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Synthesis of Multiporphyrin Containing Hyperbranched Polymers

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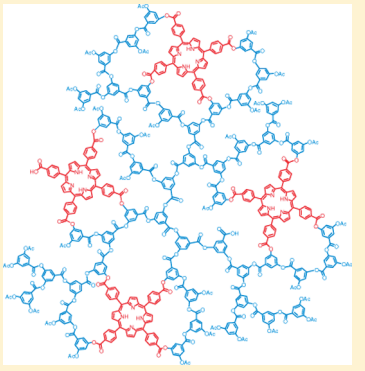
ABSTRACT: This paper describes the facile synthesis of a hyperbranched poly(aryl ester) that possesses a number of porphyrin units within its globular structure. The simple procedure utilizes commercially available starting materials which after fractionation generate a series of polymers with molecular weights between 4500 and 30 000 Da. The number of porphyrins increased with molecular weight with the largest polymer containing ~6 porphyrins. Further analysis revealed a linear relationship between the number of incorporated porphyrins and molecular weight.



INTRODUCTION

Photosynthesis is the single most important process developed by nature. Through the harvesting of solar energy, photosynthetic organisms such as plants, green algae, and cyanobacteria are ultimately responsible for providing all of the biological energy needed for higher forms of life to exist. The potential benefits of reproducing this process in an artificial system are obvious, and the challenge of understanding and replicating the light-harvesting capabilities of these organisms has led to the development of a wide range of model systems.[1−3] The photosynthetic process involves channeling light energy from a large area to a central point, using an array of chromophore molecules surrounding a reaction center.[4] In photosynthetic bacteria such as *Rhodopseudimonas*[5] and *Rhodospirillium molichianum*[6−12] (purple bacteria) the principal photosynthetic component consists of a reaction center surrounded by a symmetrical ring of chromophores in a protein matrix.

The light-absorbing chromophore employed by nature is chlorophyll, a functionalized porphyrin. Thus, it is no surprise that a large proportion of the research concerning synthetic light-harvesting models involves the synthesis of porphyrin arrays.[13] Many of these have been linear in fashion; however, more recently two- and three-dimensional (symmetrical) arrays have been investigated. The simplest of these involves linking a number of porphyrins together using covalent chemistry, such as the cross-shaped pentamers prepared by Prathapan et al.[14,15] More complex assemblies have been prepared using noncovalent chemistry; for example, Yoshiaki et al. reported a cyclic supramolecular assembly involving 12 porphyrin units.[16] In more recent work, dendrimers[17] have been used to mimic the highly ordered ringlike structure of the natural light-harvesting complex found in purple bacteria.[18] Furthermore, work within our group developed a noncovalent system using a dendrimer as a scaffold to support a large number of external porphyrins.[19] Other examples include a number of symmetrical porphyrin arrays,[20−23] such as the aromatic polyether porphyrin dendrimer prepared by Aida et al.[24−27] These types of multiporphyrin architectures have been shown to exhibit energy transfer efficiencies of over 90%; however, they are limited by the time-consuming nature of the synthesis involved.

It has recently been discovered that highly ordered and perfectly symmetrical arrangement of chromophores in photosynthetic organisms is not essential to successful light harvesting. High-resolution X-ray crystallography (2.5 Å) of the photosynthetic components of *Synechococcus elongates* (a cyanobacteria) shows a structure built from largely the same components as those found in purple bacteria, yet the chlorophyll arrangement displays no obvious symmetries.[28] This demonstrates that a highly ordered configuration is not necessary for effective light harvesting, opening up the possibility of using hyperbranched polymers to artificially study this phenomenon. The work detailed in this paper describes initial attempts to construct a simple, globular molecule possessing a number of porphyrin units, using just one synthetic step.

EXPERIMENTAL SECTION

All NMR samples were prepared using deuterated solvents supplied by Sigma-Aldrich. ^{1}H NMR was performed at 250 MHz and ^{13}C NMR at 60 MHz using a Bruker AC-250 with 5 mm CH probe. UV analysis was carried out using a Hitachi U-2010 spectrophotometer in wavelength mode. IR samples were recorded neat (without using Nujol or KBr) on a Perkin-Elmer Spectrum RX I FT-IR spectophotometer with integral

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DuraSampl IR-II. GPC was conducted at room temperature using either a high molecular weight column setup consisting of 3 × 300 mm PL gel 10 μm mixed-B or a low molecular weight setup consisting of 2 × 600 mm PL gel 5 μm (500 Å). All samples were run using Fisher GPC grade THF, supplied to the columns by a Waters 515 HPLC pump at 1.00 mL min^{-1}. Samples were prepared in THF and spiked with toluene as a flow marker, before being injected through a 200 μL sample loop with a Gilson 234 autoinjector. Sample concentration was monitored using an Erma ERC-7512 refractive index detector and where relevant by UV using a Waters Millipore Lambda Max 481 LC spectrophotometer. Data were analyzed using Polymer Laboratories proprietary software. Preparative GPC was conducted using SX-1 beads from Biorad (Biobeads).

