

# Optically active 'adjacent' type non-centrosymmetrically substituted phthalocyanines

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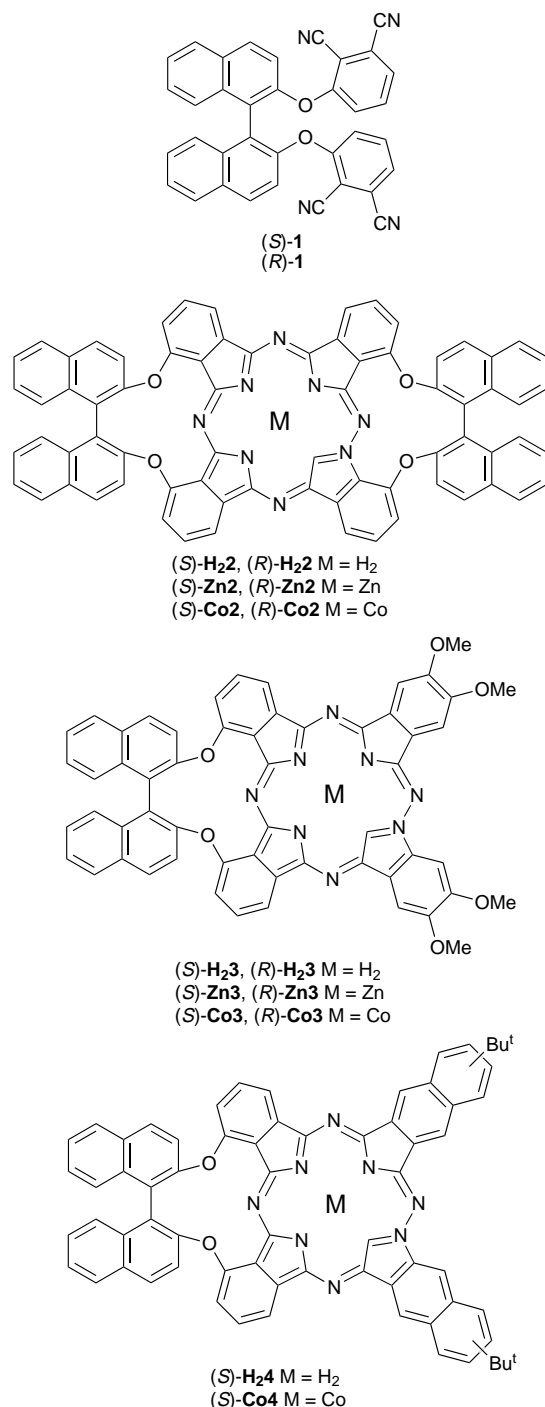
Optically active 'adjacent' type non-centrosymmetrically substituted phthalocyanines (Pcs) and benzo-substituted Pcs having  $\pi$ -systems with  $C_{2v}$  symmetry have been synthesized in high yields in a mixed condensation using bisphthalonitriles (which do not racemize under general Pc formation conditions) and a second phthalonitrile, and characterized by UV-VIS, natural and magnetic circular dichroism spectroscopy.

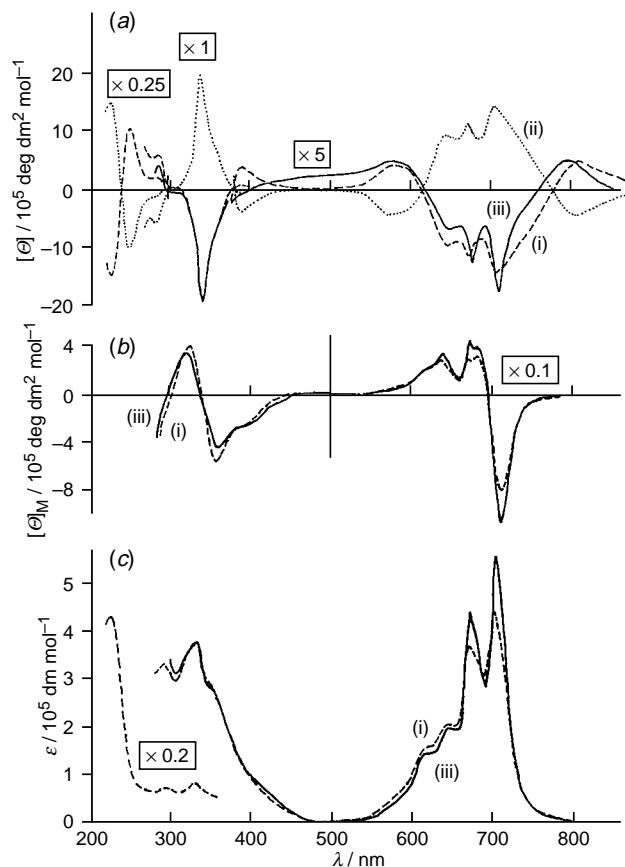
Control of the molecular symmetry of Pcs is not always easy. Here we describe a convenient route leading to *adjacent* and non-centrosymmetrically substituted *optically active* Pcs.

