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Synthesis of optically active 1,1′-binaphthyl-phthalocyanines linked via a crown ether unit

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Abstract

Novel optically active metal and metal-free phthalocyanines, substituted with 1,1′-binaphthyl crown ether units, have been synthesized and characterized.

1. Introduction

There has been considerable recent work focusing on functionalizing the periphery of phthalocyanines, with groups including alkyl, alkylamides, alkoxyl, porphyrins, oligo(ethyleneoxy), benzyloxyethoxy, crown ether, dendrimers and tetrathiafulvalene to control the supramolecular architecture and impart novel properties demanded in the fields of electronics, optoelectronics and charge transport.[1–9] Up to now, few reports have explored the process of combining chiral binaphthol groups with a phthalocyanine core.[10] Since the first report on the use of chiral binaphthyl-based crown ethers as hosts for molecular recognition, chiral binaphthol has attracted much attention. Chiral macrocycles, metal complexes, linear oligomers and polymers based on the 1,1′-binaphthyl structure have been synthesized for use in molecular recognition, asymmetric catalysis and as new functional materials.[11] Herein, the synthesis and characterization of novel structural metal and metal-free phthalocyanines (***R*** or ***S***)-**Pc** (the structure of (***S***)-**Pc** is shown in Scheme 1) substituted with optically active 1,1′-binaphthyl crown ether units is presented.

2. Results and discussion

The synthesis of the target optically active phthalocyanines was carried out as outlined in Scheme 2. The structure of optically active phthalocyanine (***R*** or ***S***)-**Pc** can be considered to

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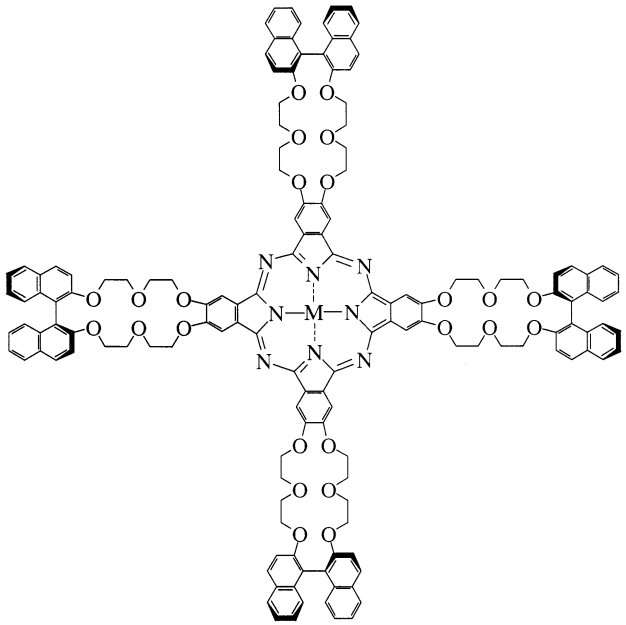
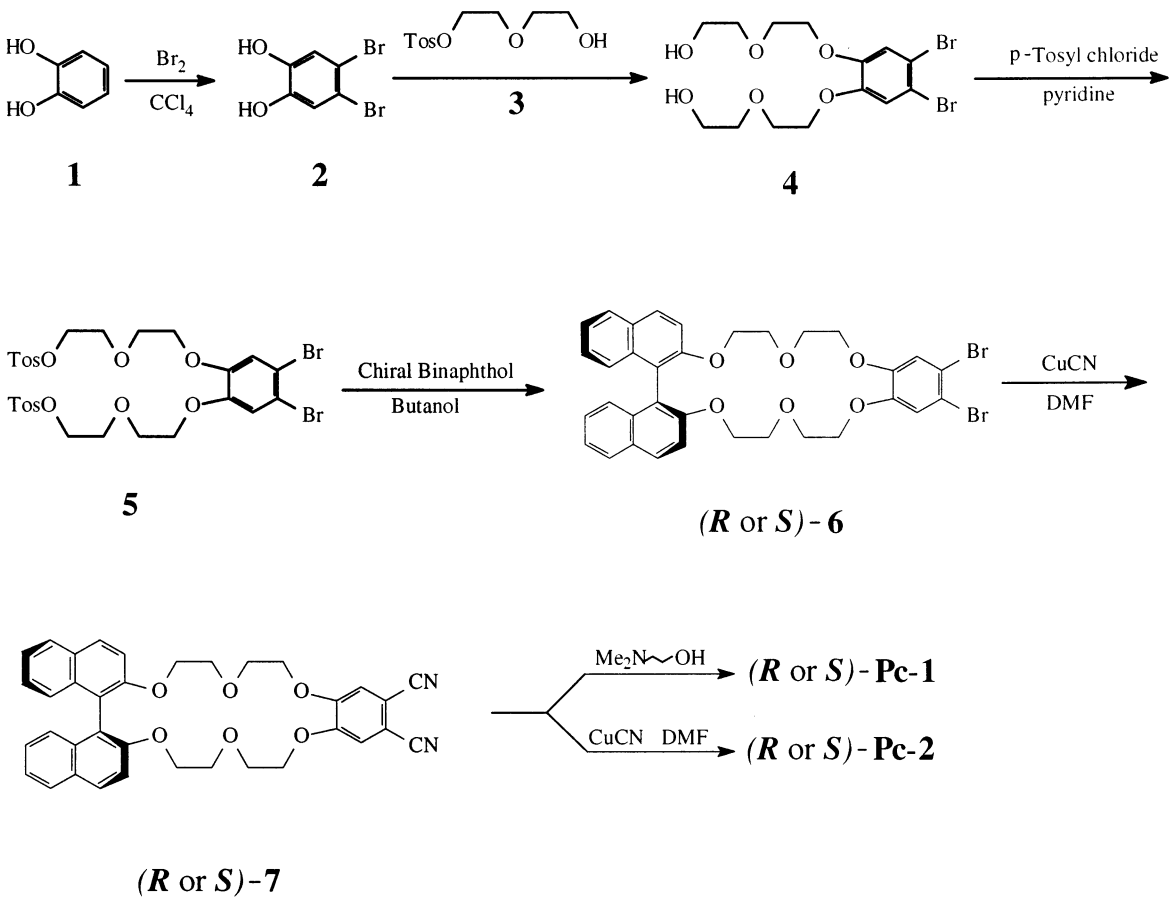


