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Structurally-tolerant self-assembly of zinc pyridyl porphyrins

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Zinc porphyrins equipped with pyridine ligands form macrocyclic assemblies in organic solvents. The assemblies have been characterised by ^{1}H NMR, UV-visible spectroscopy, X-ray crystallography and vapour pressure osmometry. The self-assembly properties of six isomeric porphyrins are relatively insensitive to the geometry of the porphyrin monomer. Changes in the internal torsion angles allow all of the porphyrins to form macrocyclic dimers but with differences in the relative orientations of the porphyrin units. The associated strain reduces the effective molarities from the value of 6 M reported previously for an 'ideal' monomer to between 0.07 and 2 M leading to dimerisation constants in the 10^5–10^6 M^{-1} range. Only one isomer has a geometry that makes dimerisation impossible without severe distortion, and this compound self-assembles to give a tetrameric macrocycle at millimolar concentrations.

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Introduction

Self-assembly is increasingly used as an alternative to covalent strategies in the synthesis of large, well-defined architectures on the molecular scale.[1] Metalloporphyrin coordination is particularly attractive because of the diversity of covalent functionality and stereochemistry possibilities accessible *via* well-established synthetic chemistry.[2] Furthermore, the distinctive physical properties of the porphyrins such as their optical, photochemical and redox activity provide different methods for characterisation of arrays of symmetry-related monomers that are not always available in studies on other oligomeric systems.[3] Nature employs complex arrays of porphyrin-type chromophores (chlorophylls) in photosynthetic energy conversion;[4] and mimicry of such systems is a potential application of self-assembled metalloporphyrin oligomers.[5]

In previous communications,[6] we reported the synthesis and characterisation of a number of designed, self-assembled oligomers based on zinc tetraphenylporphyrins connected to a pyridyl group through one of the phenyl substituents. In the case of $(Zn\mathbf{7})_2$, the dimerisation constant is $K_d = 3 \times 10^8$ M^{-1} in $CHCl_3$ solution (Fig. 1). Dimerisation is favoured by the almost ideal preorganised geometry of the monomer which is maintained by intramolecular hydrogen-bonding in the 2,6-dicarbonylpyridyl connecting arm, so that the pyridine donor nitrogen lone pair is directed normal to the plane of the porphyrin.

In this report, we show that such dimerisation is tolerant of non-ideal monomer geometries. We have synthesised a series of isomeric pyridine functionalised tetraphenylporphyrins (Zn**1**–Zn**6**, Table 1, Fig. 2) and investigated their self-assembly properties in solution and in the solid state. In all cases, the nitrogen lone pair direction is no longer orthogonal to the plane of the zinc porphyrin. Despite the unfavourable geometry and distortions required for dimerisation to take place, stable self-assembled dimers are formed for five of the six compounds.

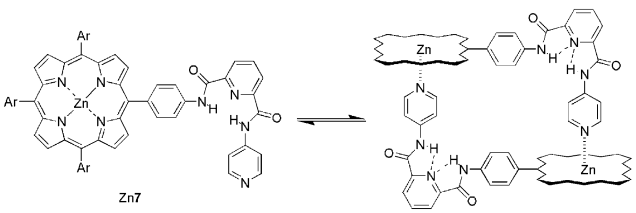

Fig. 1 Dimerisation of Zn**7**; Ar = 4-*n*-pentylphenyl (*P*).

Results and discussion

Synthesis

The zinc porphyrins were prepared from the corresponding free-base amino tetraphenylporphyrins H_2**8**, H_2**9** and H_2**10**. Two solubilising groups were investigated: *P* = 4-*n*-pentylphenyl and *EH* = 3,4-bis(2′-ethylhexyloxy)phenyl (Fig. 2). These were attached to the porphyrin rings through three of the four *meso* phenyl rings. *EH*, the more efficient solubilising group, was required to study Zn**1**, Zn**2** and Zn**3** at mM

Table 1 Regiochemistry of rings A and B and solubilising groups (Ar) in compounds Zn**1**–Zn**6** (see Fig. 2)

Porphyrin	A	B	Ar
Zn**1**	*para*	*para*	*EH or P*
Zn**2**	*para*	*meta*	*EH or P*
Zn**3**	*meta*	*para*	*EH or P*
Zn**4**	*meta*	*meta*	*P*
Zn**5**	*ortho*	*para*	*P*
Zn**6**	*ortho*	*meta*	*P*

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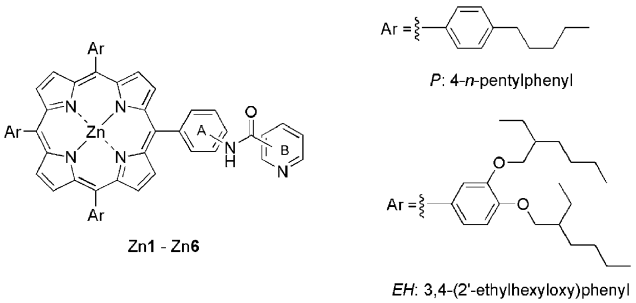
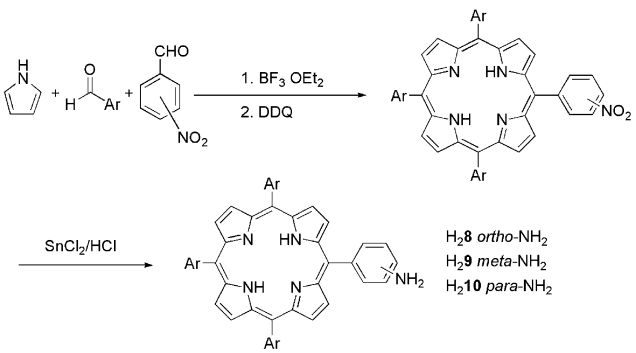


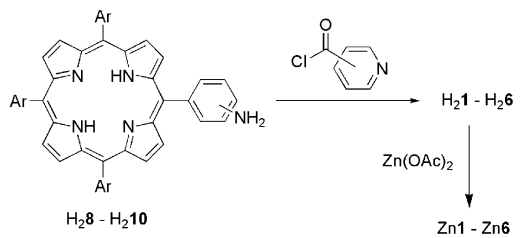
Fig. 2 General structure of compounds Zn**1**–Zn**6**.



