Porphyrin Core Star Polymers: Synthesis, Modification, and Implication for Site Isolation

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During the last years, efforts have been made to encapsulate porphyrins[1] within dendrimers to tune their photophysical,[2] electrochemical,[3] and chemical[4] properties. Work carried out in several laboratories has demonstrated the profound ability of a dendritic shell to isolate the porphyrin core moiety facilitating the design of hemeprotein mimics. Unfortunately, dendrimer synthesis is usually time-consuming, and a more rapid route to encapsulated porphyrins that preserves the architectural and functional control afforded by a dendritic shell is desired. Recent advances in the area of "living" ring opening polymerization (ROP) of ϵ-caprolactone[5] have enabled the accurate construction of star-shaped polymers.[6] We sought to take advantage of this methodology coupled with the space filling branching approach of dendrimer synthesis to achieve site isolation of porphyrins. Our approach is based on a highly branched porphyrin core that acts as a multisite initiator for the ROP of ϵ-caprolactone. Versatile modification of the core and the end-group functionalities renders the synthesis flexible, allowing one to tailor-design a variety of functional star polymers. Such materials may be of general applicability in the design of oxidation catalysts[7] as well as energy-harvesting[8] and optoelectronic devices.[9]

Starting from tetrakis(4-hydroxyphenyl)porphyrin **1a** and tetrakis(3,5-dihydroxyphenyl)porphyrin **1b**, respectively, the initiators **2a,b** were prepared via esterification employing acetonide-protected 2,2-bis(hydroxymethyl)-propionic acid[10] followed
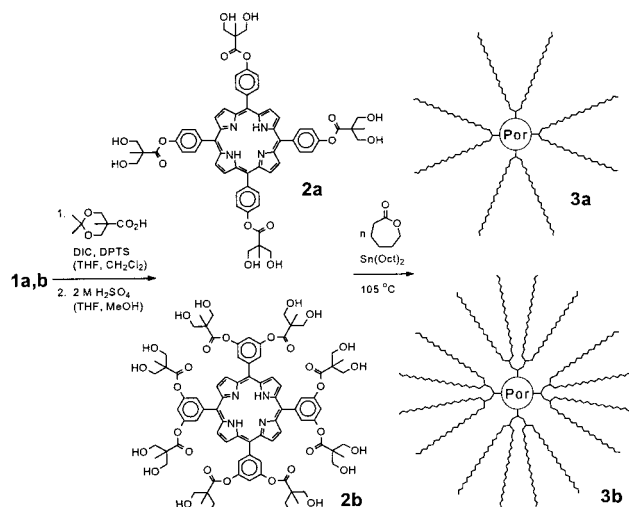
Scheme 1

Table 1. Characteristics of Porphyrin Core Star Polymers **3a,b**

	$\bar{M}_{n(target)}$	$\bar{M}_{n(NMR)}$	$\bar{M}_{n(GPC)}$	$\bar{M}_w/\bar{M}_n$
3a	19400	25400	26200	1.14
	28500	31600	34700	1.13
	37700	41800	50300	1.17
	46800	50600	58300	1.19
3b	38200	47200	56100	1.18
	56500	59900	67200	1.14
	74700	76600	82000	1.12
	93000	93700	89300	1.10

by deprotection of the diol functionalities under acidic conditions (Scheme 1). By using the methodology developed by Trollsås and Hedrick,[6a−c] we obtained star polymers **3a,b** possessing either 8 or 16 arms by bulk polymerization of ϵ-caprolactone with initiators **2a,b** and tin(II) 2-ethylhexanoate (Sn(Oct)$_2$) as the catalyst. By adjusting the monomer-to-initiator ratio, we could prepare polymers with varying chain lengths and low polydispersities in almost quantitative yields (Table 1).

