Dioxoporphyrins as Supramolecular Building Blocks: Oligomer Synthesis *via* Preassembly on a Ligand Template

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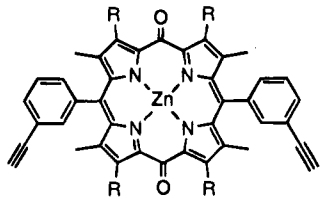
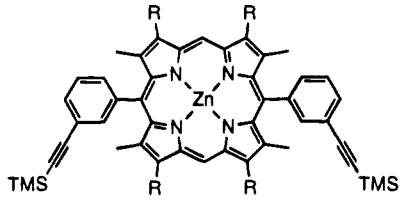
We report here that the 5,15-dioxoporphyrin unit has properties with potentially important applications in supramolecular chemistry; in particular, the great affinity of its zinc derivative for basic ligands dramatically enhances the scope and power of templated oligomer synthesis. Oxoporphyrins have been known for some time,[1] but the main focus has been on their synthesis[2] and redox activity.[3] Crystallography of zinc dioxoporphyrins shows that they are essentially planar, with shorter zinc−pyridine bonds than the corresponding porphyrin,[4] but their pyridine-binding properties in solution do not appear to have been studied previously. It transpires that their increased Lewis acidity gives them compelling advantages in certain situations and leads to a mode of templating in supramolecular chemistry which may be new.

We first isolated zinc 5,15-dioxo-10,20-bis(aryl)porphyrin **Zn1** as an unexpected but substantial side product (30%) from the nitration of **Zn2** using $AgNO_2$/MeCN.[5] **Zn1** was found to

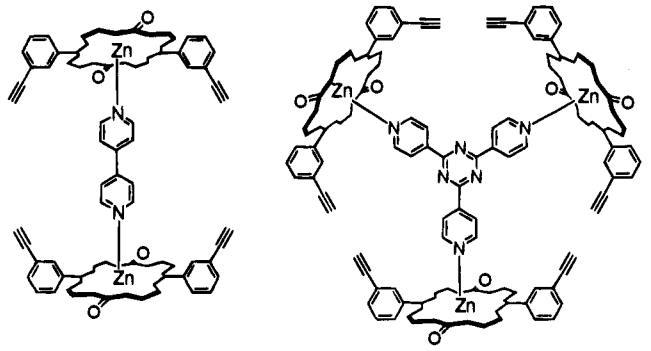


Zn1
R = CH_2CH_2COOMe



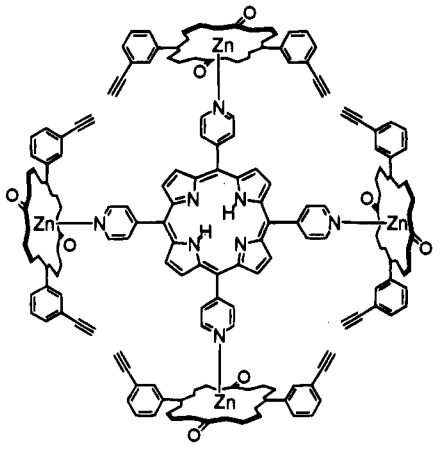
Zn2

have a binding constant of (5.2 ± 0.5) × 10^5 M^{-1} in dichloromethane at 25 °C, some 100 times stronger than that of the original porphyrin, and it therefore seemed worth exploring in its own right. We find that **Zn2** is oxidized most efficiently using thallium trifluoroacetate[6] in THF/CH_2Cl_2 (3:1), followed by quenching with sodium sulfite, to give dioxoporphyrin in 90% yield. Removal of the TMS protecting group and subsequent recrystallization from CH_2Cl_2/hexane yields pure **Zn1** in an overall yield of 75% from **Zn2**.



$(Zn1)_2$.Bipy

$(Zn1)_3$.Py_3T



$(Zn1)_4$.Py_4P

Figure 1. Complexes of **Zn1** with **Bipy**, **Py_3T**, and **Py_4P**.

Zn1 is orange in color, both as the solid and in solution, is indefinitely stable, and is much more soluble than **Zn2** in polar solvents such as methanol, acetone, and acetonitrile. Its Soret absorption at 471 nm ($\epsilon = 4.8 \times 10^4$ M^{-1} cm^{-1}) is only 10% as strong as that of **Zn2**, but the Q-band at 565 nm ($\epsilon = 2.4 \times 10^4$ M^{-1} cm^{-1}) is of similar intensity (1.1×10^4 M^{-1} cm^{-1}). On pyridine binding, these move to 467 and 558 nm, respectively, a shift in the opposite direction seen on ligation of porphyrins. A van't Hoff plot for pyridine binding to **Zn1** gives $\Delta H = -29$ kJ mol^{-1} and $T\Delta S = +3$ kJ mol^{-1} at 298 K in tetrachloroethane. Both of these values are much smaller than those for **Zn2** ($\Delta H = -38$ kJ mol^{-1} and $T\Delta S = -20$ kJ mol^{-1}), implying greater coordination of solvent in the absence of added ligand and release of solvent on pyridine binding. These differences in solvation may explain the higher solubility of **Zn1** compared with that of **Zn2**.