Scheme 1 Synthesis of porphyrins H_2**8**–H_2**10**.

concentrations, whereas Zn**4**, Zn**5** and Zn**6** exhibited sufficient solubility with the simpler pentyl groups. The benzaldehyde equipped with two *EH* solubilising substituents was prepared from 3,4-dihydroxybenzaldehyde and 2-ethylhexyl bromide. The 2-ethylhexyl group was racemic, and therefore the products Zn**1***EH*, Zn**2***EH* and Zn**3***EH* are actually mixtures of diastereoisomers. This probably improves the solubility but has little effect on the ligand binding and self-assembly properties.[5b,6b]

Reaction of pyrrole with a mixture of nitrobenzaldehyde and a benzaldehyde bearing the appropriate solubilising groups in CH_2Cl_2 with ethanol and $BF_3{\cdot}OEt_2$ gave, on oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and subsequent purification, the corresponding nitroporphyrins in up to 25% yield. Reduction with $SnCl_2$ in concentrated HCl and 1,4-dioxane proceeded in high yield to give the free base amino tetraphenylporphyrins H_2**8**, H_2**9** and H_2**10** (Scheme 1);[7] Amide coupling reactions to attach the pyridine substituents were performed with the freshly-prepared pyridine carbonyl chloride hydrochloride in CH_2Cl_2 and pyridine giving H_2**1**–H_2**6** in high yields (Scheme 2). The amides could also be prepared directly using the carboxylic acid and *N*,*N*′-



Scheme 2 Synthesis of zinc porphyrins Zn**1**–Zn**6**.

dicyclohexylcarbodiimide (DCC) in dry DMF. The free base porphyrins were then metallated with $Zn(OAc)_2$ in CH_2Cl_2 and MeOH to give the desired zinc porphyrins, Zn**1**–Zn**6**.

Characterisation of the self-assembled complexes

The ^{1}H NMR and UV-visible absorption spectra of all six zinc porphyrins show that they form stable self-assembled complexes in the μM–mM concentration range in chlorinated organic solvents. A range of techniques was used to establish the nature of the self-assembled complexes as detailed below. Although two different solubilising groups were used (*P* and *EH* in Fig. 2), no significant effects on the properties of the porphyrins were observed, so we will not distinguish between porphyrins bearing different solubilising groups in the following discussion.

Vapour pressure osmometry

The effective molecular weights of the zinc porphyrin assemblies in solution were established using vapour pressure osmometry at mM concentrations. The tetra alkyl porphyrin Zn**11***P* which has no pyridine ligands and therefore can not self-assemble was used as calibration standard. Table 2 summarises the results obtained. It is apparent that Zn**1** forms a tetrameric assembly while Zn**2**–Zn**6** all dimerise.[8]

UV-visible absorption spectroscopy

The Soret bands in the UV-visible absorption spectra of all of the zinc porphyrins, Zn**1**–Zn**6**, are red-shifted compared with the reference zinc porphyrin Zn**11**. This is characteristic of pyridine–zinc coordination interactions in these systems. The spectra are concentration-dependent, and so it was possible to determine the association constants for self-interaction, *K*, using concentration titrations. The results are presented in Table 3.

For Zn**1**, the data fit best to a tetramerisation model as expected from the vapour pressure osmometry experiments. The rest fit best to a dimerisation model. In all cases, the dimers are significantly less stable than $(Zn\mathbf{7})_2$, and this presumably reflects the reduced preorganisation of the monomer units which are not geometrically self-complementary in their lowest energy conformations.

X-Ray crystallography

Crystals of Zn**5***P* and Zn**6***P* suitable for single crystal X-ray studies were grown, and the structures obtained are shown in Fig. 3 and 4. Both porphyrins clearly form dimers in the solid state. The structures show the deviations from the expected lowest energy conformations of the monomer units, and these

Table 2 Vapour pressure osmometry data in $C_2H_2Cl_4$ at 295 K

Monomer	Aggregation factor
Zn**11***P*	1.0 ± 0.1
Zn**1***EH*	4.1 ± 0.2
Zn**2***EH*	2.0 ± 0.5
Zn**3***P*	2.3 ± 0.3
Zn**4***P*	2.3 ± 0.3
Zn**5***P*	2.1 ± 0.3
Zn**6***P*	2.3 ± 0.1

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Table 3 Stability constants and effective molarities for macrocyclisation (EM) determined by UV-visible concentration titrations at 295 K[a]

Complex	K	EM[b]/M
(Zn**1***EH*)$_4$	1×10^{12} M^{-3}	0.9
(Zn**2***EH*)$_2$	4×10^{5} M^{-1}	0.4
(Zn**3***EH*)$_2$	3×10^{5} M^{-1}	0.3
(Zn**4***P*)$_2$	7×10^{4} M^{-1}	0.07
(Zn**5***P*)$_2$	2×10^{6} M^{-1}	2
(Zn**6***P*)$_2$	1×10^{6} M^{-1}	1
(Zn**7***P*)$_2$[c]	3×10^{8} M^{-1}	6

[a] All experiments were carried out in $CHCl_3$ except for Zn**1***EH* which was measured in CH_2Cl_2. Errors are ±0.4 in log K. [b] EM was calculated according to ref. 6*a*, assuming that $K_{ref} = 1 \times 10^3$ M^{-1} from the Zn**11** 4-carboxamidopyridine complex reported previously, and the values are accurate to within an order of magnitude. [c] These data were reported previously in ref. 6*a* and uses a different reference ligand system because the ligand is based on aminopyridine rather than carboxypyridine.

are clearly required to allow the porphyrins to generate a self-assembled complex with optimal orientations of the coordinated pyridines with respect to the zinc porphyrins they interact with. The distortions are accommodated by changes in the torsion angles between the amide groups and the aromatic rings. In (Zn**6**)$_2$, the porphyrin units are parallel separated by about 9 Å, but in (Zn**5**)$_2$, the twisting about the amide-aromatic bonds results in a structure in which the two porphyrins are inclined at an angle of about 60°. The two porphyrins in the (Zn**5**)$_2$ dimer are crystallographically non-equivalent, and one of the pyridine ligands is disordered over two sites (only the more symmetric structure is shown in Fig. 3). It is interesting to note that the two dimers that crystallised well are the most stable complexes according to Table 3. The (Zn**7**)$_2$ complex has also been crystallised. The effective molarities for the other four assemblies are all less than 1 M. Since the effective molarity is the concentration at which open polymeric complexes start to compete with closed macrocycles, it is likely that the mixtures of different species that are present at high concentrations make crystallisation of the less stable systems problematic.

^{1}H NMR spectroscopy

Comparison of the ^{1}H NMR spectra of the free base porphyrins, H$_2$**1**–H$_2$**6**, with the corresponding metallated porphyrins, Zn**1**–Zn**6**, provides further information about the three-dimensional structures of the self-assembled complexes. Fig. 5 shows a representative example.

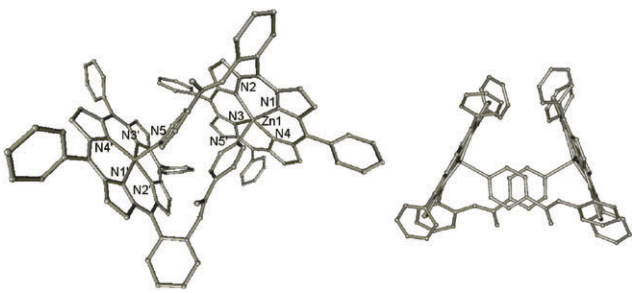

Fig. 3 Two views of the X-ray crystal structure of the self-assembled dimer (Zn**5***P*)$_2$. The solubilising groups have been removed for clarity.