(S)-(+)-**Pc-1** **M=2H**

(S)-(+)-**Pc-2** **M=Cu**

Scheme 1. The structure of optically active (***S***)-**Pc**

consist of three parts, i.e. phthalocyanine core, crown ether bridges and chiral binaphthyl end groups. It was obtained from (***R*** or ***S***)-**7**, which was prepared by standard procedures[5,13,14] as follows. Catechol **1** was brominated and subsequently alkylated with diethyleneglycol monotosylate **3** to give compound **4**. Compound **5,** prepared by tosylation of **4** with *p*-tosylchloride, was converted into (***R*** or ***S***)-**6** by reaction with optically active (***R***) or (***S***)-2,2′-dihydroxy-1,1′-binaphthyl. Then (***R*** or ***S***)-**6** was treated with CuCN in DMF to give (***R*** or ***S***)-**7**. Finally, the (***R*** or ***S***)-**Pc-1** and (***R*** or ***S***)-**Pc-2** were formed by treating (***R*** or ***S***)-**7** with (*N*,*N*-dimethylamino)ethanol, or with CuCN in DMF, respectively. In addition, (***R*** or ***S***)-**Pc-2** could also be prepared directly from (***R*** or ***S***)-**6** by treatment with an excess of CuCN in DMF. Since the target optically active phthalocyanines (***R*** or ***S***)-**Pc** were synthesized from optically pure starting materials, it is important to avoid racemization during each step. According to the report by Cram et al.[14c] the chiral configuration of 1,1′-binaphthyl molecules is relatively stable at higher temperature over extended periods of time. In our case, the possible racemization would take place mainly in the preparation of (***R***)-**7**, (***S***)-**7**, (***R***)-**Pc-2** and (***S***)-**Pc-2**. The experimental conditions, refluxing in DMF at 153°C, or heating in (*N*,*N*-dimethylamino)ethanol for 20–40 hours, were relatively mild compared with the conditions employed by Cram. In order to check that there was no racemization in these two steps, the unreacted starting materials, (***R***)-**6**, (***S***)-**6**, (***R***)-**7** and (***S***)-**7**, were recovered and their optical rotation measured. The results showed that their specific rotations were identical to the starting materials, demonstrating that there was no configurational change. The new compounds were confirmed by ^{1}H NMR, UV–vis, CD spectra measurements and elemental analysis. The MALDI-TOF MS spectra of the optically active (***R*** or ***S***)-**Pc** gave results consistent with the calculated molecular weights.



