

A VERSATILE AND RAPID APPROACH TO ENCAPSULATE FUNCTION – PORPHYRIN CORE STAR POLYMERS

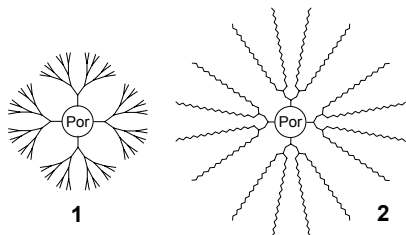
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Introduction

The encapsulation of porphyrins has attracted much interest in recent years due to its importance in a variety of fields ranging from biomimetics to materials chemistry. Mainly dendrimers **1** (Scheme 1) have been used to isolate the porphyrin moiety and tune its photophysical,¹ electrochemical,² and chemical³ behavior. Several groups have shown that the dendritic shell renders the properties of the porphyrin core and following this concept hemeprotein mimics were designed. However, a major drawback is the usually time consuming dendrimer synthesis. We sought a more rapid entry to efficiently encapsulate porphyrins that would allow for control over architecture and functionality. Our strategy⁴ is based on a highly branched porphyrin core that acts as a multisite initiator for the “living” ring opening polymerization (ROP) of ϵ -caprolactone⁵ generating porphyrin star polymers **2**.

Scheme 1

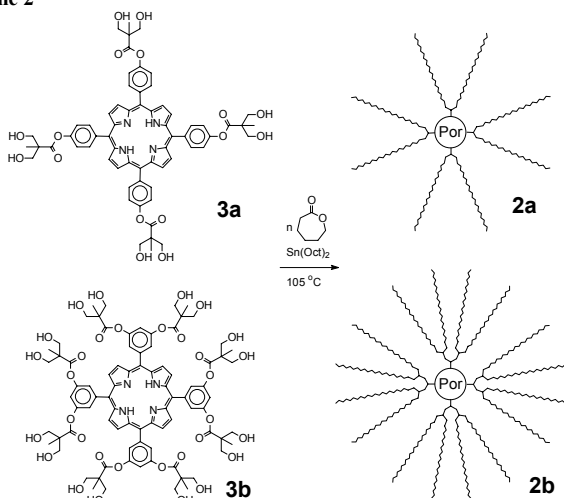


Herein, we describe the synthesis and modification of the new materials as well as their investigation with regard to site isolation using two different experimental approaches.

Results and Discussion

The initiators **3a,b** were prepared via esterification of tetrakis(4-hydroxyphenyl)porphyrin and tetrakis(3,5-dihydroxyphenyl)porphyrin, respectively, using acetamide-protected 2,2-bis(hydroxymethyl)-propionic acid⁶ followed by deprotection of the diol functionalities (Scheme 2). Bulk polymerization in ϵ -caprolactone employing the procedure by Trollsås and Hedrick^{5a-c} yielded star polymers **2a,b** possessing either 8 or 16 arms.

Scheme 2

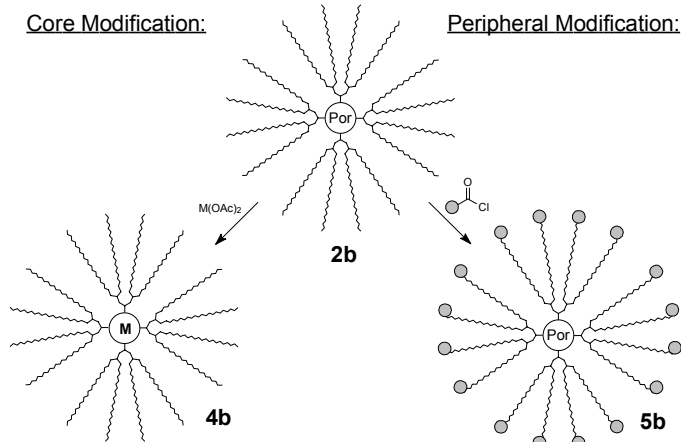


Polymers with varying molecular weights (26000 – 89000) and low polydispersities (1.10 – 1.19) were prepared in almost quantitative yields by varying the monomer to initiator ratio. A significant advantage of the high yield processes used is that the only purification required after polymerization

and modification (*vide infra*) was a precipitation into methanol. All polymers are soluble in a variety of solvents such as CHCl_3 , THF, or CH_3CN .

Further modification of the stars was accomplished by metalation of the core moiety as well as by derivatization of the hydroxyl-functional chain ends leading to an enhanced versatility of the synthesis (Scheme 3). For instance, zinc(II) was successfully inserted into the macrocyclic ligand (**4b**) and a coumarin chromophore was quantitatively introduced at each of the 16 hydroxyl chain ends via esterification using coumarin-3-carboxylic acid chloride (**5b**).

Scheme 3



Both of these compounds were used to gain information about the ability of the poly(ϵ -caprolactone) shell to isolate the porphyrin core. The zinc(II) porphyrin star was used in experiments employing an external probe and therefore evaluating the accessibility of the core.⁴ Hereby, the fluorescence quantum yields were measured in the presence of a quencher molecule, i.e. the probe (Figure 1). Stern-Volmer analysis allowed for the determination of the product of the quenching rate constant and the excited state lifetime.⁷ As the chain lengths increase, the fluorescence quantum yields (in the absence of the quencher) remain constant and the absorption as well as the fluorescence spectra do not shift, suggesting no significant change of the lifetime^{1b} and therefore leading to a direct evaluation of the quenching rate constant as a measure of the core accessibility.⁸ A strong shielding of the core moiety in the polymers compared to zinc tetrakis(4-phenyl)porphyrin (ZnTPP) as the reference was observed. This clearly shows the largely reduced penetration of the small molecule quencher through the polymeric backbone.