Synthesis of Tetracarboxyphenylporphyrin (TCPP). Propionic acid (250 mL) and 4-carboxybenzaldehyde (8.00 g, 0.053 mol) were mixed in a round-bottomed flask fitted with a condenser. The reaction mixture was heated to reflux, and pyrrole (3.70 mL, 0.053 mol) was added to the reaction vessel via syringe. Refluxing was continued with stirring for ~1 h under a constant flow of air. The product was separated from the reaction mixture by hot filtration and washed with refluxing dichloromethane followed by a small amount of cold THF. The solid purple filtrate was collected and dried under vacuum before further purification by recrystallization from MeOH/DCM. Yield: 2.62 g, 25%. ^{1}H NMR (DMSO): 13.32 (s, 4H, COO*H*), 8.80 (s, 8H, pyrrolic-β-C*H*), 8.32 (q, 16H, phenylic C*H*), −2.96 (s, 2H, N*H*). ^{13}C NMR (DMSO): δ 167.4, 145.3, 134.4, 130.4, 127.8, 119.2, 26.8. IR (cm^{-1}): 3435, 3061, 1685, 1600, 1285, 782. MS (ES), MH^+ = 790 g mol^{-1}. Elemental: C,72.86 H, 3.86 N, 7.07 O, 16.21, $C_{48}H_{30}N_4O_8$ (expected C, 72.90; H, 3.82; N, 7.09).

Multi-Free-Base-Porphyrin Hyperbranched Poly(aryl ester) 1. Tetracarboxyphenylporphyrin (1.60 g, 2.10 mmol), 3,5-diacetoxybenzoic acid (10.00 g, 42 mmol), and diphenyl ether (10.00 g) were added to a dry round-bottomed flask under nitrogen. The reaction vessel was fitted with a still head, a condenser, and collection flask before being evacuated at room temperature (20 °C) for 30 min. The system was again flushed with nitrogen. The reaction was heated to 225 °C using a heating mantle for 45 min. The temperature was reduced to 180 °C by placing in a preheated oil bath. The reaction was placed under vacuum, and acetic acid was removed for 2 h. The polymer product was isolated by precipitation from THF into methanol. Yield: 3.61 g, 31% (based on mass recovery). ^{1}H NMR ($CDCl_3$) 8.89 (br s, 8H, [TCPP] pyrrolic-β-*H*), 8.23 (8H, br d, *J* = 8.24, [TCPP] phenylic *o*-C*H*), 8.02−7.77 (br m_4, 72H, [polymer] Ar *p*-C*H*), 7.56 (d, *J* = 8.24, 8H, [TCPP] phenylic *m*-C*H*), 7.45−7.15 (br m_3, 36H, [polymer] Ar *o*-C*H*), 2.25 (br s, 108H, [polymer] CH_3). UV absorbance (CH_2Cl_2): λ_{max} nm = 420, 516, 552, 590, 647.5. GPC (HMW) M_n 6500, PD 2.19.

Multi-Zinc-Porphyrin Hyperbranched Poly(aryl ester) 2. The porphyrin cored hyperbranched polymer **1** (1.00 g) was dissolved in dichloromethane and stirred with excess $Zn(OAc)_2 \cdot H_2O$ (2.0 g, 9.11 mmol) at room temperature for 30 min. Unreacted zinc acetate was then removed via filtration, and the solvent was removed using a rotary evaporator. The crude product was then dissolved in a minimum of refluxing THF and precipitated into a large excess of ice-cold methanol. The product was then isolated via filtration. Yield: 0.719 g, 72%. ^{1}H NMR ($CDCl_3$): δ 9.03 (br s, 8H, porphyrin pyrrolic-β-H),), 9.00 (8H, br d, porphyrin phenylic *o*-CH), 8.04−7.83 (br m4, 2H, [polymer] Ar *p*-CH), 7.54 (d, 8.24, 8H, porphyrin phenylic *m*-CH), 7.54−7.25 (br m3, 1H, [polymer] Ar *o*-CH), 2.34 (br s, 3H, [polymer] CH_3. ^{13}C NMR ($CDCl_3$): δ 168.7, 162.7, 151.2, 130.9, 130.7, 121.2, 120.9, 20.9. UV Absorbance (CH_2Cl_2): λ_{max} nm = 418, 554, 590.

