Porphyrin self-assembly using a boronic acid template

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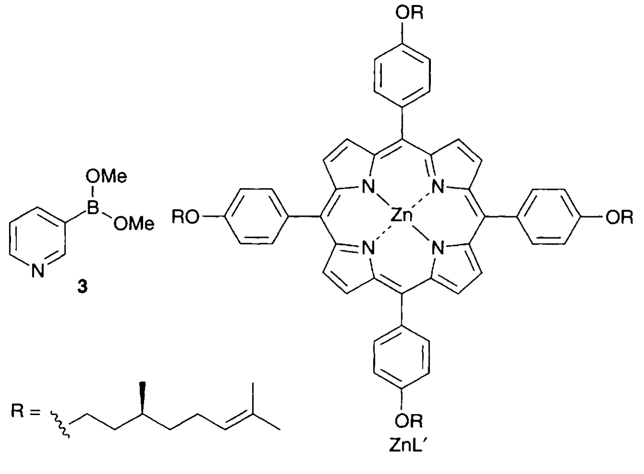
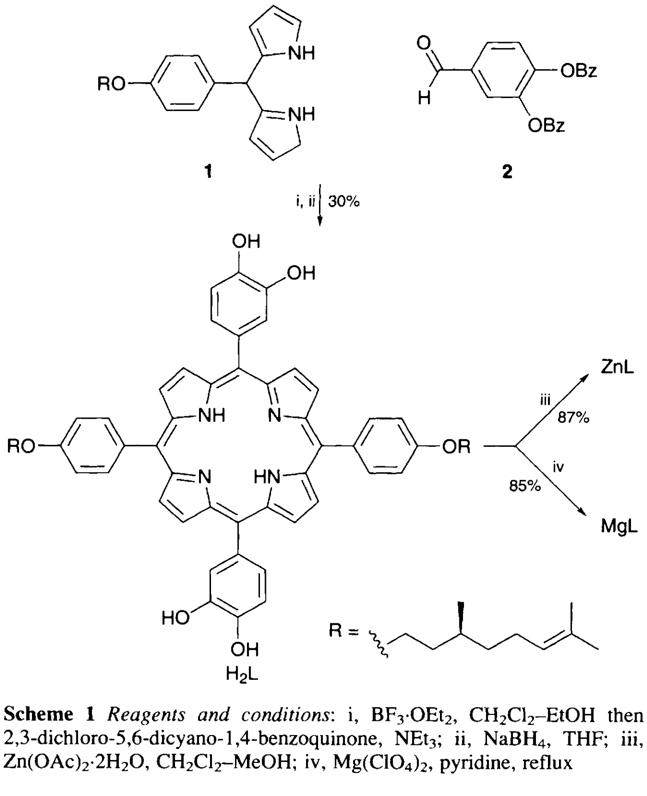
A 1 : 1 mixture of zinc dicatechol porphyrin ZnL and pyridine-3-boronic acid 3 self-assembles into dimers; the corresponding magnesium dicatechol porphyrin MgL assembles into a polymer.

Self-assembly is emerging as an increasingly viable method for constructing large molecular architectures quickly and efficiently.[1] Porphyrins are particularly suitable building blocks for non-covalent synthesis due to their attractive photophysical,[2] spectroscopic,[3] geometrical,[4] catalytic[5] and synthetic properties.[6] The self-assembly of various porphyrin architectures *via* pyridine–metal coordination has been reported.[7] To date, all such systems employ a single molecule combining both the pyridine ligand and the metal acceptor atom. The facilitating role of non-covalent templates in macrocycle synthesis is well known, and it occurred to us that introducing a non-covalent link between the porphyrin and the pyridine ligand would be advantageous. In the field of molecular recognition chemistry, the boronic acid–diol interaction has recently received renewed interest, in part due to its relatively high strength for a reversible interaction with sugars in solution.[8] Although the boronic acid–diol interaction is covalent, it is reversible and in rapid equilibrium, and can thus be treated in an analogous fashion to more classical non-covalent recognition structures, such as hydrogen bonds. In this communication, we report the results of combining these two motifs to generate new self-assembled porphyrin-containing superstructures.

