

# 1,4-Dibutoxy-2,3-di(4-pyridyl)-8,11,15,18,22,25-hexakis(hexyl)-phthalocyaninato zinc, a self-assembled coordination polymer in the solid state

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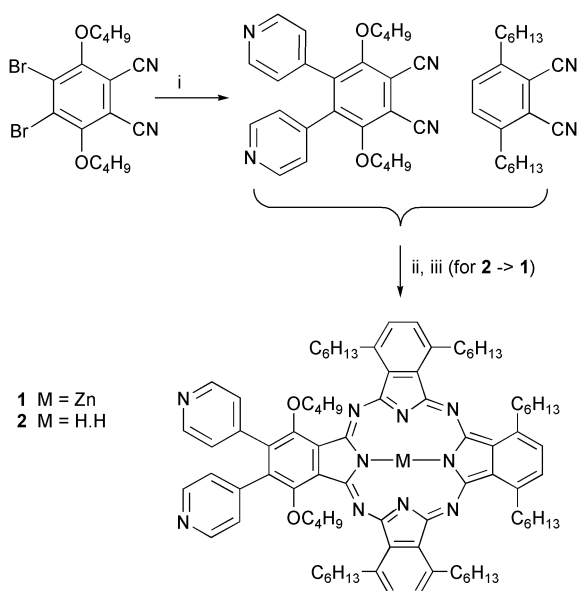
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The title compound forms intermolecular zinc–nitrogen coordinated species in solution and self-assembles to form a coordination polymer in the solid state, the X-ray structure for which shows that the unit cell contains eight macrocycle units in two chains comprising both enantiomeric forms as ABBA/BAAB sequences.

Phthalocyanines show a propensity to form co-facial or near co-facial molecular assemblies. This type of packing is well documented for the crystal state<sup>1</sup> but is also evident among aggregated molecules in solution<sup>2</sup> and in the long columnar stacks of liquid crystal phases exhibited by derivatives bearing long alkyl chains.<sup>3</sup> In an earlier study we proposed<sup>4</sup> that a hexa-octyl pyridino[3,4]tribenzoporphyrzine metallated with zinc(II) forms 'edge-to-face' rather than non-cofacial aggregates in the solution phase, resulting from the pyridyl N atom of one molecule complexing with the zinc centre of a second. We have now explored this type of self-assembled structure further using a phthalocyanine bearing two pyridyl substituents **1**. A crystal structure determination, which we believe to be the first of a non-uniformly substituted phthalocyanine, establishes that the compound indeed self-assembles edge-to-face to form a 'zigzag' polymer in the solid state.

Compound **1** was prepared according to Scheme 1. The 4,5-dibromo-3,6-dibutoxyphthalonitrile precursor<sup>5</sup> was reacted with pyridine-4-boronic acid under Suzuki conditions to give 4,5-dipyridyl-3,6-dibutoxyphthalonitrile along with a smaller amount of 4-pyridyl-3,6-dibutoxyphthalonitrile. The former was cross-cyclotetramerised with 3,6-dihexylphthalonitrile to form the metal-free phthalocyanine **2**. Compound **2** was metallated using zinc acetate to form **1**.

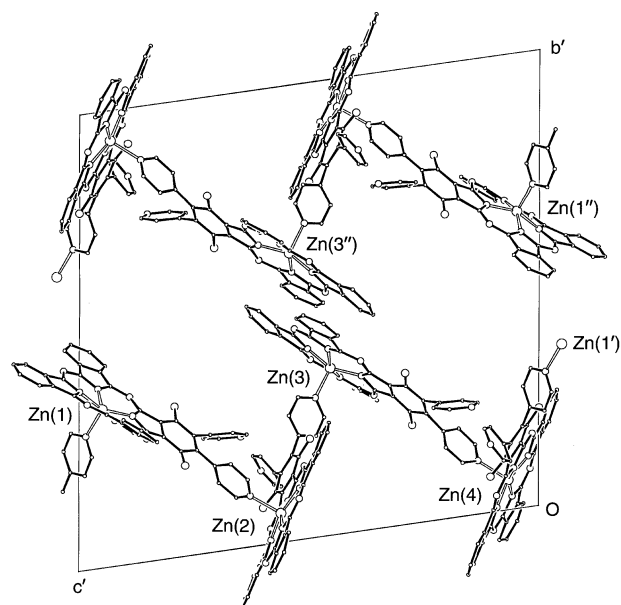


**Scheme 1** Reagents and conditions: i, pyridine-4-boronic acid,  $(\text{PPh}_3)_4\text{Pd}$ ,  $\text{CsF}$ , dry DME, reflux under  $\text{N}_2$ , 45%; ii, Li, BuOH, reflux, AcOH, 10%. iii,  $\text{Zn}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ , BuOH, reflux, 85%.