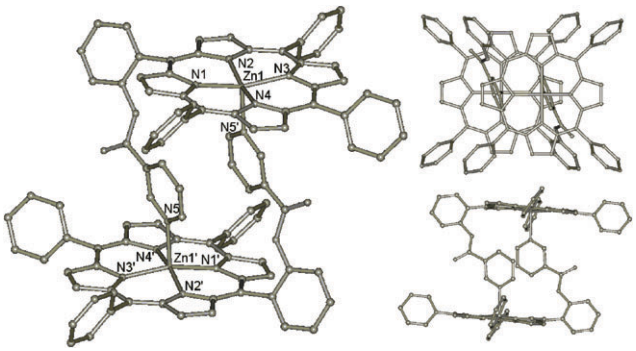

Fig. 4 Three views of the X-ray crystal structure of the self-assembled dimer (Zn**6***P*)$_2$. The solubilising groups have been removed for clarity.

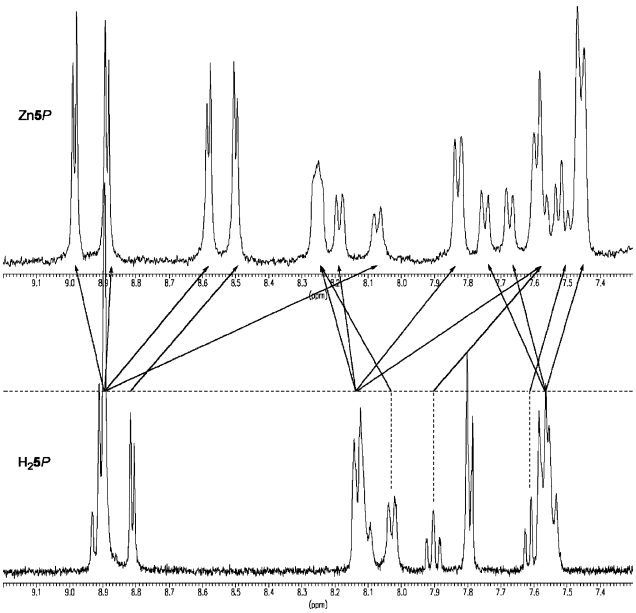

Fig. 5 The aromatic region of the ^{1}H NMR spectra of H$_2$**5***P* and Zn**5***P* in $CDCl_3$ at 295 K. Arrows connect signals that change upon metallation.

The spectra of the zinc porphyrins are significantly more complex than the corresponding free-base porphyrins. The number of signals observed for the protons on the aryl solubilising groups increases on metallation. This shows that the two faces of the porphyrin become non-equivalent on complexation. The rotation about the *meso*-phenyl bonds is slow on the NMR timescale, but in the free-base porphyrins, the two faces of the porphyrin are in similar environments, so no splitting is observed. When self-assembly takes place, one face of the porphyrin is on the inside of the complex and experiences the ring current of neighbouring porphyrin, while the other is on the outside, and the associated signals are not strongly perturbed by complexation. The complexation-induced changes in chemical shift are collected in Fig. 6. The ^{1}H NMR spectra are concentration independent (0.1–10 mM) as expected from the association constants in Table 3, which suggest that the complexes should be fully assembled at mM concentrations. The signals due to the protons on the pyridine groups exhibit the largest shifts, because coordination of the

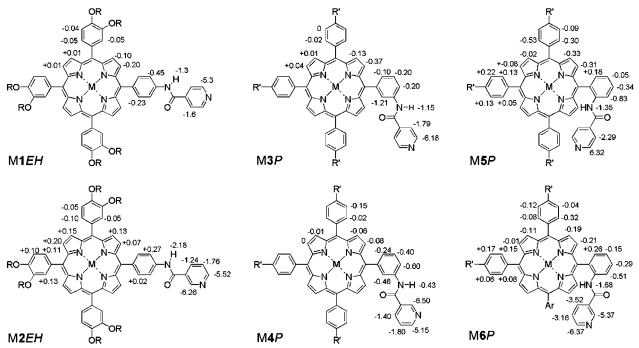

Fig. 6 Limiting complexation-induced chemical shift changes calculated by comparing the ^{1}H NMR spectra of H_2**1**–H_2**6** and Zn**1**–Zn**6**. The values are corrected for the effects of metallating the porphyrin and coordination of pyridine using data for H_2**11** and the Zn**11**–pyridine complex; M = 2H or Zn, R = 2-ethylhexyl, R′ = *n*-pentyl.

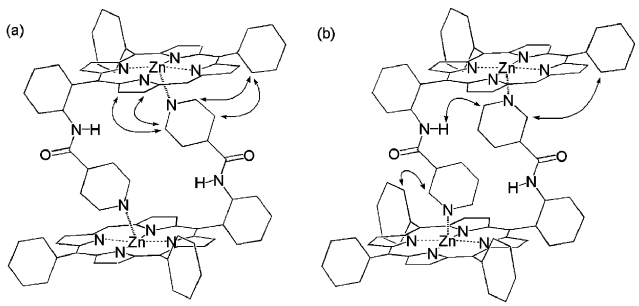

Fig. 7 Intermolecular NOEs observed in ROESY spectra of (a) (Zn**5**)$_2$ and (b) (Zn**6**)$_2$ in $CDCl_3$ at 295 K.

pyridine nitrogen to the zinc places the pyridine in the centre of the shielding region of the porphyrin ring current.[2,6*c*,9]

ROESY spectra of Zn**5** and Zn**6** allowed the identification of a number of unambiguous intermolecular NOEs consistent with the X-ray crystal structures (Fig. 7). In these systems, the porphyrin *meso* phenyl group is substituted in the *ortho* position, and so the complexes are more compact and more rigid than the other systems. There is more exchange broadening in the less stable complexes, and it was not possible to identify unambiguous intermolecular NOEs for Zn**1**–Zn**4** even at low temperatures (218 K).

Conclusions

We have previously shown that an optimally preorganised rigid zinc porphyrin–pyridine conjugate forms a stable self-assembled dimer with an effective molarity of 6 M and a dimerisation constant of 3×10^8 M^{-1}. In this paper, we show that this type of assembly is remarkably tolerant of significant deviations from the ideal geometry. Five of the six zinc porphyrins reported here form relatively stable self-assembled dimers, and the effective molarities range from 0.07 to 2 M with dimerisation constants in the range 10^5–10^6 M^{-1}. Thus by distorting a small number of torsion angles away from their ideal geometries, the monomer units are able to adopt conformations compatible with dimerisation. These conformational changes account for the reduction in stability compared with the ideal system, Zn**7**. The systems based on the *ortho*-amino porphyrin have higher effective molarities for cyclisation (1–2 M) and are more rigid and compact than the other systems, and consequently they were much easier to characterise by all of the techniques discussed above. The dimers based on the *meta*-amino porphyrin have effective molarities that are an order of magnitude lower, and the effective molarity for the *para*-amino porphyrin system that dimerises is an order of magnitude lower again. The other *para*-amino porphyrin system, Zn**1**, presumably has an even lower effective molarity for dimerisation, but it has an ideal geometry for assembling into a tetrameric macrocycle, and this is what is observed in this case. In conclusion, it seems that almost any zinc porphyrin equipped with a pyridine ligand will self-assemble to form a macrocylic dimer, unless there are very strong geometric constraints to prevent this.†

