A Molecular Switch for Control of Conformation: Strained Intramolecular Co-ordination in 4,4'-Bipyridyl-capped Zinc Porphyrins

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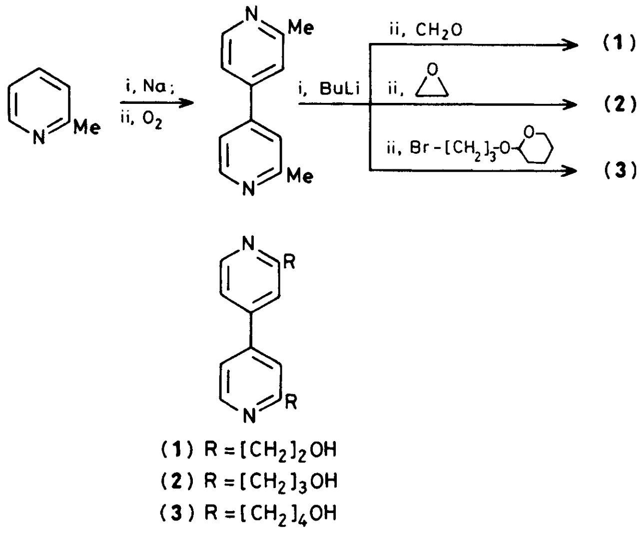
Intramolecular co-ordination between the nitrogens of the cap and the central metal ion in the title compounds forces the porphyrin and bipyridyl groups to be perpendicular: addition of an external ligand releases the bipyridyl ligand which then lies parallel to the porphyrin.

We report here the synthesis and properties of a molecular 'switch' which can be set at will to give either of two quite different molecular conformations. The design of the switch arises from the following information and logic. The formally four-co-ordinate ion at the centre of a metallo-porphyrin or -chlorin is often a Lewis acid, seeking one or more axial ligands to satisfy its co-ordination demands; in the absence of ligand, aggregation occurs.[1] The ligands may be covalently attached to the macrocycle and bind intramolecularly,[2,3] or may be added separately. In the presence of an excess of the ligand, magnesium can become partly six co-ordinate[2—4] but zinc remains exclusively five co-ordinate.[1,5] It follows that if intramolecular ligand binding to zinc is accompanied by strain, then addition of external ligand will release the strain and lead to a dramatic conformational change. We illustrate the operation of this process in 4,4'-bipyridyl-capped zinc porphy-

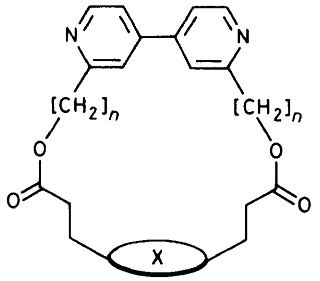


Scheme 1

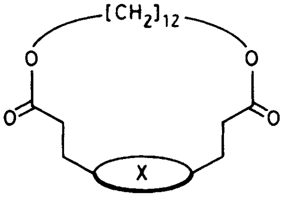
Table 1. N.m.r. properties of capped porphyrins.[a]

Compound	Upfield ring current shift (p.p.m.).[b]		
	H_α	H_β	H_δ
(4)	2.0	4.0	3.0
(5)	0.75	1.3	2.25
(6)	0.85	1.1	1.55
(7)		Aggregated	
(7) + Lutidine[c]	1.6	3.2	3.0
(8)	2.6	1.7	2.1
(8) + Lutidine[c]	0.9	1.3	2.25
(9)	3.8	1.5	1.5
(9) + Lutidine[c]	0.9	0.8	1.3

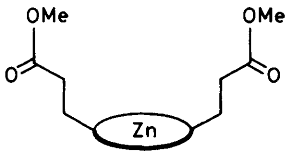
[a] ^1H N.m.r. spectra were acquired at 250 or 400 MHz in CD_2Cl_2. [b] For pyridine protons in the cap, relative to corresponding non-capped diol. [c] A sufficient excess of lutidine was added that further addition gave no change.



(4) $n = 2$, $X = H_2$
(5) $n = 3$, $X = H_2$
(6) $n = 4$, $X = H_2$
(7) $n = 2$, $X = Zn$
(8) $n = 3$, $X = Zn$
(9) $n = 4$, $X = Zn$



(10) $X = H_2$
(11) $X = Zn$



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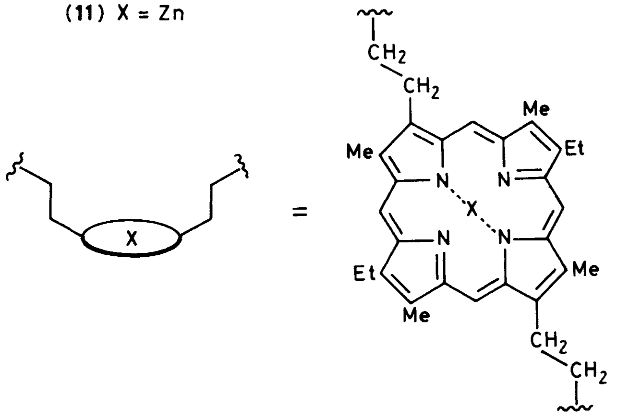

