

An optically-active subphthalocyanine dimer

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A subphthalocyanine (SubPc) dimer linked by racemic 1,1'-binaphth-2,2'-dioxy (BINOL), **1**, has been synthesized and characterized by 1- and 2-D ¹H NMR, high resolution mass spectrometry (FAB), X-ray crystallography and electronic absorption spectroscopy. Additionally, the dimer derived from optically-active (*R*)-(+)-BINOL, **2**, has been made and studied using CD and MCD spectroscopies.

Nearly twenty year after they were first reported^{1,2} the subphthalocyanine (SubPc) macrocycles began to attract attention because of their interesting optical and nonlinear optical properties,^{3–5} and their ability to serve as precursors in the formation of unsymmetrical phthalocyanines (Pcs).⁶ These cone-shaped, 14 π -electron systems display two intense electronic spectral features similar to those of their higher homologues, the 18 π -electron Pcs: the Q-band at 565 nm ($\epsilon = 90\,000\text{ M}^{-1}\text{cm}^{-1}$) and the Soret band at 305 nm (55 000), both of which are blue-shifted relative to the Pcs.

Monosubstituted phthalonitriles produce racemic mixtures of a pair of regioisomeric SubPcs with C_3 and C_1 symmetry.^{7–11} The separation of both the SubPc regioisomers and, using a chiral HPLC column, the enantiomeric forms, have been reported by Claessens and Torres.⁹ Kobayashi *et al.*¹¹ have published a circular dichroism study of SubPcs with C_3 symmetry.

We report here the synthesis and spectroscopic characterization of a chiral SubPc dimer in which two SubPc macrocycles are linked by the *R* enantiomer of BINOL [(*R*)-(+)-1,1'-bi-2-naphthol] (Fig. 1).¹² Although the molecule has approximate C_2 symmetry, the local C_{3v} symmetry of the SubPc units is, in fact, preserved. The optical activity of **2** is thus derived not from the SubPc's peripheral substitution pattern but rather from the chirality of the linking BINOL unit. Also described is the X-ray crystal structure of the compound derived from racemic BINOL, the first structurally characterized bis-SubPc complex.

Both **1** and **2** were prepared by refluxing 0.86 g of SubPc (2.0 mmol) and 0.27 g of either racemic or (*R*)-(+)-BINOL (0.94 mmol) in 15 mL of dry 1,2,4-trichlorobenzene for 72 hours. The reaction mixture was flash chromatographed on silica, eluting first with *n*-hexane to remove the trichlorobenzene, next with toluene to remove unreacted SubPc and small amounts of the SubPc–BINOL 1 : 1 adduct, and finally with toluene–ethyl acetate (20 : 1). The toluene–ethyl acetate solution was rotary

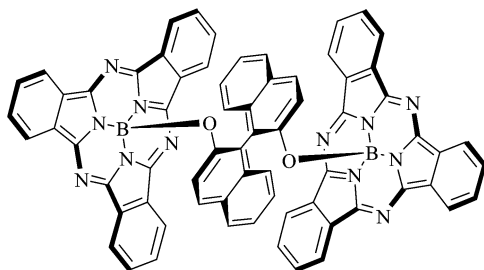
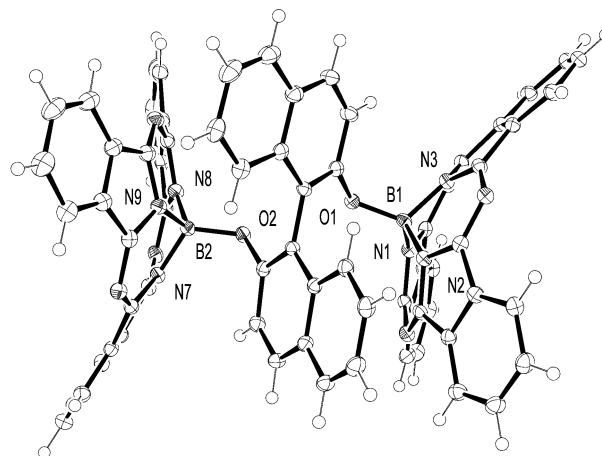
evaporated to dryness. The microcrystalline product was recrystallized from toluene–*n*-hexane, collected by vacuum filtration, washed several times with *n*-hexane and dried under vacuum at 76 °C for 24 h.[†]