Multi-Iron-Porphyrin Hyperbranched Poly(aryl ester) 3. The porphyrin cored hyperbranched polymer **1** (1.0 g), $FeCl_2$ (2.5 g, 19.7 mmol), and 2,6-lutidine (0.44 mL, 3.75 mmol) were dissolved in THF. The reaction mixture was refluxed for 4 h. Unreacted $FeCl_2$ was then removed via filtration, and the solvent was reduced by rotary evaporation. The crude product was then dissolved in a minimum of refluxing THF and precipitated into a large excess of ice-cold methanol. The product was then isolated via filtration. Yield 0.752 g, 75%. UV absorbance (CH_2Cl_2): λ_{max} nm = 419, 510, and 585.

Fractionation of Multi-Porphyrin Hyperbranched Poly-(aryl ester). Preparative GPC was performed using biobeads swelled overnight in THF. These were then loaded onto a standard glass chromatography column (~3 cm diameter), with a small amount of sand used to stop the beads from floating. The solvent was then changed to dichloromethane by flushing the column under gravity. The crude/bulk multiporphyrin hyperbranched polyarylester (1.00 g) was loaded onto the column in the minimum amount of DCM. The solvent flow was controlled by gravity, and sample fractions (5 mL) were collected before being monitored with analytical GPC (with similar fractions being combined).

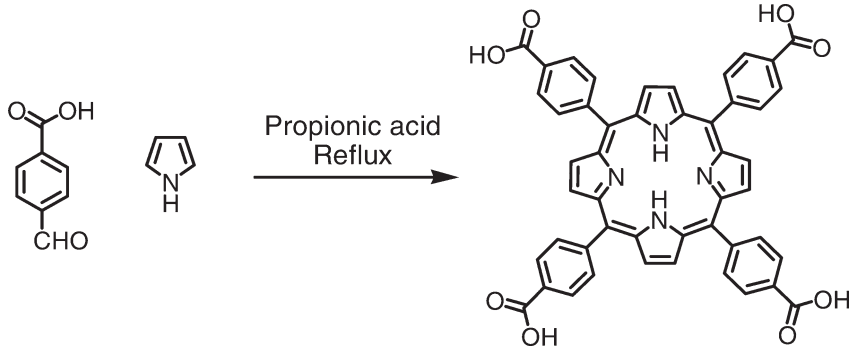
RESULTS AND DISCUSSION

Fréchet has previously reported the synthesis of a hyperbranched polymer possessing a number of porphyrin units within a globular structure. The polymer was prepared via ring-opening polymerization using an $A_2 + B_3$ approach which possessed M_n values of around 10 000 Da and contained up to ten porphyrins units.[29] Although successful, the method suffered from high polydispersity and lengthy reaction times. In addition, the porphyrin used was a monofunctionalized tetraphenylporphyrin which is not easy to synthesize or purify.[30] We have recently used a different system based on poly(3,5-diacetoxybenzoic acid) to construct a HBP possessing just a single porphyrin unit at the core. The reaction time for this synthesis was measured in hours rather than days, and molecular weights of over 20 000 Da were achieved with polydispersities as low as 1.19.[31−35] It was thought that if these properties could be carried through for a multi-porphyrin system, the resulting polymer would represent an improvement on the existing method. Considering the original synthesis of the porphyrin cored polymer,[36] it was proposed that "reversing" the functionality of the tetraacetoxyphenylporphyrin core molecule to give tetracarboxyphenylporphyrin (TCPP) would enable a multi-porphyrin polymer to be produced. Although this methodology could lead to unwanted cross-linking, any such material can be removed easily via filtration. Overall, the synthetic procedure is very simple and does not generate mixtures, and the products are easy to purify. Thus, using the same basic method to synthesize a porphyrin cored HBP, a copolymerization of 3,5-diacetoxybenzoic acid and TCPP was conducted.

