Synthesis and Properties of 1,4,8,11,15,18,22,25-Octaalkoxy-2,3,9,10,16,17,23,24-octakis(phenylthio)phthalocyaninato Copper(II)

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1,4,8,11,15,18,22,25-Octaalkoxy-2,3,9,10,16,17,23,24-octakis(phenylthio)phthalocyaninato copper(II) was synthesized. They were easily soluble in organic solvents and their Q-bands showed bathochromic shifts about 100 nm compared with unsubstituted phthalocyaninato copper(II). Their properties were examined.

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Interest in exploiting the attractive optical and electrical properties of phthalocyanine (Pc) ring system continues to grow rapidly [1]. We have investigated the synthesis and properties of Pc derivatives [2-6]. Pc shows strong absorption in the visible region (the Q-band). Introduction of electron-donating substituents onto the benzene rings results in the large red shift. There is, therefore, the potential for turning the Q-band absorption to match the wavelengths of GaAlAs laser light (semiconductor laser light) [7]. However, the problem of the low solubility of Pc in organic solvents needs to be overcome if the application of Pc derivatives in the recording devices is to be realized. Substituents so placed should cause substantial disruption of the strong lattice forces of the parent Pc and hence help confer solubility. On the other hand, 1,4,8,11,15,18,22,25-octaalkoxyphthalocyaninato zinc(II) gave attractive properties by electrochemical measurements [8]. The electrolysis, using a potential sweep method, of 1,4,8,11,15,18,22,25-octaalkoxy-ZnPc afforded the formation of an electrochemically-active thin film. Several physicochemical measurements indicated that the metal-ring structure of 1,4,8,11,15,18,22,25-octaalkoxy-ZnPc was maintained in the electrodeposited film.

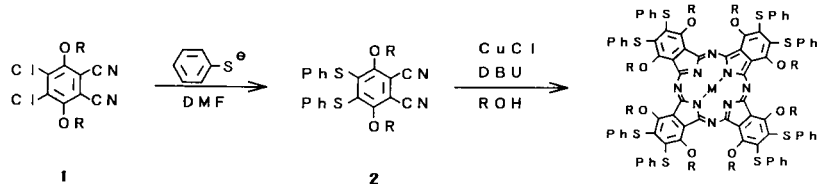
The present paper describes the synthesis and properties of hexadeca substituted Pc containing alkoxy and phenylthio groups.

Results and Discussion.

Synthetic pathways to 1,4,8,11,15,18,22,25-octaalkoxy-2,3,9,10,16,17,23,24-octakis(phenylthio)-CuPc (**3**) are summarized in the Scheme. Intermediates, 1,2-benzenedicarbonitrile derivatives (**1**) were prepared from 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in two steps according to reference [9]. The reaction of **1** with benzenethiolate anion gave the precursor, 3,6-dialkoxy-4,5-bis(phenylthio)-1,2-benzenedicarbonitrile (**2**). In the ^{1}H-nmr spectra, the signals of the aromatic protons of **2** appeared as a multiplet at δ 6.90-7.30 ppm. In the ir spectra, the absorptions of the C-H out-of-plane bending vibration of the monosubstituted benzene ring were observed at 684-753 cm^{-1}. The ms and elemental analysis consist of the molecular formula. Cyclization of **2** in the presence of 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) and copper(I) chloride in alcohol gave **3**. *trans*-Alkoxylation reactions might occur during the cyclization of 1,2-benzenedicarbonitrile derivatives having alkoxy groups [9]. In the present work, *trans*-alkoxylation reactions were taken into consideration, **2a** and **2b** were cyclized using ethanol or pentanol as a solvent, respectively. The ir showed absorptions of alkoxy and phenyl groups of **3**. The FAB-ms and elemental analysis consist of the molecular formula. In the electronic spectra of **3** in toluene, the Pc system was characterized by strong absorption bands in the uv-visible region (the Soret bands) and in the near infrared region (the Q-band). The yield of **3b** was better than that of **3a** on account of the reaction temperature.

Compounds **3** have bathochromic shifts of the Q-bands

Scheme



1 2 3 : M = Cu

	R
a	C_2H_5
b	C_5H_{11}

about 25 nm compared with 1,4,8,11,15,18,22,25-octakis-(octyloxy)-CuPc because of electron donation of the phenylthio groups [9]. Compounds **3** were soluble in aromatic hydrocarbons, haloalkanes, aryl halides and acetone. Alkoxy and phenylthio groups caused substantial disruption of the strong lattice forces of the parent Pc to lead to high solubility. The solubility of **3a** and **3b** in acetone at 20° were 6.7 x 10^{-6} and 2.0 x 10^{-4} mole/ℓ, respectively. Compound **3b** was more soluble than **3a**. The combination of strong near infrared absorption and the solubility in organic solvents, which are characteristics of the dyes examined in this study, is excellent for exploitation in a recording device using a semiconductor laser [7]. The thermal behavior of **3** was investigated by TG-DTA and DSC under a nitrogen atmosphere at a heating rate of 10°/minute. Their thermograms exhibited endothermic peaks before decomposition, **3a**, 217°; **3b**, 123°. Based on the phase transitions as they were not accompanied by a weight loss.

