

Hyperbranched porphyrins—a rapid synthetic approach to multiporphyrin macromolecules

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A new class of porphyrin containing hyperbranched polymers has been prepared *via* proton-transfer polymerisation utilising an $A_2 + B_3$ approach, thus providing an accelerated entry into the construction of branched multiporphyrin architectures.

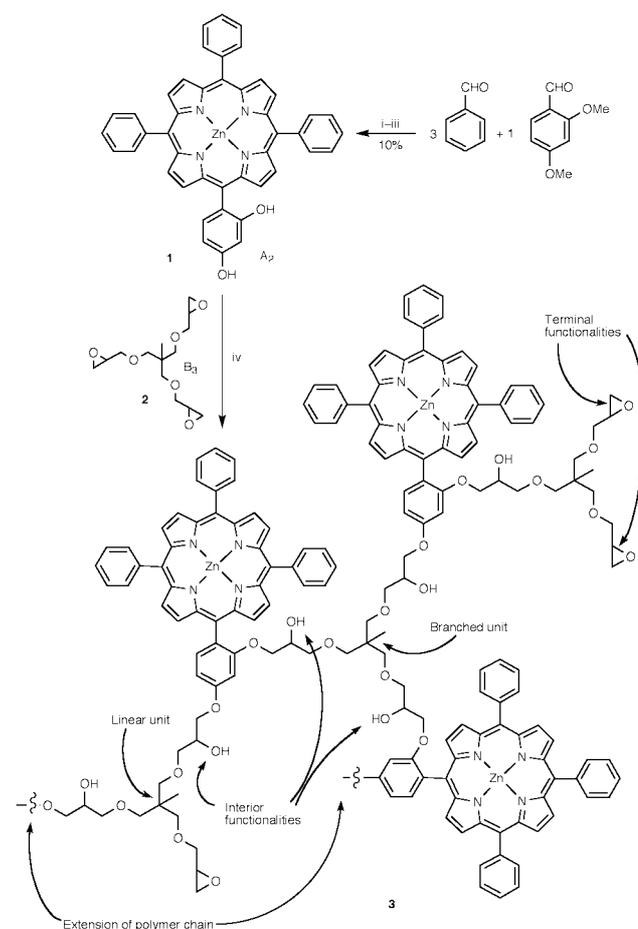
In recent years, significant effort has been made to prepare and study covalently linked multiporphyrin arrays¹ due to their promising role in artificial photosynthesis.² The incorporation of porphyrin units into the framework of a dendrimer³ is of special interest since the dendritic architecture allows for maximum interactions between the chromophores, a necessary condition for efficient energy and electron transfer processes. However, access to such multiporphyrin compounds represents a difficult synthetic challenge, thus only low generation dendritic porphyrins have been prepared to date.^{1,4}

We report on an alternative approach to the construction of branched multiporphyrin architectures that takes advantage of the rapid one pot synthesis used for generating hyperbranched polymers.⁵ This approach is based on our recent work in proton transfer polymerisation⁶ that used an $A_2 + B_3$ route for the preparation of hyperbranched aliphatic polyethers.⁷ The system described herein is designed following similar principles. In this case, bisphenolic porphyrin **1** serves as the A_2 monomer and the aliphatic trisepoxide **2**⁸ serves as the B_3 monomer (Scheme 1).

Initiation of the polymerisation is expected to proceed *via* deprotonation of the phenol by the base catalyst. This should be followed by ring opening of an epoxide substituent by the nucleophilic phenoxide. Regeneration of phenoxide should then occur by an efficient proton transfer from a different phenol to the formed secondary alkoxide.⁷ This process leads to a highly branched polyether architecture incorporating multiple porphyrin units.⁹ It was envisaged that the formed polymer chain in the *ortho*-position of the *meso*-phenyl substituents would lead to good solubility by decreasing the porphyrin–porphyrin stacking interactions. The metalated derivative, *e.g.* zinc complex, was chosen to prevent participation of the pyrrole hydrogens in the proton transfer event.

