Synthesis and behavior of novel phthalocyanines possessing intramolecular crown ether bridges between their different aromatic rings for effective extraction multi metal inclusion

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Abstract

Novel Cu- and Co-phthalocyanines (7a–e, 8a, b) possessing intramolecular crown ether bridges between their different aromatic rings were successfully synthesized from the reaction of the corresponding bisphthalonitriles (6a–e) bearing polyethyleneoxy chains in the presence of CuCl and CoCl₂, respectively. As 1,8-diazabicyclo [5.4.0]-7-undecene (DBU) was used as a base in n-pentanol at reflux temperature for 30 h under N₂ atmosphere, these new phthalocyanines were found to be characteristic of satisfactory solubility in some of organic solvents, and showed strong absorption bands in ultraviolet and visible wave length region (λ_max ≈ 719–739 nm). Extraction experiment of metal chlorides (NaCl, KCl, MgCl₂, CaCl₂, CeCl₃, ZnCl₂, FeCl₃) in chloroform was carried out by using Cu-phthalocyanine (7b) bearing two intramolecular bridges with tri(ethyleneoxy) chains. Among these metal salts, 7b formed a complex (9b) with only FeCl₃, which showed a dark-red amorphous solid. Spectroscopic analysis of the complex (9b) indicated that original strong absorption bands near 738 nm characteristic for phthalocyanines completely disappeared, and new two strong bands appeared near 799–853 nm. FAB-MASS spectrum of the complex (9b) showed that new strong peaks came out in the region centered at m/z = 1879 and 1881 besides original peaks in the region centered at 1488, which corresponded to molecular peak of the starting phthalocyanine (7b). These facts indicated that the complex (9b) included two molecules of FeCl₃ into the protonated crown ether bridges of the phthalocyanine skeleton. Furthermore, it was found that the complex (9b) was transformed to the original phthalocyanine (7b) quantitatively by treatment with triethylamine. © 2005 Elsevier Ltd. All rights reserved.

Keywords: Cu-phthalocyanine; Co-phthalocyanine; bisphthalonitrile; Crown ether bridge; Metal chloride/phthalocyanine complex; FeCl₃ selective including; UV red-shift; FAB-MASS; Amorphous

1. Introduction

Phthalocyanines have been well-known as color materials with high molecular absorption constants in visible and UV spectra, possessing some of excellent features of anti-chemicals, heat-resistance, and anti-oxidation. Thus, phthalocyanines have been used only for pigment or dyestuff. Because of their insolubility to organic solvent, their application was considerably limited [1]. Since phthalocyanine derivatives soluble in organic solvent have been developed in recent years, usages of the colorstuffs have been largely increased. In addition, importance of such derivatives has been found in organic functional materials for information technology, semiconductors, and photosensitizers. Phthalocyanines with novel and high functionalities developed by improvement of behaviors on photochemical absorption and conductivity may be expected to possess much potentiality as high performance materials for information technology.

On the other hand, crown ether compounds are known to extract specific metals or metal salts according to specific cavity size of each of crown ether [2]. For example, syntheses and some behaviors of phthalocyanines bearing crown ether rings between same aromatic rings were reported by Sielckne [3] and Kobayashi [4]. Only, spectroscopic data demonstrated that some metals were inserted between two molecules of these phthalocyanines...
in a sandwich style in a solution [5]. Furthermore, phthalocyanines bearing a 2,2-dialkyl-1,3-propanediol [6] and a binaphthol [7] groups were only synthesized, but no characteristic properties and behaviors were reported.

We have focused phthalocyanines including more than two different metals in one molecule, since such phthalocyanine seems to show interesting optical, magnetic and electronic functions. Also, no phthalocyanines bearing crown ether rings bridges between their different aromatic rings have incidentally synthesized as yet. In these phthalocyanines, the crown ether cavities may include metals or metal salts besides the central metal easier than usual crown ether rings, because nine atoms consist of a same plane to make a size of cavities relatively rigid.

In the present study, we wish to describe efficient syntheses of novel phthalocyanines bearing intramolecular two crown ether bridges between their different aromatic rings. Furthermore, successful isolation of a complex consisting of a Cu-phthalocyanine with FeCl3, in which each of two molecules of FeCl3 may be selectively included into each cavity of the two protonated crown ether rings of the starting phthalocyanine, as shown in Fig. 1.

