.05 mmol) and lithium (26 mg, 3.74 mmol) were placed in a glass reactor, and THF (3 mL) was added under Ar. The solution was also treated as described above, resulting in **6** (a mixture of two isomers) in 47% yield (21.6 mg); blue−green powder; ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.00–2.10 (m, 30H), 3.60–5.40 (m, 8H), 8.04–9.38 (m, 6H); FABMS (*m*/*z*) 926.2 (M$^+$); MALDI-TOFMS (*m*/*z*) 927.94 (MH$_2^+$).

Preparation of 1,4,8,11,15,18,22,25-Octaoctyl-2,3,9,10,16,17,-23,24-tetrakis(*o*-xylylenedithio)phthalocyaninato Nickel(II) (4-Ni). Compound **4** (247 mg, 0.12 mmol) and Ni(OAc)$_2$·4H$_2$O (250 mg, 1.0 mmol) were placed in a glass reactor, and DMF (20 mL) was added under Ar. The solution was stirred at 150 °C for 2.5 h, cooled to room temperature and was then poured into ice water. The green precipitate was filtered, and the residue was washed with MeOH. After drying, the product was purified by column chromatography (Wakogel C-300HG, *n*-hexane/CHCl$_3$ = 1:1). Upon recrystallization, **4-Ni** was obtained in 91% yield (230.8 mg); green powder; mp 91 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 0.68–0.84 (m, 24H), 1.07–1.38 (m, 64H), 1.47–1.75 (m, 32H), 3.82–4.82 (m, 32H), 6.81–7.29 (m, 16H); MALDI-TOF MS (*m*/*z*) 2131.395 (MH$^+$).

Preparation of Tetrakistrithiolophthalocyaninato Nickel(II) (7-Ni). Compound **4-Ni** (107.8 mg, 0.05 mmol) and lithium (30.5 mg, 4.39 mmol) were placed in a glass reactor. The mixture was treated by a method similar to that described above (the reaction time was 1 h) and **7-Ni** was obtained in 66% yield (61.5 mg). Brownish-green powder; mp 201 °C; ^{1}H NMR (600 MHz, CDCl$_3$): δ = 0.76 (t, *J* = 7.1 Hz, 24H), 1.08–1.20 (m, 48H), 1.26 (quint, *J* = 7.3 Hz, 16H), 1.47 (quint, *J* = 7.3 Hz, 16H), 1.80 (quint, *J* = 7.5 Hz, 16H), 4.35 (br, 16H); ^{13}C NMR (150 MHz, CDCl$_3$): δ = 14.0, 22.6, 29.2, 29.5, 29.6, 30.2, 31.8, 34.2, 133.9, 134.4, 144.7, 146.3; MALDI-TOF MS (*m*/*z*) 1842.854 (MH$^+$).

NMR Measurement for Phthalocyanine (7) in CDCl$_3$/TFA-*d*. ^{1}H and ^{13}C NMR were measured for **7** in chloroform-*d* containing 5 vol % of TFA-*d*; ^{1}H NMR (400 MHz, CDCl$_3$/TFA-*d*) δ = 0.87 (t, *J* = Hz, 24H), 1.14–1.41 (m, 64H), 1.53 (quint, *J* = 7.1 Hz, 16H), 1.59–1.86 (m, 16H), 3.43 (dt, *J* = 17.3, 5.3 Hz, 8H), 4.25 (dt, *J* = 17.3, 5.3 Hz, 8H); ^{13}C NMR (100 MHz, CDCl$_3$/TFA-*d*) δ = 14.0, 22.7, 29.27, 29.33, 29.5, 30.0, 31.9, 34.1, 126.1, 137.1, 144.1, 150.9.