Experimental

Physical methods

UV-visible concentration titrations were carried out to determine the stability constants of the various assemblies. A concentrated solution (3×10^{-4} M) of zinc porphyrin was prepared and added in measured quantities that increased roughly logarithmically to a sample cell, which initially contained 2.5 cm^3 of solvent. The concentration range in the cell spanned values from 1×10^{-8} to 1×10^{-4} M and typically 25 spectra were recorded in each titration. The absorbances at five different wavelengths in the Soret (400–450 nm) and Q bands (550–600 nm) were monitored. The dimerisation or tetramerisation constants were determined from these data using non-linear least-squares curve fitting. The results from different wavelengths tended to be spread over approximately one order of magnitude, so the average values are quoted with an estimated error of ±0.4 in log *K*.

Vapour pressure osmometry was carried out using a Wescor 5500 Vapour Pressure Osmometer. Calibration of the osmometer was carried out using standard solutions of benzophenone in $CHCl_3$, spanning the concentration range 0–150 mmol kg^{-1}. The response was validated using a reference porphyrin, Zn**11***P*, which gave an aggregation number of 1. This confirms that no porphyrin aggregation other than through coordination interactions takes place at the concentrations of interest. Errors are based on multiple measurements for each sample.

Synthesis

Aminoporphyrins H_2**8**, H_2**9** and H_2**10** were synthesised according to published procedures.[7] Nicotinoyl and isonicotinoyl chlorides were freshly prepared by heating the corresponding carboxylic acids to reflux in $SOCl_2$ containing

† By comparison with the dimeric assemblies reported here, it seems likely that the system in ref. 6*b* that we previously assigned as a macrocyclic trimer based on vapour pressure osmometry data was a self-assembled dimer. The monomer was considerably more flexible than those described here, and the effective molarity of 100 M that we reported for trimer assembly is an order of magnitude higher than we have observed in any other system. Reanalysis of the ref. 1*b* data as a dimerisation process gives a much more sensible value of 0.2 M for the effective molarity.

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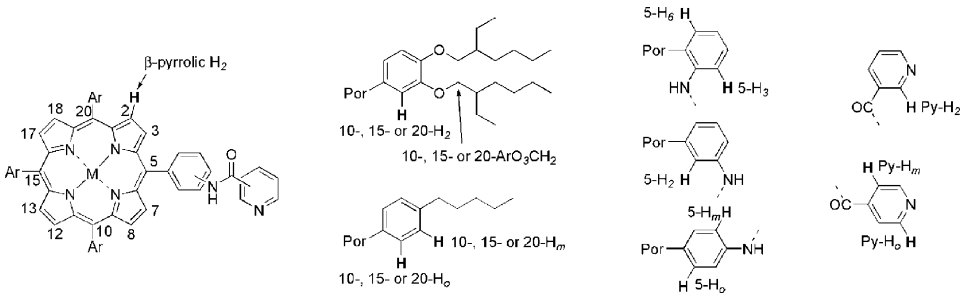

Fig. 8 Labelling scheme for NMR data; Por = C5 of the porphyrin ring.

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catalytic DMF for 2–3 h followed by removal of solvent under vacuum, and they were used without further purification. The labelling scheme used for the NMR data is outlined in Fig. 8.

Typical procedure for amide couplings to give $H_2$1–$H_2$6

The corresponding aminoporphyrin (24.5 mg, 0.03 mmol, 1 equiv.) was dissolved in dry CH_2Cl_2 (10 ml) and pyridine (0.7 ml) was added. The reaction mixture was protected from light and stirred with nicotinoyl chloride hydrochloride (53 mg, 0.3 mmol, 10 equiv.) for 14 h. The reaction mixture was washed with 1 M HCl (3 × 20 ml), 0.5 M NaOH (1 × 40 ml) and water (1 × 50 ml). The combined organic layers were dried over Na_2SO_4, filtered and the solvent was removed *in vacuo*. Pre-adsorption onto silica and purification by column chromatography (2.5 × 11 cm) using 80% CH_2Cl_2–20% petroleum ether (200 ml) gave the first band containing a trace amount of the aminoporphyrin starting material. The desired product was obtained by elution with 2% CH_3OH–98% CH_2Cl_2 (200 ml) and recrystallisation from $CHCl_3$–CH_3OH as a purple powder (yields 70–90%).

5-{4-[*N*-(4-Pyridylcarboxy)]aminophenyl}-10,15,20-tris(4-pentylphenyl)-21*H*,23*H*-porphine, $H_2$1*P*

Mp 275–278 °C; ^{1}H NMR ($CDCl_3$, 250 MHz): δ (ppm) 8.89 (10H, m, β-pyrrolic $H_{2,3,7,8,12,13,17,18}$ and Py-H_o), 8.29 (2H, d, 5-H_o), 8.20 (1H, s, amide NH), 8.14 (6H, d, 10-, 15- and 20-H_o), 8.08 (2H, d, 5-H_m), 7.90 (2H, d, Py-H_m); 7.58 (6H, d, 10-, 15- and 20-H_m), 2.98 (6H, t, $ArCH_2$), 1.95 (6H, qnt, $ArCH_2C$-H_2), 1.56 (12H, m, CH_2), 1.03 (9H, t, CH_3), −2.73 (2H, s, porphyrin NH); UV-Vis (CH_2Cl_2): λ_{max} (ε) 421 (380 000), 518 (18 000), 554 (11 000), 593 (5500); 649 nm (5600 mol^{-1} dm^3 cm^{-1}); MS (+ve FAB): *m*/*z* (%) 945 (100) (M^+ − H: $C_{65}H_{64}N_6O$ requires 946.27).

5-{{4-[*N*-(4-Pyridylcarboxy)]aminophenyl}-10,15,20-tris[3,4-bis(2-ethylhexoxyphenyl)]-21*H*,23*H*-porphine, $H_2$1*EH*

Mp 178–180 °C; ^{1}H NMR ($CDCl_3$, 250 MHz): δ (ppm) 8.90 (6H, m, β-pyrrolic H), 8.80 (4H, m, β-pyrrolic H + Py-H_o), 8.28 (2H, d, 5-H_o), 8.05 (2H, d, 5-H_m), 7.85 (2H, d, Py-H_m), 7.75 (3H, s, 10-, 15- and 20-H_2), 7.68 (3H, d, 10-, 15- and 20-H_6), 7.22 (3H, d, 10-, 15- and 20-H_5), 4.12 (6H, d, ArO_3CH_2), 3.95 (6H, d, ArO_4CH_2), 1.90 (3H, m, ArO_3CH_2CH), 1.80 (3H, m, ArO_4CH_2CH), 0.80–1.70 (84H, m, CH_2, CH_3), −2.75 (2H, s, porphyrin NH); UV-Vis ($CHCl_3$): λ_{max} (ε): 422 (381 000), 519 (17 700), 557 (12 000), 594 (5350), 650 nm (5150 mol^{-1} dm^3 cm^{-1}); MS (+ve FAB): *m*/*z* (%): 1504 (100) (M^+: $C_{98}H_{130}N_6O_7$ requires 1504.14).