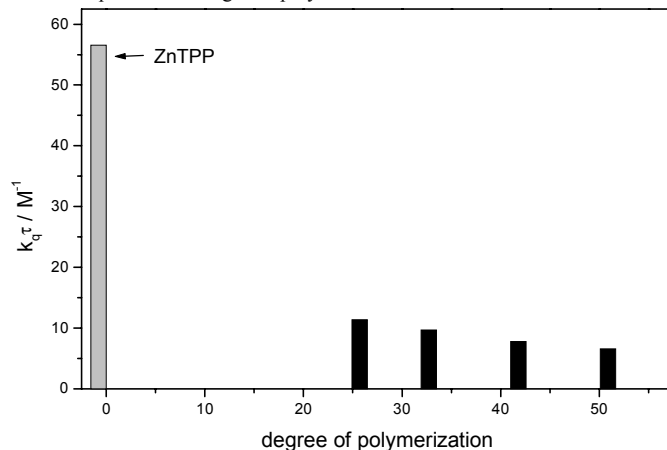


Figure 1. Fluorescence quenching experiments for the series of 16-arm zinc(II) porphyrin stars employing methyl viologen as quencher in CH_3CN .

Since the fluorescence quenching experiments did not allow for an evaluation of the solvent effect on the site isolation due to the low solubility of the probe in non-polar solvents, an alternative approach was used to gain further insight into the polymer conformation as a function of solvation.

Energy transfer experiments were performed on coumarin-terminated stars (*vide supra*). The energetic match between the emission of the coumarin donors and the absorption of the porphyrin acceptor leads to an efficient and extremely distance dependent resonance energy transfer process.⁹ Therefore, the difference in average distance of the chain ends relative to the core was evaluated from the energy transfer efficiencies. As illustrated in Figure 2, the same compound exhibited a more quenched emission from the donors and a more enhanced emission from the acceptor in the bad solvent CH₃CN compared to the good solvent CHCl₃.

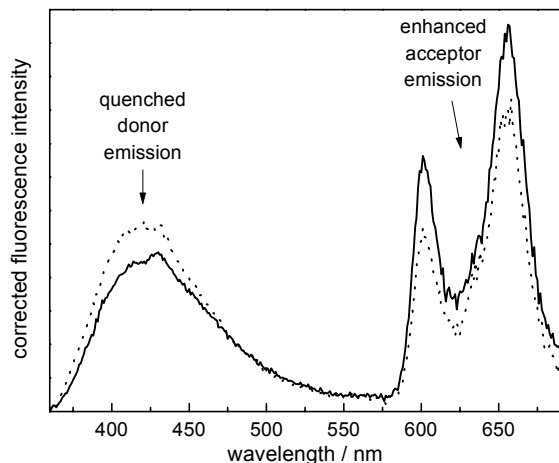
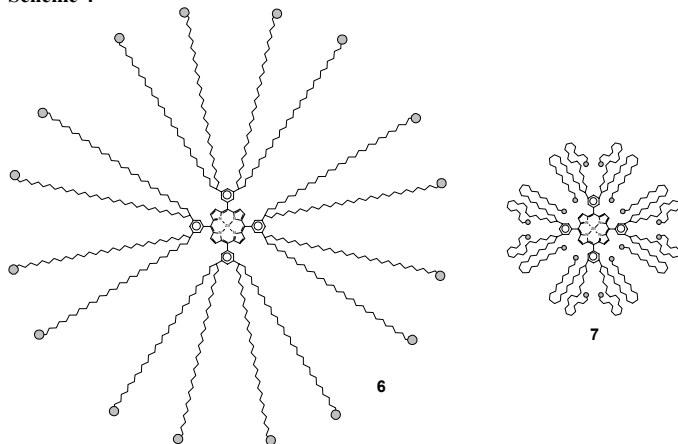


Figure 2. Emission spectra of coumarin-terminated stars in CHCl₃ (-----) and CH₃CN (—) after excitation of the coumarin donors ($\lambda_{exc} = 350\text{nm}$).

We therefore suggest that a structural collapse in the bad solvent (7) leads to reduced average donor-acceptor distance and therefore higher energy transfer efficiency compared to the more extended conformation adopted in a good solvent (6) (Scheme 4). Studies to relate the observed transfer efficiencies to experimentally determined molecular size data are currently underway.

Scheme 4



Conclusions

Novel porphyrin core star polymers have been synthesized via ROP of ϵ -caprolactone using branched porphyrin initiators. This methodology should prove of general applicability to achieve site isolation of functional molecules. Versatile modification of the core and the chain ends renders the synthesis flexible, allowing one to tailor-design a variety of functional star polymers. The shell is constructed in a one pot procedure involving no chromatography and the shell thickness can be controlled by the chain length and the solvent as shown by fluorescence quenching experiments as well as intramolecular energy transfer measurements. Such materials may be of general applicability in the design of optoelectronic devices¹⁰ since site isolation has been proven to

be crucial to achieve high luminescence efficiencies.¹¹ In addition, these compounds are potentially useful for solar energy conversion.¹²

Acknowledgement. Financial support from the AFOSR-MURI program and the National Science Foundation (NSF-DMR 9816166) is acknowledged with thanks.

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