The ¹H NMR resonances of the linking BINOL group display considerable upfield shifts and chemical shift dispersion as a result of the diamagnetic ring currents from the two SubPc units. The protons in the BINOL 3- and 3'-positions, in particular, are seen at 5.06 ppm.

A thermal ellipsoid plot of **1** is shown in Fig. 2.[‡] The SubPc macrocycles display their familiar bowl shape and are separated by 5.57 Å, the distance between the boron atoms. The planes of the macrocycles, as determined by the N₃ coordination sphere about the central boron atoms, are inclined at 18.2° to each other, while the least squares planes of the BINOL naphthalene units form an angle of 69.1°.

Fig. 3 shows the magnetic circular dichroism (MCD), circular dichroism (CD), and electronic absorption spectra of the optically-active dimer, **2**, in CH₂Cl₂. The Q band region was deconvoluted simultaneously for the three spectra using the same band-centre and bandwidth parameters (the obtained components are shown using broken lines and Gaussian line shape).¹³ The solid and broken lines in the inset display the experimental and simulated CD spectra in the Q₀₀ band region, which confirms substantial reproducibility of the deconvolution calculation. In addition, the oscillator strength (*f*) and transition energies obtained from molecular orbital calculations¹⁴ are overlaid with the absorption spectrum.

The Q band of **2** appeared at 562 nm, which is shorter by several nanometers than those of normal SubPc monomers (*ca.* 565–567 nm).¹⁵ In the calculation, split Q bands of similar intensity were estimated at 561 (*f* = 0.6831) and 557 (0.6047) nm, suggesting that the shorter wavelength side of the Q band peak is a complex superposition of many vibrational bands.¹⁶ On the longer wavelength side of the Q band, two weak

Fig. 1 BINOL([SubPc]B)₂, **1**.Fig. 2 ORTEP representation of **1** (50% ellipsoids). Only the boron atoms and their N₃O coordination spheres are labelled.

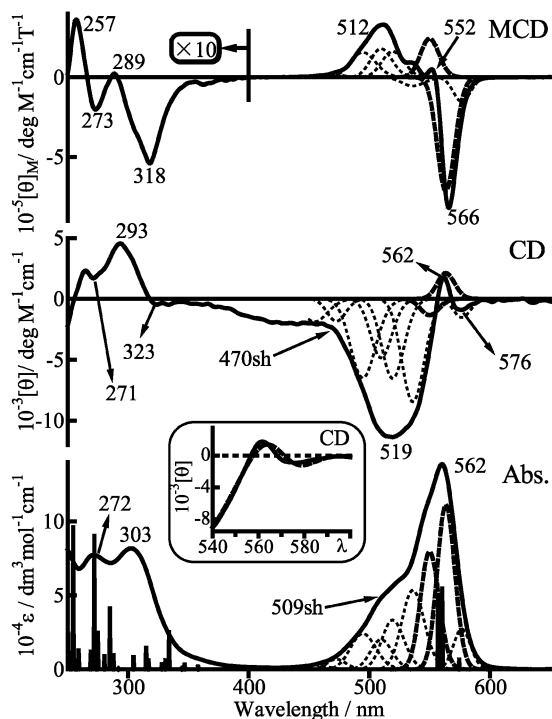


Fig. 3 Electronic absorption, CD, and MCD spectra (from bottom to top) of **2** in CH_2Cl_2 . The calculated transition energies and oscillator strength are overlaid with the absorption spectrum. Deconvoluted individual Gaussian peaks are shown with a dotted line on each of the spectra. The inset shows the Q band region of the CD (solid line) and simulated (dashed line) spectra.

