A Rigid, Laterally Bridged Binuclear Subphthalocyanine: the First Dimer of Aromatic Macrocyclic Complexes containing Boron

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The synthesis and characterisation of a subphthalocyanine and its planar binuclear dimer: the first example of an aromatic macrocyclic dimer containing boron is reported.

Phthalocyanines consist of four isoindoline units and a variety of their binuclear[1] and multimer[2] complexes have been reported to date. However, no description has appeared on the binuclear and/or multimer of the so-called subphthalocyanines[3] and superphthalocyanines.[4] These compounds are, as inferred from their name, relatives of phthalocyanines, but are composed of three or five isoindoline units, respectively, as opposed to four units in phthalocyanines. We now report the first example of a binuclear subphthalocyanine, *i.e.* a laterally bridged binuclear subphthalocyanine 1, together with its mononuclear control molecule 2. To our knowledge, even the electronic absorption spectrum of monomeric subphthalocyanines has not been shown in previous literature and compound 1 is the first example of MN_3 (M = boron) aromatic macrocyclic dimers.

Condensation of an excess of 4-*tert*-butylphthalonitrile, 1,2,4,5-tetracyanobenzene and diphenylboron bromide (Ph_2BBr) (mole ratio = 20:1:5) in argon-saturated 1-chloro-naphthalene for 10 min at 260 °C[3a] gave a crude mixture of 1 and 2, after silica-gel chromatography. From this mixture, pure 1 (azure coloured) and 2 (magenta coloured) have been obtained in 2.8 and 24% yields, respectively, after gel permeation chromatography using a Bio-beads SX-2 (Biorad) column. Compound 2 was also obtained by similar treatment (10 min at 260 °C in 1-chloronaphthalene) of 4-*tert*-buytyl-phthalonitrile and Ph_2BBr in 43–48% yield.[3a] Mass spectrometry using fast atom bombardment (FAB) gave ion peaks at 1094 [M^+, 7 (relative intensity)], 934 (M^+ − 2Br, 84) and 154(100) for 1 and 643 (M^+, 27) and 563 (M^+ − Br, 100) for 2; these compounds were further characterised by IR, NMR and

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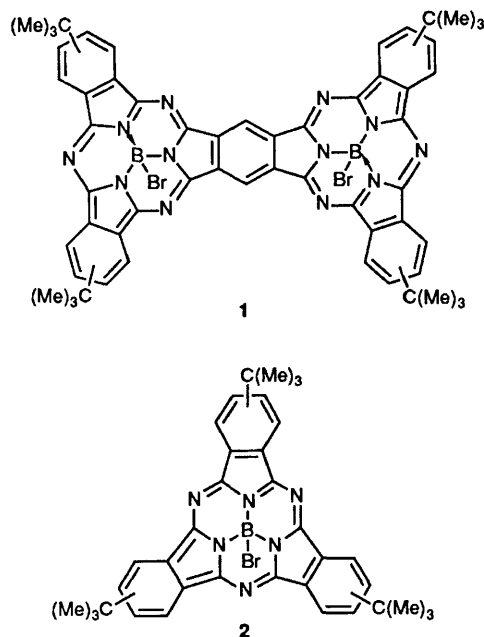
elemental analysis.[†] Both **1** and **2** show IR absorption at 890 cm^{-1} ascribable to B–Br vibrations[‡] and their NMR spectra are broad and complex because of their bent nature and large ring current effect.[†] Even proton signals in the *tert*-butyl group spread between δ 1.2 and 1.6, as seen in a phthalocyanine,[5] and aromatic protons appeared as a multiplet between δ 7.2–8.4 in deuteriated chloroform (ref. TMS).