Our key starting materials are compounds **1** which can be obtained *via* a single step high yielding reaction (more than 90%) from commercially available (*S*)-(-)- or (*R*)-(+)-2,2'-dihydroxy-1,1'-binaphthyl and 3-nitrophthalonitrile without optical loss.<sup>1,2</sup> The most important property of compounds **1** is that they do not racemize under general Pc synthesis conditions because of the large steric hindrance due to the two bulky dicyanophenoxy groups, and of course no opposite isomer is produced. In addition, since the distance between the two phenoxy groups is close to the minimum to link two adjacent benzene rings of Pc, the formation of oligomeric Pcs is suppressed. Compounds (*S*)-**1** and (*R*)-**1** were converted to isoindoline derivatives by bubbling ammonia gas in dry MeOH<sup>3</sup> followed by reaction with 2 equiv. of 4,5-dimethoxyisoindoline<sup>4</sup> in refluxing *N,N*-dimethylaminoethanol for 3 h.<sup>3</sup> After evaporation of the solvent, the residue was separated on a basic alumina column (Act III) using CH<sub>2</sub>Cl<sub>2</sub>-MeOH (9:1 v/v) and then CH<sub>2</sub>Cl<sub>2</sub>-pyridine (1:1 v/v). The blue-green fraction was collected and separation was attempted by gel-permeation chromatography using Bio-beads SX-2 (Bio-rad) and CH<sub>2</sub>Cl<sub>2</sub>-MeOH (9:1 v/v). Three blue-green bands appeared, but the separation between the first and second bands was too small to effect separation. The third band (blue) was identified as (*S*)-**H<sub>2</sub>2** and (*R*)-**H<sub>2</sub>2** with two binaphthyl units *via* FAB mass spectroscopy (5-7%).<sup>2,5,6</sup> The first and second bands were accordingly mixed together and then separated on a column of Bio-beads SX-8 using THF as eluent. The first band was collected and recrystallized from CH<sub>2</sub>Cl<sub>2</sub>-EtOAc and then THF-EtOAc to give the optically active non-centrosymmetric (*S*)-**H<sub>2</sub>3** and (*R*)-**H<sub>2</sub>3** as a blue-green powder in 21-26% yield. Similarly, (*S*)-**H<sub>2</sub>4** was prepared from the diiminoisoindoline derivatives of (*S*)-**1** and 6-*tert*-butyl-2,3-dicyanophthalene in 9% yield. Interestingly, the NMR signal of the pyrrole protons of (*S*)-**H<sub>2</sub>4** appeared at two separate positions, one at  $\delta$ -2.40 and the other at -4.05 (one proton each).<sup>2</sup> Judging from the fact that the ring current in naphthalocyanine (Nc) is smaller than that in Pc,<sup>7</sup> the signal from the former may be attributed to a pyrrole proton at the naphthalene ring site. The zinc and cobalt derivatives [*i.e.* (*S*)-**Zn3**, (*R*)-**Zn3**, (*S*)-**Co3**, (*R*)-**Co3** and (*S*)-**Co4**] were prepared by refluxing (*S*)-**H<sub>2</sub>3** and (*R*)-**H<sub>2</sub>3** with Zn(OAc)<sub>2</sub> and CoCl<sub>2</sub>, and (*S*)-**H<sub>2</sub>4** with CoCl<sub>2</sub>, as previously described.<sup>1</sup>

