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Synthesis of Cobalt Phthalocyanine Derivatives and their Cyclic Voltammograms

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ABSTRACT

Metal phthalocyanine derivatives exhibit high electron transfer abilities. Metal phthalocyanine derivatives are insoluble in most common organic solvents, a factor which has inhibited their use in functional materials using their electron transfer properties. We report here the synthesis of three kinds of cobalt phthalocyanine derivatives: cobalt phthalocyanine tetrasulfonic acids, cobalt phthalocyanine octacarboxylic acids and cobalt octakis(hexyloxymethyl)phthalocyanines, and a new type of phthalocyanine derivative, cobalt anthraquinocyanine. The electron transfer behavior of this cobalt phthalocyanine derivatives was examined with cyclic voltammetry. Cobalt phthalocyanine tetrasulfonic acid and cobalt phthalocyanine octacarboxylic acid exhibited irreversible redox behavior and the cyclic voltammograms of cobalt anthraquinocyanine exhibited properties similar to that of cobalt phthalocyanine octacarboxylic acids. © 1997 Elsevier Science Ltd

Keywords: Metal phthalocyanine derivatives, metal anthraquinocyanine, cyclic voltammetry, electron transfer.

INTRODUCTION

Metal phthalocyanines and their derivatives are potential functional materials for use as organic conductors [1], photoconductors [2], gas sensors [3] and catalysts [4]. Metal phthalocyanines and their derivatives are known to exhibit high electron transfer abilities, but can only be utilized in a few fields because of their lower solubility in common organic solvents.

The expected functions of metal phthalocyanine derivatives are almost all based on a redox or electron transfer reaction. The electron transfer of metal phthalocyanine is estimated by the electrode reaction, since they have many applications in thin layer films. The electron transfer properties of metal phthalocyanine derivatives can be utilised not only to make thin layer films but also to fix soluble ones. It is necessary, therefore, to examine the redox behavior of metal phthalocyanine derivatives in order to evaluate their use for further applications.

We have synthesized three kinds of cobalt phthalocyanine derivatives, i.e. cobalt phthalocyanine tetrasulfonic acid [5], cobalt phthalocyanine octacarboxylic acid [6] and cobalt octakis(alcoxyalkyl)phthalocyanine [7–11]. Metal octakis(alcoxyalkyl)phthalocyanines which have long alcoxyalkyl groups have been reported to exhibit thermotropic liquid crystalline behavior [12]. The cobalt octakis(alcoxyalkyl)phthalocyanine, synthesized in this work has hexyloxymethyl groups at the peripheral (2,3,9,10,16,17,23,24) positions, and we have additionally synthesized a new type of phthalocyanine derivative [13] which has four 9,10-anthraquinone (anthraquinone) units, and which is expected to possess a higher electron transfer property.

Cyclic voltammograms (CVs) were measured for the above soluble cobalt phthalocyanine derivatives and metal anthraquinocyanine in order to examine their electron transfer properties.

RESULTS AND DISCUSSION

Synthesis

Cobalt phthalocyanine tetrasulfonic acid (1)

Cobalt phthalocyanine tetrasulfonic acid (**1**) was synthesized from 4-sulfophthalic acid, the appropriate metal halide and urea, as shown in Scheme 1.

Phthalocyanine sulfonic acids can be prepared by two processes, namely, the urea synthesis method from sulfonated phthalic derivatives, and by sulfonation of the parent phthalocyanine. In this work, the former process was employed since the latter could not be controlled with respect to the number and orientation of the sulfonic acid groups.