Results and Discussion

Preparation of Unsymmetric Phthalocyanines and Related Compounds. The starting compound, 4,5-bis(benzylthio)-3,6-diethylphthalonitrile (**1**), was prepared from 1,4-diethyltetrabromobenzene via four reaction steps.[8] There are three approaches for preparing unsymmetrically substituted phthalocyanines: a statistical cyclization reaction of two different types of phthalonitriles,[5c,k,7g,11] a ring-expansion treatment of subphthalocyanine with diiminoisoindoline,[7h,12] and a solid-state reaction of two types of phthalonitriles on macromolecular carriers.[13] We decided to adopt the statistical cyclization approach. Compound **1** was mixed with *t*-butylphthalonitrile in a 1:3 ratio and then treated with lithium alkoxide in *n*-hexanol at 100 °C (Scheme 1). A blue−green solid that precipitated out of the solution was filtered, dried, and purified giving 2,3-bis(benzylthio)-1,4-diethyl-tri(*t*-butyl)phthalocyanine (**2**) in 23% yield together with tetrakis-(benzylthio)tetraethyl-di(*t*-butyl)phthalocyanine (**3**) (9%), tetra(*t*-butyl)phthalocyanine [***t*Bu$_4$Pc**] (68%), and **PcSBn** (trace). However, 2,3,9,10,16,17-hexakis(benzylthio)-1,4,8,11,15,18-hexaethyl-*t*-butylphthalocyanine could not be detected in the reaction mixture. As Wöhrle et al. reported in the literature,[11b] it seems that compound **3** could consist of two isomers, 2,3,16,17-tetrakis(benzylthio)-1,4,15,18-tetraethyl-di(*t*-butyl)phthalocyanine (**3a**) and 2,3,9,10-tetrakis(benzylthio)-1,4,8,11-tetraethyl-di(*t*-butyl)phthalocyanine (**3b**), which cannot be resolved. Compounds **2** and **3** are soluble in the most commonly used organic solvents with the exception of methanol and acetonitrile.

Although the ^{1}H NMR spectra of **2** and **3** contain very complex signals because of the randomly substituted *t*-butyl groups, the benzyl and ethyl groups can be observed in each spectrum. In the UV–visible absorption spectra, the Q-band

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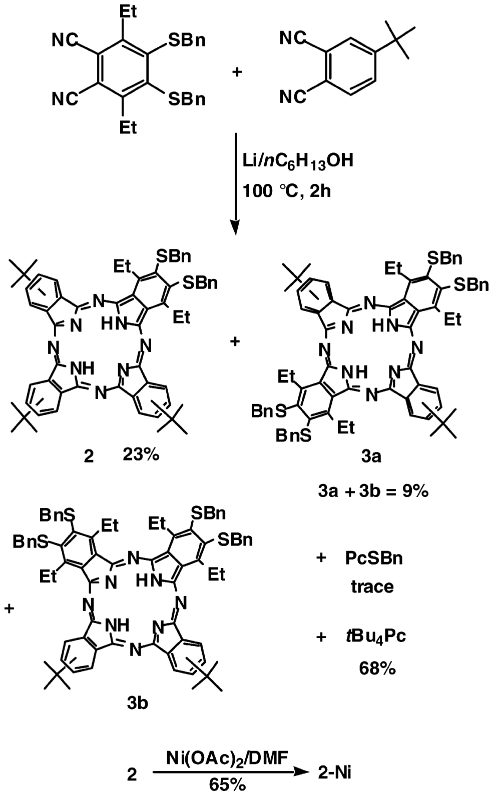
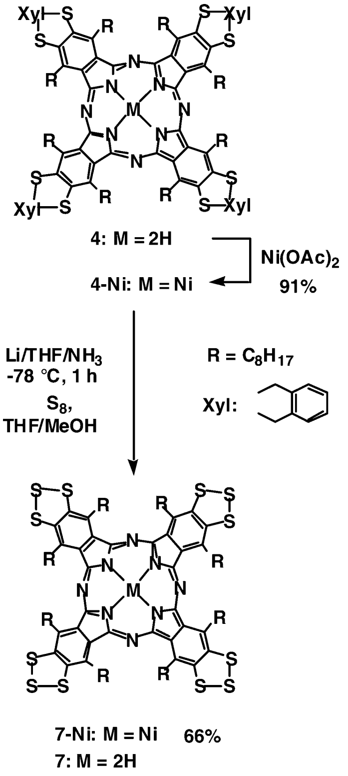
Scheme 1