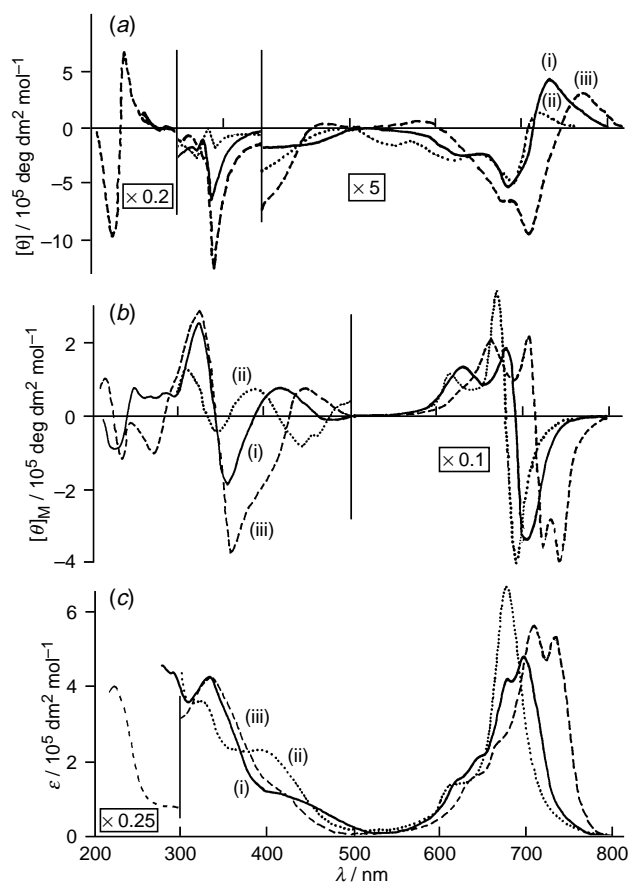
Fig. 1 shows the electronic absorption, magnetic circular dichroism (MCD) and circular dichroism (CD) spectra of (*S*)-**H<sub>2</sub>2** and (*R*)-**H<sub>2</sub>2** in two solvents. In the absorption spectra, the four component Q band, characteristic of metal-free Pc, is

seen and the spectra on the shorter wavelength side of the Soret band are to some extent deformed by the superimposition of the absorption due to the <sup>1</sup>L<sub>a</sub> transition of naphthalene.<sup>8</sup> In the 220-250 nm region, a strong absorption attributable to the <sup>1</sup>B<sub>u</sub> transition of the naphthalene moiety is observed. The MCD





**Fig. 1** (a) CD, (b) MCD and (c) electronic absorption spectra of (i) (*S*)-**H<sub>2</sub>2** and (ii) (*R*)-**H<sub>2</sub>2** in THF and (iii) (*S*)-**H<sub>2</sub>2** in toluene



**Fig. 2** (a) CD, (b) MCD and (c) electronic absorption spectra of (i) (*S*)-**H<sub>2</sub>3**, (ii) its (pyrrole proton) deprotonated species and (iii) (*S*)-**H<sub>2</sub>4** in THF

spectra are characteristic of the metal-free Pcs, producing Faraday *B*-terms approximately corresponding to the absorption maxima or shoulders.<sup>9</sup> Although the solvent effect is discernible in the absorption and MCD spectra, it is most clearly seen in the CD spectra. The shape of the spectrum in toluene is similar to that in the absorption spectrum, while in THF it deviates significantly, as seen typically in the Q band region, reflecting perhaps a tendency to higher aggregation trend in the latter solvent.<sup>10</sup> Thus, subtle differences in the absorption spectra are amplified in the CD spectra. Corresponding to the main Soret and Q band, the *R* and *S* enantiomers show mainly positive and negative CD envelopes, respectively.