Recrystallisation from THF/MeOH afforded shiny dark green prisms, mp  $>290^\circ\text{C}$ , the X-ray crystal structure for which is shown in Fig. 1.<sup>†</sup> There are four independent phthalocyanine moieties in the unit cell, (1)-1, (1)-2, (1)-3 and (1)-4, centred on Zn(1)–Zn(4), respectively. Each zinc has square pyramidal coordination and the apical Zn–pyridine bonds link the molecules in an infinite polymer chain. Such a chain is reminiscent of that reported earlier for zinc 5,10,15-triphenyl-20-pyridylporphyrin.<sup>7</sup> Unlike the latter, **1**, though possessing a plane of symmetry in the monomeric state, generates a chiral complex upon coordination. Fig. 1 shows that the unit (1)-1, (1)-2, (1)-3 and (1)-4 contains the two enantiomers, (A and B) in the sequence ABBA. This unit packs with chains of the racemic sequence, BAAB, *i.e.* (1)-1'', (1)-2'', (1)-3'' and (1)-4'', related by a centre of symmetry. There is partial overlap of near neighbour macrocyclic rings of the two polymer chains, *e.g.* (1)-3 and (1)-3''.

Fig. 2 shows the structure of one of the individual molecules, (1)-1, with the six hexyl groups included. As expected the zinc atom is out of the plane of the four coordinating ring N atoms, by 0.438(7) Å. Its bond to the pyridine N is *ca.* 0.13 Å longer than the mean length of the bonds to the macrocycle's four coordinating N atoms. Key bond lengths and angles for all four variants of **1** are shown in Table 1. These show very similar patterns in the four residues but considerable variation in the out-of-base-plane displacement of the zinc atoms towards the neighbouring pyridine ligand.

The visible and near-IR spectrum of the polymeric structure was measured of a burnished film, *i.e.* one in which crystals are gently smeared onto a glass slide. The multi-band absorption

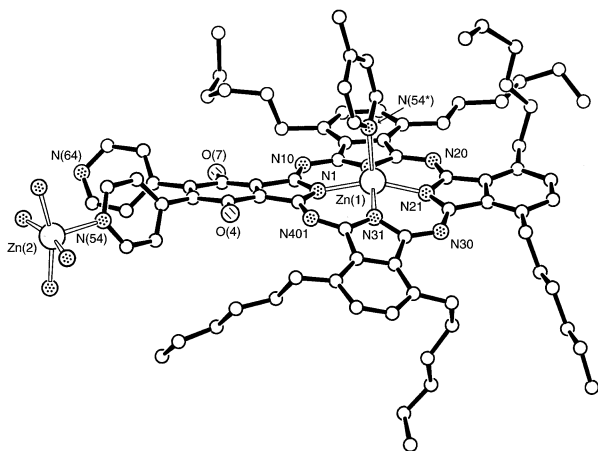


**Fig. 1** The linking of molecules in the crystal of **1**. The substituent hexyl and butyl groups have been omitted for clarity. The primed suffixes indicate symmetry operations: 'x, y, z – 1; ''1 – x, 1 – y, 1 – z.

**Table 1** Dimensions about the zinc atoms. Bond lengths (Å) and angles (°) with esds in parentheses

Parameters for residues (1)- <i>n</i>	(1)-1	(1)-2	(1)-3	(1)-4
Zn( <i>n</i> )-N(1)	2.043(12)	2.067(16)	2.059(11)	2.035(14)
Zn( <i>n</i> )-N(11)	1.955(12)	2.021(14)	2.028(13)	2.039(13)
Zn( <i>n</i> )-N(21)	2.033(11)	1.994(14)	2.005(12)	1.992(12)
Zn( <i>n</i> )-N(31)	2.036(13)	2.064(14)	2.028(15)	2.049(13)
Zn( <i>n</i> )-N(54*)	2.143(12)	2.156(12)	2.163(14)	2.173(11)
Mean Zn-N(base) <sup>a</sup>	2.02(2)	2.04(2)	2.030(11)	2.029(13)
N(11)-Zn( <i>n</i> )-N(1)	86.4(6)	87.8(7)	87.3(5)	88.0(6)
N(21)-Zn( <i>n</i> )-N(1)	154.9(5)	164.6(4)	155.0(5)	160.9(4)
N(31)-Zn( <i>n</i> )-N(1)	86.7(6)	87.0(8)	86.9(6)	88.4(6)
N(11)-Zn( <i>n</i> )-N(21)	88.4(5)	91.5(6)	87.0(6)	88.4(5)
N(11)-Zn( <i>n</i> )-N(31)	154.9(5)	163.8(4)	157.9(6)	162.7(4)
N(21)-Zn( <i>n</i> )-N(31)	87.6(5)	89.5(7)	89.3(6)	89.5(6)
N(1)-Zn( <i>n</i> )-N(54*)	95.8(4)	91.5(4)	95.5(4)	90.9(4)
N(11)-Zn( <i>n</i> )-N(54*)	98.3(4)	99.6(4)	100.7(4)	101.4(4)
N(21)-Zn( <i>n</i> )-N(54*)	109.2(3)	103.7(4)	109.5(4)	108.2(4)
N(31)-Zn( <i>n</i> )-N(54*)	106.4(4)	95.9(4)	101.1(4)	95.5(4)
N-Zn-N( <i>cis</i> , base) <sup>b</sup>	87.3(4)	88.9(10)	87.6(6)	88.6(3)
N-Zn-N( <i>trans</i> , base) <sup>b</sup>	154.91(3)	164.2(4)	156.4(14)	161.8(10)
N-Zn-N(from apex) <sup>b</sup>	102(3)	98(3)	102(3)	99(4)
Displacement of Zn from N <sub>4</sub> base mean-plane	0.438(7)	0.276(6)	0.415(7)	0.320(5)