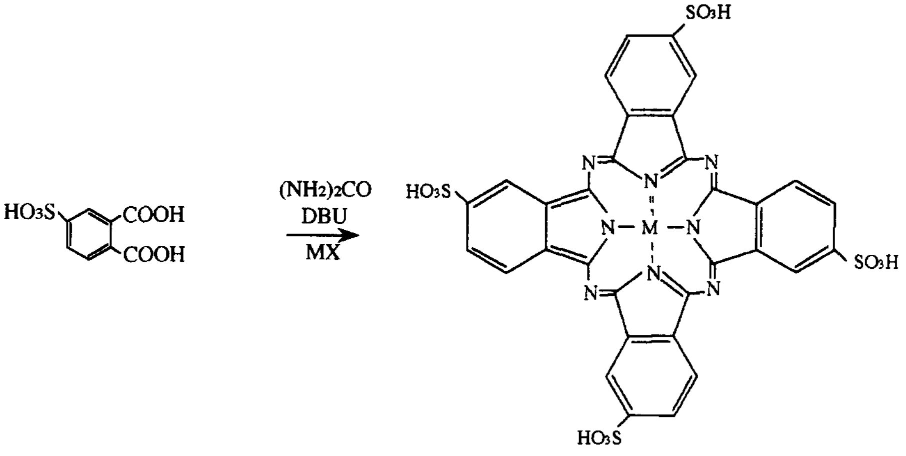
Phthalocyanine tetrasulfonic acids are prepared from monosulfonated phthalic derivatives, and the metal salts of phthalocyanine tetrasulfonic acids are water soluble [14]. Metal phthalocyanine tetrasulfonic acids have been used as dyes for natural and synthetic textile fibers.

The synthetic pathway to cobalt phthalocyanine tetrasulfonic acid (**1**) used in this study is shown in Scheme 1; IR and electronic spectral data are given in the Experimental. The position of the absorption peaks of the product is in agreement with literature data [15]. Metal phthalocyanine derivatives exhibit the strongest electron absorption peak around the 680 nm region (Q band), which can be attributed to the allowed π–π^* transition. The data obtained confirm the formation of cobalt phthalocyanine tetrasulfonic acid (**1**).

Cobalt phthalocyanine octacarboxylic acid (2)

Cobalt phthalocyanine octacarboxylic acid (**2**) was synthesized from benzene-1,2,4,5-tetracarboxylic dianhydride (pyromellitic dianhydride), metal halide and urea, as shown in Scheme 2.

In general, the synthesis of phthalocyanines starts from 1,2-benzenedicarbonitriles or 1,2-benzenedicarboxylic anhydride. The pyromellitic dianhydride used in this work gives monomeric to pentameric phthalocyanines [6]. This is because the starting material is a bifunctional reagent, bringing about polycyclotetramarization in the phthalocyanine synthesis. For this reason, the product was synthesized using the reaction conditions for the monomer preparation [6]. It has been reported that octasubstituted phthalocyanines synthesized from pyromellitic anhydride have functional groups such as carboxylic acid, imide or amide at the peripheral points [6]. The presence of these functional groups was evaluated by IR spectroscopy. The IR spectrum of the synthesized cobalt octasubstituted phthalocyanine gave a characteristic pattern of imide groups in the region of 1600–1800 cm^{-1}; the



(1)

Scheme 1

functional group was changed from imide to acid by hydrolysis with KOH, as shown by the characterization data in the Experimental.

Cobalt octakis(hexyloxymethyl)phthalocyanine (7)