2. Experimental section

As starting compounds, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (1), various alkyl iodides, p-toluenesulfonyl chloride, tri- and tetraethyleneglycols, 1,8-diazabicyclo[5.4.0]-7-undecene (DBU), other organic and inorganic reagents were purchased from Aldrich Chemical Co. Ltd, Tokyo Kasei Kogyo Co. Ltd or Nacalai Tesque Ltd and were used without any further purification. N,N-Dimethylformamide (DMF) was dried on CaH2, and then distilled under reduced pressure. Merk silica gel 60 was used for column chromatography.

1H- and 13C NMR spectra were measured by a JEOL JNM-EX-400 (400 and 100 MHz) spectrometer or a JEOL JNM-GX-270 (270 and 67.8 MHz) spectrometer, respectively, with TMS as an internal standard. IR spectra were measured by a JASCO IR-810 spectrometer or JASCO FT/IR-400 Plus spectrometer. Mass spectra were obtained using a Shimadzu GC-14B or GC-18A with FID using a capillary column packed with DB-17. The apparatus of elemental analysis was Yanaco CHN CORDER MT-6. Melting point was measured by a Yanaco MP-J3

2.1. 2,3-Dichloro-5,6-dicyano-1,4-hydroquinone (2)

Treatment of 1 (35.0 g, 0.154 mol) with Na2S2O4 aq. (40.0 g, 0.23 mol in 500 ml water) in toluene was carried out at room temperature for 20 min. Resultant product was filtrated by Nutsche funnel, and was washed by water and hexane. Compound 2 was obtained as a white powder (31.7 g, Y=90%).

IR (KBr, cm\(^{-1}\)): 3220, 2260, 1580, 1460, 1360, 1280, 1200, 1080, 890, 780, 750, 700; \(^{1}\)H NMR (400 MHz, d6-DMSO) \(\delta\): 3.40 (brs, 2H, OH); 13CN MR (d6-DMSO) \(\delta\): 148.89, 127.24, 111.78, 99.64; APCI-MS \(m/z\) (%): 230

2.2. General procedure for synthesis of 2,3-dichloro-5,6-dicyano-4-alkoxyhydroquinone (3a–d)

A mixture of 2 (22.9 g, 100 mmol), K2CO3 (27.6 g, 200 mmol), propyl iodide (110 mmol) in DMF was stirred at 70–80 °C for 30 h. Resultant product was extracted by ethyl acetate, and was washed by brine. Extracted organic layer was dried by anhydrous MgSO4. Solvent of organic layer was evaporated by rotary evaporator. Product was purified by column chromatography using hexane:ethyl acetate (1:3) as a developing solvent. All the products with propyl, pentyl and octyl chains were identified by comparison of their spectroscopic behaviors (IR, \(^{1}\)H NMR, \(^{13}\)C NMR, MASS) with those of authentic samples [8].

2.2.1. 2,3-Dichloro-5,6-dicyano-4-n-propoxyhydroquinone (3a) [8]

Cream-color powder, Y=66%. IR (KBr, cm\(^{-1}\)) : 3330, 2950, 2880, 2240, 1560, 1450, 1390, 1340, 1250, 1190, 1080, 1010, 960, 900, 780; \(^{1}\)H NMR (400 MHz, d6-DMSO) \(\delta\): 3.82 (t, \(J=6.6\) Hz, 2H, Ar-OCH2CH2CH3), 1.72–1.70 (m, 2H, -CH2-), 0.98 (t, \(J=6.6\) Hz, 3H, -CH3); \(^{13}\)C NMR (d6-DMSO) \(\delta\): 148.89, 127.24, 111.78, 99.64; APCI-MS \(m/z\) (%): 269 (M\(^+\))
2.2.2. 2,3-Dichloro-5,6-dicyano-4-n-pentyloxyhydroquinone (3b) [8]

