



Syntheses and properties of functionalized oxacalix[4]arene porphyrins

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Abstract—Six new functionalized oxacalix[4]arene porphyrins have been synthesized via a high-yielding ‘3+1’ condensation between *meso*-(3,5-dihydroxyphenyl)triphenylporphyrin and readily available new fluorodinitrobenzene-containing trimers. The X-ray structure of one linear trimer is presented. The synthesis of a porphyrin containing two oxacalix[4]arene moieties is also reported using a similar strategy. ¹H NMR data and computer calculations using the AM1 semiempirical method incorporated into the Spartan program indicate that the oxacalix[4]arene porphyrins adopt 1,3-alternating conformations. The photophysical properties of the oxacalix[4]arene porphyrins were investigated.

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1. Introduction

The mechanisms of proton-coupled electron transfer (PCET) processes, which occur in many natural systems,^{1–3} have been the subject of several investigations using model porphyrin-based compounds.^{4,5} Such studies indicate that either a face-to-face or side-to-side arrangement of the acid–base and redox sites are crucial for efficient proton and electron transfers.⁶ On the other hand, the recognition that the hydrogen-bond framework in heme model systems is a determinant of heme structure and function has resulted in the targeted synthesis of model systems containing one or more hydrogen-bond functionalities.^{7–10} Some such porphyrins were found to have interesting structural and electronic properties, particularly the so-called ‘hangman’ porphyrins, which are potential model systems for investigations of both hydrogen-bond frameworks and energy transfer agents in natural systems.^{6,11–19} Hangman porphyrins bearing hydrogen synthons with different pK_a values have been reported^{6,13–19} and the acidity of these systems was found to influence both the speed and the stability of the catalyst in proton-coupled O–O activation reactions.^{6,15c} These types of porphyrins are attractive PCET model systems since they allow the control of both the proton and electron transfers while providing the opportunity to introduce a hydrogen-bond active group with specific proton-donating ability and arrangement relative to the metalloporphyrin redox site.⁶ However, the synthesis of such models presents several challenges due to very long and tedious synthetic

routes currently available and the lack of susceptibility to modular modifications of the target systems.¹⁴

Calixarenes have been extensively studied in recent years because of their interesting chemical and physical properties.^{20–32} However, heterocalixarenes are far less prevalent in the chemical literature. Among those, oxacalixarenes are especially scarce, despite the fact that their modest yield synthesis was first reported in 1966.²⁶ Although this flexible route based on a nucleophilic aromatic substitution can be used to efficiently synthesize highly functionalized oxacalixarenes, it requires high temperature with extended reaction time. Recently, Katz et al.³⁰ made a significant improvement in oxacalixarene synthesis by choosing selective bases and solvents to let the reaction proceed at room temperature and in high yields. We have recently reported the synthesis of calixarene-locked bisporphyrins via the nucleophilic aromatic substitution reaction of 1,5-difluoro-2,4-dinitrobenzene with a 3,5-dihydroxyphenyl-containing porphyrin.³³ Synthetic routes to the unsymmetric heterocalixarenes are few, especially for oxacalixarenes, although Wang and Yang²⁴ recently developed a fragment-coupling synthesis of O- and N-bridged calixarenes using triazine; the reaction in general needs a long time to go to completion.

Herein we report the first efficient preparation and properties of functionalized unsymmetrical oxacalixarene porphyrins via a ‘3+1’ condensation of readily available aryl trimers with *meso*-(3,5-dihydroxyphenyl)porphyrins. Due to the unique discrete 1,3-alternating conformations of oxacalix[4]arenes,^{20–33} we envisioned the design and synthesis of porphyrin-oxacalix[4]arene systems containing hydrogen

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synthons in a face-to-face arrangement relative to the porphyrin macrocycle, for application as heme model systems. Our synthetic strategy involves the preparation of a series of novel unsymmetrical oxacalix[4]arenes by nucleophilic aromatic substitution of functionalized *meta*-dihydroxybenzenes with 1,5-difluoro-2,4-dinitrobenzene.

2. Results and discussion

The synthesis of functionalized oxacalix[4]arene porphyrins **1a–c** from readily available dihydroxybenzenes **2a–c** is shown in Scheme 1. The linear aryl trimers **3a–c** were readily prepared on a multi-gram scale in 75–85% yield, by reacting **2a–c** with 3 equiv of 1,5-difluoro-2,4-dinitrobenzene and 4 equiv of finely ground K_2CO_3 (<80 μm) in acetone at room temperature for 1–2 h. The amount of symmetrical oxacalix[4]arene byproducts resulting from this reaction was minimized by using acetone as the solvent and 3 equiv (rather than two) of 1,5-difluoro-2,4-dinitrobenzene. The linear trimers **3a–c** shared characteristic 1H NMR spectra, showing two downfield singlets (around 8.9 ppm) for the protons next to the carbons bearing the NO_2 groups, and two upfield singlets (around 6.9 ppm) for the protons next to the carbons bearing the fluorines. The structure of trimer **3c** was further confirmed by crystallography at $T=150$ K (see Fig. 1). The crystals were destroyed by cooling to temperatures lower than 150 K, apparently as a result of a phase change. The C–F distances are 1.331(2) and 1.334(2) Å.