The spectra of (*S*)-**H<sub>2</sub>3** and its deprotonated species and (*S*)-**H<sub>2</sub>4** are shown in Fig. 2. Compared with the spectra in Fig. 1, the Q bands are broadened and shifted to longer wavelength, and the CD spectra are mostly negative in sign through the Q and Soret regions. The Q band of (*S*)-**H<sub>2</sub>4** lies at longer wavelength and is stronger than that of (*S*)-**H<sub>2</sub>3**. (*S*)-**Co4** also shows the Q<sub>0-0</sub> band at longer wavelength (708 nm in CH<sub>2</sub>Cl<sub>2</sub>) than is usual for CoPcs.<sup>9</sup> In compounds **1–4**, the binaphthyl moiety of all the *S* isomers is right-handed while that of the *R* isomers is left-handed, judging from the CD pattern in the 220–270 nm region.

The method shown here has general applicability, and the yields are very high for a reaction of this type. Diphthalonitriles linked by short chains (*ca.* 5–6 atoms) can be used as precursors of non-centrosymmetric Pcs such as **2–4**.

## Notes and References

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1 Reaction was carried out at room temperature for three days (C. C. Leznoff, S. M. Marcuccio, S. Greenberg and A. B. P. Lever, *Can. J. Chem.*, 1985, **63**, 623).

- All compounds gave satisfactory elemental analytical data. *Selected data for 1*: Off-white needle [silica, benzene–EtOAc (2 : 1 v/v), *R<sub>f</sub>* 0.58], recrystallized from MeCN–Et<sub>2</sub>O, mp 230–231 °C; yield: 95.2 and 90.4% for (*S*)-**1** and (*R*)-**1**, respectively. [ $\alpha$ ]<sub>D</sub> –29.2 and 29.6 for (*S*)-**1** and (*R*)-**1**, respectively (*c* 1, CH<sub>2</sub>Cl<sub>2</sub>);  $\delta$  (60 MHz, CDCl<sub>3</sub>) 7.7–8.1 (m, 4 H), 7.0–7.6 (m, 14 H); *m/z* (EI) 538 (100%, [M<sup>+</sup>]); For **H<sub>2</sub>2**:  $\delta$ <sub>H</sub> (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 6.0–9.2 (m, 36 H, arom), –4.54 (s, 2 H, pyrrole); *m/z* (FAB) 1078.3 (100%, [M<sup>+</sup>]); a yield by direct methods was 35.7% for (*S*)-**H<sub>2</sub>2**, recrystallized from CH<sub>2</sub>Cl<sub>2</sub>–MeOH. For **Co2**: *m/z* (FAB) 1135 (54%, [M<sup>+</sup>]), 533 (41), 459 (100). For **H<sub>2</sub>3**: *m/z* (FAB) 916 (100%, [M<sup>+</sup>]). For **Zn3**:  $\delta$ <sub>H</sub> (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 6.5–8.7 (m, 22 H, arom), 4.15 (br s, 12 H, OCH<sub>3</sub>). For (*S*)-**H<sub>2</sub>4**:  $\delta$  (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 6–9 (m, 28 H, arom), 1.3–1.8 (m, 18 H, CH<sub>3</sub>), –2.40 (br s, H, pyrrole H at naphthalene site), –4.05 (br s, H, pyrrole H at benzene site). Since, as shown in Fig. 1, UV–VIS absorption, MCD and especially CD spectra change depending on the solvent the details of these spectra will be reported in a full paper.
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- J. Metz, O. Schneider and M. Hanack, *Inorg. Chem.*, 1984, **23**, 1065.
- Compound (*S*)-**H<sub>2</sub>2** and (*R*)-**H<sub>2</sub>2** can be obtained from two molecules of (*S*)-**1** and (*R*)-**1** as a blue powder in 30–36% yield.
- Compounds similar to **2** but linked by two alkyl chains have been reported (C. C. Leznoff and D. M. Drew, *Can. J. Chem.*, 1996, **74**, 307).
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- In the absence of aggregation, the shapes of the CD spectra of allowed transitions are similar to that of the electronic absorption spectrum, aside from its sign (W. Moffitt and A. Moscowitz, *J. Chem. Phys.*, 1959, **30**, 648).

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