Cream-color powder, Y = 63%. IR (KBr, cm⁻¹): 3350, 2950, 2860, 2230, 1560, 1440, 1390, 1240, 1260, 1190, 1080, 1000, 960, 900, 780; ¹H NMR (400 MHz, d₆-DMSO) δ: 3.88 (t, J = 6.8 Hz, 2H, Ar-OCH₂CH₂CH₃), 1.72 (quint, J = 6.8 Hz, 2H, -CH₂-), 1.44–1.35 (m, 4H, -CH₂-), 0.91 (t, J = 6.8 Hz, 2H, -CH₃); ¹³C NMR (d₆-DMSO) δ: 165.19, 141.42, 132.22, 131.80, 118.14, 114.61, 106.12, 94.97, 75.21, 29.04, 27.43, 21.83, 13.82; APCI-MS m/z (%): 297 (M⁺)

2.2.3. 2,3-Dichloro-5,6-dicyano-4-isopentyloxyhydroquinone (3c) [8]

Cream-color powder, Y = 78%. IR (KBr, cm⁻¹): 3340, 2950, 2870, 2250, 1560, 1450, 1390, 1340, 1260, 1200, 1080, 1040, 1000, 950, 900, 780; ¹H NMR (400 MHz, d₆-DMSO) δ: 4.10 (t, J = 6.6 Hz, 2H, Ar-OCH₂CH₂CH₃), 1.85–1.82 (m, 1H, (CH₃)₂CH-), 1.66 (quint, J = 6.6 Hz, 2H, -CH₂-), 0.93 (d, J = 6.6 Hz 6H, -CH₃); ¹³C NMR (d₆-DMSO) δ: 154.66, 150.87, 133.88, 129.15, 113.47, 113.07, 108.35, 101.77, 74.11, 38.17, 24.23, 22.33; APCI-MS m/z (%): 297 (M⁺)

2.2.4. 2,3-Dichloro-5,6-dicyano-4-octyloxyhydroquinone (3d) [8]

Cream-color powder, Y = 75%. IR (KBr, cm⁻¹): 3300, 2950, 2860, 2230, 1560, 1440, 1390, 1340, 1260, 1190, 1080, 1000, 960, 900, 780; ¹H NMR (270 MHz, d₆-DMSO) δ: 4.16 (t, J = 6.6 Hz, 2H, Ar-OCH₂CH₂CH₂-), 1.87 (quint, J = 6.6 Hz, 2H, -CH₂-), 1.53–1.48 (m, 4H, -CH₂CH₃), 0.89 (t, J = 6.6 Hz, 3H, -CH₃); ¹³C NMR (d₆-DMSO) δ: 165.19, 141.42, 132.22, 131.80, 118.14, 114.61, 106.12, 94.97, 75.21, 29.04, 27.43, 21.83, 13.82; APCI-MS m/z (%): 340 (M⁺)

2.3. Procedure for preparation of 1,8-bis(p-tosyloxy)-3,6-dioxaoctane (5a) [9]

A solution of p-toluene sulfonic chloride (41.94 g, 0.22 mol) in dichloromethane (60 ml) was added dropwise to a mixture of tetraethylene glycol 4b (15.02 g, 0.1 mol), pyridine (18.96 g, 0.24 mol) and dichloromethane (40 ml) at −5 to 5 °C. The experimental procedure was followed in the similar manner to that of 5a. Compound 5b was isolated by column chromatography using hexane:ethyl acetate (1:1), and was obtained as a colorless liquid (38.7 g, Y = 62%).

IR (KBr, cm⁻¹): 2900, 1600, 1450, 1350, 1170, 1010, 920, 810, 770, 660; ¹H NMR (400 MHz, d₆-DMSO) δ: 7.79 (d, J = 8.3 Hz, 4H, ArTs), 7.34 (d, J = 8.3 Hz, 4H, ArTs), 4.15 (t, J = 4.9 Hz, 4H, OCH₂-), 3.68 (t, J = 4.9 Hz, 4H, OCH₂-), 3.56 (s, 8H, OCH₂-), 2.45 (s, 6H, -CH₃); ¹³C NMR (d₆-DMSO) δ: 144.79, 132.87, 129.78, 127.91, 70.65, 70.47, 69.21, 68.61, 21.59; APCI-MS m/z (%): 503 (M⁺)

2.5. General procedure for synthesis of 1,8-bis(2',3'-dichloro-5',6'-dicyano-4'-alkoxyphenoxo)-3,6-dioxaentane (6a–e)

A mixture of 3a (4.16 g, 15.4 mmol), K₂CO₃ (4.84 g, 35 mmol), triethylene glycol ditosylate (3.21 g, 7 mmol) in CH₃CN (250 ml) was stirred under reflux condition for 90 h. After the removal of CH₃CN with reduced pressure, product was extracted by ethyl acetate, and was washed by brine. Extracted organic layer was dried by anhydrous MgSO₄. Ethyl acetate was evaporated by rotary evaporator. Product was purified by column chromatography using hexane:ethyl acetate (5:2). Compound 6a was obtained as a colorless powder (0.87 g, 19%). Similar manners were carried out for products 6b–6e. All the products were identified as follows.