To tune the properties of these materials, we accomplished further modification of the dendritic stars by metalation of the core moiety as well as by derivatization of the hydroxyl-functional chain ends (Scheme 2). Insertion of zinc(II) into the free base porphyrin gave **4b**, which is easily identified by its characteristic electronic absorption spectrum in the Q-band region[11] (Figure 1a). Introduction of the dye coumarin at each of the 16 hydroxyl chain ends of **3b** was easily accomplished by esterification with coumarin-3-carboxylic acid chloride affording **5b**. The additivity of the individual coumarin chromophore units contributes to the large absorption in the UV region of the spectrum (Figure 1a). The proton NMR spectra of **3b** and **5b** (Figure 1b) reveal a significant downfield shift of the signal associated with the end groups of **3b** (CH_2OH) by conversion to the coumarin esters in **5b**. Due to the energetic match between the emission of the coumarin donors and the absorption of the porphyrin acceptor, compounds such as **5b** offer the opportunity of efficient light harvesting and resonance energy transfer.[12] Further studies of these processes are currently underway.

A significant advantage of the high yield processes used is that the only purification required after polymerization, metalation,

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(6) (a) Trollsås, M.; Hedrick, J. L.; Mecerreyes, D.; Dubois, P.; Jerôme, R.; Ihre, H.; Hult, A. *Macromolecules* **1997**, *30*, 8508. (b) Trollsås, M.; Hedrick, J. L.; Mecerreyes, D.; Dubois, P.; Jerôme, R.; Ihre, H.; Hult, A. *Macromolecules* **1998**, *31*, 2756. (c) Trollsås, M.; Hedrick, J. L. *J. Am. Chem. Soc.* **1998**, *120*, 4644, and references therein.
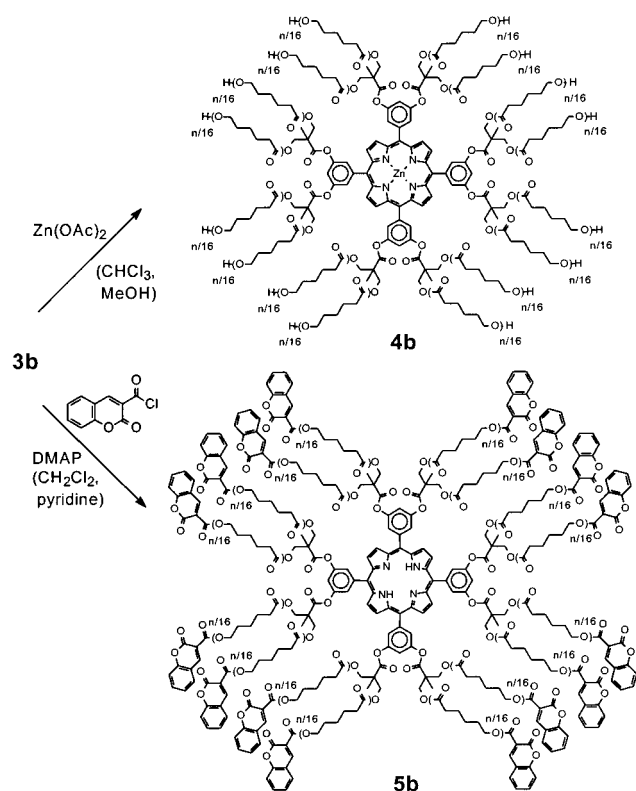
(7) Detailed review are given in (a) Sheldon, R. A., Ed. *Metalloporphyrins in Catalytic Oxidations*; Marcel Dekker: New York, 1994. (b) Montanari, F., Casella, L., Eds. *Metalloporphyrin Catalyzed Oxidations*; Kluwer: London, 1995.

(8) For a recent discussion, see Freemantle, M. *Chem. Eng. News* **1998**, (10/26), 37.

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(12) For a related study, see Gilat, S. L.; Adronov, A.; Fréchet, J. M. J. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 1422.

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Communications to the Editor

Scheme 2

and end group modification was a precipitation into methanol. All polymers are soluble in a variety of solvents such as $CHCl_3$, THF, or CH_3CN.

To evaluate the ability of the polyester backbone to effectively isolate the porphyrin moiety, we studied the accessibility of the core in two series of zinc porphyrin star polymers (**4a,b**) by fluorescence-quenching experiments. Stern–Volmer analysis allowed for the determination of the $k_q\tau$ values (the product of the quenching rate constant and the excited-state lifetime) using methyl viologen as the electron acceptor quencher[13] (Figure 2). 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 τ^{2b} and therefore leading to a direct evaluation of k_q as a measure of the core accessibility.[14] The results show a strong shielding of the core moiety in the polymers compared to zinc tetraphenylporphyrin (ZnTPP) as the reference, clearly demonstrating the largely reduced penetration of the small molecule quencher through the polymeric backbone. Extrapolation indicates a rather steep decline in core accessibility with increasing degree of polymerization. The data also suggest that the chain length rather than the number of arms is crucial in achieving isolation of the core unit. These findings are in agreement with recent theoretical work[15] showing the interaction between the arms near the core unit to be more pronounced giving rise to a dense packing in the interior.