Scheme 2



of **2** is observed as a split broad signal (see Supporting Information). If an unsymmetrically substituted phthalocyanine consists of two different types of benzopyrrole components (A and B) in a 1:1 ratio and exhibits a split Q-band, it can safely be concluded that the compound is the ABAB (trans) rather than the AABB (cis) isomer.[4c,14] A broad split Q-band is also observed for **3**. This suggests strongly that compound **3** is a mixture of the ABAB (trans) **3a** and AABB (cis) **3b** isomers. The Q-band absorptions for **2** and **3** are red-shifted relative to that of tetra(*t*-butyl)phthalocyanine, and the magnitude of the red shift is affected by the number of peripheral benzylthio and ethyl groups. The structures of **2** and **3** were confirmed by MALDI-TOF MS. The anticipated parent peaks were observed at $m/z = 982.719$ for **2** and $m/z = 1227.94$ for **3**.

Compounds **2** and **4** were treated with nickel(II) acetate in DMF to produce phthalocyaninato nickel(II) complexes (**2-Ni**) and (**4-Ni**) in 65 and 91% yields, respectively (Schemes 1 and 2).[15] The ^{1}H NMR spectrum of **2-Ni** contains complex sets of peaks arising from the *t*-butyl groups similar to that observed for **2**. The ^{1}H NMR spectrum of **4-Ni** is similar to that of **4**. The Q-bands of **2-Ni** and **4-Ni** lie at shorter wavelengths and have narrower band widths than those of the corresponding metal-free derivatives. The structures of **2-Ni** and **4-Ni** were confirmed by MALDI-TOF MS. The anticipated parent peaks were observed at $m/z = 1038.512$ [MH$^+$] for **2-Ni** and $m/z = 2131.395$ [MH$^+$] for **4-Ni**. The complexation of **3** with nickel(II) acetate was attempted by a method similar to that described above but the reaction gave an insoluble material, and the structure could not be determined.

Debenzylation and Sulfurization of Phthalocyanines. The S−C bond of the benzylthio or xylylenedithio groups can easily be cleaved through a Birch reduction, and the thiolate anions which are generated can be functionalized upon reaction with several electrophiles.[8,9,16] The presence of at least one substituent at the benzene ring positions next to the trithiole ring is required to stabilize the benzotrithiole derivatives.[17] The C−S bonds of **2** and **2-Ni** were reductively cleaved according to a procedure we have described previously to construct four trithiole rings on the phthalocyanine.[9] Typically, two benzyl groups are removed from **2** by using lithium metal in THF/liquid ammonia at −78 °C, and then elemental sulfur is added to the reaction mixture (Scheme 3). After purification, monotrithiolophthalocyanine (**5**) is obtained in 30% yield. When the ^{1}H NMR spectrum of **5** is measured in chloroform-*d*, no peak is observed for the benzyl group (see Supporting Information). In the UV–vis spectrum, the Q-band of **5** is observed to lie close to that of **2** (Figure 1a). A similar treatment of **2-Ni** with lithium/THF/ammonia and elemental sulfur gave **5-Ni** in 96% yield. The Q-band of **5-Ni** lies at similar wavelength to that of **2-Ni** at higher

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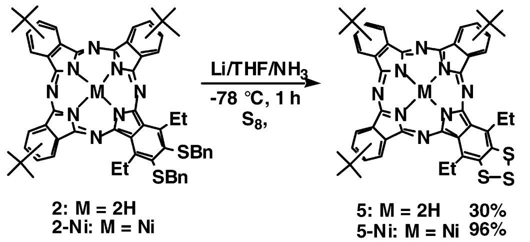
(14) (a) Kobayashi, N.; Miwa, H.; Nemykin, V. N. *J. Am. Chem. Soc.* **2002**, *124*, 8007–8020. (b) Kibayashi, N.; Fukuda, T. *J. Am. Chem. Soc.* **2002**, *124*, 8021–8034. (c) Kobayashi, N.; Mack, J.; Ishii, K.; Stillman, M. J. *Inorg. Chem.* **2002**, *41*, 5350–5363.