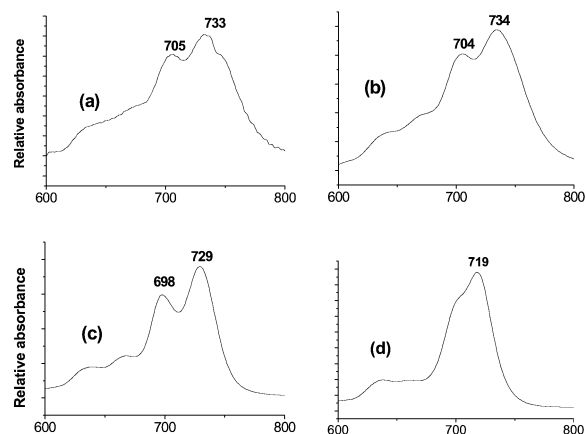
<sup>a</sup> N(base) refers to the four N atoms of the phthalocyanine core. <sup>b</sup> Mean values.



**Fig. 2** View of (1)-1, with its adjoining pyridyl ligand, coordinated through N(54\*), and, bonded to N(54), the coordination sphere of Zn(2). The butyl groups (attached to the O atoms) and hydrogen atoms have been omitted for clarity.

envelope is shown as Fig. 3(a). A spin coated film of **1** obtained from a solution in THF gives rise to a closely similar spectrum, Fig. 3(b), implying that the film contains a comparable molecular assembly.

The behaviour of **1** in solution is solvent dependent. A similar electronic absorption envelope to that of the polymer is observed in the spectrum of the compound in CH<sub>2</sub>Cl<sub>2</sub> solution, Fig. 3(c). However, the bands in the latter show a small hypsochromic shift, which may be attributed to the presence of lower aggregates. Addition of one drop of pyridine to the solution evidently breaks down these aggregates, giving a new spectrum, Fig. 3(d), which is superimposable upon that obtained



**Fig. 3** Visible and near-IR spectrum (600–800 nm) of **1** as (a), a burnished film; (b), a spin coated film; (c) as a solution in CH<sub>2</sub>Cl<sub>2</sub>, and (d), as (c) but after addition of one drop of pyridine.

for **1** in THF solution. Disruption of the solution phase aggregates is also observed by <sup>1</sup>H NMR spectroscopy. The spectrum of **1** in CDCl<sub>3</sub> shows no signals for pyridyl protons at chemical shifts downfield of those for phthalocyanine ring protons. This is consistent with an equilibrium which, on time average, contains a significant amount of edge-to-face aggregates. Addition of pyridine-*d*<sub>5</sub> to the solution changes the spectrum to show pyridinoid proton signals at 8.62 and 7.40 ppm for uncomplexed pyridine rings.

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## Notes and references

† *Crystal data*: C<sub>86</sub>H<sub>110</sub>N<sub>10</sub>O<sub>2</sub>Zn, *M* = 1381.2, triclinic, space group *P* $\bar{1}$  (no. 2), *a* = 19.979(4), *b* = 27.995(9), *c* = 28.253(8) Å,  $\alpha$  = 98.52(2),  $\beta$  = 90.19(1),  $\gamma$  = 92.27(2)°, *V* = 15 615(7) Å<sup>3</sup>. *Z* = 8, *D*<sub>c</sub> = 1.175 g cm<sup>-3</sup>, *F*(000) = 5936, *T* = 140(1) K,  $\mu$ (Mo-K $\alpha$ ) = 3.7 cm<sup>-1</sup>,  $\lambda$ (Mo-K $\alpha$ ) = 0.71069 Å. Diffraction intensities measured on a Rigaku R-Axis IIC image plate diffractometer with rotating anode X-ray source. Total no. of reflections recorded, to  $\theta_{\max}$  = 20° (limit of useful data in this poorly diffracting sample), was 45 798 of which 26 641 unique (*R*<sub>int</sub> = 0.119); 14 910 'observed' with *I* > 2 $\sigma$ . Structure determination by direct methods shows four independent Zn-phthalocyanine complex molecules; refinement by full-matrix least-squares methods. The non-hydrogen atoms (except in disordered side-chains) refined with anisotropic thermal parameters. Hydrogen atoms (except in disordered sections) included in idealised positions and 'riding'. Refinement with the low quality data gave rather unreliable displacement parameters for some atoms which were then refined isotropically. Final *wR*<sub>2</sub> = 0.346 and *R*<sub>1</sub> = 0.216 for all 26 641 reflections; for the 'observed' data only, *R*<sub>1</sub> = 0.146. Highest difference peaks (to ca. 1.2 e Å<sup>-3</sup>) close to zinc atoms. CCDC 191667. See <http://www.rsc.org/suppdata/cc/b2/b207873m/> for crystallographic data in CIF or other electronic format.

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