Scheme 2. The synthesis of optically active (***R*** or ***S***)-**Pc**

Fig. 1 shows the CD and UV–vis spectra of (***R***)-**Pc-1** and (***S***)-**Pc-1** in $CHCl_3$. The UV–vis spectrum of (***S***)-**Pc-1**, consisting of two closely spaced Q bands at 700 nm ($\varepsilon=333000$) and 662 nm ($\varepsilon=272000$), together with two associated vibrational overtones at 600 nm ($\varepsilon=57800$) and 640 nm ($\varepsilon=102000$), is characteristic of monomeric metal free phthalocyanines in dilute $CHCl_3$ solution (2×10^{-5} mol/L).[15] In addition, a broad Soret absorption around 300 nm is observed, and a weaker absorption in the 400–500 nm region may involve the ether oxygen lone pairs. The CD spectra of (***R***)-**Pc-1** and (***S***)-**Pc-1** in $CHCl_3$ (1×10^{-4} mol/L), display a strong absorption at the ^1B_b transition band, as well as a weak absorption at the Q band wavelength. In the case of (***R***)-**Pc-1**, the spectrum shows intense negative first and positive second Cotton effects at the ^1B_b transition band: 240 nm ($\Delta\varepsilon=930$). On the other hand, the ^1L_a transition around 290 nm ($\Delta\varepsilon=110$) exhibits a single Cotton effect with weak intensity.[16]

The CD and UV–vis spectra of (***R***)-**Pc-2** and (***S***)-**Pc-2** in $CHCl_3$ are shown in Fig. 2. Comparing the spectrum of (***S***)-**Pc-2** with that of (***S***)-**Pc-1**, the difference appears at the Q band. The sharp Q band absorption at 678 nm ($\varepsilon=337000$), together with two weak absorptions in the UV–vis spectrum of (***S***)-**Pc-2**, are assigned to a π–π^* transition of the monomeric metallated phthalocyanine.