(15) Phthalocyanine (**4**) was prepared by the procedure reported previously (ref. 9).

(16) (a) Velázquez, C. S.; Broderick, W. E.; Sabat, M.; Barrett, A. G. M.; Hoffman, B. M. *J. Am. Chem. Soc.* **1990**, *112*, 7408–7410. (b) Velázquez, C. S.; Fox, G. A.; Broderick, W. E.; Anderson, K. A.; Anderson, O. P.; Barrett, A. G. M.; Hoffman, B. M. *J. Am. Chem. Soc.* **1992**, *114*, 7416–7424.

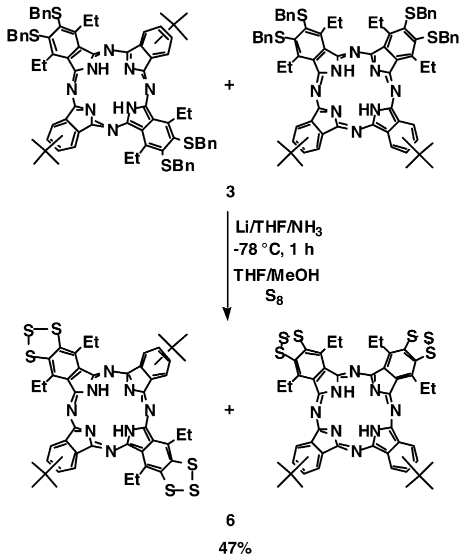
(17) Kimura, T.; Ogawa, S.; Sato, R. *Mini Rev. Org. Chem.* **2007**, *4*, 15–29.

Scheme 3



energy than the Q-band of **5** with a relatively broad bandwidth (Figure 1b). Although the ^{1}H NMR spectrum of **5-Ni** is complex, the disappearance of the benzyl group signals can be confirmed (see Supporting Information). MALDI-TOF MS experiments were carried out for **5** and **5-Ni**. The molecular ion peaks observed at $m/z = 832.345$ [M$^+$] and $m/z = 888.277$ [M$^+$], respectively, are consistent with the presence of trithiole rings. In contrast, no signal consistent with a phthalocyanine containing a pentathiepin ring was found in either spectrum.

Scheme 4



Compounds **3** and **4-Ni** were treated with a procedure similar to that described above to produce bistrithiolophthalocyanine (**6**) in 47% yield and nickel tetratkisrithiolophthalocyanine (**7-Ni**) in 66% yield (Schemes 2 and 4). It should be noted that compound **6** may be a mixture of two isomers. No peaks of the benzyl groups were observed in the ^{1}H NMR spectrum of **6**. Similarly, no signals for the xylylene group are observed in the ^{1}H NMR spectrum of **7-Ni** (see Supporting Information). The Q-band absorption of **6** is observed to lie close to that of **3** (Figure 1c). The Q-band of **7-Ni** lies at 737.5 nm, at higher energy than the Q-band of **7** with a significantly narrower bandwidth (Figure 2a). The structures of **6** and **7-Ni** were confirmed by MALDI-TOF MS. The molecular ion peaks were observed as anticipated at $m/z = 927.94$ [MH_2^{+}] for **6** and $m/z = 1842.854$ [MH$^+$] for **7-Ni**.