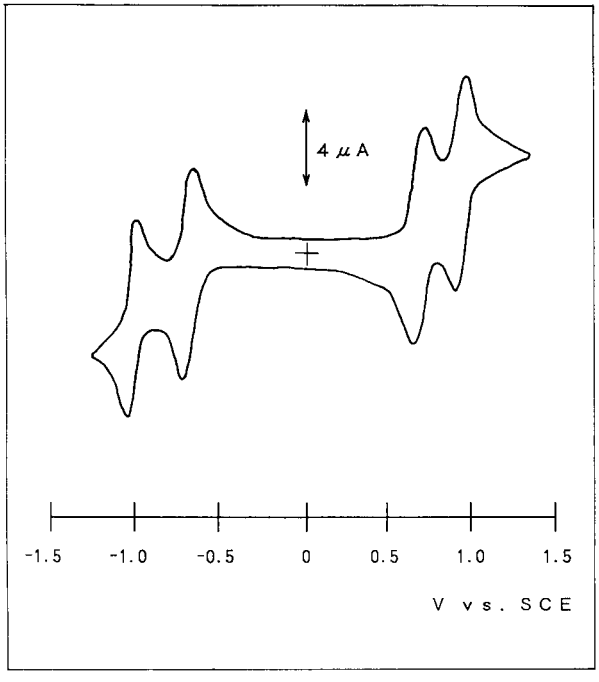


Figure. Cyclic voltammogram of **3a** (1.25 x 10^{-3} mole/ℓ) in methylene chloride containing 0.1 mole/ℓ of TBAP. Scan rate = 100 mV/s.

In the electrochemical measurements, the stability limits of methylene chloride with tetra-*n*-butylammonium perchlorate (TBAP) (0.1 mole/ℓ) were +1.7 to −1.7V *vs.* the saturated calomel electrode (SCE). In the working potential window, two reduction and two oxidation peaks of **3** were observed. Cyclic voltammograms of **3a** and **3b** were almost identical. A typical cyclic voltammogram of **3a** at 100 mV/s in methylene chloride containing TBAP (0.1 mole/ℓ) is shown in the Figure. From its general shape, **3a** appear to be reversible, four reduction-oxidation peaks corresponding to dianion/monoanion, monoanion/neutral molecule, neutral molecule/monocation and monocation/dication processes were observed. The values of the peak potentials obtained at several scan rates are given at −1.08, −0.74, 0.75 and 1.00 V *vs.* SCE, respectively. The cyclic voltammogram of **3a** did not change by repeated potential sweeps in the range of −1.0 to 1.7 V.

EXPERIMENTAL

The ir, ms and electronic absorption spectra were measured with a Perkin-Elmer FTIR-1640, a Shimadzu QP-1000 or a JEOL DX303 and a Shimadzu UV-2100 spectrometers, respectively. The FAB-ms spectra were obtained using *m*-nitrobenzyl alcohol as the viscous matrix. The ^{1}H-nmr spectra were recorded with a JEOL PMX60Si with TMS as the internal standard. Thermal properties were measured by the use of a Rigaku TG-DTA and a Seiko Denshi DSC. Solubility in acetone at 20° was calculated from the molecular extinction coefficients [11,12].

Electrochemical Measurements.

The solvent, methylene chloride, was washed with sulfuric acid and distilled. Fresh distillate was used for the measurements. The supporting electrolyte, TBAP, was recrystallized twice from ethyl acetate-hexane (5:1), and dried under vacuum at 100° for 20 hours before use. The concentrations of **3a** and **3b** were 1.25 x 10^{-1} mole/ℓ and 1.10 x 10^{-1} mole/ℓ containing 0.1 mole/ℓ TBAP, respectively. The electrochemical measurements were carried out under a nitrogen atmosphere at 20° with a Nichikakeisoku NP-G1002E potentio/galvanostat and a Rikadenki X-Y recorder RW-21. The SCE reference electrode, the platinum wire working electrode and the counter electrode were set in an electrochemical cell. Scan rates were 50, 100, 200 mV/s.

3,6-Diethoxy-4,5-bis(phenylthio)-1,2-benzenedicarbonitrile **2a**.