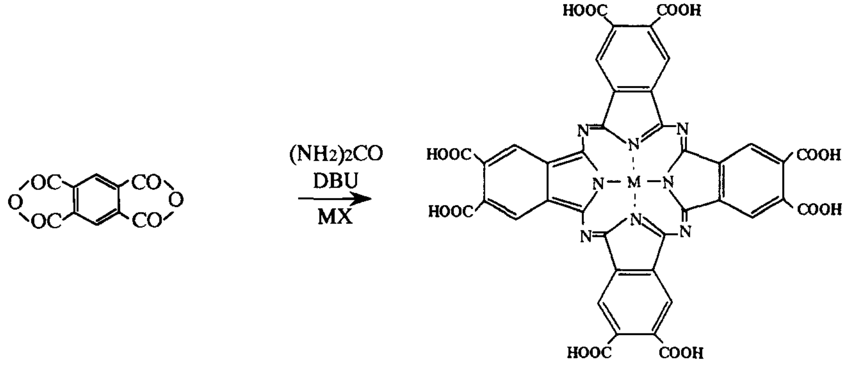
Scheme 3 shows the synthesis of cobalt octakis(hexyloxymethyl)phthalocyanine (**7**). Metal octakis(alcoxyalkyl)phthalocyanine derivatives were first reported by Powlowski and Hanack, who synthesized a series of metal octakis(alcoxymethyl)phthalocyanine derivatives [7]. This work reports the syntheses of metal octakis(alcoxymethyl)phthalocyanine derivatives in which the carbon number of the alcoxylic groups was one, two or more than 12, no data was reported where the number of carbon atoms of the carboxylic group was three to 11. Metal octakis(alcoxyalkyl)phthalocyanine derivatives having long alkyl chains possess thermotropic liquid crystalline properties [12, 16]. The synthesized cobalt octakis(hexyloxymethyl)phthalocyanine (**7**) exhibited no thermotropic liquid crystalline behavior, due to the relatively shorter side chains. Relevant characterization data for compound **7** is shown in the Experimental, and is in accord with the proposed structure.

Cobalt anthraquinocyanine (11)

The synthetic pathway to cobalt anthraquinocyanine (**11**) is shown in Scheme 4.

To date, only iron and oxivanadium anthraquinocyanines have been reported by Freyer [17]. Though Freyer synthesized anthraquinocyanines from 2,3-dicyanoanthraquinone [17], anthraquinone-2,3-dicarboxylic acid and urea were used in this present work.

IR and electronic spectral data (Experimental) confirm the formation of the anthraquinocyanine ring.



(2)

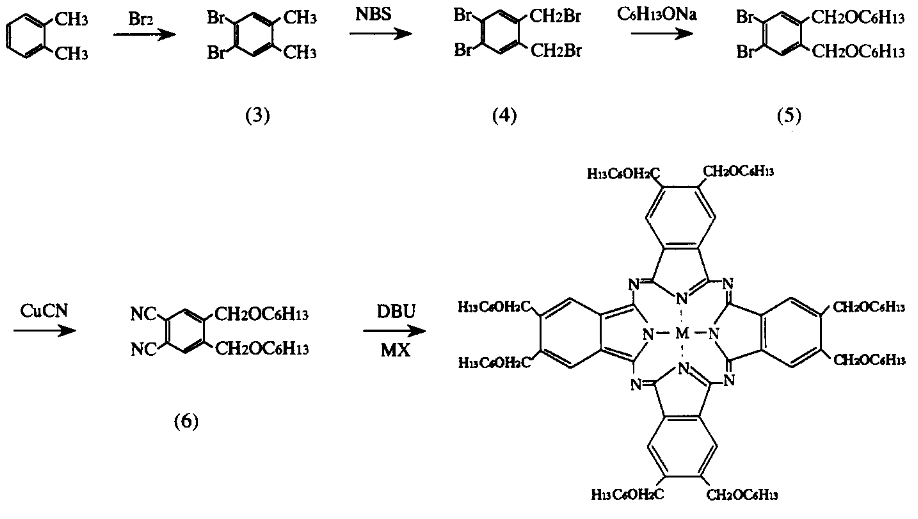
Scheme 2

Solubility

The synthesized cobalt phthalocyanine derivatives (**1**, **2**, **7** and **11**) exhibited excellent solubility in organic solvents such as DMSO, DMF, pyridine, etc. The increased solubility is attributed to the reduction of intermolecular interaction of phthalocyanine ring by the substituents.