2.5.1. 1,8-Bis(2',3'-dichloro-5',6'-dicyano-4'-n-propoxyphenoxo)-3,6-dioxaentane (6a)

Y = 19%; mp 105–108 °C. IR (KBr, cm⁻¹): 2970, 2230, 1430, 1390, 1350, 1250, 1140, 1020, 940, 840, 780; ¹H NMR (400 MHz, d₆-DMSO) δ: 4.40 (t, J = 4.4 Hz, 4H, OCH₂-), 4.18 (t, J = 6.8 Hz, 3H, Ar-OCH₂CH₂CH₃), 4.13 (t, J = 6.8 Hz, 2H, Ar-OCH₂CH₂CH₃), 3.88 (t, J = 4.4 Hz, 4H, OCH₂-), 3.68 (s, 4H, OCH₂-), 1.91 (sexet, 6H, J = 6.8 Hz, 4H, -CH₂-); ¹³C NMR (d₆-DMSO) δ: 155.35, 155.31, 135.19, 135.03, 112.20, 109.37, 108.64, 75.12, 70.73, 70.31, 23.33; APCI-MS m/z (%): 656 (M⁺); Anal. calc'd for C₂₃H₂₀O₃N₃: C 51.24, H 3.99, N 8.54; found: C 50.98, H 3.97, N 8.29.

2.5.2. 1,8-Bis(2',3'-dichloro-5',6'-dicyano-4'-n-pentyloxyphenoxo)-3,6-dioxaentane (6b)

Y = 60%; mp 79–80 °C. IR (KBr, cm⁻¹): 2950, 2240, 1420, 1360, 1240, 1120, 1030, 950, 780; ¹H
NMR (400 MHz, d<sub>6</sub>-DMSO) δ: 4.42 (t, J = 4.4 Hz, 4H, OCH<sub>2</sub>-), 4.21 (t, J = 4.0 Hz, 4H, Ar-OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 3.88 (t, J = 4.4 Hz, 4H, OCH<sub>2</sub>-), 3.68 (s, 4H, OCH<sub>2</sub>-), 1.91 (quint, 4H, J = 6.8 Hz, 4H, -CH<sub>2</sub>-); 1.54–1.37 (m, 8H, -CH<sub>2</sub>-), 0.95 (t, J = 6.8 Hz, 6H, -CH<sub>3</sub>); 13<sup>C</sup> NMR (d<sub>6</sub>-DMSO) δ: 154.94, 154.89, 134.72, 134.63, 114.81, 109.87, 108.31, 74.82, 70.33, 69.92, 29.23, 27.29, 21.94, 13.56; APCl-MS m/z (%): 713 (M<sup>+</sup>); Anal. calcld. for C<sub>39</sub>H<sub>46</sub>Cl<sub>4</sub>N<sub>4</sub>O<sub>6</sub>: C 53.95, H 4.81, N 7.86; found: C 53.76, H 4.81, N 7.68.

2.5.3. <sup>1</sup>H NMR (270 MHz, d<sub>6</sub>-DMSO) δ: 4.40 (t, J = 4.5 Hz, 4H, OCH<sub>2</sub>-), 4.24 (t, J = 6.6 Hz, 3H, Ar-OCH<sub>2</sub>CH<sub>3</sub>), 4.19 (t, J = 6.6 Hz, 1H, Ar-OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 3.88 (t, J = 4.5 Hz, 4H, OCH<sub>2</sub>-), 3.69 (s, 4H, OCH<sub>2</sub>-), 1.89 (octet, J = 6.6 Hz, 2H, (CH<sub>3</sub>)<sub>2</sub>CH); 1.78 (q, J = 6.6 Hz, 4H, (CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>); 0.99 (d, J = 6.6 Hz, 12H, -CH<sub>3</sub>); 13<sup>C</sup> NMR (d<sub>6</sub>-DMSO) δ: 155.25, 155.15, 153.10, 134.92, 112.13, 108.95, 75.24, 75.12, 70.73, 70.31, 38.65, 24.74, 22.53; APCl-MS m/z (%): 713 (M<sup>+</sup>); Anal. calcld. for C<sub>39</sub>H<sub>46</sub>Cl<sub>4</sub>N<sub>4</sub>O<sub>6</sub>: C 53.95, H 4.81, N 7.86; found: C 53.76, H 4.81, N 7.68.

