

Synthesis and Applications of Tetrabenzoporphyrins

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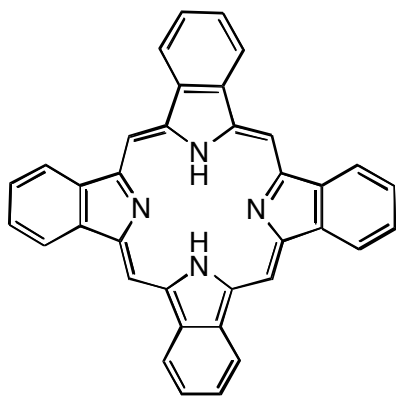
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Tetrabenzoporphyrins (such as **1** and **2**) bear four benzene rings fused to the pyrrolic positions of a porphyrin macrocycle, and are often regarded as the porphyrin analogues of phthalocyanines. Because of the extension of the π -conjugation system, these molecules display high chemical stability and unique photophysical and electrochemical properties. Tetrabenzoporphyrins typically form highly stable metal complexes with a variety of metal ions; for example, the Mg(II) and Zn(II) complexes of tetrabenzoporphyrins are considerably more stable than Mg(II) and Zn(II) porphyrins.

One of the major drawbacks to the study of the tetrabenzoporphyrin macrocycle and its applications has been the limited synthetic routes to these compounds in pure form, and their low solubility, in part due to their high tendency for π - π stacking.



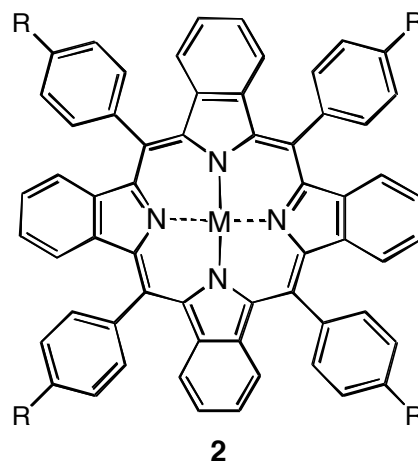
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Until recently benzo-functionalized tetrabenzoporphyrins were normally obtained from high temperature condensations of phthalimidine derivatives and/or phenyl-containing carboxylic acids in the presence of metal templates, which invariably produced mixtures of the corresponding metallo-tetrabenzoporphyrins.^{e.g.1} High temperature Rothmund-type condensations of isoindoles with formaldehyde or benzaldehydes in the presence of metal templates have also been used to prepare metallo-tetrabenzoporphyrins.^{e.g.2} The harsh conditions used in these syntheses only allowed the introduction of a few inert substituents at the benzo positions. On the other hand, direct functionalization (e.g.

sulfonation) of the tetrabenzoporphyrin produces mixtures of mono- and poly-functionalized tetrabenzoporphyrins. Recently, we and others have reported alternative routes to these systems, from precursors such as cycloalkyl- and bicyclic-fused pyrroles.³⁻⁵

A few years ago we reported a new synthesis of tetrabenzoporphyrin **1**, from oxidation of a butanoporphyrin precursor.³ Herein we report our latest developments in the synthesis and characterization of soluble tetrabenzoporphyrin systems, such as **2**. These macrocycles are obtained either by condensation of a 3:4-butanopyrrole with *p*-substituted benzaldehydes, followed by oxidation to tetrabenzoporphyrin, or by the [2+2] MacDonald condensation route using two different dipyrromethanes, to prepare unsymmetric systems.

We will also report the spectroscopic, photophysical and novel electrochemical properties of our tetrabenzoporphyrin macrocycles and their precursors, and their applications, for example in the fields of biology and medicine.



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R = hydrophilic group

M = diamagnetic metal ion

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