Cyclic voltammograms

Figure 1 shows CVs of cobalt phthalocyanine tetrasulfonic acid (**1**), cobalt phthalocyanine octacarboxylic acids (**2**), cobalt octakis(hexyloxymethyl)phthalocyanine (**7**) and cobalt anthraquinocyanine (**11**). The CV of **1** exhibited the irreversibility characteristic, and consisted of three step one-electron reduction waves and one step one-electron oxidation wave. Cobalt phthalocyanine octacarboxylic acid (**2**) was similar to **1**. The first oxidation waves of **2** appeared near +0.8 V vs Ag/AgCl, and the first reduction potentials were about −1.0 V vs Ag/AgCl. In general, oxidations of transition metal phthalocyanines are electrochemically irreversible [18], and the potential is about 1.0 V vs the standard hydrogen electrode (SHE) [19, 20]. Clack *et al.* reported that the first reduction potential of copper and zinc phthalocyanines occurs near −0.8 V vs SHE and cobalt phthalocyanine appears at −0.37 V vs SHE [21]. The redox of metal phthalocyanine derivatives are due to the interaction between the phthalocyanine ring and the central metal [22]. Compounds **1** and **2** showed positive oxidation potential in comparison with the unsubstituted derivative which was reported by Orihara *et al.* [23]. Car-



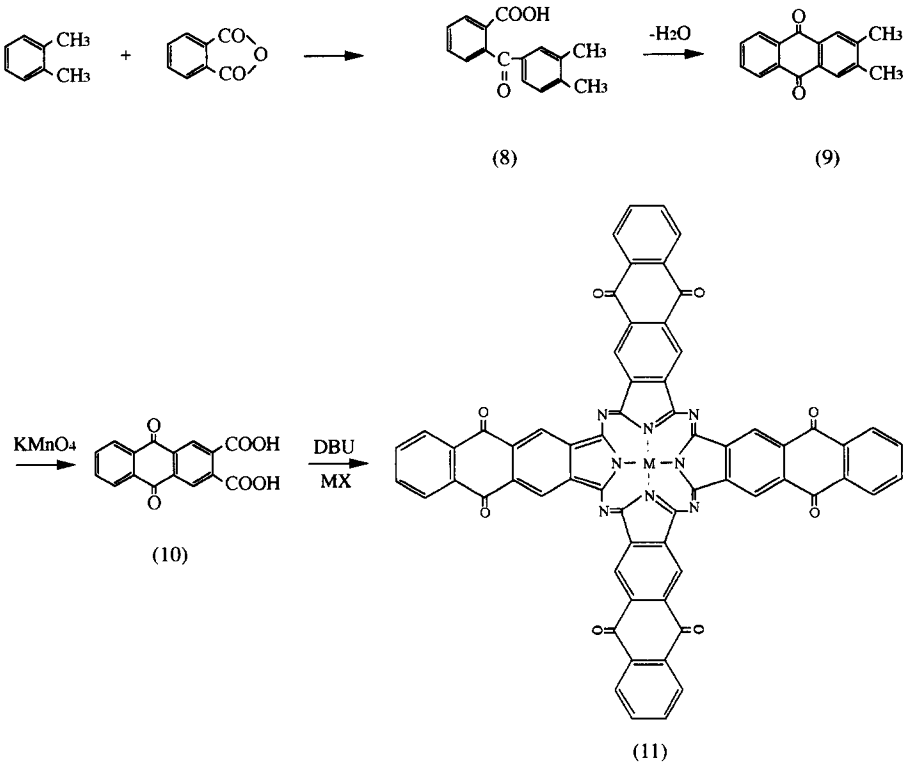
Scheme 3

boxylic and sulfonic groups are electron-withdrawing, which would be expected to decrease the electron charge in the phthalocyanine ring. Thus, the change in the oxidation potential is due to the type of substituents, and the effect depends also on the number of substituents.

The reduction and the oxidation of metal phthalocyanine derivatives occur both at the central metal and on the phthalocyanine ring [19–23]. For copper and zinc phthalocyanine derivatives, the central metal oxidation does not show until the phthalocyanine ring is oxidized [19–23], whereas iron and cobalt phthalocyanine derivatives show ring oxidation after the central metal oxidation, and reduction was followed by the reduction of the central metal [19–23].

The hexyloxymethyl substituent is an electron-donating group and would thus be expected to increase the negative charge on the phthalocyanine ring.

Cobalt anthraquinocyanines give similar CVs to cobalt phthalocyanine octacarboxylic acid (**2**). The anthraquinone ring in the cobalt anthraquinocyanine (**11**) molecule acts as the electron-withdrawing group. Hence, the redox behavior of (**11**) is much the same as **2**.