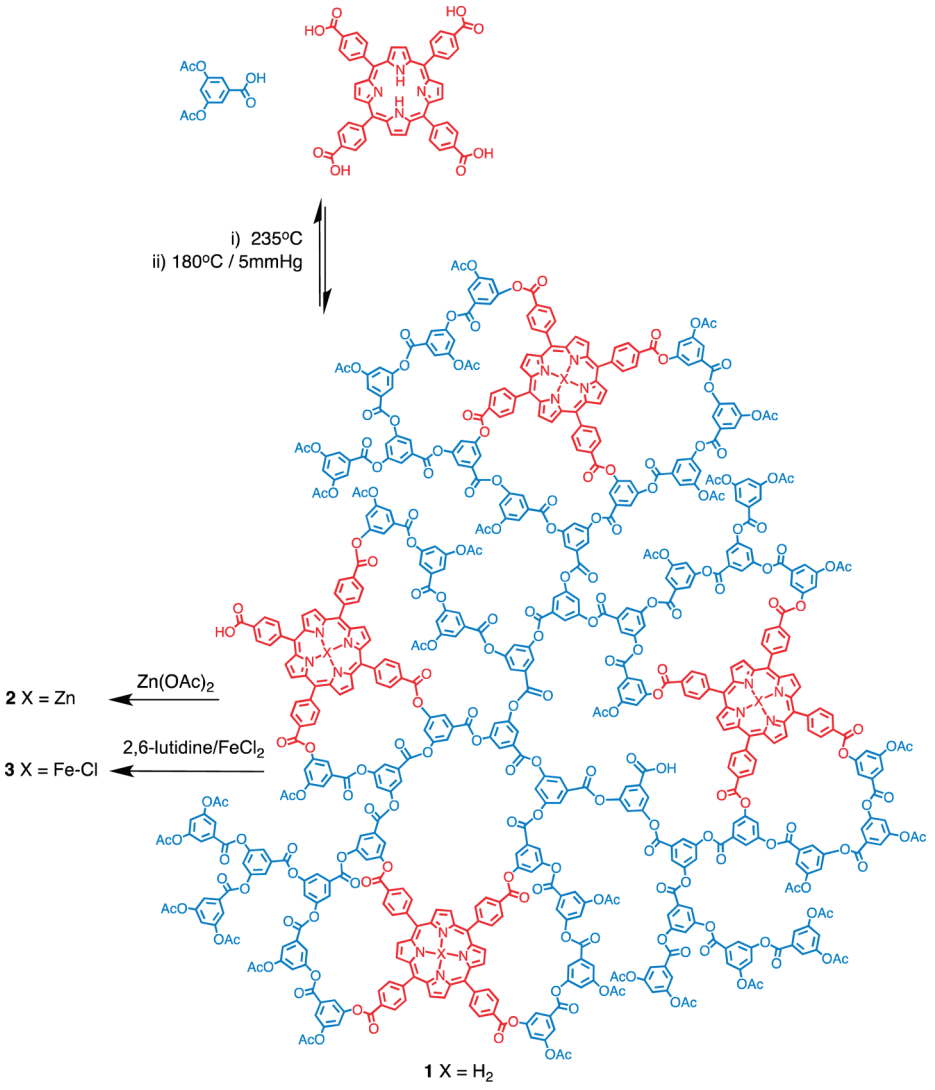
Tetracarboxyphenylporphyrin was synthesized by refluxing 4-carboxybenzaldehyde with pyrrole in propionic acid for 1 h, as shown in Scheme 1.[37] The product was isolated by hot filtration and recrystallized from methanol/dichloromethane.

Once synthesized, the porphyrin could be copolymerized with 3,5-diacetoxybenzoic acid. The polymer was prepared on a 10 g scale with respect to the monomer using an equal mass of diphenyl ether (solvent) and 5 mol % of tetracarboxyphenylporphyrin, as shown in Scheme 2. The polymerization was carried out using the same conditions developed in our earlier work.[36] Specifically, the mixture was heated to 225 °C for 45 min followed by removal of acetic acid under vacuum at 180 °C for 2 h, after which the polymer mixture was dissolved in refluxing THF, leaving behind a portion of insoluble material presumable to be cross-linked polymer. On precipitation into methanol, a red-brown polymer product was isolated (3.6 g, ~35% yield based on mass). The color of the polymer provided an early

Scheme 1. Synthesis of Tetracarboxyphenylporphyrin



Scheme 2. Synthesis of Multi-Porphyrin Hyperbranched Poly(3,5-diacetoxybenzoic acid)



indication of the presence of porphyrin. This was confirmed by ^{1}H NMR, which displayed characteristic resonances from the polymer, in addition to two broad peaks attributable to the pyrrolic and phenylic protons on the porphyrin at 8.8−8.9 and 8.3−8.4 ppm, respectively. Although this confirmed that porphyrin was contained in the polymer mixture, it was not possible to determine conclusively that the polymer contained covalently incorporated porphyrin by ^{1}H NMR.