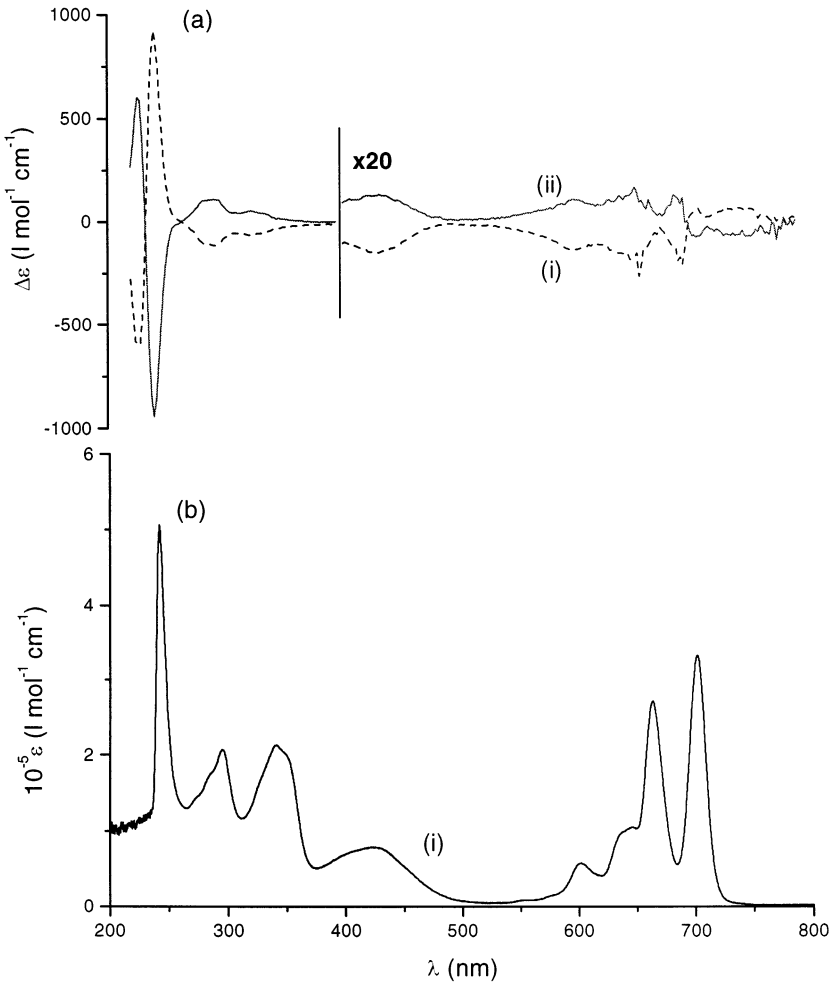


Figure 1. (a) CD and (b) UV–vis spectra of (i) (***S***)-**Pc-1** and (ii) (***R***)-**Pc-1** in $CHCl_3$

According to chiral exciton coupling theory,[16] the binaphthyl moieties of (***R***)-**Pc-1** and (***R***)-**Pc-2** are negative, which is correlated with a left-handed helicity between the two long axes of naphthalene chromophores, while those of (***S***)-**Pc-1** and (***S***)-**Pc-2** are positive and of right-handed helicity, judging from the CD pattern in the 220–300 nm region. The introduction of the optically active binaphthyl moieties on the periphery of phthalocyanines induces the CD absorption of (***R***)-**Pc-1**, (***S***)-**Pc-1**, (***R***)-**Pc-2** and (***S***)-**Pc-2** at Q bands and Soret bands.[10]

3. Experimental

All solvents were dried before use. Catechol was recrystallized from toluene. *p*-Toluenesulfonyl chloride was recrystallized from hexane. (*N*,*N*-Dimethylamino)ethanol and DMF were freshly distilled before use. (±)-2,2′-Dihydroxy-1,1′-binaphthyl was resolved according to the method reported by Cai and co-workers.[12] (***R***)- and (***S***)-2,2′-dihydroxy-1,1′-binaphthyl were obtained with specific rotations of $[\alpha]_D = +34.4$ and $[\alpha]_D = -34.1$ (*c* 1, THF), respectively.