Fig. 1 shows the absorption, magnetic circular dichroism (MCD), emission and excitation spectra of **1** and **2**. The shape of the absorption spectrum of **2** is similar to that of a metallophthalocyanine,[6] but the bands are generally shifted to the blue, that is *ca.* 120–130 nm in the *Q* band region (*ca.* 3000–3500 cm^{-1}) and 20–30 nm in the *B* (Soret) band region (*ca.* 2000–3500 cm^{-1}), reflecting the smaller π-conjugated system than in phthalocyanines. Considering that the *Q* band of superphthalocyanines appears at *ca.* 910–930 nm,[4] it is found that the *Q* band energy changes *ca.* 3000–3600 cm^{-1} per isoindoline unit, *i.e.* on passing from subphthalocyanine to phthalocyanine and further to superphthalocyanine. The absorption coefficients of the main *Q* and Soret bands are smaller than those of general phthalocyanines.[6] The *Q* band MCD spectrum of **2** appears to be composed of a superimposition of Faraday *B* terms.[7] Given the somewhat cone-shaped nature of subphthalocyanines,[3b] the MCD spectrum may be interpreted under the *C₃ᵥ* or *D₃ₕ* approximation. The positions of MCD peaks or a trough in the *Q* band region are approximately the same as those of absorption shoulders or a peak. Emission and excitation spectra of **2** are in a mirror=image relationship. A fluorescence quantum yield (φ$_F$) of 0.61 was obtained in chloroform by the use of tetraphenylporph-
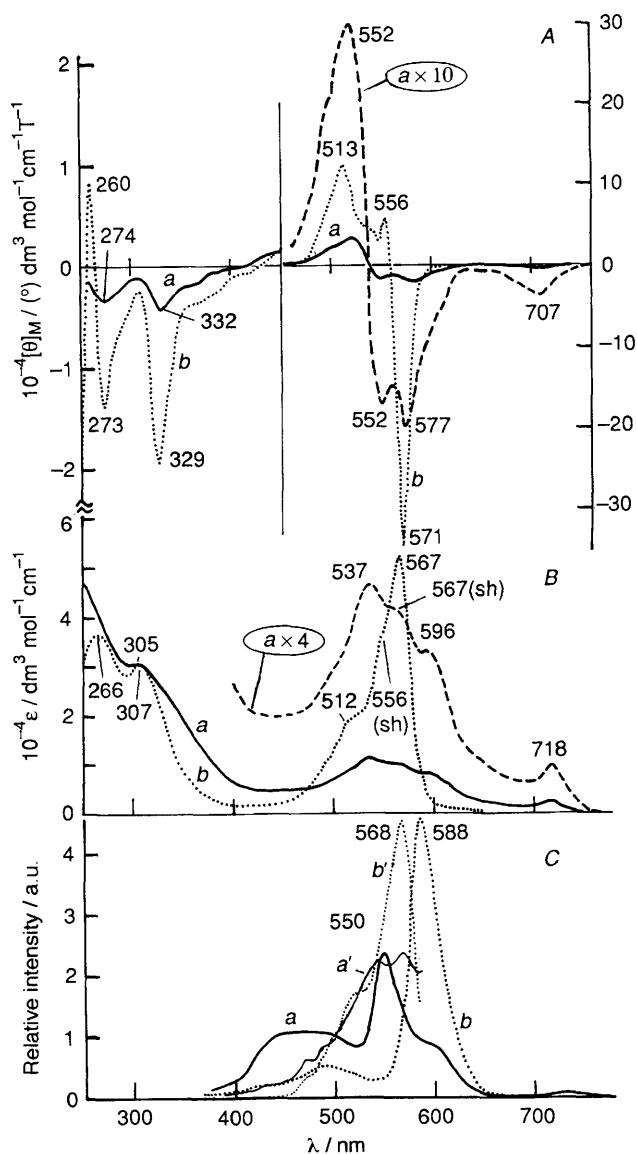

Fig. 1 MCD (*A*) UV–VIS-near IR absorption (*B*) and emission and excitation (*C*) spectra of **1** (curves *a* and *a'*) and **2** (curves *b* and *b'*) in deaerated chloroform. Excitation was at 360 nm. Magnetic field = 1.09 T. [1] and [2] in fluorescent experiments was *ca.* 10^{-7} mol dm^{-3}. Note the encircled magnification factor.

yrin in aerated benzene as a calibrant (φ$_F$ = 0.11);[8] the lifetime was determined from the decay curve by the use of the least-squares method to be 2.1 ns.

The absorption spectrum of **1** is quite different from that of **2** or a planar binuclear phthalocyanine[9a] and tetrabenzoporphyrin[9b] recently reported. A broad and very weak *Q* band, indicative of intramolecular electronic coupling,[10] is seen with an additional small peak at 718 nm. The MCD intensity of **1** is much weaker than that of **2** especially in the *Q* band region, and a MCD trough observed for **2** at 571 nm splits into two small troughs. A positive (negative in sign) *B* term is observed corresponding to the near-IR absorption band. From the absorption and MCD spectra in the *Q* region, the exciton splitting is estimated to be about 1800–1900 cm^{-1}, which is comparable to that of binuclear phthalocyanines.[5,10] A *Q* band *S₁* emission of roughly half the intensity of that of **2** is detected with an unusually broad excitation spectrum as observed for a planar binuclear tetrabenzoporphyrin.[9b] Weak emission may be a reflection of non-planarity in **1**, since covalently bound relatively flexible porphyrin[11] and phthalo-

cyanine[10] dimers emit more weakly than monomeric species because of intramolecular quenching. A lifetime of 3.3 ns was obtained.§

A previous X-ray crystallographic study[3b] substantiated that subphthalocyanines are cone-shaped because of constraint arising from three isoindoline units. Nevertheless, the above data indicate that both 1 and 2 indeed have strong aromaticity. Weak emission and a broad, very weak Q band and the appearance of a near IR band in 1 indicate intramolecular excitonic interaction between the two chromophore units in this molecule.[10,12]

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§ This value and 2.1 ns of 2 are much smaller than the lifetimes of the S_1 emission of a laterally bridged planar binuclear tetrabenzoporphyrin (9.80 ns)[9b] and phthalocyanine (4.26 ns) (unpublished datum) in the same solvent. In addition, the fact that the lifetime of 1 (a dimer) is longer than that of 2 (a monomer) is contrary to the general result. The reason for these results are presently unclear.