The large affinity of **Zn1** for pyridine ligands means that multicomponent complexes are readily assembled: thus 82% of the **Zn1** in a mixture of 0.2 mM **Zn1** and 0.1 mM 4,4′-bipyridyl (Bipy) in dichloromethane solution is calculated to be present as the 2:1 complex (Figure 1), compared with only 15% for the corresponding porphyrin solution. Even more strikingly, replacement of Bipy by 0.05 mM 5,10,15,20-tetrapyridylporphyrin (Py_4P) should lead to 67% of the **Zn1** being present as the 4:1 complex versus 2% for the porphyrin analogue.[7]

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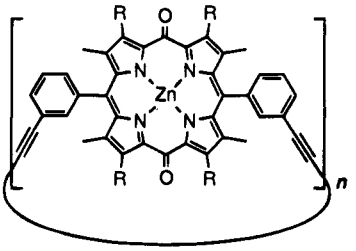
The ease of assembly of multicomponent complexes has major implications for the synthesis of oligomers on a ligand template: Glaser–Hay coupling of **Zn1** (at ~2 × 10^{-4} M) in the absence of any template yields about 40% each of cyclic trimer $\mathbf{Zn_3}$**4** and tetramer $\mathbf{Zn_4}$**5** with very little dimer $\mathbf{Zn_2}$**3**.This



$\mathbf{Zn_2}$**3** $n = 2$

$\mathbf{Zn_3}$**4** $n = 3$

$\mathbf{Zn_4}$**5** $n = 4$

behavior is similar to that observed with the parent porphyrin,[8] although the small yield of dimer is slightly surprising. However, addition of 0.5 molar equiv of Bipy to the reaction mixture completely changes the course of the reaction: cyclic dimer is now produced almost quantitatively as the only detectable product. Similarly, 0.33 molar equiv of s-tripyridyltriazine (Py_3T) leads to virtually exclusive formation of cyclic trimer, while 0.25 molar equiv of Py_4P gives >70% of cyclic tetramer. All of these dioxoporphyrin oligomers can readily be isolated and purified by recrystallization, as no similarly-sized molecules are present to interfere. The result involving the formation of the tetramer is particularly gratifying: the porphyrin analogue can be prepared efficiently only by templated dimerization of the linear dimer,[9] which is itself not easy to prepare on a large scale, while the dioxoporphyrin tetramer can be obtained on an arbitrarily large scale in one step. The ligands are readily removed by protonation with 10% TFA/MeOH, giving the free base compounds, which may then be remetalated.

These synthetic results are consistent with preassembly of all the oligomer components around the ligand, as shown in Figure 1, before any covalent chemistry takes place. Preassembly of one or two components on a template is relatively common,[10] but self-assembly of more complex systems usually involves either the trapping of a reactive intermediate on the pathway by added template[9] or the *sequential* complexation of pairs of intermediates, as in Stoddart's catenane and rotaxane syntheses.[11,12]

A series of NMR competition experiments with a range of porphyrin trimers shows that the hexaoxo trimer $\mathbf{Zn_3}$**4** binds Py_3T with a binding constant at least 800 times greater than that of the corresponding porphyrin trimer, i.e., $>10^{12}$ M^{-1}. This is consistent with the facts that the maximum possible association rate is diffusion controlled (10^9–10^{10} M^{-1} s^{-1}) and the dissociation rate observed in the competition experiments is slower than 10^{-3} s^{-1}.

The lack of overall aromaticity implied by the cross-conjugated structure of dioxoporphyrins leads to a complete loss of ring current shifts:[13] the pyrrole NH protons in $\mathbf{H_2}$**1** resonate at +12.37 ppm, compared with −2.48 ppm in $\mathbf{H_2}$**2**.[1] Similarly, the limiting shifts for bound pyridyl ligands are scarcely different from their initial values in free solution; in all cases, $\Delta\delta < 1$ ppm by comparison with shifts of up to 7.1 ppm within porphyrin cavities. The absence of dramatic NMR shifts on binding appears to be the only way in which dioxoporphyrins are less attractive as building blocks than their parent porphyrins.[14] The dioxoporphyrin oligomers all gave satisfactory positive FAB-MS spectra; indeed, in the presence of ligand templates, molecular ions were readily obtained for $\mathbf{Zn_3}$**3**·Bipy (M^+ = 2160), $\mathbf{Zn_3}$**4**·Py_3T (M^+ = 3320; M^{2+} = 1659), and $\mathbf{Zn_4}$**5**·Py_4P (M^+ = 4629; M^{2+} = 2315).

Dioxoporphyrins represent a simple but highly effective tuning of the porphyrin moiety. They offer new opportunities for creating templated or self-assembled supramolecular systems, and their catalytic abilities in Diels–Alder[15] and acyl-transfer reactions[16] are currently being explored.

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(7) The alkyne groups will, of course, be randomly oriented rather than all facing inward as shown in Figure 1, but the rate of aryl rotation (~1 s^{-1}) is fast compared with the reaction used to couple the alkynes together.

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(14) *Meso*-nitrated Zn porphyrins are alternative building blocks that retain the full advantage of ring current effects, but their preparation and binding properties are slightly less convenient than those of dioxoporphyrins (McCallien D. W. J.; Sanders, J. K. M. to be published). Another possibility is to use conventional porphyrins but with more strongly ligating central metal ions, such as Fe, Co, or Ru. These, however, suffer several disadvantages as general building blocks: the metals are less easily removed than Zn; some of the oxidation states are paramagnetic and/or oxygen sensitive; and their coordination chemistry is more complex, with two axial ligation sites rather than one for Zn.

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