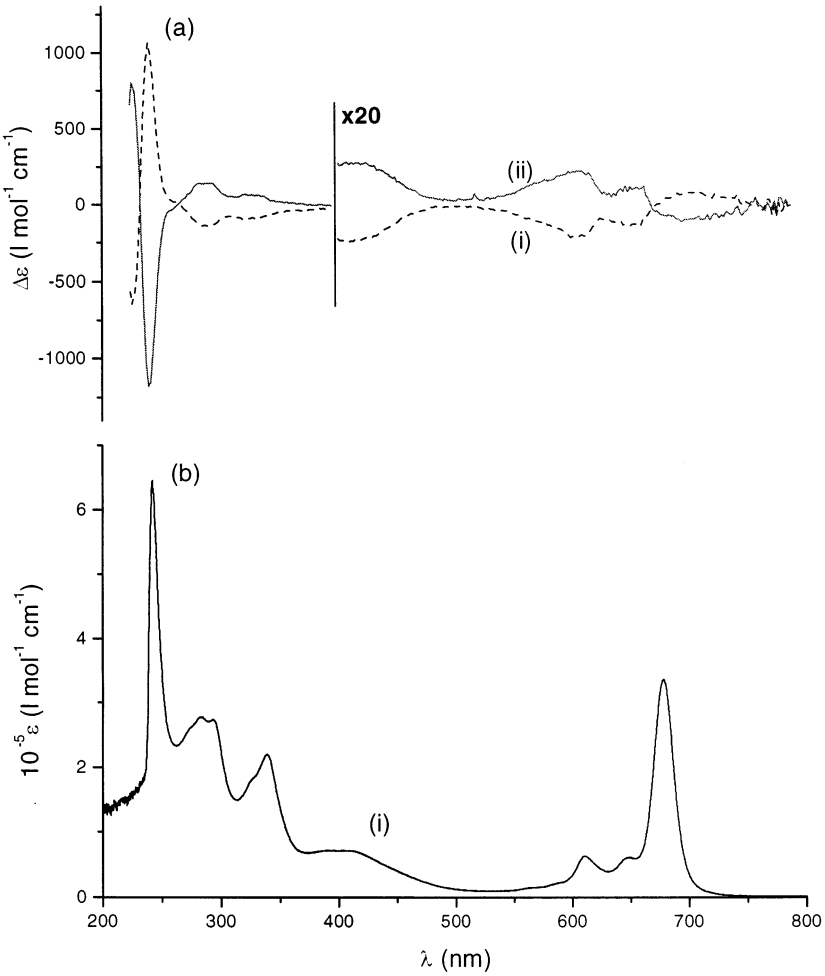


Figure 2. (a) CD and (b) UV–vis spectra of (i) (***S***)-**Pc-2** and (ii) (***R***)-**Pc-2** in $CHCl_3$

4,5-Dibromocatechol **2** was prepared according to a literature procedure.[13] All other reagents were used as supplied, without further purification.

^{1}H NMR spectra were recorded on a UNITY-200 instrument, with TMS as an internal standard. MALDI-TOF MS was detected on an Instrum Biflex III spectrometer with α-cyano-4-hydroxycinnamic acid (CCA) as a matrix. Optical rotations were determined on Perkin–Elmer 241 MC at 589 nm. Circular dichroism (CD) was measured at room temperature on a CD-6 spectropolarimeter. UV–vis spectra were obtained with a TU-120 spectrophotometer. Elemental analyses were measured with a Heraeus CHN-RAPID instrument.

*3.1. 5-Tosyloxy-3-oxa-1-pentanol **3***

4-Toluenesulfonyl chloride (28.5 g, 0.15 mol) in methylene chloride (150 ml) was added dropwise to a well-stirred ice-cooled solution of the diethylene glycol (60 ml, 0.63 mol), triethylamine (80 ml, 0.57 mol) in methylene chloride (200 ml) over 1 h. The solution was stirred at room temperature overnight, and then washed with 1N HCl and water. The organic layer was

dried over anhydrous sodium sulfate and concentrated. The residue was dissolved in ethanol and then cooled at 5°C. The diethylene glycol ditosylate was separated as white crystals with mp 87–89°C. After filtration, the filtrate was concentrated, and the residue was purified by silica gel chromatography with 1:2 (v/v) ethyl acetate–petroleum ether (60–90°C) as the eluent to give the product **3** as a yellowish oil (14 g, 36%). ^{1}H NMR ($CDCl_3$): δ 2.4 (s, 3H, CH_3), 3.4–3.7 (m, 6H, CH_2), 4.1–4.2 (m, 2H, CH_2), 7.3–7.9 (m, 4H, ArH); elemental anal. calcd for $C_{11}H_{16}O_5S$: C, 50.77; H, 6.15. Found: C, 50.82; H, 6.44.

3.2. 1,2-Bis[2′-(2″-hydroxyethoxy)ethoxy]-4,5-dibromobenzene ***4***

Potassium carbonate (5.6 g, 40 mmol) was added under nitrogen to a stirred solution of dibromocatechol **2** (5.36 g, 20 mmol) and 5-tosyloxy-3-oxa-1-pentanol **3** (11.3 g, 43 mmol) in methyl cyanide (90 ml). The reaction mixture was refluxed for 24 h and then concentrated. The residue was shaken with water and extracted with methylene chloride. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate and then concentrated. The residue was purified by silica gel chromatography with 1:1 (v/v) ethyl acetate–petroleum ether (60–90°C) as the eluent to give the product **4** as a viscous oil (5.2 g, 59%). ^{1}H NMR ($CDCl_3$): δ 3.47 (s, 2H, OH), 3.6–4.2 (m, 16H, CH_2), 7.1 (s, 2H, ArH); elemental anal. calcd for $C_{14}H_{20}O_6Br_2$: C, 37.83; H, 4.50. Found: C, 37.49; H, 4.79.