The asymmetric zinc porphyrin A_2 monomer **1**[†] is accessible in gram quantities *via* a three step procedure in 10% overall yield. The polymerisations employed equimolar ratios of the monomers as a 0.2 M solution in THF at 60 °C using a catalytic amount of base (25 mol% per phenolic group). The successful incorporation of both monomers into the polymer backbone was monitored by matrix assisted laser desorption ionisation time of flight (MALDI-TOF) mass spectrometry (Fig. 1). Unfortunately, ionisation of higher molecular weight material becomes increasingly difficult by the MALDI technique. Therefore, gel permeation chromatography (GPC)[‡] was used as an additional complementary method for MW analysis (Fig. 2). The kinetic growth profile appeared as expected for a polycondensation reaction (Fig. 2, inset).^{6,7} Upon reaching MW ~ 10 000,[§] the reaction was stopped by removing the heating source, and the resulting polymer **3**[¶] was purified by precipitation into methanol (THF–MeOH 1:50) giving rise to a fairly narrow polydispersity (PD) of less than 2 (Fig. 2). Control over MW can be achieved easily by variation of reaction time (typically a few

days). We reason that slow polymerisation is due to the high dilution conditions made necessary by the relatively low



Scheme 1 Reagents and conditions: i, pyrrole, EtCO₂H, PhNO₂, 120 °C; ii, BBr₃, CH₂Cl₂, 0 °C to room temp.; iii, Zn(OAc)₂, CHCl₃–MeOH, reflux; iv, KOBu^t, THF, heat.

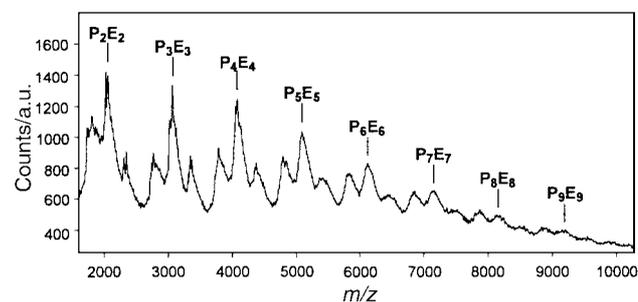


Fig. 1 MALDI-TOF mass spectrum of the polymerisation mixture showing the incorporation of the porphyrin (P) and epoxide (E) monomers. The peaks at lower (higher) mass of each major peak correspond to the loss (addition) of one epoxide unit.

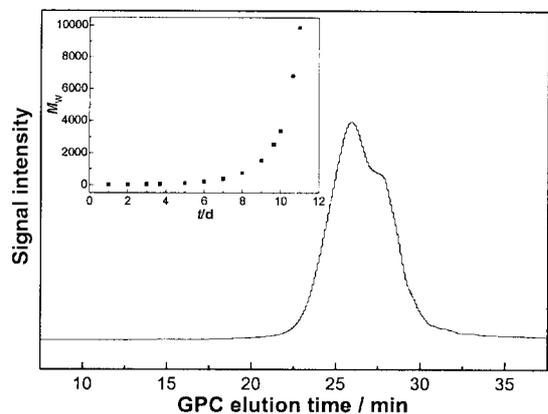


Fig. 2 GPC trace of polymer **3** after precipitation into MeOH (MW = 9900; PDI = 1.9). The inset shows polymer growth as a function of time for a polymerisation run at 60 °C.

solubility of **1**. Higher temperatures result in faster polymer growth, as well as increased PD of the polymers. The polymers were obtained as dark purple powders in 50–60% yields after precipitation, and showed good solubility in a variety of solvents such as CHCl_3 , THF and DMSO.