5-{4-[*N*-(3-Pyridylcarboxy)]aminophenyl}-10,15,20-tris(4-pentylphenyl)-21*H*,23*H*-porphine, $H_2$2*P*

Mp 257–259 °C; ^{1}H NMR ($CDCl_3$, 250 MHz): δ (ppm) 9.28 (1H, s, Py-H_2), 8.86 (8H, m, β-pyrrolic H and Py-H_4), 8.37 (1H, d, Py-H_6), 8.26 (2H, d, 5-H_o), 8.15 (1H, s, amide NH), 8.12 (6H, m, 10-, 15- and 20-H_o), 8.01 (2H, d, 5-H_m), 7.50 (1H, dd, Py-H_5), 7.55 (6H, m, 10-, 15- and 20-H_m), 2.94 (6H, t, $ArCH_2$), 1.92 (6H, m, $ArCH_2CH_2$), 1.58 (12H, m, CH_2); 1.02 (9H, t, CH_3); −2.73 (2H, s, porphyrin NH); UV-Vis ($CHCl_3$): λ_{max} (ε) 422 (400 000), 518 (14 900), 555 (7870), 594 (3940), 649 nm (4720 mol^{-1} dm^3 cm^{-1}); MS (+ve FAB): *m*/*z* (%): 946 (100) (M^+: $C_{65}H_{65}N_6O$ requires 946.27).

5-{4-[*N*-(3-Pyridylcarboxy)]aminophenyl}-10,15,20-tris[3,4-bis(2-ethylhexoxyphenyl)]-21*H*,23*H*-porphine, $H_2$2*EH*

Mp 86–88 °C; ^{1}H NMR ($CDCl_3$, 250 MHz): δ (ppm) 9.30 (1H, s, Py-H_2), 8.90 (9H, m, β-pyrrolic H and Py-H_4) 8.35 (2H, m, Py-H_6 and amide NH), 8.25 (2H, d, 5-H_o), 8.08 (2H, d, 5-H_m), 7.80 (3H, s, 10-, 15- and 20-H_2), 7.70 (3H, d, 10-, 15- and 20-H_6), 7.52 (1H, dd, Py-H_5), 7.21 (3H, d, 10-, 15- and 20-H_5), 4.18 (6H, d, ArO_4CH_2), 3.98 (6H, d, ArO_3CH_2), 1.95 (3H, m, ArO_4CH_2CH), 1.84 (3H, m, ArO_3CH_2CH), 0.80–1.75 (84H, m, CH_2, CH_3), −2.73 (2H, s, porphyrin NH); UV-Vis ($CHCl_3$): λ_{max} (ε) 427 (313 000), 520 (12 700), 559 (7450), 595 (2810), 650 nm (2930 mol^{-1} dm^3 cm^{-1}); MS (+ve FAB): *m*/*z* (%) 1504 (100) (M^+: $C_{98}H_{130}N_6O_7$ requires 1504.14).

5-{3-[*N*-(4-Pyridylcarboxy)]aminophenyl}-10,15,20-tris(4-pentylphenyl)-21*H*,23*H*-porphine, $H_2$3*P*

Mp 258–260 °C; ^{1}H NMR ($CDCl_3$, 250 MHz): δ (ppm) 8.90 (8H, s, β-pyrrolic H), 8.72 (2H, d, Py-H_o), 8.30 (1H, s, 5-H_2), 8.20 (1H, d, 5-H_6), 8.12 (6H, m, 10-, 15- and 20-H_o), 8.07 (1H, d, 5-H_4), 7.73 (1H, t, 5-H_5), 7.68 (2H, d, Py-H_m), 7.54 (6H, m, 10-, 15- and 20-H_m), 2.96 (6H, m, $ArCH_2$), 1.95 (6H, m, $ArCH_2CH_2$), 1.57 (12H, m, CH_2), 0.98 (9H, t, CH_3), −2.85 (2H, s, porphyrin NH); UV-Vis ($CHCl_3$): λ_{max} (ε) 423 (88 300), 518 (15 300), 554 (10 500), 592 (8510), 647 nm (8070 mol^{-1} dm^3 cm^{-1}); MS (+ve FAB): *m*/*z* (%) 945 (100) (M^+ − H: $C_{65}H_{65}N_6O$ requires 946.27).

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5-{3-[*N*-(4-Pyridylcarboxy)]aminophenyl}-10,15,20-tris[3,4-bis(2-ethylhexoxyphenyl)]-21*H*,23*H*-porphine, $H_2$3*EH*

^{1}H NMR ($CDCl_3$, 250 MHz): δ (ppm) 8.94 (6H, m, β-pyrrolic $H_{2,8,12,13,17,18}$), 8.85 (2H, d, β-pyrrolic $H_{3,7}$), 8.79 (2H, d, Py-H_o), 8.35 (1H, s, 5-H_2), 8.25 (1H, d, 5-H_6), 8.08 (2H, m, amide NH and 5-H_4), 7.80 (1H, t, 5-H_5), 7.75 (5H, m, Py-H_m and 10, 15- and 20-H_2), 7.69 (3H, d, 10, 15- and 20-H_6), 7.22 (3H, d, 10, 15- and 20-H_5), 4.16 (6H, d, ArO_3CH_2), 3.98 (6H, d, ArO_4CH_2), 2.0–0.80 (90H, m, CH_2 and CH_3), −2.78 (porphyrin NH); UV-Vis ($CHCl_3$): λ_{max} (ε) 426 (389 000), 519 (22 000), 558 (13 000), 593 (10 000), 649 nm (9000 mol^{-1} dm^3 cm^{-1}); MS (+ve FAB): *m*/*z* (%): 1504 (M^+: $C_{98}H_{130}N_6O_7$ requires 1504.14).

5-{3-[*N*-(3-Pyridylcarboxy)]aminophenyl}-10,15,20-tris(4-pentylphenyl)-21*H*,23*H*-porphine, $H_2$4*P*

Mp 246–248 °C; ^{1}H NMR ($CDCl_3$, 250 MHz): δ (ppm) 9.16 (1H, d, Py-H_2), 8.91 (8H, m, β-pyrrolic H), 8.76 (1H, d, Py-H_4), 8.35 (1H, m, 5-H_2), 8.23 (2H, m, 5-H_6 and Py-H_6), 8.10 (6H, d, 10-, 15- and 20-H_o), 8.05 (1H, d, 5-H_4), 7.80 (1H, t, 5-H_5), 7.55 (6H, d, 10-, 15- and 20-H_m), 7.42 (1H, dd, Py-H_5), 7.40 (1H, amide NH), 2.95 (6H, t, $ArCH_2$), 1.92 (6H, m, $ArCH_2CH_2$), 1.58 (12H, m, CH_2), 1.04 (9H, t, CH_3), −2.85 (2H, s, porphyrin NH); UV-Vis ($CHCl_3$): λ_{max} (ε) 423 (152 000), 518 (18 900); 554 (9540); 592 (5450); 647 nm (4540 mol^{-1} dm^3 cm^{-1}); MS (+ve FAB): *m*/*z* (%): 945 (100) (M^+ − H: $C_{65}H_{65}N_6O$ requires 946.27).