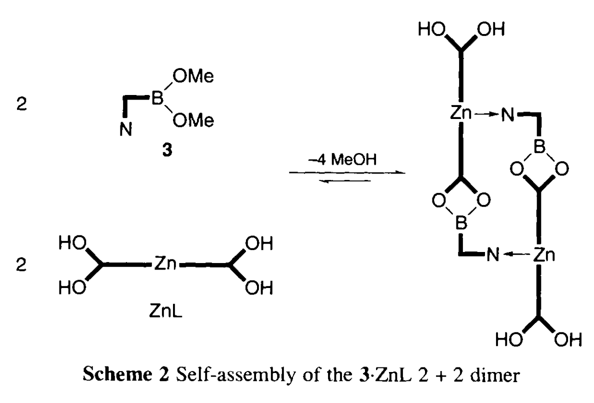
The synthesis of the porphyrin components ZnL and MgL from precursors **1** and **2** is outlined in Scheme 1.† Addition of 1 equiv. of pyridine-3-boronic acid dimethyl ester **3** to the free-base porphyrin H_2L induced no significant UV–VIS spectral change in CH_2Cl_2 solution. In contrast, addition of **3** to a CH_2Cl_2 solution of ZnL (10^{-5} mol dm^{-3}) caused shifts typical of Zn–pyridine interactions. A titration binding study revealed an unusually high association constant, K_a = 11 000 dm^3 mol^{-1}.‡ This compares very favourably with the interaction between **3** and the reference porphyrin ZnL′, where K_a = 340 dm^3 mol^{-1}, and indicates that a high degree of cooperativity is achieved in the cyclisation process.[9] VPO (vapour phase osmometry) measurements in $CHCl_3$ (25 °C) confirmed the 2 + 2 dimeric nature of the 1 : 1 complex between **3** and ZnL, as shown in Scheme 2, with an average molecular weight of 2538 ± 240 g mol^{-1} (M_w ZnL = 1050, M_w **3** = 151).

In contrast to the five-coordinate ZnL, MgL has a six-coordinate metal centre, and can therefore coordinate to two pyridine ligands. A 2 : 1 mixture of **3** and MgL therefore ought to form multi-porphyrin chains rather than isolated dimers

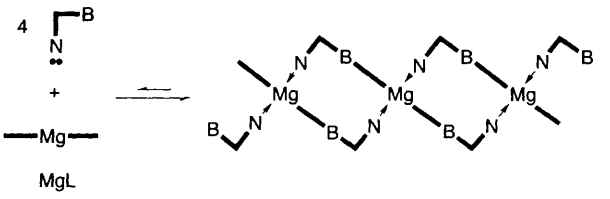




Scheme 1 *Reagents and conditions*: i, $BF_3{\cdot}OEt_2$, CH_2Cl_2–EtOH then 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, NEt_3; ii, $NaBH_4$, THF; iii, $Zn(OAc)_2{\cdot}2H_2O$, CH_2Cl_2–MeOH; iv, $Mg(ClO_4)_2$, pyridine, reflux



Scheme 2 Self-assembly of the **3**·ZnL 2 + 2 dimer



Scheme 3 Self-assembly of the **3**·MgL polymer

(Scheme 3). VPO could not be used to determine the molecular weight of the **3**·MgL assembly due to the sparing solubility of MgL in $CHCl_3$, but the polymeric nature was confirmed by light-scattering measurements in dilute solution ($CHCl_3$, 25 °C), which indicated a molecular weight of approximately 10^9 g mol^{-1}.§ As MgL has chiral solubilising groups, derived from *S*-(+)-citronellyl bromide, it might be expected that the polymer displays CD (circular dichroism) effects, but this was not the case. This is in contrast to the another self-assembled chiral boronic acid polymer based on sugars.[10] Evidently the chirality of the side-chains is too far removed from the porphyrin core to induce regular helicity to the polymer.

The combination of two separate reversible equilibrium interactions, namely the metal–pyridine and boronic acid–diol interactions, has allowed us to generate new porphyrin-containing supramolecular assemblies. In particular, a unique type of polymer is generated with a 1 : 2 mixture of six-coordinate MgL and template molecule **3**. This opens up the possibilities of constructing novel photoactive materials by self-assembling the components in solution.