Scheme 4

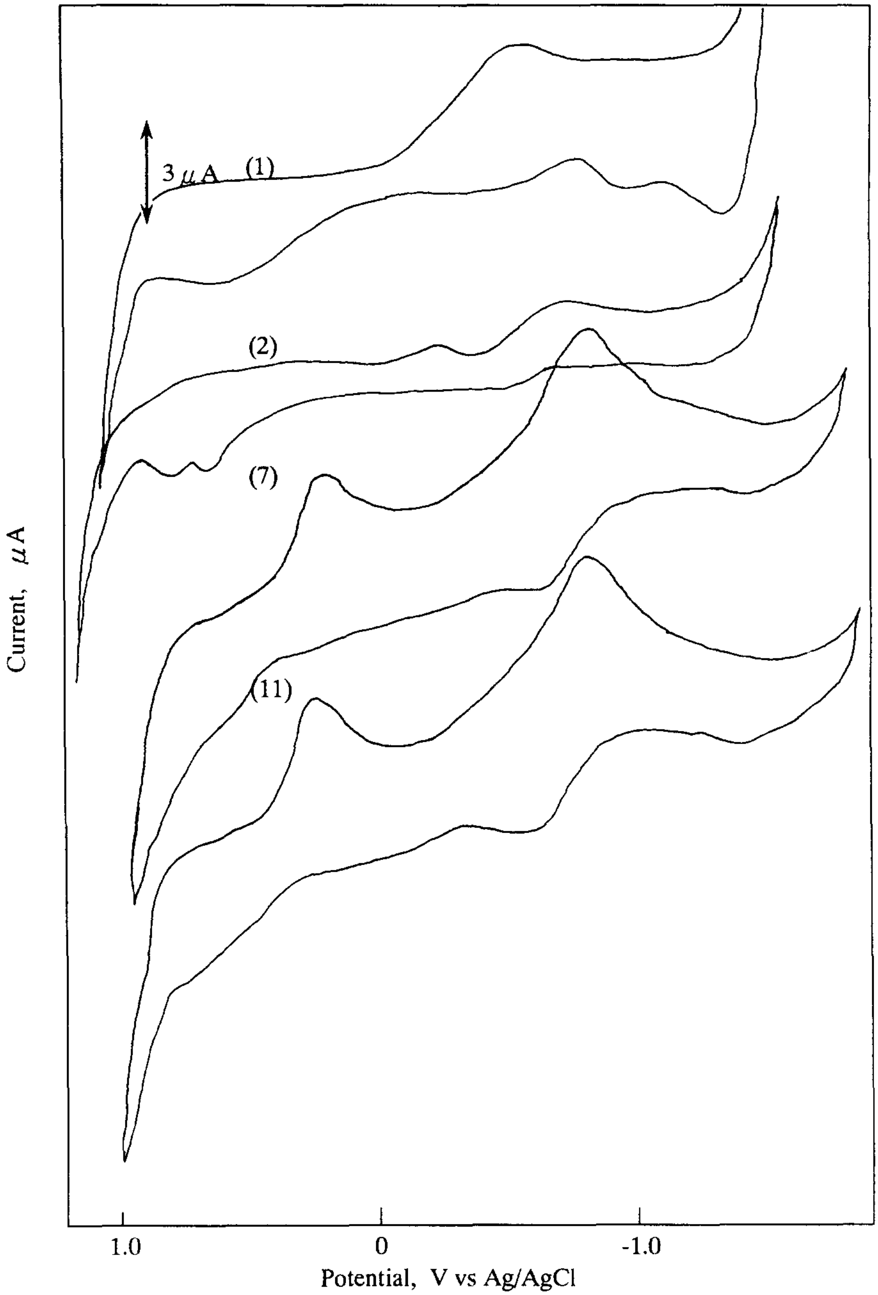


Fig. 1. Cyclic voltammograms of metal phthalocyanine derivatives in DMSO with 0.1 M TBAP, scan rate: 50 mV/s: (**1**) cobalt phthalocyanine tetrasulfonic acid; (**2**) cobalt phthalocyanine octacarboxylic acid; (**7**) cobalt octakis(hexoxymethyl)phthalocyanine; (**11**) cobalt anthraquinocyanine.