The benzenethiolate ion was generated from diphenyl disulfide (4.00 g, 18.3 mmoles) with sodium borohydride (0.800 g, 21.0 mmoles) in dry DMF (20 ml) under a nitrogen atmosphere [10]. After the solution was heated at 60° for 15 minutes, **1a** (4.00 g, 14.0 mmoles) in dry DMF (80 ml) was added. The mixture was heated at 65° for 22 hours. The product was extracted with chloroform, the organic layer was washed with water, dried over magnesium sulfate and evaporated to dryness. The residue was purified by chromatography over silica gel using chloroform as the eluent. The fraction was recrystallized from chloroform-hexane (3:1) to give pale yellow prisms of **2a** (1.84 g, 30%), mp 130-131°; ir (potassium bromide): 3071 (C-H), 2979-2885 (C-H), 2231 (C≡N), 1235 (C-O-C), 1025 (C-O-C), 752 (C-H), 700 (C-H) cm^{-1}; ^{1}H-nmr (carbon tetrachloride): δ = 1.28 (t, J = 6.4 Hz, 6H, CH_3), 4.10 (q, J = 7.0 Hz, 4H, CH_2), 6.90-7.30 (m, aromatic, 10H); ms: m/z 432 (M^+).

Anal. Calcd. for $C_{24}H_{20}N_2O_2S_2$ (MW 432.57): C, 66.64; H, 4.66; N, 6.48. Found: C, 66.41; H, 4.77; N, 6.48.

3,6-Bis(pentyloxy)-4,5-bis(phenylthio)-1,2-benzenedicarbonitrile **2b**.

The same procedure gave **2b** as yellow needles, yield 17%, mp 50-51°; ir (potassium bromide): 3071 (C-H), 2960-2856 (C-H), 2224 (C≡N), 1235, (C-O-C), 1044 (C-O-C), 739 (C-H), 684 (C-H) cm^{-1}; ^{1}H-nmr (carbon tetrachloride): δ = 0.93 (t, J = 6.0 Hz, 6H, CH_3), 1.10-1.90 (m, 12H, C_3H_6), 4.10 (t, J = 6.6 Hz, 4H, CH_2), 6.90-7.30

(m, aromatic 10H); ms: m/z 516 (M^+).

Anal. Calcd. for $C_{30}H_{32}N_2O_2S_2$ (MW 516.73): C, 69.73; H, 6.24; N, 5.42. Found: C, 69.46; H, 6.27; N, 5.28.

1,4,8,11,15,18,22,25-Octaethoxy-2,3,9,10,16,17,23,24-octakis-(phenylthio)phthalocyaninato Copper(II) **3a**).

A solution of 3,6-diethoxy-4,5-bis(phenylthio)-1,2-benzenedicarbonitrile **2a** (0.50 g, 1.2 mmoles), copper(I) chloride (0.038 g, 0.39 mmole) and DBU (0.27 g, 1.8 mmoles) in ethanol (5 ml) was refluxed under a nitrogen atmosphere for 10 hours. Methanol was added and the precipitate was filtered, washed with dilute hydrochloric acid and water, purified by chromatography over silica gel using toluene as the eluent, and recyrstallized from toluene-methanol (1:1) to give greenish plates **3a** (21 mg, 4%), mp 305° dec; ir (potassium bromide): 3051 (C-H), 1578, 1477, 1419, 1215 (C-O-C), 1024 (C-O-C), 753 (C-H), 701 (C-H); uv-vis (toluene): λ max 368 (log ε 4.57), 690 (4.59), 774 (5.31); ms: (FAB, *m*-nitrobenzyl alcohol) m/z 1791 (M^+).

Anal. Calcd. for $C_{96}H_{80}N_8O_8S_8Cu$ (MW 1793.81): C, 64.28; H, 4.50; N, 6.25. Found: C, 64.18; H, 4.67; N, 6.12.

1,4,8,11,15,18,22,25-Octakis(pentyloxy)-2,3,9,10,16,17,23,24-octakis(phenylthio)phthalocyaninato Copper(II) **3b**.

The same procedure gave **3b** as greenish plates, yield 48%, mp 285° dec; ir (potassium bromide): 3051 (C-H), 2953-2867 (C-H), 1584, 1478, 1419, 1219 (C-O-C), 1107 (C-O-C), 735 (C-H), 687 (C-H); uv-vis (toluene): λ max 368 (log ε 4.69), 692 (4.70), 777 (5.39); ms: (FAB, *m*-nitrobenzyl alcohol) m/z 2127 (M^+).

Anal. Calcd. for $C_{120}H_{128}N_8O_8S_8Cu$ (MW 2130.46): C, 67.65; H, 6.06; N, 5.26. Found: C, 67.35; H, 6.16; N, 5.13.

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