2.5.4. <sup>1</sup>H NMR (270 MHz, d<sub>6</sub>-DMSO) δ: 4.40 (t, J = 4.3 Hz, 4H, OCH<sub>2</sub>-), 4.20 (t, J = 6.6 Hz, 3H, Ar-OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 4.16 (t, J = 6.6 Hz, 1H, Ar-OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 3.88 (t, J = 4.3 Hz, 4H, OCH<sub>2</sub>-), 3.69 (s, 4H, OCH<sub>2</sub>-), 1.88 (quint, J = 6.6 Hz, 2H, Ar-OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>); 1.50 (m, 4H, -CH<sub>2</sub>-), 1.31 (m, 16H, -CH<sub>2</sub>-), 0.89 (t, J = 6.6 Hz, 6H, -CH<sub>3</sub>); 13<sup>C</sup> NMR (d<sub>6</sub>-DMSO) δ: 155.25, 155.16, 135.10, 134.91, 112.16, 109.33, 108.59, 75.14, 70.30, 31.84, 30.02, 29.29, 25.66, 22.71, 14.19; APCl-MS m/z (%): 797 (M<sup>+</sup>); Anal. calcld. for C<sub>39</sub>H<sub>46</sub>Cl<sub>4</sub>N<sub>4</sub>O<sub>6</sub>: C 53.95, H 4.81, N 7.86; found: C 53.76, H 4.81, N 7.68.

2.5.5. <sup>1</sup>H NMR (400 MHz, d<sub>6</sub>-DMSO) δ: 4.41 (t, J = 4.4 Hz, 4H, OCH<sub>2</sub>-), 4.21 (t, J = 6.8 Hz, 4H, Ar-OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 3.89 (t, J = 4.4 Hz, 4H, OCH<sub>2</sub>-), 3.89 (t, J = 4.4 Hz, 4H, OCH<sub>2</sub>-), 3.69–3.60 (m, 8H, OCH<sub>2</sub>-), 1.89 (quint, J = 6.8 Hz, 4H, -CH<sub>2</sub>-CH<sub>2</sub>CH<sub>3</sub>); 1.54–1.38 (m, 8H, -CH<sub>2</sub>-), 0.95 (t, J = 6.8 Hz, 6H, -CH<sub>3</sub>); 13<sup>C</sup> NMR (d<sub>6</sub>-DMSO) δ: 155.35, 153.17, 135.01, 112.19, 109.33, 108.64, 75.15, 70.75, 70.47, 70.25, 29.60, 27.64, 22.30, 13.93; APCl-MS m/z (%): 757 (M<sup>+</sup>); Anal. calcld. for C<sub>34</sub>H<sub>40</sub>Cl<sub>4</sub>N<sub>4</sub>O<sub>6</sub>: C 53.14, H 5.07, N 7.02.

2.6. General procedure for synthesis of 2,3,9,10,16,17,23,24-Octachloro-4,8,12-tetraalkoxy-1,5:11,15-bis(3<sup>′</sup>,3<sup>′</sup>,6<sup>′</sup>,6<sup>′</sup>-dioxaetoate- and 3<sup>′</sup>,3<sup>′</sup>,6<sup>′</sup>,6<sup>′</sup>-trioxanodecanes-1<sup>′</sup>,8<sup>′</sup>- and -1<sup>′</sup>,11<sup>′</sup>-dioxy) phthalocyaninato copper(II) (7a–e)

A mixture of 6a–e (1 mmol), 1,8-diazabicyclo[5.4.0]7-undecene (0.30 g, 2 mmol), and CuCl (0.07 g, 0.7 mmol) in n-pentanol (15 ml) was stirred under reflux condition for 30 h under nitrogen. After the reaction, methanol was added to reaction mixture. Resultant precipitate was filtered by suction filter. And then, product was purified by column chromatography using chloroform:ethanol (20:1). All the products with different length of alkyl chains were identified by spectroscopic methods (IR, UV, FAB-MASS), and elemental analysis as follows.
55.10, H 5.60, N 6.76; found: C 55.06, H 5.67, N 7.32; mp > 300 °C; FAB-MS m/z (%): 1657.1 (M+).