transitions were predicted at 578 ($f = 0.0004$) and 575 (0.0821) nm, which correspond to forbidden transitions of a nearly cofacial, but slightly oblique, sandwich type **1**.¹⁷ In accord with the calculated result, there is no intense absorption to the longer wavelength of the Q band peak at 562 nm. We can thus state with some confidence that the optimum structure used for the calculation adequately represents the structure of **2** in solution. The longer wavelength component of the Q band (at 561 nm) is composed of transitions from the localized HOMO to localized HOMO + 1 in one SubPc unit and the localized HOMO - 1 to localized LUMO in the other SubPc unit.

Similarly, the shorter wavelength component (at 557 nm) is composed of two transitions from the HOMO to LUMO + 3 and the HOMO - 1 to LUMO + 2. Accordingly, these two allowed transitions are considered to arise from an excitonic interaction, and accompanying CD generation can be expected.¹⁷ Since the transition dipole moment of SubPc lies in the SubPc plane, an exciton coupled model predicts CD signs changing from + to - on going from longer to shorter wavelengths,¹⁸ differing from the experiment (Fig. 3, middle). The result of band deconvolution, however, suggests that the negative CD observed at 576 nm corresponds to forbidden transitions predicted at 578 and 575 nm,¹⁹ and therefore that the real Q band CD signals are those detected at 564 nm (+) and 550 nm (-) (this is also supported from the correspondence to the MCD spectra). This example demonstrates that an incorrect analysis can result if band deconvolution is not performed *a priori*, and that even weak CD signals can be analyzed by an exciton coupled method following band deconvolution. The ratio of the positive CD envelope at 564 nm and negative envelope at 550 nm is *ca.* 1 : 1.9, giving asymmetric curves. This asymmetric CD curve can be rationalized by an induced CD on the SubPc by the chiral binaphthyl unit.²⁰

In summary, we have synthesized the first example of an optically-active binuclear subphthalocyanine and characterized

it using electronic absorption, CD and MCD spectroscopies, semi-empirical molecular orbital calculations and have determined the X-ray crystal structure of the racemic form.

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Notes and references

† Yield: 0.12 g (12%); mp > 300 °C (**1**), 290–310 °C (dec.) (**2**); ¹H NMR (300, MHz, CDCl_3): δ = 5.12 (d, J = 8.8 Hz, 2H), 6.00 (d, J = 8.4 Hz, 2H), 6.43 (t, J = 7.2 Hz, 2H), 6.85 (t, J = 7.4 Hz, 2H), 7.20 (d, J = 8.9 Hz, 2H), 7.47 (d, J = 7.9 Hz, 2H), 7.71 (m, 12H), 8.50 (m, 12H); UV-vis (CH_2Cl_2): λ_{max} = 562 nm (ϵ = 140 000 $\text{M}^{-1} \text{cm}^{-1}$), 550 (sh), 525 (sh), 303 (85 000); HRMS (FAB): M^+ = 1074.3286 (calc'd for $\text{C}_{68}\text{H}_{36}\text{B}_2\text{N}_{12}\text{O}_2$: 1074.3290); elemental analysis calcd for $\text{C}_{68}\text{H}_{36}\text{B}_2\text{N}_{12}\text{O}_2$: C, 75.99; H, 3.38; N, 15.64; found: C, 76.58; H, 4.11; N, 14.62%; TLC, R_f = 0.46 (silica; ethyl acetate-*n*-hexane, 1 : 1).