*3.3. 1,2-Bis[2′-(2″-(*p*-toluenesulfonyloxy)ethoxy)ethoxy]-4,5-dibromobenzene* ***5***

p-Toluenesulfonyl chloride (17 g, 89 mmol) in pyridine (30 ml) was added to a solution of 1,2-bis[2′-(2″-hydroxyethoxy)ethoxy]-4,5-dibromobenzene **4** (16.6 g, 37.4 mmol) in pyridine (30 ml) with stirring at −18°C. The mixture was stirred for 48 h at −10°C, and then poured over ice, acidified with aqueous HCl and extracted with methylene chloride. The combined organic layers were washed with water, dried over anhydrous sodium sulfate and then concentrated. The residue was purified by silica gel chromatography with 1:1 (v/v) ethyl acetate–petroleum ether (60–90°C) as the eluent to give the product **5** as a viscous oil (24.7 g, 88%). ^{1}H NMR ($CDCl_3$): δ 2.40 (s, 6H, CH_3), 3.7–4.2 (m, 16H, CH_2), 7.05 (s, 2H, ArH), 7.27 (d, 4H, ArH), 7.74 (d, 4H, ArH); elemental anal. calcd for $C_{28}H_{32}O_{10}Br_2S_2$: C, 44.68; H, 4.26. Found: C, 44.56; H, 4.47.

*3.4. 2,3-(4′,5′-Dibromobenzo)-11,12:13,14-di(1′,2′-naphtho)-1,4,7,10,15,18-hexaoxacycloeicosa-2,11,13-triene (***R** *or* **S)-*****6***

1,2-Bis[2′-(2″-(*p*-toluenesulfonyloxy)ethoxy)ethoxy]-4,5-dibromobenzene **5** (9.9 g, 13.1 mmol) was added dropwise to a mixture of (***S***)-2,2′-dihydroxy-1,1′-binaphthyl (3.76 g, 13.1 mmol) and NaOH (1.15 g, 28.8 mmol) in boiling butanol (70 ml) stirred under nitrogen. The mixture was refluxed for 16 h and evaporated under reduced pressure. The residue was shaken with water and extracted with methylene chloride. The combined organic layers were washed with water, dried over anhydrous sodium sulfate and then concentrated. The residue was purified by silica gel chromatography with 5:1, and then 3:1 (v/v) ethyl acetate–petroleum ether (60–90°C) as the eluent to give the product (***S***)-**6** as a white foamy solid (4.6 g, 51%). Similarly, (***R***)-**6** was prepared (49%). ^{1}H NMR ($CDCl_3$): δ 3.5–4.2 (m, 16H, CH_2), 7.03 (s, 2H, ArH), 7.2–7.5 (m, 8H, ArH), 7.8 (m, 4H, ArH); *m*/*z* (MALDI-TOF) 694.39 (M^+); elemental anal. calcd for $C_{34}H_{30}O_6Br_2$: C, 58.79; H, 4.32. Found: C, 58.89; H, 4.67 for (***S***)-**6** and C, 59.00; H, 4.82 for

(*R*)-**6**; mp 81–83°C for (*S*)-**6** and 82–83°C for (*R*)-**6**; $[\alpha]_D = -142$ and 140 (*c* 1, $CHCl_3$) for (*S*)-**6** and (*R*)-**6**, respectively.

*3.5. 2,3-(4′,5′-Dicyanobenzo)-11,12:13,14-di(1′,2′-naphtho)-1,4,7,10,15,18-hexaoxacycloeicosa-2,11,13-triene (***R** *or* **S***)-***7**

A mixture of (*S*)-**6** (1.39 g, 2 mmol), CuCN (0.54 g, 6 mmol), and pyridine (0.1 ml) in DMF (20 ml) was refluxed under nitrogen for 40 h. The mixture was cooled to room temperature and then poured into aqueous ammonia. After stirring for 2 h, the mixture was extracted with methylene chloride. The combined organic layers were washed with water, dried over anhydrous sodium sulfate and then concentrated. The residue was purified by silica gel chromatography with 3:1, and then 2:1 (v/v) ethyl acetate–petroleum ether (60–90°C) as the eluent to give the product (*S*)-**7** as a white foamy solid (0.86 g, 73%). Similarly, (*R*)-**7** was prepared (70%). ^{1}H NMR ($CDCl_3$): δ 3.4–4.2 (m, 16H, CH_2), 7.09–7.5 (m, 10H, ArH), 7.8 (m, 4H, ArH); elemental anal. calcd for $C_{36}H_{30}O_6N_2$: C, 73.72; H, 5.12; N, 4.78. Found: C, 73.24; H, 5.46; N, 4.97 for (*S*)-**7** and C, 73.73; H, 4.85; N, 4.95 for (*R*)-**7**; mp 100–102°C for (*S*)-**7** and 98–101°C for (*R*)-**7**; $[\alpha]_D = -187$ and 184 (*c* 1, $CHCl_3$); for (*S*)-**7** and (*R*)-**7**, respectively.