5-{2-[*N*-(4-Pyridylcarboxy)]aminophenyl}-10,15,20-tris(4-pentylphenyl)-21*H*,23*H*-porphine, $H_2$5*P*

Mp 194–197 °C; ^{1}H NMR ($CDCl_3$, 250 MHz): δ (ppm) 8.91 (7H, m, 5-H_3 and β-pyrrolic $H_{2,8,12,13,17,18}$), 8.81 (2H, d, β-pyrrolic $H_{3,7}$), 8.13 (6H, m, 10-, 15- and 20-H_o), 8.03 (2H, d, 5-H_6), 7.90 (1H, t, 5-H_4), 7.79 (3H, m, amide NH and Py-H_o), 7.58 (1H, t, 5-H_5), 7.53 (6H, m, 10-, 15- and 20-H_m), 6.29 (2H, d, Py-H_m), 2.98 (6H, t, $ArCH_2$), 1.93 (6H, m, $ArCH_2CH_2$), 1.54 (12H, m, $ArCH_2CH_2$), 1.05 (9H, m, CH_3), −2.70 (2H, s, porphyrin NH); UV-Vis ($CHCl_3$): λ_{max} (ε) 420 (138 000); 518 (16 100); 554 (7790); 593 (4740); 647 nm (3260 mol^{-1} dm^3 cm^{-1}); MS (+ve FAB): *m*/*z* (%): 945 (100) (M^+ − H: $C_{65}H_{65}N_6O$ requires 946.27).

5-{2-[*N*-(3-Pyridylcarboxy)]aminophenyl}-10,15,20-tris(4-pentylphenyl)-21*H*,23*H*-porphine, $H_2$6*P*

Mp 118–122 °C; ^{1}H NMR ($CDCl_3$, 250 MHz): δ (ppm) 8.82 (7H, m, β-pyrrolic $H_{2,8,12,13,17,18}$ and 5-H_3), 8.74 (2H, d, β-pyrrolic $H_{3,7}$), 8.05 (8H, m, 10-, 15- and 20-H_o, and 5-H_6), 7.82 (2H, m, 5-$H_{4,5}$), 7.66 (1H, s, Py-H_2), 7.48 (7H, m, 10-, 15- and 20-H_o and Py-H_4), 6.62 (1H, d, Py-H_6), 6.35 (1H, dd, Py-H_5), 2.90 (6H, m, $ArCH_2$), 1.85 (6H, m, $ArCH_2CH_2$), 1.48 (12H, m, CH_2), 0.95 (9H, t, CH_3), −2.88 (2H, s, porphyrin NH); UV-Vis ($CHCl_3$): λ_{max} (ε) 422 (404 000), 519 (19 400), 556 (9180), 593 (5100), 695 nm (5100 mol^{-1} dm^3 cm^{-1}); MS (+ve FAB): *m*/*z* (%): 945 (100) (M^+ − H: $C_{65}H_{65}N_6O$ requires 946.27).

Typical metallation procedure to give Zn1–Zn6

The corresponding free-base porphyrin (17 mg, 0.018 mmol) and $Zn(OAc)_2$ (40 mg, 0.18 mmol, 10 eq) were stirred in 3 : 1 CH_2Cl_2–CH_3OH (10 ml) for 60 min. The solvent was removed *in vacuo*, and the reaction mixture was passed through a plug of basic alumina (1.5 × 5.2 cm) using 2% CH_3OH in CH_2Cl_2. Crystallisation from $CHCl_3$–CH_3OH afforded the desired product as a purple powder (yields 85–95%).

{5-{4-[*N*-(4-Pyridylcarboxy)]aminophenyl}-10,15,20-tris(4-pentylphenyl)-21,23-porphinato}zinc, Zn1*P*

^{1}H NMR ($CDCl_3$, 250 MHz): δ (ppm) 8.90 (2H, d, β-pyrrolic H), 8.88 (2H, d, β-pyrrolic H), 8.82 (2H, d, β-pyrrolic H), 8.67 (2H, d, β-pyrrolic H), 8.09 (2H, d, 15-H_o), 8.05 (4H, d, 10- and 20-H_o), 7.97 (2H, d, 5-H_o), 7.51 (2H, d, 5-H_m), 7.49 (4H, d, 10- and 20-H_m), 7.46 (2H, d, 15-H_m), 7.13 (1H, s, amide NH), 6.15 (2H, bs, Py-H_m), 3.27 (2H, br, Py-H_o), 2.92 (6H, t, $ArCH_2$), 1.90 (6H, qnt, $ArCH_2CH_2$), 1.51 (12H, m, CH_2), 1.01 (9H, t, CH_3); MS (+ve FAB): *m*/*z* (%) = 1005 (100) (M^+: $C_{65}H_{62}N_6OZn$ requires 1009.78).

{5-{4-[*N*-(4-Pyridylcarboxy)]aminophenyl}-10,15,20-tris[3,4-bis(2-ethylhexoxyphenyl)]-21,23-porphinato}zinc, Zn1*EH*

Mp 238–240 °C; ^{1}H NMR ($CDCl_3$, 250 MHz): δ (ppm) 8.90 (4H, s, β-pyrrolic $H_{12,13,17,18}$), 8.80 (2H, d, β-pyrrolic $H_{2,8}$), 8.65 (2H, d, β-pyrrolic $H_{3,7}$), 8.05 (2H, d, 5-H_o), 7.85 (1H, s, 15-H_2), 7.80 (2H, s, 10- and 20-H_2), 7.70 (1H, d, 15-H_6), 7.65 (2H, d, 10- and 20-H_6), 7.60 (2H, d, 5-H_m), 7.2–7.25 (3H, m, 10-, 15- and 20-H_5) 6.25 (2H, bs, Py-H_m), 4.05 (6H, d, ArO_3CH_2), 3.90, (6H, d, ArO_4CH_2), 3.50, (2H, bs, Py-H_o), 1.90 (3H, m, ArO_3CH_2CH), 1.80 (3H, m, ArO_4CH_2CH), 0.80–1.70 (84H, m, CH_2, CH_3); UV-Vis ($CHCl_3$): λ_{max} (ε) 427 (312 000), 552 (20 200), 593 nm (7550 mol^{-1} dm^3 cm^{-1}); MS (+ve FAB): *m*/*z*: 1567 (M^+), 3134 (M_2^+), 4700 (M_3^+), 6270 (M_4^+) ($C_{98}H_{128}N_6O_7Zn$ requires 1567.51).

