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Hyperbranched porphyrins—a rapid synthetic approach to multiporphyrin macromolecules

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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 A2 + B3 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 arrays due to their promising role in artificial photosynthesis. The incorporation of porphyrin units into the framework of a dendrimer 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.

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. This approach is based on our recent work in proton transfer polymerisation that used an A2 + B3 route for the preparation of hyperbranched aliphatic polyethers. The system described herein is designed following similar principles. In this case, bisphenolic porphyrin serves as the A2 monomer and the aliphatic trisepoxide serves as the B3 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. This process leads to a highly branched polymer architecture incorporating multiple porphyrin units. 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 A2 monomer 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). Upon reaching MW ~ 10000, the reaction was stopped by removing the heating source, and the resulting polymer 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.
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 into MeOH (MW = 9900;
PDI = 1.9). The inset shows polymer growth as a function of time for a
polymerisation run at 60 °C.

In summary, we have developed for the first time hyper-
branched polymers incorporating porphyrin chromophores. The
described methodology allows for the rapid synthesis of
multiporphyrin architectures facilitated by the ease of purifica-
tion, e.g. no chromatography, and it should be of general
applicability. Such polymers could serve as interesting materi-
als for a variety of photophysical and electrochemical studies as
well as for the construction of optoelectronic devices. 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
1 Selected data for I: M20 300 MHz, CHCl3, 25 °C, TMS) 8.96 (d, 3JH,H)
5 H, 8H, [6-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, 3JH,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+ CaH2N2O2Zn
requires 708.1504); λmax(CHCl3)/nm (ε/103 mol–1·cm–1) 425 (517000),
551 (19600), 593 (3200); λmax(CHCl3)/nm (ε/10000) 602, 651.
2 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.
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kD.
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