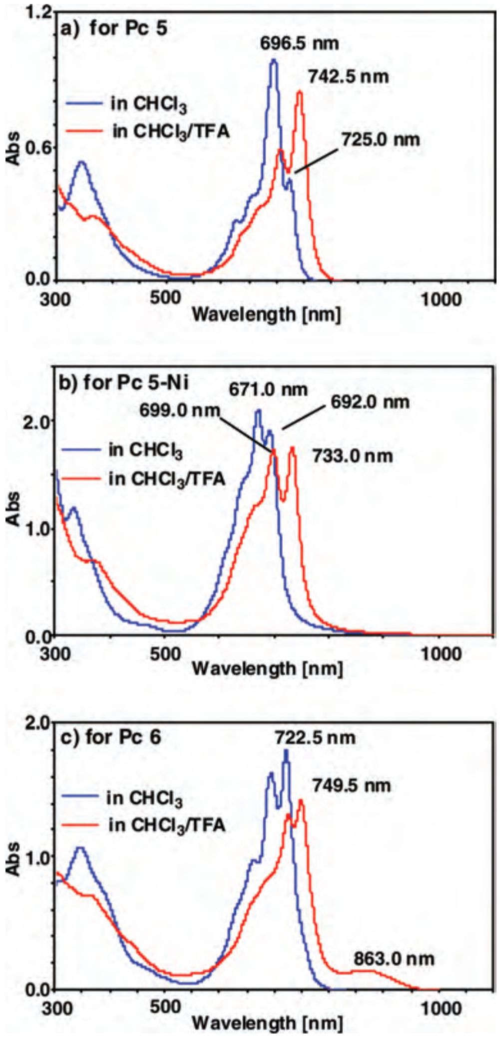


Figure 1. UV–visible absorption spectra of phthalocyanines **5**, **5-Ni**, and **6**.

UV–vis Absorption Spectroscopy for Charged Species. It has been reported previously that phthalocyanines and related compounds can be protonated with acids to produce cationic species and that this results in substantial changes

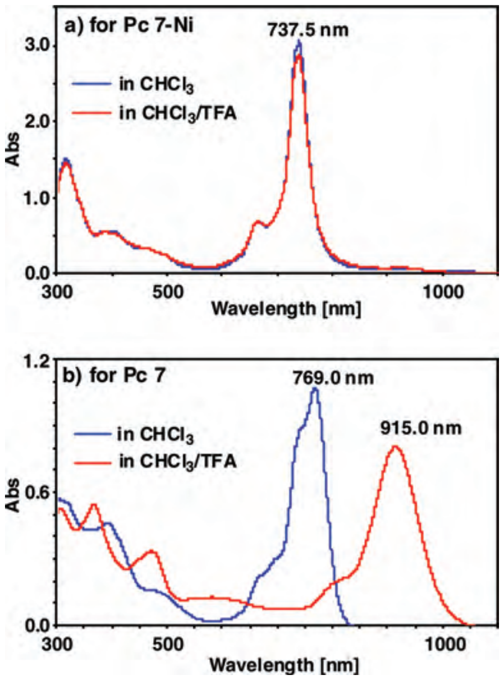


Figure 2. UV–visible absorption spectra of phthalocyanines **7** and **7-Ni**.

in the UV–visible spectra.[7a,18,19] Cationic species of **5**, **5-Ni**, **6**, **7**, and **7-Ni** were prepared in chloroform containing 5 vol % of TFA (Figures 1 and 2).[20] The major absorption bands of the cationic species of **5** are shifted to longer wavelength by about 18 nm (Figure 1a), while the cationic species of **6** exhibits two types of Q bands. One is a red-shifted signal by 27 nm, while another weaker band is observed at 863 nm (Figure 1c). Interestingly, the Q-band of **7** lies at 769 nm while that measured of the cationic species generated in chloroform/TFA is observed at 915 nm (Figure 2b). Protonation clearly has a drastic impact on the π-system. As described previously, the Q-band of **7** is observed at 887 nm in concentrated sulfuric acid despite low solubility of **7** so the protonation clearly proceeds in chloroform/TFA (5 vol %) as well as in concentrated sulfuric acid. If the positive charge generated on the phthalocyanine delocalizes to the trithiole ring, the trithiole moiety may adopt a planar rather than an envelope conformation, which could result in steric congestion between the eight octyl groups.

The UV–vis spectrum of **7** (2.7×10^{-5} mol/L) was measured in the presence of 1 to 100 equiv of TFA to examine the effect of acid concentration. The spectra did not change under these conditions, and a large excess of TFA had to be added to observe further spectral changes. When further TFA was added to bring the solution up to 2500 equiv, the 769 nm band gradually decreased in intensity, while the addition of 5000 equivalents of TFA resulted in a new band at 912 nm (see Supporting Information). These bands are probably associated with mono and diprotonated species, respectively. An increase to 15 000 equiv (ca. 3 vol %) resulted in the spectral changes shown in Figure 2b.