‡ Single crystals of BINOL([SubPc]B)₂, **1** were grown in chloroform and formed as the disolvate. Data collection was carried out on a Bruker SMART 1000 diffractometer that was equipped with a CRYO Industries low temperature apparatus. Crystal data. $\text{C}_{70}\text{H}_{38}\text{B}_2\text{Cl}_6\text{N}_{12}\text{O}_2$, M = 1313.44, triclinic, a = 13.7625(7), b = 15.0790(8), c = 16.2905(10) Å, α = 71.493(2), β = 68.488(2), γ = 78.757(2)°, U = 2970.7(3) Å³, T = 90 K, space group $P\bar{1}$ (no. 2), Z = 2, $\mu(\text{Mo-K}\alpha)$ = 0.35 mm^{-1} , 39325 reflections measured, 17067 unique (R_{int} = 0.044) which were used in all calculations. The final $wR(F^2)$ was 0.130 (all data). CCDC 203809. See <http://www.rsc.org/suppdata/cc/b3/b301563g/> for crystallographic data in .cif or other electronic format.

- 1 A. Meller and A. Ossko, *Monatsh. Chem.*, 1972, **103**, 150.
- 2 H. Kietaibl, *Monatsh. Chem.*, 1974, **153**, 405.
- 3 S. H. Kang, Y.-S. Kang, W.-C. Zin, G. Olbrechts, K. Wostyn, K. Clays, A. Persoons and K. Kim, *Chem. Commun.*, 1999, 1661.
- 4 G. Olbrechts, K. Wostyn, K. Clays, A. Persoons, S. H. Kang and K. Kim, *Chem. Phys. Lett.*, 1999, **308**, 173.
- 5 C. G. Claessens, D. González-Rodríguez and T. Torres, *Chem. Rev.*, 2002, **102**, 835.
- 6 N. Kobayashi, R. Kondo, S.-I. Nakajima and T. Osa, *J. Am. Chem. Soc.*, 1990, **112**, 9640.
- 7 C. G. Claessens and T. Torres, *Chem. Eur. J.*, 2000, **6**, 2168.
- 8 C. G. Claessens and T. Torres, *Eur. J. Org. Chem.*, 2000, 1603.
- 9 C. G. Claessens and T. Torres, *Tetrahedron Lett.*, 2000, **41**, 6361.
- 10 C. G. Claessens and T. Torres, *J. Am. Chem. Soc.*, 2002, **124**, 14522.
- 11 N. Kobayashi and T. Nonomura, *Tetrahedron Lett.*, 2002, **43**, 4253.
- 12 Binuclear SubPcs in which two SubPcs share a benzene ring were recently reported: C. G. Claessens and T. Torres, *Angew. Chem., Int. Ed.*, 2002, **41**, 2561; T. Fukuda, J. R. Stork, R. J. Potucek, M. M. Olmstead, B. C. Noll, N. Kobayashi and W. S. Durfee, *Angew. Chem., Int. Ed.*, 2002, **41**, 2565.
- 13 N. Kobayashi, T. Fukuda and D. Lelièvre, *Inorg. Chem.*, 2000, **39**, 3632.
- 14 MO calculations: The molecular geometry of **1** was optimized at the semiempirical AM1 level employing the HyperChem software. Configuration interaction was calculated using single electron excited states within 9 eV at the AM1 level. The optimized structure was practically identical with the observed structure in the solid state.
- 15 N. Kobayashi, T. Ishizaki, K. Ishii and H. Konami, *J. Am. Chem. Soc.*, 1999, **121**, 9096.
- 16 The Q band of SubPc monomer was calculated at 572 nm (AM1 level).
- 17 N. Harada and K. Nakanishi, *Circular Dichroic Spectroscopy. Exciton Coupling in Organic Stereochemistry*, University Science Books, Mill Valley, CA, 1983.
- 18 A weak CD signal is expected, given the distance between the SubPc centers and their relative orientation.
- 19 It is difficult to determine whether this band originates from the forbidden transition, vibronic band, or aggregated species.
- 20 G. Beer, C. Niederal, S. Grimme and J. Daub, *J. Angew. Chem., Int. Ed.*, 2000, **39**, 3252.