Table 2. Ligand dependence of u.v.–visible spectra.[a]

Compound	$\lambda_{max.}$ (nm) CH_2Cl_2	CH_2Cl_2 + pyridine
(7)	404, 532, 570	414, 543, 578
(8)	404, 534, 570	412, 540, 576
(9)	414, 540, 574	412, 540, 576
(11)	400, 530, 567	412, 540, 576
(12)	402, 530, 568	413, 542, 578

[a] *Ca.* 10^{-5} M in CH_2Cl_2.

rins. These capped materials are also precursors for models of photosynthesis.[6]

The bipyridyl diols **(1)**—**(3)**† were prepared from 2-picoline as shown in Scheme 1. High dilution coupling[7] of the diols with *meso*-porphyrin-II-di-acid chloride gave the capped compounds **(4)**—**(6)** in 40—50% yield. Zinc insertion with $Zn(OAc)_2$ gave **(7)**—**(9)**. Similarly, zinc was inserted into **(10)**[8] to give the model compound **(11)**.

The n.m.r. spectra (Table 1) of all compounds had only a single set of aromatic signals for the bipyridyl groups, demonstrating rapid flipping about the central γ–γ' bond. The free base porphyrins **(5)** and **(6)** have very similar conformations (A), with H_δ pointing on average down towards the porphyrin ring.[9] The porphyrin–bipyridyl distance is quite large, and no nuclear Overhauser effects (n.O.e.s) are seen from one moiety across to the other. The pyridine nitrogens are accessible to solvent and are readily methylated.[6] By contrast, **(4)** takes up a strained conformation (B).‡ H_β is most shifted, and there are n.O.e.s between H_α and the porphyrin ethyl group. The pyridine nitrogens are inaccessible and are not easily methylated by methyl iodide.

In the absence of added ligand, **(7)** and **(11)** gave the broad n.m.r. signals which are characteristic of aggregation;[1] addition of 1 equivalent of pyridine or 3,5-lutidine gave sharp spectra with shifts similar to the metal-free compounds. In contrast, **(8)** and **(9)** gave well-resolved spectra with unusual shifts in the absence of ligand, indicating that the bipyridyl group was binding intramolecularly. Addition of an excess of lutidine restored the metal-free shifts.

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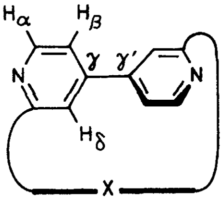
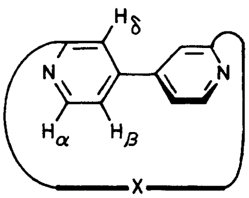
† All new compounds gave satisfactory u.v., n.m.r., and mass spectra.

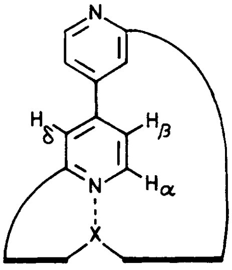
‡ This strain is reflected in the isolation, during the synthesis of **(4)**, of 10% yield of a dimer containing two porphyrin and two bipyridyl units.



(A)



(B)



(C)

Ring current calculations[9] show that the conformation of (**9**) in the absence of external ligand is as shown in (C); the large upfield shift of H_α and the equal shifts of H_β and H_δ are highly characteristic (Table 1). There is rapid exchange of binding between the two ends of the bipyridyl group. In the presence of added ligand, (**9**) takes up the 'metal-free' conformation (A). Since intramolecular binding is greatly favoured entropically and lutidine is a similar ligand to the bipyridyl, the efficiency of this switch can be attributed to the strain associated with conformation (C). This strain is apparent in molecular models.

In (**8**) the strain is larger: the bipyridyl shifts for H_α and H_β are roughly midway between those of metal-free (**5**) and the fully-bound (**9**); this implies an equilibrium between conformations (A) and (C). The addition of lutidine makes conformation (C) highly unfavourable and the 'metal-free' shifts of (A) are observed exclusively. The strain of intramolecular binding is too great for (**7**), and only aggregation occurs.

These conclusions are strengthened by u.v.–visible spectra (Table 2). The pyridine adducts of (**11**) and (**12**) show the expected[5] substantial red shifts by comparison with the pure compounds. The spectrum of (**9**) is red shifted in the absence and presence of pyridine, and that of (**8**) is partially shifted in the absence of pyridine. This partial shift probably arises from the overlap of unresolved shifted and unshifted peaks; similar effects are seen with chlorophyll co-ordination equilibria.[4]

The corresponding magnesium complexes exhibit similar intramolecular co-ordination chemistry, but are, as expected, not efficient switches because significant six-co-ordination occurs.

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