GPC analysis using UV detection set at 420 nm confirmed that porphyrin was indeed incorporated into the polymer and also

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showed M_n and polydispersity of the bulk polymer was 6500 Da and 2.19, respectively.[32,38] The chromatogram showed a strong UV absorbance from the porphyrin across the complete molecular weight range but also contained a distinct UV active peak around 800 Da, which was attributed to unincorporated porphyrin. This "free" TCPP was removed via repeated washing with methanol until the washings were colorless. The GPC was repeated, and the chromatogram of this purified polymer was marked by the absence of the low molecular weight peak attributed to free porphyrin, confirming successful removal.

Mass spectrometry was carried out on a polymer sample collected from the tail end of a GPC analysis; the spectrum showed the polymer contained covalently incorporated porphyrin. Peaks were observed at 178 mass intervals, corresponding to a value of $m/z = 178n + 790$, where 178 is the mass of the monomer residue, n is the number of monomer residues, and 790 is the mass of the porphyrin. The level of porphyrin incorporation in the purified bulk polymer was determined using UV/visible spectrophotometry to be around 4 mol % with respect to monomer residues. Because of the reversible nature of the polymerization mechanism, it was expected that the 5 mol % porphyrin in the feed would be maintained in the polymer. However, the data are somewhat biased toward the monomer, suggesting that only 80% of the porphyrin became incorporated into the bulk polymer. This can be accounted for by considering the nature of the polymerization; as the reaction progresses, some polymer molecules will become cross-linked to such an extent to become insoluble. The polymers contained within this insoluble portion are likely to contain a higher than average proportion of porphyrin (i.e., cross-linker). Therefore, as a result of this insolubility, these porphyrins are effectively removed from the equilibrium. This will result in a net reduction in porphyrin concentration within the soluble polymer mixture (relative to monomer). Although this will be more pronounced for higher molecular weight polymers, the remaining polymer/porphyrin mixture should become re-equilibrated, distributing the porphyrin evenly.

To confirm the level of porphyrin incorporation across the complete molecular weight range and to determine whether any multiporphyrin polymers had been produced, the bulk polymer was fractionated using preparative GPC. The fractions were analyzed using UV/visible spectrophotometry; solutions were prepared in dichloromethane for each polymer fraction and diluted to known concentrations of manageable UV/vis absorbance (i.e., diluted to UV concentration with respect to porphyrin). Using a Beer−Lambert plot of free porphyrin in dichloromethane, the number of moles of porphyrin contained in each solution was calculated. These values were then used todetermine the relative mass contribution of both the porphyrin moieties and the monomer residues for each polymer fraction and thus the moles of monomer residue. This allowed a porphyrin-to-monomer ratio to be calculated for each fraction. The results of this analysis are given in Table 1.

Plotting molecular weight vs the number of incorporated porphyrins shows a linear relationship between the two (Figure 1). This confirms the level of porphyrin incorporation is constant across all molecular weights and not biased toward either high or low molecular weight fractions. This supports the percent porphyrin calculations obtained for each fraction (Table 1), which indicated a relatively even porphyrin incorporation with an average value of 3.8%. In an attempt to prepare a polymer with a greater number of porphyrins, the reaction was repeated with an increased reaction time. However, despite attempts to modify the reaction conditions, this proved unsuccessful and in all cases only served to increase the level of cross-linking such that a negligible amount of product was recovered.

Table 1. Analysis of Porphyrin Content for Fractionated Polymer

fraction	M_n	porphyrin polarity (μM)	monomer polarity (μM)	% porphyrin	porphyrins/polymer[a]
bulk	6500	0.191	4.76	3.9	1
1	29000	0.181	4.82	3.6	6
2	20000	0.189	4.78	3.8	4
3	13000	0.180	4.82	3.6	3
4	9000	0.186	4.79	3.7	2
5	6500	0.189	4.78	3.8	1
6	4500	0.197	4.75	4.0	1

[a] Rounded to the nearest integer.