The metal anthraquinocyanine structure consists of a central metal, a porphyrazine ring and four anthraquinone units. Anthraquinone is known to have high oxidation and reduction properties, and its CV shows a typical reversible two step one-electron redox reaction. Cobalt anthraquinocyanine (**11**), however, was observed to have a redox property similar to **1** noted above.

EXPERIMENTAL

Cobalt phthalocyanine tetrasulfonic acid (1) [5]

12.3 g (50 mmol) 4-sulfophthalic acid, 30.0 g (0.50 mol) urea, 30 mmol cobalt chloride ($CoCl_2$), 1 g 1,8-diazabicyclo[5,4,0] undec-7-ene (DBU) and 150 ml 1,2,4-trichlorobenzene were heated to 210°C for 3 h. The product was filtered, washed with benzene to remove 1,2,4-trichlorobenzene, and dried in vacuum to constant weight; yield 75%. IR ν_{max} cm^{-1}: 3000 (C—H), 1720 (C—C), 1450 (C—H), 1380 (S—O), 1050 (C—H), 770 (C—H); UV λ_{max} nm: 688.5, 649.0, 354.0, 213.0. Calculated for $C_{32}H_{16}N_8O_{12}S_4Co$ C, 42.86; H,1.80; N, 19.45. Found C, 42.91; H, 2.08; N,19.67.

Cobalt phthalocyanine octacarboxylic acid (2) [6]

2.50 g (11.5 mmol) pyromellitic dianhydride, 13.0 g (0.22 mol) urea, 23.5 mmol $CoCl_2$, and 0.1 g DBU, were heated to 250°C until the reaction mixture was fused. The reaction residue was washed with water, acetone and 6 N HCl.

After drying, the solid obtained was hydrolyzed, viz. 30 g crude product, 30 g KOH and 90 ml water were heated for 8 h at 100°C. The mixture was diluted with 200 ml water and filtered. The filtrate was acidified to pH 2 with concentrated HCl. The blue product which precipitated was separated from the liquor using a centrifuge. The solid was washed with water three times, and then dried; yield 30%. IR ν_{max} cm^{-1}: 3390–3000 (C—H), 1750 (C—O), 1480 (C—H), 1060 (C—H), 720 (C—O); UV λ_{max} nm: 684.0. Calculated for $C_{40}H_{16}N_8O_{16}Co$ requires C, 57.44; H, 2.14; N, 14.90. Found C, 57.86; H, 2.14; N, 14.52.

Cobalt octakis(alcoxyalkyl)phthalocyanine [7]

1,2-Dibromo-4,5-dimethyl benzene (3)[8]

To a stirred mixture of 166 g (1.56 mol) *o*-xylene, 2 g iodine and 3 g iron were placed, at 5–10°C, 500 g (3.12 mol) bromine was added dropwise, over 7 h. The reaction mixture was then poured into water and filtered. The precipitate was washed with 3% aq NaOH and then recrystallized from methylcyclohexane; yield 49%, mp 86.6°C. IR ν_{max}^{KBr}cm^{-1}: 2950, 1740, 1440, 1340, 1120, 880, 640, 440; ^{1}H NMR (CCl_4, δ/ppm):2.1 (*s*, 6H), 7.36 (*s*, arom, 2H). $C_8H_8Br_2$:calc. C 36.66%, H 3.05%, found C 36.40%, H 3.08%; MS $[M]^+ m/z = 264$.