{5-{4-[*N*-(3-Pyridylcarboxy)]aminophenyl}-10,15,20-tris[3,4-bis(2-ethylhexoxyphenyl)]-21,23-porphinato}zinc, Zn2*EH*

Mp >298 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 9.10 (2H, d, β-pyrrolic $H_{3,7}$), 9.05 (2H, d, β-pyrrolic $H_{12,18}$), 9.03 (2H, d, β-pyrrolic $H_{13,17}$), 8.97 (2H, d, β-pyrrolic $H_{2,8}$), 8.27 (4H, m, 5-$H_{o,m}$), 7.93 (1H, br s, 15-H_2), 7.81 (1H, m, 15-H_6), 7.75 (2H, s, 10- and 20-H_2), 7.58 (2H, d, 10- and 20-H_6), 7.31 (1H, d, 15-H_5), 7.21 (2H, d, 10- and 20-H_5), 7.11 (1H, d, Py-H_6), 6.17 (1H, br s, amide NH), 5.76 (1H, t, Py-H_5), 4.24 (2H, d, 15-ArO_4CH_2), 4.18 (4H, d, 10- and 20-ArO_4CH_2), 4.06 (2H, d, 15-ArO_3CH_2), 3.96 (4H, d, 10- and 20-ArO_3CH_2), 3.38 (1H, br s, Py-H_4), 3.04 (1H, br s, Py-H_2), 1.95 (3H, m, $ArO_4CH_2CH_2$), 1.84 (3H, m, $ArO_3CH_2CH_2$), 1.75–1.25 (48H, m, CH_2), 1.10–0.80 (CH_3); UV-Vis ($CHCl_3$, 3.91 × 10^{-5} M): λ_{max} (ε) 430 (58 900); 438 (62 400); 566 (792); 609 nm (639 mol^{-1} dm^3 cm^{-1}); MS (+ve FAB): *m*/*z* (%): 1567 (100) (M^+: $C_{98}H_{128}N_6O_7Zn$ requires 1567.51).

{5-{3-[*N*-(4-Pyridylcarboxy)]aminophenyl}-10,15,20-tris(4-pentylphenyl)-21,23-porphinato}zinc, Zn3*P*

Mp >298 °C; ^{1}H NMR ($CDCl_3$, 250 MHz): δ (ppm) 8.94 (2H, m, β-pyrrolic $H_{13,17}$), 8.91 (2H, m, β-pyrrolic $H_{12,18}$), 8.77 (2H, d, β-pyrrolic $H_{2,8}$), 8.53 (2H, d, β-pyrrolic $H_{3,7}$), 8.0–8.15 (7H, m, 5-H_6 and 15-, 10-, and 20-H_o), 7.88 (1H, d, 5-H_4), 7.45–7.55 (7H, m, 5-H_5 and 10-, 15- and 20-H_m), 7.09 (1H, s, 5-H_2), 6.99

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(1H, s, amide NH), 5.89 (2H, d, Py-H_m), 2.96 (6H, m, $ArCH_2$), 2.54 (2H, br s, Py-H_o), 1.95 (6H, m, $ArCH_2CH_2$), 1.57 (12H, m, CH_2), 0.98 (9H, t, CH_3); UV-Vis ($CHCl_3$, 3.91×10^{-5} M): λ_{max} (ε) 429 (106 000); 561 (4300); 602 nm (2060 mol^{-1} dm^3 cm^{-1}); MS (+ve FAB): m/z (%): 1006 (100) (M^+: $C_{65}H_{63}N_6ZnO$ requires 1009.78), 2017 (31) (M_2^+: $C_{130}H_{126}N_{12}O_2Zn_2$ requires 2019.56).

{5-{3-[*N*-(4-Pyridylcarboxy)]aminophenyl}-10,15,20-tris[3,4-bis(2-ethylhexoxyphenyl)]-21,23-porphinato}zinc, Zn3*EH*

^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.98 (4H, m, β-pyrrolic $H_{12,13,17,18}$), 8.81 (2H, m, β-pyrrolic $H_{2,8}$), 8.53 (2H, br, β-pyrrolic $H_{3,7}$), 8.09 (1H, m, 5-H_6), 7.93 (1H, m, 5-H_4), 7.78 (2H, s, 10- and 20-H_2), 7.65–7.70 (4H, m, 15-H_2 and 10-, 15- and 20-H_6), 7.57 (1H, m, 5-H_5), 7.15–7.2 (4H, m, 10-, 15- and 20-H_5 and 5-H_2), 6.97 (1H, s, amide NH), 5.94 (2H, br s, Py-H_m), 4.00 (12H, m, 10-, 15- and 20-$ArO_{3,4}CH_2$), 2.65 (2H, br s, Py-H_o), 1.95–0.81 (66H, m, CH_2 and CH_3); MS (+ve FAB): m/z (%): 1567 (100) (M^+: $C_{98}H_{128}N_6O_7Zn$ requires 1567.51).

{5-{3-[*N*-(3-Pyridylcarboxy)]aminophenyl}-10,15,20-tris(4-pentylphenyl)-21,23-porphinato}zinc, Zn4*P*

Mp 195–198 °C; ^{1}H NMR ($CDCl_3$, 250 MHz): δ (ppm) 8.98–8.83 (8H, m, β-pyrrolic $H_{2,3,7,8,12,13,17,18}$), 8.08 (6H, m, 10-, 15- and 20-H_o), 7.99 (1H, d, 5-H_6), 7.89 (1H, s, 5-H_2), 7.51–7.39 (8H, m, 5-$H_{4,5}$ and 10-, 15- and 20-H_m), 6.97 (1H, br, amide NH), 6.83 (1H, d, Py-H_6), 5.62 (1H, t, Py-H_5), 3.61 (1H, br, Py-H_4), 2.97–2.30 (7H, m, Py-H_2 and $ArCH_2$), 1.95–0.85 (28H, m, CH_2 and CH_3); UV-Vis ($CHCl_3$): λ_{max} (ε) 426 (681 000), 551 (28 800), 601 nm (7190 mol^{-1} dm^3 cm^{-1}); MS (+ve FAB): m/z (%): 1007 (100) (M^+: $C_{65}H_{63}N_6ZnO$ requires 1009.78), 2017 (1.6) (M_2^+: $C_{130}H_{126}N_{12}Zn_2O_2$ requires 2019.56).