It has been reported that the protonation of metal-free tetrazaporphyrin and phthalocyanine can occur not only on the central pyrrole nitrogen atoms but also on the nitrogen atoms at the meso positions, and that the extent of protonation depends on the acidity and acid concentration.[7a,17] UV–vis spectra were recorded for **5-Ni** and **7-Ni** under conditions similar to those described above to determine the effect of protonation at the peripheral meso positions. The absorption bands of the protonated form of **5-Ni** in chloroform/TFA (5 vol %) shift to longer wavelength by about 40 nm and exhibit significantly broader band widths (Figure 1b).

In contrast, the spectrum of **7-Ni** was unchanged in the presence of 5 vol % of TFA in chloroform (Figure 2a). A large excess of TFA was added to examine the effect of protonation at the peripheral meso positions. When 20 vol % TFA was used as a solvent, a new absorption appeared at 819 nm (see Supporting Information). The intensity of this band increased in the presence of 50 vol % TFA. The 737.5 nm band did not disappear although it shifted slightly to longer wavelength. This suggests that **7-Ni** is significantly harder to protonate than **7**.

NMR Spectroscopy. The NMR spectra of **7** and **7-Ni** were measured using chloroform-*d* and chloroform-*d* containing 5 vol % of TFA-*d* (chloroform-*d*/TFA-*d*). When the ^{1}H NMR spectrum of **7** was measured in chloroform-*d*/TFA-*d*, the signals of the $-CH_2-$ connected directly to the benzene ring and of the next $-CH_2-$ are observed as two split signals (Figure 3b) and appear at slightly higher field than was the case in chloroform-*d* (Figure 3a). The other signals of the octyl group were observed at slightly lower field. The splitting of the $-CH_2-$ signal could be caused by hindered rotation of the octyl group due to the steric congestion with the trithiole ring. An interaction between the meso nitrogen atoms and TFA, possibly based on hydrogen bonding, may be responsible. In the ^{13}C NMR spectrum of **7** in chloroform-*d*, the two signals for the pyrrole carbons could not be observed because of the effect of proton alternation between the four central nitrogen atoms. It has been reported previously that the ^{13}C NMR signals of phthalocyanine derivatives exhibit a coalescence point with respect to the central pyrrole rings at around room temperature based on tautomerization.[21]

In contrast, when the ^{13}C NMR spectrum of **7** was measured in chloroform-*d*/TFA-*d* (5 vol %) (see Supporting Information), only four phthalocyanine skeleton signals were observed in the spectrum at $\delta = 126.1, 137.1, 144.1, 150.9$. This result suggests that the two nonprotonated nitrogen atoms in the pyrrole rings of **7** are deuterated by TFA-*d*, and the two protons on the pyrrole nitrogen atoms are exchanged with deuterium to form a completely symmetrical structure.

The ^{1}H NMR spectrum of **7-Ni** measured in chloroform-*d* shows the signal of the $-CH_2-$ group, which is connected directly to the benzene ring at a slightly higher field than was the case with **7** (see Supporting Information). In contrast, the signal of the $-CH_2-$ groups of **7-Ni** linked to the benzene ring was not observed in the ^{1}H NMR spectrum measured in chloroform-*d*/TFA-*d* (5 vol %) although signals for other protons of the octyl group were observed at a slightly lower field than those measured in chloroform-*d*. Because the UV–vis spectrum of **7-Ni** in chloroform/TFA (5 vol %) is similar to that measured without TFA, the extent of deuteration of **7-Ni** must be limited. The free rotation of the octyl groups may be hindered by the interaction between the meso nitrogen atoms and TFA-*d*. A limited interaction between **7-Ni** and TFA is anticipated with a fast exchange between the various possible structures, similar to the tautomerization of the two inner protons, resulting in broadened NMR signals. Furthermore, although the ^{13}C NMR signal for the phthalocyanine macrocycle can be observed

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(18) (a) Bernstein, P. A.; Lever, A. B. P. *Inorg. Chim. Acta* **1992**, *198–200*, 543–555. (b) Stuzhin, P. A. *J. Porphyrins Phthalocyanines* **1999**, *3*, 500–513.