2.6.5. 2,3,9,10,16,17,23,24-Octachloro-4,8,18,22-tetra-n-pentyloxy-1,25:11,15-bis(3′,6′,9′-trioxaoctane-1′,11′-dioxy) phthalocyaninato copper(II) (7e)

Green amorphous solid, Y = 60%. IR (KBr, cm⁻¹): 2950, 2850, 1650, 1560, 1430, 1220, 1110, 1040, 960, 790; UV–vis (chloroform) λmax nm (log ε): 327 (4.62), 348 (4.61), 663 (4.45), 739 (5.04); Anal. calcd for C₆₈H₇₆Cl₈CuN₈O¹₄: C 51.80, H 4.86, N 7.55; found: C 51.31, H 4.72, N 7.86; mp > 300 °C; FAB-MS m/z (%): 1576.5 (M+).

2.7. General procedure for synthesis of 2,3,9,10,16,17,23,24-octachloro-4,8,18,22-tetra-n-pentyloxy-1,25:11,15-bis(3′,6′,9′-trioxaoctane-1′,8′- and -1′,11′-dioxy) phthalocyaninato cobalt(II) (8a, b)

A mixture of 6b or 6e (1 mmol), 1,8-diazabicyclo[5.4.0]-7-undecene (0.30 g, 2 mmol), and CoCl₂ (0.09 g, 0.7 mmol) in n-pentanol (15 ml) was stirred under reflux condition for 30 h under nitrogen. After the reaction, methanol was added to reaction mixture. Produced precipitate was filtrated by suction filter, and then product was purified by column chromatography using chloroform:ethanol (20:1). The products of 8a and 8b were identified by spectroscopic methods (IR, UV, FAB-MASS), and elemental analysis.

2.7.1. 2,3,9,10,16,17,23,24-Octachloro-4,8,18,22-tetra-n-pentyloxy-1,25:11,15-bis(3′,6′,9′-trioxaoctane-1′,8′-dioxy) phthalocyaninato cobalt(II) (8a)

Dark blue amorphous solid, Y = 35%. IR (KBr, cm⁻¹): 2930, 2850, 1540, 1430, 1260, 1220, 1100, 1040, 960, 790; UV–vis (chloroform) λmax nm (log ε): 318 (4.76), 651 (4.57), 721 (4.98); Anal. calcd for C₆₈H₇₆Cl₈CoN₈O¹₄: C 51.96, H 4.87, N 7.13; found: C 51.49, H 5.09, N 7.39; mp > 300 °C; FAB-MS m/z (%): 1571.9 (M+).

2.7.2. 2,3,9,10,16,17,23,24-Octachloro-4,8,18,22-tetra-n-pentyloxy-1,25:11,15-bis(3′,6′,9′-trioxaoctane-1′,11′-dioxy) phthalocyaninato cobalt(II) (8b)

Dark blue amorphous solid, Y = 36%. IR (KBr, cm⁻¹): 2930, 2850, 1600, 1430, 1330, 1260, 1220, 1100, 1030, 950, 790; UV–vis (chloroform) λmax nm (log ε): 318 (4.76), 651 (4.57), 721 (4.98); Anal. calcd for C₆₈H₇₆Cl₈CoN₈O¹₄: C 51.96, H 4.87, N 7.13; found: C 51.49, H 5.09, N 7.39; mp > 300 °C; FAB-MS m/z (%): 1571.9 (M+).