Initial photophysical studies revealed only slight changes in the absorption behaviour of polymer **3** compared to monomer **1**, suggesting rather weak electronic coupling of the porphyrin units (Fig. 3).¹⁰ However, a 30% decrease in fluorescence intensity of **3** compared to **1** was observed (Fig. 3, inset). This finding is attributed to an enhanced self-quenching of the chromophores within the macromolecule, presumably by cofacial interactions.

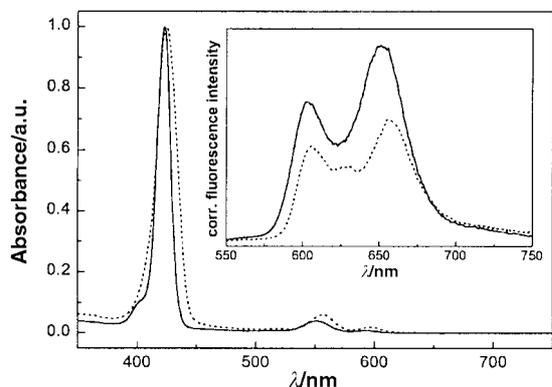


Fig. 3 UV-VIS absorption spectra of monomer **1** (—) and polymer **3** (···) in CHCl_3 . The inset shows the corrected fluorescence spectra in CHCl_3 ($\lambda_{\text{exc}} = 420 \text{ nm}$).

In summary, we have developed for the first time hyperbranched polymers incorporating porphyrin chromophores. The described methodology allows for the rapid synthesis of multiporphyrin architectures facilitated by the ease of purification, e.g. no chromatography, and it should be of general applicability. Such polymers could serve as interesting materials for a variety of photophysical and electrochemical studies as well as for the construction of optoelectronic devices.¹¹ Furthermore, structural modification of these polymers by transmetalation or derivatisation of residual functional groups should provide a diverse set of new materials.

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Notes and references

† Selected data for **1**: δ_{H} (300 MHz, CHCl_3 , 25 °C, TMS) 8.96 (d, $^3J(\text{H,H})$ 5 Hz, 8H, $\beta\text{-H}$), 8.19–8.21 (m, 6H, Ph-H), 7.72–7.80 (m, 9 + 1H, Ph-H + 6'-H), 6.72–6.76 (s and d, $^3J(\text{H,H})$ 8 Hz, 1 + 1H, 3'- and 5'-H), 5.12 (br s, 1H, OH), 5.04 (br s, 1H, OH); FAB-HRMS: m/z 708.1487 (M^+ , $\text{C}_{44}\text{H}_{28}\text{N}_4\text{O}_2\text{Zn}$ requires 708.1504); $\lambda_{\text{max}}(\text{CHCl}_3)/\text{nm}$ ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) 423 (517 000), 551 (19 600), 593 (3200); $\lambda_{\text{em}}(\text{CHCl}_3)/\text{nm}$ ($\lambda_{\text{exc}} = 420 \text{ nm}$) 602, 651.

‡ The MW values of polymer **3** as given by GPC are merely estimates due to the differences in hydrodynamic volume between **3** and the polystyrene standards used for GPC calibration.

§ Polymers of much higher molecular weight (MW > 50 000) can be obtained; however, the polydispersity increases significantly above 10 kD.

¶ Selected data for **3**: GPC† (THF): $M_w = 9900$, $M_n = 5100$, PDI = 1.9; δ_{H} (300 MHz, $\text{DMSO}-d_6$, 25 °C) 8.72 (br s, $\beta\text{-H}$), 8.13 (br s, Ph-H), 7.72 (br s, Ph-H + 6'-H), 6.94 (br s, 3'- and 5'-H), 1.2–4.3 (very br, CH_2CHOH , CH_2CHOH and CH_2CHOH), 0.9 (br s, CH_3); $\lambda_{\text{max}}(\text{CHCl}_3)/\text{nm}$ ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) 425, 557, 597; $\lambda_{\text{em}}(\text{CHCl}_3)/\text{nm}$ ($\lambda_{\text{exc}} = 420 \text{ nm}$) 606, 655.

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