(19) Kobayashi, N.; Nonomura, T.; Nakai, K. *Angew. Chem., Int. Ed.* **2001**, *40*, 1300–1303.

(20) Emission spectra for **2**, **2-Ni**, **3**, **5**, **5-Ni**, and **6** were measured in chloroform. Although the emission of the two nickel complexes could not be observed, **2**, **3**, **5**, and **6** exhibited weak emission at 703 and 734 nm for **2** ($\lambda_{exc} = 699.5$ nm), at 706 and 733 nm for **3** ($\lambda_{exc} = 690.0$ nm), at 708 and 733 nm for **5** ($\lambda_{exc} = 719.5$ nm), and at 703 and 733 nm for **6** ($\lambda_{exc} = 662.0$ nm).

(21) (a) It has been reported that the tautomerization of inner protons affects the signals of ^{1}H NMR and ^{13}C NMR spectra; Abraham, R. J.; Hawkes, G. E.; Smith, K. M. *Tetrahedron Lett.* **1974**, 1483–1486. (b) Abraham, R. J.; Hawkes, G. E.; Hudson, M. F.; Smith, K. M. *J. Chem. Soc., Perkin Trans. 2* **1975**, 204–211. (c) Cook, M. J.; Cracknell, S. J.; Moore, G. R.; Osborne, M. J.; Williamson, D. J. *Magn. Reson. Chem.* **1991**, *29*, 1053–1060.

Table 1. Redox Potentials of Phthalocyanines

	$E_{1/2}$ (V)			
compound	second oxidation	first oxidation	first reduction	second reduction
2	0.69	0.47	−1.07	−1.41
2-Ni	0.67	0.35	−1.21	−1.57
3	0.91	0.57	−1.04	−1.39
PcSBn	0.72	0.49	−1.02	−1.31
5	0.75	0.48	−1.18 (Ep)	
5-Ni	0.76	0.44	−1.30 (Ep)	
6		0.90 (Ep)	−1.23 (Ep)	
7	0.82	0.56	−1.04	
7-Ni		0.64	−1.21 (Ep)	

in the case of **7-Ni** in chloroform-*d* ($\delta = 133.9$, 134.4, 144.7, 146.3), the spectrum measured in chloroform-*d*/TFA-*d* (5 vol %) contains six octyl carbon signals but no signals for the aromatic carbons and two octyl carbons next to the benzene ring. This demonstrates that the structure of **7-Ni** is unsymmetric in solution because of the interaction between the meso nitrogen atoms and TFA-*d* and the fast exchange of interacting positions.

Electrochemical Properties. The redox potentials were measured by cyclic voltammetry using Ag/AgNO$_3$ as a reference electrode to determine the electrochemical properties (Table 1). The CV of compound **2** (two benzylthio groups) contains two reversible oxidation ($E_{1/2} = 0.47$ and 0.69 V) and two reversible reduction potentials ($E_{1/2} = -1.07$ and −1.41 V). In the case of **3** (four benzylthio groups), there are two reversible oxidation ($E_{1/2} = 0.57$ and 0.91 V) and two reversible reduction potentials ($E_{1/2} = -1.04$ and −1.39 V). The oxidation potentials of **2** (two benzylthio and three *t*-butyl groups) are lower than those of **3** (four benzylthio and two *t*-butyl groups). It appears, therefore, that the peripheral substituents cause a slight variation based on their inductive effects. The nickel complex **2-Ni** also exhibited two reversible oxidation potentials ($E_{1/2} = 0.35$ and 0.67 V) and two reversible reduction potentials ($E_{1/2} = -1.21$ and −1.57 V).

