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## A simple synthesis of pyridine-tethered porphyrins

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## Abstract

Zinc porphyrin **4**, in which a pyridine ligand is tethered to the 3-position of a *meso*-phenyl substituent via a nine-atom spacer, has been synthesised and is found to exist as the intramolecularly bound complex in solution. © 2000 Elsevier Science Ltd. All rights reserved.

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Metalloporphyrins which bear tethered ligands capable of reversible binding to the central metal ion are potentially important as synthetic mimics of biological catalysts (such as cytochromes)<sup>1</sup> and as sensors. With the latter application in mind, we sought a straightforward synthesis of pyridine-tethered porphyrins which could be easily adapted to influence the intramolecular binding. A few examples of such tethered porphyrins are known.<sup>1,2</sup> However, a simple molecular model indicated that novel porphyrin **4**, in which a pyridine is attached to the 3-position of a *meso*-phenyl group via a nine-atom spacer, would form a relatively strain-free intramolecular complex. More importantly, it was envisaged that **4** could be easily synthesised by a general procedure and modification would allow access to a range of derivatives.

Porphyrin 4 was synthesised as shown in Scheme 1. Sodium was dissolved in 1,6-hexane diol and the alkoxide solution treated with 4-picolyl chloride. The resulting alcohol 1 was coverted to the chloride 2, using thionyl chloride, and used to alkylate mono-hydroxy porphyrin 3 (made by a statistical condensation of pyrrole with benzaldehyde and 3-hydroxybenzaldehyde<sup>3</sup>). Metallation with zinc acetate afforded tethered porphyrin 4.<sup>4</sup> Monomethoxy porphyrin  $5^4$  was also prepared by methylation and metallation of 3.

The absorption spectrum of model porphyrin **5** undergoes changes typical for zinc porphyrins<sup>5</sup>  $(\lambda_{max} = 419 \text{ nm in CH}_2\text{Cl}_2, \lambda_{max} = 428 \text{ nm when fully complexed with pyridine in CH}_2\text{Cl}_2$  (pK = 3.8)). The absorption spectrum for **4** is essentially identical to that of the **5**:pyridine complex. The spectrum is not concentration dependent, implying that **4** exists as the intramolecularly

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Scheme 1. Reagents and conditions: (i) HO(CH<sub>2</sub>)<sub>6</sub>ONa/HO(CH<sub>2</sub>)<sub>6</sub>OH (74%); (ii) SOCl<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub> (54%); (iii) propionic acid, reflux 30 min (5%); (iv) K<sub>2</sub>CO<sub>3</sub>, TBAI, MEK, reflux 12 h (92%); (v) zinc acetate, DMF (93%); (vi) K<sub>2</sub>CO<sub>3</sub>, (CH<sub>3</sub>)<sub>2</sub>SO<sub>4</sub>, TBAI, MEK, reflux 12 h (74%); (vii) zinc acetate, DMF (91%)

complexed species. This deduction is supported by the <sup>1</sup>H NMR spectrum of **4**, which shows the pyridine hydrogens shielded by the porphyrin ring current.<sup>4</sup>

The use of this and related derivatives for sensor applications and catalysis is currently being explored.

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- 4. Selected characterisation data. Compound 4: m.p. 197–200°C;  $\delta_{\rm H}$  (300 MHz, CDCl<sub>3</sub>) 1.4–1.8 (8H, m), 2.40 (2H, d, J 6.3 Hz, pyridine-H<sub>2,6</sub>), 2.92 (2H, t, J 5.6 Hz), 3.49 (2H, s), 3.87 (2H, t, J 7.6 Hz), 5.48 (2H, d, J 6.3 Hz, pyridine-H<sub>3,5</sub>), 7.23 (1H, m), 7.55–7.75 (11H, m), 8.12–8.28 (7H, m), 8.8–8.9 (8H, m); acc. mass (FAB) found 884.3036 (M+H), C<sub>56</sub>H<sub>46</sub>N<sub>5</sub>O<sub>2</sub>Zn = 884.2943. Compound 5: m.p. > 290°C;  $\delta_{\rm H}$  (300 MHz, CDCl<sub>3</sub>) 3.98 (3H, s), 7.33 (1H, dd, J 8.2 Hz, 2.6 Hz), 7.64 (1H, t, J 7.4 Hz), 7.72–7.84 (11H, m), 8.20–8.26 (6H, m), 8.94–9.02 (8H, m); acc. mass (FAB) found 707.1812 (M+H), C<sub>45</sub>H<sub>31</sub>N<sub>4</sub>OZn = 707.1789.
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