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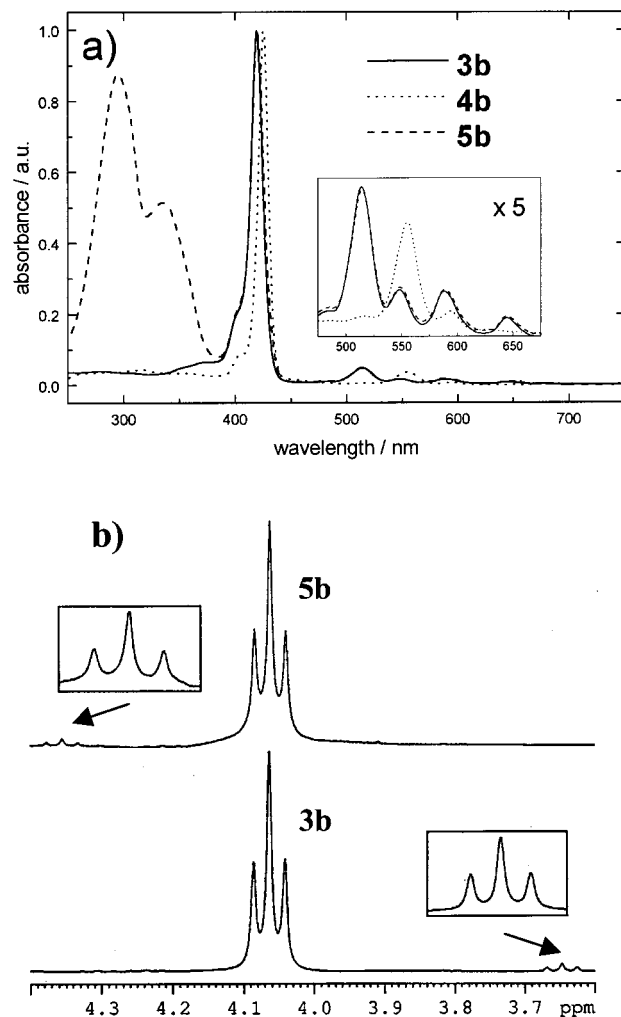

Figure 1. (a) UV/Vis spectra of **3b**, **4b**, and **5b** in $CHCl_3$. (b) ^1H NMR spectra of **3b** and **5b** in $CDCl_3$.
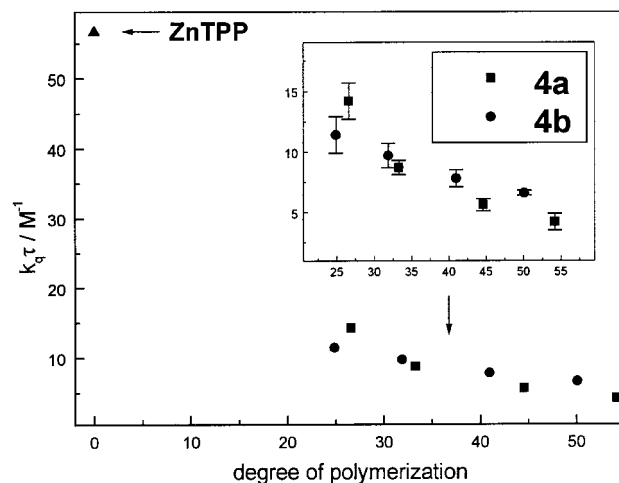

Figure 2. Fluorescence quenching for two series of zinc porphyrin star polymers having 8 arms (**4a**) and 16 arms (**4b**). The $k_q\tau$ values are derived from Stern–Volmer analysis in acetonitrile employing methyl viologen as the quencher.

Supporting Information Available: Experimental details and chemical characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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