2.8. Procedure for formation of a complex (9b) of FeCl₃ with 2,3,9,10,16,17,23,24-octachloro-4,8,18,22-tetra-n-pentyloxy-1,25:11,15-bis(3′,6′,9′-trioxaoctane-1′,8′-dioxy) phthalocyaninato copper(II) (7b)

An amount of ferric chloride (FeCl₃; 0.34 g, 2.1 mmol) was added into chloroform solution containing Cu-phthalocyanine (7b; 1.04 g, 0.7 mmol), and the solution was stirred at room temperature overnight. Then, after evaporation of chloroform under reduced pressure, the resulting solid was

Scheme 1. Synthesis route of phthalocyanines (7a–e, 8a, b) bearing intramolecular polyethyleneoxy bridges between their different aromatic rings.
poured into toluene. After stirring the suspension solution at room temperature for 3 h, unsolved precipitation was filtered off through disposal filter with mesh size of 4.0 µm. After the filtrate was dried in vacuo, the solid obtained was washed with toluene on suction filter. Then, the resulting solid was purified by re-crystallization from a mixed solvent of toluene and hexane. Dark-red solid was filtered with suction, washed and dried at vacuum. The solid obtained (0.13 g, Y = 10%) was tentatively characterized by spectroscopic methods (IR, UV, FAB-MASS).

IR (KBr, cm⁻¹): 3223, 2956, 2933, 2870, 1780, 1705, 1614, 1465, 1427, 1373, 1354, 1240, 1112, 1074, 1021, 954, 841; UV–vis (chloroform) λmax (nm): 324, 357, 513, 799, 853; FAB-MS m/z (%): 1879, 1881 (M⁺).

3. Results and discussion

3.1. Synthesis of phthalocyanines bearing intramolecular crown ether bridges between different aromatic rings

Novel phthalocyanines bearing intramolecular crown ether bridges were successfully synthesized according to the reaction scheme, as shown in Scheme 1.

The compounds, 2,3-dichloro-5,6-dicyano-1,4-hydroquinone monoalkyl ethers (3a–d), were prepared in 63–78 yields by monoalkylation of 2,3-dichloro-5,6-dicyano-1,4-hydroquinone (DDHQ) (2), obtained by reduction of the corresponding 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (1) with Na₂S₂O₄, with the corresponding alkyl iodide in the presence of anhydrous K₂CO₃ as a base in DMF at 70–80 °C for 30 h. The result was shown in Table 1.

Then, the remaining hydroxyl group of the hydroquinone monoalkyl ether was alkylated with ditosylates (5a, b) of tri- and tetra(ethylene) glycol (4a, b) in the presence of anhydrous K₂CO₃ as a base in CH₃CN at reflux to give the corresponding bisphthalonitriles (6a–e), respectively. Here, two hydroquinone rings were connected with tri- and tetra(ethyleneoxy) groups via the reaction of ether bond formation in about 44–60% yield. The result of the coupling reaction was summarized in Table 2.

Finally, Cu-phthalocyanines bearing intramolecular crown ether bridges between their different aromatic rings 7a–e were successfully prepared from the corresponding bisphthalonitriles 6a–e in the presence of CuCl using 1,8-diazabicyclo[5.4.0]-7-undecane (DBU) as a base in n-pentanol at reflux temperature for 30 h under nitrogen atmosphere. The resulting crude phthalocyanines 7a–e were purified by column chromatography followed by recrystallization in chloroform and methyl alcohol. The manner formed green amorphous solids 7a–e, as shown in Table 3.

In a similar manner, Co-phthalocyanines possessing crown ether bridges between their different aromatic rings (8a, b) were also synthesized from the corresponding...
bisphthalonitriles, Here, CoCl₂ was used instead of CuCl for the Co-phthalocyanine (Table 4).

Some attempts to prepare the corresponding metal-free phthalocyanines by some reductive methods have unfortunately resulted in failures possibly because of much instability of the metal-free ones.

3.2. Behaviors of absorptivity of phthalocyanines (7a–e, 8a, b)

It was found that all the Cu- and Co-phthalocyanines (7a–e, 8a, b) obtained in this study were able to dissolve into some of organic solvents such as chloroform, dichloromethane and toluene but insoluble in those such as ethyl acetate, diethyl ether and hexane. Their identification was carried out through spectroscopic methods (IR, UV, and FAB-MASS) and elemental analysis. Fig. 2 shows absorption spectra of Cu- and Co-phthalocyanines in chloroform. In 250–900 nm, soret bond in the ultraviolet region and Q band in near-infrared region were observed. It was noted that Cu- and Co-phthalocyanines showed strong characteristic absorption bands at λmax = 739 and 719 nm, respectively, in the Q-band (Table 5).