When the redox potentials of **5** and **5-Ni** (one trithiole ring) were measured using a similar procedure, two reversible oxidation potentials (**5**: $E_{1/2} = 0.48$ and 0.75 V and **5-Ni**: $E_{1/2} = 0.44$ and 0.76 V) and one irreversible reduction potential were observed. In contrast, irreversible oxidation and reduction potentials were observed for **6** (two trithiole rings). The redox potentials of **7-Ni** (four trithiole rings) were found to consist of one reversible oxidation potential ($E_{1/2} = 0.64$ V) and one irreversible reduction potential ($E_p = -1.21$ V), while the CV of the metal-free derivative **7** contains two reversible oxidation couples and one quasi-reversible reduction couple. In the case of the benzylthio derivatives, **2** and **2-Ni**, and the trithiole derivatives, **5** and **5-Ni**, the first oxidation potential of the nickel complex is lower than that of the metal-free phthalocyanine. In contrast, in the case of the trithiole derivatives **7** and **7-Ni**, the first oxidation potential of the nickel complex is higher than that of the metal-free phthalocyanine. The first oxidation potentials of **5** and **5-Ni** are lower than those of **7** and **7-Ni**. The order of the first oxidation potential is **7-Ni** > **7** > **5** > **5-Ni**. The protonation of phthalocyanine in CHCl$_3$/TFA can be expected to be related to the order of the first oxidation potentials. The protonation, therefore, proceeds for **5**, **5-Ni**, and **7** in chloroform/TFA (5 vol %) but not for **7-Ni**.

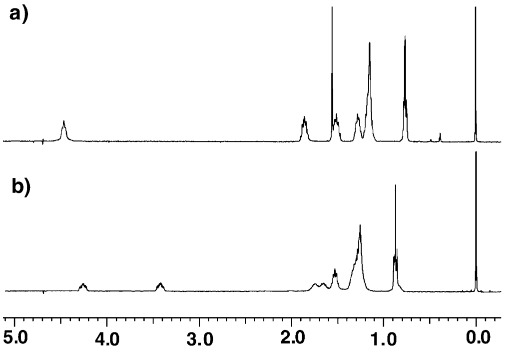

Figure 3. 400 MHz ^{1}H NMR for **7**, (a) measured in CDCl$_3$ and (b) measured in CDCl$_3$/TFA-*d*.

Conclusion

Phthalocyanines (**2**) and (**3**) were prepared by the statistical reaction of two phthalonitriles. Nickel complexes **2-Ni** and **4-Ni** were then obtained from a complexation reaction of phthalocyanines (**2**) and (**4**). Compounds **2**, **2-Ni**, **3**, and **4-Ni** were reacted with lithium/THF/ammonia at −78 °C and then with elemental sulfur to form phthalocyanines with trithiole rings, **5**, **5-Ni**, **6**, and **7-Ni**. The Q-bands observed for **5**, **5-Ni**, **6**, and **7** measured in chloroform/TFA (5 vol %) exhibit a large red shift, which is not observed in the case of **7-Ni**. This suggests that the cationic species of **5**, **5-Ni**, **6**, and **7** are generated by protonation and that the positive charge strongly affects the π-systems. The protonation of **7-Ni** was found to require a large excess of TFA. It appears that the protonation of phthalocyanines **5**, **5-Ni**, **6**, **7**, and **7-Ni** is strongly related to their first oxidation potential. Analysis of the ^{13}C NMR data demonstrated that **7** has a completely symmetric structure in chloroform-*d*/TFA-*d* (5 vol %) solution, which suggests that the metal-free phthalocyanine is protonated with TFA at the inner two nitrogen atoms. Although the Q-band absorption of **7-Ni** in chloroform/TFA (5 vol %) solution is very similar to that measured in chloroform, the ^{1}H and ^{13}C NMR spectra measured in chloroform-*d*/TFA-*d* (5 vol %) are significantly different from those measured in chloroform-*d*. It should be noted that the changes observed in the NMR spectra of **7** and **7-Ni** could be caused by the protonation of either the inner nitrogen atoms or the interaction of peripheral meso nitrogen atoms with TFA.

Supporting Information Available: Listings of ^{1}H NMR spectra for **2**, **2-Ni**, **3**, **4-Ni**, **5**, **5-Ni**, **6**, **7**, and **7-Ni**, ^{13}C NMR spectra for **7** and **7-Ni**, and UV–visible absorption spectra for **2**, **2-Ni**, **3**, **7**, and **7-Ni** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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