The reaction of *meso*-(dihydroxyphenyl)triphenylporphyrin **2d** (obtained by a mixed aldehyde condensation followed by demethylation using BBr_3 according to the literature)³⁵ and trimers **3a–c** produced the target functionalized oxacalix[4]arene porphyrins in 80–86% yields (Scheme 1); 4 equiv of finely ground K_2CO_3 in DMSO were required, at room temperature, for 30 min to 3 h (until complete

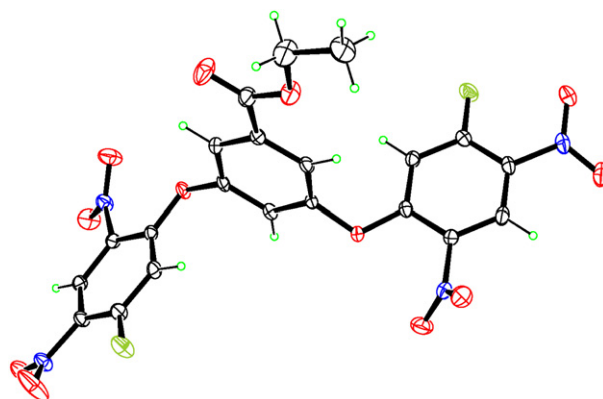
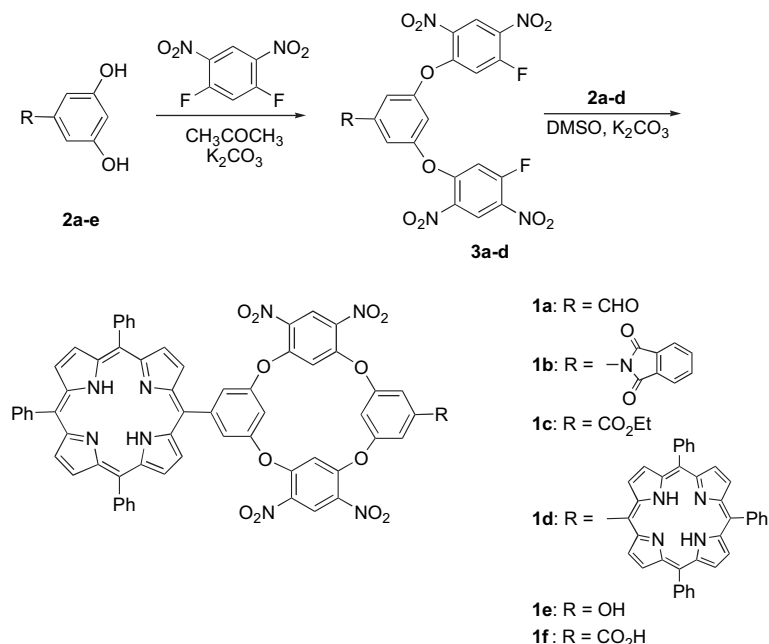


Figure 1. Molecular structure of trimer **3c**.

disappearance of the starting materials as monitored by TLC). These fragment-coupling reactions are very efficient and no higher analogs were detected compared with other fragment-coupling reactions reported in the literature.^{20–25} The porphyrin-containing trimer **3d** was also prepared in 80% yield from the reaction of porphyrin **2d** with an excess of 1,5-difluoro-2,4-dinitrobenzene in acetone at room temperature. A side product in this reaction was the symmetric oxacalix[4]arene bisporphyrin **1d**. Using DMSO as the solvent in place of acetone resulted in a lower yield of the trimer product and increased the yield of bisporphyrin **1d**. However, the coupling of porphyrin-containing trimer **3d** with **2a–c** and **2e** in DMSO, in the presence of finely ground K_2CO_3 , resulted in low yields (10–25%) of the corresponding oxacalix[4]arene porphyrins **1a–c** and **1e**. The major product from these reactions was invariably the symmetric oxacalix[4]arene bisporphyrin **1d**,³³ obtained from scrambling of trimer **3d** under the reaction conditions. The thermodynamic reversibility of oxacalixarene formation during nucleophilic substitution has been studied and confirmed



Scheme 1. Synthesis of functionalized oxacalix[4]arene porphyrins.

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