1,2-Dibromo-4,5-bis(bromomethyl)benzene (4)[9, 10]

A mixture of 30.2 g (0.11 mol) 1,2-dibromo-4,5-dimethylbenzene (**3**) 42.7 g (0.24 mol) *N*-bromosuccinimide (NBS) and 0.08 g 2,2″-azobis(isobutyro)nitrile was heated to 80°C for 8 h. After removing the 100 ml of carbon tetrachloride solvent, the crude product was recrystallized from heptane and dried in vacuum; yield 21%, mp 84.7°C. IR ν_{max}^{KBr}cm^{-1}:3000, 1650, 1460, 1200, 950, 620, 440;^{1}H NMR (CCl_4, δ/ppm):4.43 (*s*, 4H), 7.53 (*s*, arom, 2H). $C_8H_6Br_4$: calc. C 22.78%, H 1.43%, found C 22.72%, H 1.51%; MS $[M]^+$ $m/z = 422$.

1,2-Dibromo-4,5-bis(hexyloxymethyl)benzene (5)[11]

Sodium was dissolved in 112 g (1.18 mol) of hexanol and 5.00 g (0.13 mol) of 1,2-dibromo-4,5-bis(bromomethyl)benzene (**4**) was then added. The temperature was gradually raised to 155°C and the mixture stirred for 90 min. Excess hexanol was removed by distillation and 100 ml water added to dissolve the salt by-products. The resultant mixture was extracted with diethyl ether, the organic layer was washed with a little water and dried over calcium chloride. Diethyl ether was distilled off, leaving the product, 1,2-dibromo-4,5-bis(hexyloxymethyl)benzene (**5**) as a brown liquid; yield 88%. IR ν_{max}^{KBr} cm^{-1}: 2900, 1670, 1240, 1095, 630. ^{1}H NMR (CCl_4, δ/ppm): 0.89 (*s* ,6H), 1.28 (*m*, 16H), 3.52 (*s*, 4H), 4.45 (*s*, 4H), 7.53 (*s*, arom, 2H).

1,2-Dicyano-4,5-bis(hexyloxymethyl)benzene (6)[12]

A mixture of 15.2 g (33.8 mmol) 1,2-dibromo-4,5-bis(hexyloxymethyl)benzene (**5**), 13.6 g (96.6 mmol) copper cyanide and 100 ml *N,N*-dimethylformamide (DMF) was refluxed for 5 h, then cooled, and poured into 170 ml aq ammonia. The mixture was stirred for 10 min, and filtered. The bluish residue was washed with water, dried, and Soxhlet extracted with diethyl ether to give **6** in 66% yield. IR ν_{max}^{KBr} cm^{-1}: 3200, 2100, 1240, 1095, 630. $C_{22}H_{32}N_2O_2$: calc. C 74.11%, H 9.04%, N 7.85%, found C 75.05%, H 9.37%, N 7.82%; MS $[M]^+$ $m/z = 357$.

Cobalt octakis(hexyloxymethyl)phthalocyanine (7)

2.00 g (5.61 mmol) 1,2-dicyano-4,5-bis(hexyloxymethyl)benzene (**6**), 11.8 mmol $CoCl_2$, and 0.1 g DBU in 20 ml hexanol were refluxed for 5 h and the cooled liquor filtered; yield 10%. IR ν_{max} cm^{-1}: 3300 (C—H), 2900 (C—H), 1590 (C—C), 1150 (C—O), 1090 (C—H); UV λ_{max}nm: 665.0. $C_{88}H_{128}N_8O_8Co$: calc. C 70.87, H 8.63, N 7.51, found C 70.18, H, 8.40, N 7.43.

Cobalt anthraquinocyanine

*o-Xyloyl-o-benzoic acid (**8**)[13]*

10.7 g (0.13 mol) of *o*-xylene in 25 ml chloroform was added dropwise to a mixture of 16.3 g (0.11 mol) phthalic dianhydride and 14 g anhydrous aluminium chloride. The reaction mixture was refluxed for 1 h and the liquor then poured into a mixture of 30 g ice and 20 ml concentrated HCl, and then filtered. The product was recrystallized from diethyl ether; yield 81%, mp 170.6°C. IR ν_{max}^{KBr} cm^{-1}: 3450, 2900, 1760, 1680, 1600, 1400, 1225, 1100, 900, 710. ^{1}H NMR (CCl_4, δ/ppm): 2.27 (*s*, 6H), 7.36–8.00 (*m*, arom, 7H). $C_{16}H_{14}O_3$: calc. C 75.57%, H 5.55%, found C 75.03%, H 5.49% ; MS$[M]^+$ m/z =254.