Comparison of absorption spectra of Cu-phthalocyanine was made in differences of alkoxy groups and length of polyethyleneoxy groups of 7a–e. Little influences were observed on difference in wavelength of maximum absorption of these Cu-phthalocyanine. This suggested that these alkyl chains had no influence of Cu-coordinate bond of the phthalocyanine. In difference of chemical structure in their central metals, the resultant absorption spectra of Cu- and Co-phthalocyanines having n-pentyl group led to some difference in wavelength of Q-bands. These was tendency of blue shift of the solet and Q bands of Co-phthalocyanine relative to those of Cu-phthalocyanine.

On the other hand, it is quite interesting to include two different metals in one molecule of the phthalocyanines bearing intramolecular crown ether bridges between their different aromatic rings. Thus, similar extraction nature with crown ethers would be expected for the phthalocyanine.
The extraction experiments of a variety of metal halides with phthalocyanines (7b) were carried out in a chloroform solution. Each of various metal halides such as NaCl, KCl, MgCl₂, CaCl₂, CeCl₃, ZnCl₂, and FeCl₃ was added into the chloroform solution of 7b with stirring for 24 h at room temperature. After evaporation of the solvent followed by purification, a dark-red solid was isolated only when FeCl₃ was used as metal halide. Other metal chlorides had no color change of green solid in the phthalocyanine. As shown in Fig. 3, UV spectrum of the resulting dark-red solid means extraction of FeCl₃ from its chloroform solution into phthalocyanine (7b) ring. Thus, almost complete disappearance of strong Q-band (\(\lambda_{\text{max}} = 738 \text{ nm}\)) was observed in the Cu-phthalocyanine (7b), and new appearance was seen in two new absorptions band near \(\lambda_{\text{max}} = 799\) and 853 nm region. These Q-bands were distinctly different from those of the Cu-phthalocyanine before FeCl₃ extraction as presented in Fig. 3. Therefore, the extraction of FeCl₃ by the phthalocyanine perturbed the phthalocyanine ring coordinate with changing its \(\pi\)-conjugate band.

Furthermore, in order to confirm this, FAB-MASS spectrum of the complex (9b) was observed. It was found that new strong peaks came out in the region centered at \(m/z = 1879\) and 1881 besides original peaks in the region centered at 1488. These facts supported that two molecules of FeCl₃ were included into each of crown ether rings with the two protonated forms in the phthalocyanine skeleton as shown in the complex (9b) (Fig. 4). Namely it was reasonable that the iron inclusion changed dramatically the absorption spectrum of the Cu-phthalocyanine.

We attempted treatment of excess of trimethylamine to observe spectral change of the Fe inclusion-Cu-phthalocyanine (9b). The manner changed the color of the chloroform solution from dark red to green. As shown in Fig. 3, the absorption spectrum of the treated phthalocyanine was the same as that of Cu-phthalocyanine (7b). The FAB-MASS spectrum of the treated phthalocyanine had main peak of \(m/z = 1488\) corresponding to 7b. These evidences strongly indicated that the phthalocyanine (7b) equilibrated with the complex (9b) according to the reaction inserted in Fig. 4.

4. Conclusion

In this study, novel synthetic method of phthalocyanines bearing intramolecular crown ether bridges between their different aromatic rings has been successfully developed for the first time. These phthalocyanines were identified by IR and UV spectra, FAB-MS and element analysis.

Furthermore, selective formation and isolation of a novel complex consisting of the Cu-phthalocyanine with a couple of tris(ethyleneoxy) groups and ferric chloride was accomplished by extraction experiment of metal salts by Cu-phthalocyanines in chloroform. The complex was found to show two new absorptions which were distinctly different from those of phthalocyanine itself and FeCl₃. Furthermore, FAB-MASS spectroscopy of the complex indicated that each of the two molecules of FeCl₃ was included into each of the two protonated crown ether bridges of the phthalocyanine skeleton in the complex. Treatment of the complex with triethylamine brought about quantitative transformation to the original phthalocyanine.

Further study of application of these novel phthalocyanines and their complex with metal salts is on progress.

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