*3.6. Tetrakis[11,12:13,14-di(1′,2′-naphtho)-1,4,7,10,15,18-hexaoxacycloeicosa-2,11,13-trieno]-phthalocyanine (***R** *or* **S***)-Pc-1*

A mixture of (*S*)-**7** (300 mg, 0.51 mmol) and (*N*,*N*-dimethylamino)ethanol (1.5 ml) was stirred under nitrogen at 120°C for 20 h. After cooling to room temperature, it was purified by silica gel chromatography with 1:0, 2:3, and then 3:7 (v/v) ethanol–chloroform as the eluent to give the product (*S*)-**Pc-1** as a dark green solid (88 mg, 29%). Similarly, (*R*)-**Pc-1** was prepared (23%). ^{1}H NMR ($CDCl_3$): δ 3.2–4.2 (br m, 64H, CH_2), 6.9–8.2 (br m, 56H, ArH); mp >210°C; *m*/*z* (MALDI-TOF) 2347.35 (M^+) for (*S*)-**Pc-1** and 2347.60 (M^+) for (*R*)-**Pc-1**; UV–vis λ ($CHCl_3$), 700 nm ($\varepsilon = 333000$), 662 nm ($\varepsilon = 272000$), 640 nm ($\varepsilon = 102000$), 602 nm ($\varepsilon = 57800$), 425 nm ($\varepsilon = 78100$), 340 nm ($\varepsilon = 213000$), 294 nm ($\varepsilon = 207000$).

*3.7. Tetrakis[11,12:13,14-di(1′,2′-naphtho)-1,4,7,10,15,18-hexaoxacycloeicosa-2,11,13-trieno]-phthalocyaninatocopper (***R** *or* **S***)-Pc-2*

3.7.1. Procedure I

A mixture of (*S*)-**7** (117 mg, 0.2 mmol) and CuCN (54 mg, 0.6 mmol) in DMF (0.5 ml) was refluxed under nitrogen for 24 h. After cooling to room temperature, a small amount of methylene chloride was added to dissolve any solid formed, and then the solution was poured into aqueous ammonia. After stirring for 2 h, the mixture was extracted with methylene chloride. The combined organic layers were washed with water, dried over anhydrous sodium sulfate and concentrated. The residue was purified by silica gel chromatography with 1:0, 2:3 and then 3:7 (v/v) ethanol–chloroform as the eluent to give the product (*S*)-**Pc-2** as a dark green solid (50 mg, 42%). Similarly, (*R*)-**Pc-2** was prepared (37%).

3.7.2. Procedure II

A mixture of (*S*)-**6** (694 mg, 1 mmol), CuCN (0.45 g, 5 mmol), and pyridine (0.15 ml) in DMF (2 ml) was refluxed under nitrogen for 24 h. After the same treatment as in Procedure I, the

crude product was purified by silica gel chromatography with 1:0, 2:3 and then 3:7 (v/v) ethanol–chloroform as the eluent to give the product (***S***)-**Pc-2** as a dark green solid (420 mg, 70%). (***R***)-**Pc-2** was prepared similarly (68%). ^{1}H NMR ($CDCl_3$): δ 3.2–4.2 (br m, 64H, CH_2), 6.9–8.2 (br m, 56H, ArH); mp >260°C; *m*/*z* (MALDI-TOF) 2407.56 (M^+) for (***S***)-**Pc-2** and 2407.60 (M^+) for (***R***)-**Pc-2**; UV–vis λ ($CHCl_3$), 678 nm (ε=337000), 656 nm (ε=61300), 610 nm (ε=63600), 410 nm (ε=71700), 338 nm (ε=221000), 283 nm (ε=278000).

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