*2,3-Dimethylanthraquinone (**9**)[13]*

This was obtained by heating 18 g *o*-xyloyl-*o*-benzoic acid (**8**) and 2 ml of concentrated sulfuric acid to 150°C. The crude product was recrystallized from benzene; yield 35%, mp 212.5°C. IR ν_{max}^{KBr}cm^{-1}: 2900, 2600, 1675, 1420, 1300, 780, 710. ^{1}H NMR (CCl_4, δ/ppm): 2.22 (*s*, 6H), 7.26–7.65 (*m*, arom, 6H). $C_{16}H_{12}O_2$: calc. C 81.33%, H 5.12%, found C 80.89%, H 5.02%; MS$[M]^+$ m/z=236

*Anthraquinone-2,3-dicarboxylic acid (**10**)[13]*

A solution of 4 g (16.9 mmol) 2,3-dimethylanthraquinone (**9**) in 4.36 ml concentrated sulfuric acid was added to 160 g of water, and 12 g potassium permanganate ($KMnO_4$) was added gradually to the solution. Reaction was allowed to continue at 90–95°C for 10 min with stirring; excess $KMnO_4$ was then removed with oxalic acid. The crude product was filtered and washed with hot water. The product dissolved in hot dilute ammonia solution, unreacted 2,3-dimethylanthraquinone being filtered off. Anthraquinone-2,3-dicarboxylic acid (**10**) was precipitated from the filtrate by addition of HCl. The material was filtered, washed with hot water and dried; yield 66%, mp 325.0°C. IR ν_{max}^{KBr} cm^{-1}: 3450, 2900, 1690, 1600, 1400, 1260, 770, 700. ^{1}H NMR (CCl_4, δ/ppm): 7.27 (*s*, arom, 6H). $C_{16}H_8O_6$: calc. C 64.87%, H 2.72%, found C 64.26%, H 2.51%.

*Cobalt anthraquinocyanine (**11**)*

1.00 g (3.30 mmol) anthraquinone-2,3-dicarboxylic acid (**10**), 2 g (34.0 mmol) urea, 6.75 mmol $CoCl_2$ and 0.1 g DBU were heated to 210°C until the reaction mixture was fused. The reaction residue was digested with water, filtered, and the product dried; yield 23%. ν_{max} cm^{-1}: 3300 (C—H), 2900 (C—H), 1690 (C—O), 1470 (C—H), 980 (C—H), 780 (C—H); λ_{max} nm: 688.0. $C_{64}H_{24}N_8O_8Co$: calc. C 70.46, H 2.22, N 10.27, found C 70.17, H 2.26, N 10.30.

INSTRUMENTATION

IR spectra were recorded on a Shimadzu IR-435 spectrometer. ^{1}H NMR spectra were recorded at 15 mg ml^{-1} in chloroform-*d* on a Nihon Denshi EX-90 spectrometer. Electronic spectra were measured on a Shimadzu UV-2100, ultraviolet-visible spectrometer from 0.025 mg cm^{-3} in pyridine or 0.1N sodium hydroxide solution. Elemental analyses were carried out using a Perkin-Elmer 2400 equipment. Melting points were measured with a Mettler FP-5 apparatus.

Cyclic voltammetry of soluble metal phthalocyanine derivatives and metal anthraquinocyanine were carried out with a BAS CV-50W voltammetric analyzer at room temperature in dimethylsulfoxide containing a 0.10 mol dm^{-3} solution of tetrabutylanmonium perchlorate. Cyclic voltammograms were recorded by scanning the potential at the rate of 50 mV s^{-1}. The working and counter electrodes were platinum wires and the reference electrode was a silver (Ag)/ silver chloride (AgCl) saturated sodium chloride electrode.

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