Footnotes

† *Selected spectroscopic data* for H_2L: ^1H NMR (300 MHz, $CDCl_3$–CD_3OD): δ 8.95 (4 H, br, β pyrrolic H), 8.88 (4 H, br, β pyrrolic H), 8.10 (4 H, d, *J* 9 Hz, phenyl H), 7.72 (2 H, s, phenyl H), 7.56 (2 H, d, *J* 8 Hz, phenyl H), 7.29 (4 H, d, *J* 9 Hz, phenyl H), 7.20 (2 H, d, *J* 8 Hz, phenyl H), 5.20 [2 H, m, $CH_2C\mathit{H}C(CH_3)_2$], 4.2 (4 H, $OC\mathit{H}_2CH_2$, hidden), 2.2–1.2 (14 H, m), 1.74 [6 H, s, $CH_2CHC(C\mathit{H}_3)_2$], 1.64 [6 H, s, $CH_2CHC(C\mathit{H}_3)_2$], 1.10 [6 H, d, *J* 6 Hz, $OCH_2CH(C\mathit{H}_3)CH_2$], −2.7 (2 H, v br, inner NH), SIMS-MS: *m*/*z* 987 [MH^+], UV–VIS (CH_2Cl_2) [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})] 424 (3.4 × 10^5), 458 (6.6 × 10^4), 526 (1.2 × 10^4), 556 (7.4 × 10^3), 591 (3.9 × 10^3), 652 (5.7 × 10^3), 691 (1.3 × 10^4).

ZnL: ^1H NMR (300 MHz, $CDCl_3$–CD_3OD): δ 8.90 (8 H, br, β pyrrolic H), 8.11 (4 H, d, *J* 9 Hz, phenyl H), 7.70 (2 H, s, phenyl H), 7.34 (2 H, d, *J* 8 Hz, phenyl H), 7.28 (4 H, d, *J* 9 Hz, phenyl H), 7.20 (2 H, d, *J* 8 Hz, phenyl H), 5.20 [2 H, m, $C\mathit{H}_2CHC(CH_3)_2$], 4.22 (4 H, br, $OC\mathit{H}_2CH_2$), 2.2–1.2 (14 H, m), 1.74 [6 H, s, $CH_2CHC(C\mathit{H}_3)_2$], 1.66 [6 H, s, $CH_2CHC(C\mathit{H}_3)_2$], 1.10 [6 H, d, *J* 6 Hz, $OCH_2CH(C\mathit{H}_3)CH_2$], SIMS-MS: *m*/*z* 1049 [MH^+], UV–VIS (CH_2Cl_2) [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})] 430 (4.1 × 10^5), 557 (2.1 × 10^4), 598 (1.1 × 10^4).

MgL: ^1H NMR (300 MHz, $CDCl_3$–CD_3OD): δ 8.94 (4 H, br, β pyrrolic H), 8.87 (4 H, br, β pyrrolic H), 8.12 (4 H, d, *J* 9 Hz, phenyl H), 7.80 (2 H, s, phenyl H), 7.39 (2 H, d, *J* 8 Hz, phenyl H), 7.27 (4 H, d, *J* 9 Hz, phenyl H), 7.19 (2 H, d, *J* 8 Hz, phenyl H), 5.21 [2 H, m, $C\mathit{H}_2CHC(CH_3)_2$], 4.24 (4 H, br, $OC\mathit{H}_2CH_2$), 2.2–1.2 (14 H, m), 1.74 [6 H, s, $CH_2CHC(C\mathit{H}_3)_2$], 1.69 [6 H, s, $CH_2CHC(C\mathit{H}_3)_2$], 1.10 [6 H, d, *J* 6 Hz, $OCH_2CH(C\mathit{H}_3)CH_2$], SIMS-MS: *m*/*z* 1009 [MH^+], UV–VIS (CH_2Cl_2) [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})]: 428 (3.5 × 10^5), 572 (1.9 × 10^4), 616 (1.1 × 10^4), 656 (1.1 × 10^3), 738 (3.9 × 10^3).

‡ Binding constant errors are approximately ±10%. The use of two components in the assembly allows the quantitative evaluation of the assembly process to be undertaken more accurately than with single-component systems, as titration binding studies can be performed in addition to dilution measurements. Unfortunately, ^1H NMR could not be used to monitor the assembly of **3**·ZnL. At room temperature in the absence of competitive solvents, the spectra were so broadened as to derive no useful analytical data, and could be sharpened only by increasing the temperature and/or the addition of competitive solvents [$(CD_3)_2SO$, MeOD] so as to disrupt the complex.

§ Light scattering measurements were carried out by Otsuka Electronics Ltd., Osaka, Japan on an Otsuka DLS-7000 instrument. An average of three measurements at four concentrations in the range 2–4 mg dm^{-3} yielded a molecular weight of 1.26 (±0.02) × 10^9 g mol^{-1} and gave a linear ($r > 0.99$) Berry plot.

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