{5-{2-[*N*-(4-Pyridylcarboxy)]aminophenyl}-10,15,20-tris(4-pentylphenyl)-21,23-porphinato}zinc, Zn5*P*

Mp 294–297 °C; ^{1}H NMR ($CDCl_3$, 250 MHz): δ (ppm) 8.99 (2H, d, β-pyrrolic $H_{13,17}$), 8.89 (2H, d, β-pyrrolic $H_{12,18}$), 8.58 (2H, d, β-pyrrolic $H_{2,8}$), 8.50 (2H, d, β-pyrrolic $H_{3,7}$), 8.26 (2H, m, 5-H_6 and 15-H_o'), 8.18 (1H, d, 15-H_o), 8.08 (1H, d, 5-H_3), 7.83 (2H, d, 10- and 20-H_o), 7.75 (1H, d, 15-H_m'), 7.66 (1H, d, 15-H_m), 7.60 (2H, d, 10- and 20-H_m'), 7.56 (1H, d, 5-H_4), 7.53 (1H, t, 5-H_5), 7.44 (4H, m, 10- and 20-H_m and 10- and 20-H_m'), 6.44 (1H, s, amide NH), 4.00 (2H, d, Py-H_m), 3.14 (2H, t, 15-$ArCH_2$), 2.98 (4H, t, 10- and 20-$ArCH_2$), 1.97 (2H, m, 15-$ArCH_2CH_2$), 1.89 (4H, m, 10- and 20-$ArCH_2CH_2$), 1.60 (12H, m, CH_2), 1.47 (2H, d, Py-H_o), 1.15 (3H, t, 15-CH_3), 1.11 (6H, t, 10- and 20-CH_3); UV-Vis ($CHCl_3$, 1.49×10^{-6} M): λ_{max} (ε) 425 (318 000), 557 (11 700), 606 nm (6370 mol^{-1} dm^3 cm^{-1}); MS (+ve FAB): m/z (%): 1006 (100) (M^+: $C_{65}H_{63}N_6ZnO$ requires 1009.78), 2017 (80) (M_2^+: $C_{130}H_{126}N_{12}Zn_2O_2$ requires 2019.56).

{5-{2-[*N*-(3-Pyridylcarboxy)]aminophenyl}-10,15,20-tris(4-pentylphenyl)-21,23-porphinato}zinc, Zn6*P*

Mp > 298 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.81 (d, 2H, β-pyrrolic $H_{13,17}$); 8.71 (d, 2H, β-pyrrolic $H_{12,18}$); 8.63 (2H, d, β-pyrrolic $H_{2,8}$), 8.53 (2H, d, β-pyrrolic $H_{3,7}$), 8.31 (2H, d, 5-$H_{3,6}$), 8.15 (1H, d, 15-H_o'), 8.08 (1H, d, 15-H_o), 7.86 (2H, d, 10- and 20-H_o'), 7.67 (3H, m, 5-H_5 and 10- and 20-H_o), 7.62 (1H, d, 15-H_m'), 7.53 (1H, m, 5-H_4), 7.50 (1H, d, 15-H_m), 7.42 (2H, d, 10- and 20-H_m'), 7.37 (2H, d, 10- and 20-H_m), 6.35 (1H, s, amide NH), 3.19 (1H, br, Py-H_5), 3.10 (1H, s, Py-H_6), 2.96 (2H, t, 15-$ArCH_2$), 2.86 (4H, t, 10- and 20-$ArCH_2$), 2.30 (1H, br s, Py-H_2), 1.95 (2H, m, 15-$ArCH_2CH_2$), 1.85 (4H, qnt, 10- and 20-$ArCH_2CH_2$), 1.51 (12H, m, CH_2), 1.10 (1H, br, Py-H_4), 1.05 (3H, t, 15-CH_3), 0.99 (6H, t, 10- and 20-CH_3); UV-Vis ($CHCl_3$, 4.95×10^{-6} M): λ_{max} (ε) 428 (192 000); 562 (13 700); 604 nm (6870 mol^{-1} dm^3 cm^{-1}); MS (+ve FAB): m/z (%): 1008 (100) (M^+: $C_{65}H_{63}N_6ZnO$ requires 1009.78).

X-Ray crystallography‡

Data for $(Zn5P)_2$ were measured on a Siemens Smart CCD area detector on the single-crystal diffraction station (No. 9.8) at the Daresbury Laboratory Synchrotron Radiation Source (Zr-Kα radiation, λ = 0.68888 Å) with an Oxford Cryosystems Cryostream Cooler at 160(2) K. Data for $(Zn6)_2$ were collected at 160(2) K on a Bruker SMART-CCD diffractometer with graphite monochromated Mo-Kα radiation.

Crystal data for $(Zn5P)_2$. $Zn_2C_{131}H_{128.78}N_{12}O_{3.39}$, M = 2056.27; red plates, 0.08 × 0.08 × 0.03 mm, monoclinic, space group $P2_1/n$, a = 17.9304(6), b = 28.2171(11), c = 22.5392(8) Å, β = 109.8510(10)°, V = 10726.0(7) Å^3, Z = 4, D_c = 1.273 g cm^{-3}, μ = 0.509 mm^{-1} (Zr-Kα radiation λ = 0.68888 Å), $F(000)$ = 4344. A total of 59 944 reflections were collected in the range $1.16 \leq \theta \leq 25.0°$, 20 722 unique ($R_{int}$ = 0.0625) were used in the structural analysis. The structure was solved by direct methods and refined by full-matrix least squares on F^2 (SHELXTL NT[XI]) to $R1$ = 0.0536 (for 12 447 $F > 4\sigma(F)$); $wR2$ = 0.1685, S = 0.980 for all 20 722 unique data and 1474 refined parameters. A semi-empirical absorption correction was applied based on symmetry equivalent and repeated reflections (minimum and maximum transmission coefficients 0.597 and 1.000). Minimum and maximum final electron density −0.696 and 0.808 e Å^{-3}. Four of the terminal pentyl chains and the linking pyridyl ligand are disordered over two sites. The structure also contains a methanol of crystallisation which was refined isotropically with hydrogens positioned geometrically and a disordered water of crystallisation which was refined to an occupancy of 39%. No hydrogen atoms were fixed to the water.

Crystal data for $(Zn6P)_2$. $ZnC_{65}H_{62}N_6O$, M = 1008.58; purple needle, 0.52 × 0.17 × 0.15 mm, triclinic, space group $P\bar{1}$, a = 13.8860(10), b = 14.1.454(10), c = 15.4484(11) Å, α = 115.083(2), β = 101.118(2), γ = 96.010(2)°, V = 2636.7(3) Å^3, Z = 2, D_c = 1.270 g cm^{-3}, μ = 0.156 mm^{-1} (Mo-Kα radiation; λ = 0.71073 Å), $F(000)$ = 1064. A total of 19 571 reflections were collected in the range $1.51 \leq \theta \leq 28.81°$, 11 851 unique ($R_{int}$ = 0.0256) were used in the structural analysis. The structure was solved by direct methods and refined by full-matrix least squares on F^2 (SHELXTL NT) to $R1$ = 0.0509 (for 8311 $F > 4\sigma(F)$); $wR2$ = 0.1443, S = 1.062 for all 11 851 unique data and 594 refined parameters

‡ CCDC reference numbers 140806 and 140807. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b704571a

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with allowance for the thermal anisotropy of all non-hydrogen atoms. A semi-empirical absorption correction was applied based on symmetry equivalent and repeated reflections (minimum and maximum transmission coefficients 0.672 and 0.802). Minimum and maximum final electron density −0.372 and 0.452 e $Å^{-3}$.

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