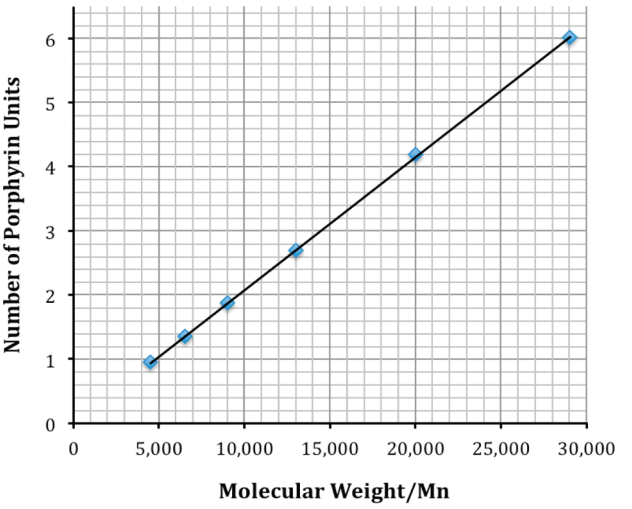

Figure 1. Plot of porphyrin number (rounded to the nearest integer) vs polymer molecular weight (M_n) for the fractionated polymer.

Having demonstrated the basic synthetic and purification procedures, it was next appropriate to probe whether these macromolecules could be modified further. As some of the intended applications require metalated porphyrins, it was important to establish that metal insertion could be carried out into the internal porphyrins without harming or damaging the polymeric backbone. As such, zinc insertion was attempted which if successful would allow nitrogen coordination and ligand binding. This proved to a relatively facile task; as shown in Scheme 2, the bulk polymer was dissolved in dichloromethane and an excess of $Zn(OAc)_2$ added. The solution was then gently refluxed and monitored by UV/vis absorption to follow the reduction in the number of Q bands from four to two. After 30 min the reaction was deemed complete, and unreacted $Zn(OAc)_2$ was removed via filtration. Solvent was then removed by rotary evaporation and purified by precipitation into cold methanol from refluxing THF. The four Q bands at 516, 552, 590, and 647.5 nm present in the UV/vis spectrum of the starting material were replaced by two new resonances at 554 and 590 nm, confirming the metalation was a success. To probe the possibility of further functionalization, insertion of iron was also attempted. This was deemed

appropriate as iron-containing porphyrins have a number of important applications in biology and catalysis. As iron is slightly larger than zinc, a more rigorous reaction procedure was required but a similar work-up was sufficient. The bulk polymer was dissolved in THF, and an excess of $FeCl_2$ was added alongside 2,6-lutidine. The solution was heated to reflux and once more monitored by UV/vis absorption. After 4 h the reaction was complete and unreacted $FeCl_2$ removed via filtration. The product was purified by precipitation into cold methanol from refluxing THF. The UV/vis absorption spectra was similar to that obtained from the zinc sample, with the four Q bands of the freebase porphyrin polymer **1** being replaced by two peaks at 510 and 565 nm. Although a ^{1}H NMR spectrum could not be obtained for the iron sample, GPC analysis of both the zinc and iron containing polymers confirmed that metalation had not destroyed or damaged the polymer. The M_n of both products remained unchanged, although the polydispersity was slightly reduced due to the additional purification step that also removed small oligomers.

In conclusion, a simple one-step procedure for synthesizing HBPs with multiple porphyrins was achieved. After purification and fractionation using preparative size exclusion chromatography, a series of "dendrimer"-like polymers were obtained. The method produced a range of polymers which contained an upper molecular weight of ~29 000 and possessed 6 internal porphyrins. Analysis of the fractions revealed a linear relationship between the level of porphyrin incorporation and molecular weight, suggesting an even distribution of porphyrins across all polymer fractions. The 4 mol % level of incorporation achieved was very close to the 5 mol % of porphyrin added at the start of the reaction. Any differences were attributed to losses from cross-linking and oligomers which were removed from the system during purification. Any attempt to increase the proportion of porphyrin content failed due to increased levels of cross-linking. Furthermore, successful metalation of the porphyrins was demonstrated via the insertion of zinc and iron which did not cleave or damage the polymer. The catalytic and binding properties of these polymers are currently being investigated.

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