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Synthesis and Properties of Hyperbranched Conjugated Porphyrins

Zhuping Fei,[†] Binsong Li,[†] Zhishan Bo,*,[†] and Ran Lu*,[‡]

State Key Laboratory of Polymer Physics and Chemistry, CAS Key Lab of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China, and College of Chemistry, Jilin University, 119 JieFang Road, Changchun 130023, China

zsbo@iccas.ac.cn

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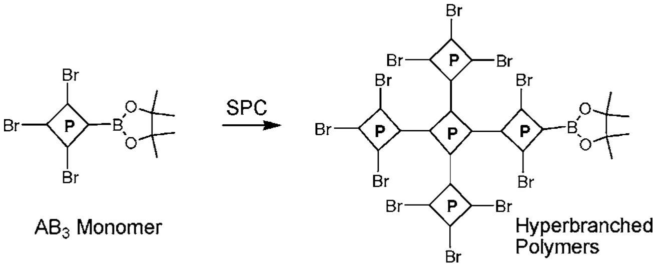
ABSTRACT



Hyperbranched conjugated porphyrin arrays were prepared by one-pot Suzuki polycondensation of AB_3 and $AB_3 + C_4$ approaches.

Two families of three-dimensional macromolecules, dendrimers and hyperbranched polymers, have gained growing scientific interest.[1] Monodisperse, well-defined, and highly branched dendrimers are prepared by time-consuming multistep reactions,[1a,b] whereas irregularly branched and polydisperse hyperbranched polymers are prepared by one-pot reactions, which makes the large-scale synthesis possible at a reasonable cost. The synthesis of many kinds of hyperbranched polymers has been well documented.[1c−e]

In recent years, giant multiporphyrin dendritic arrays have attracted considerable scientific attention because they have been considered as ideal models of mimicking the natural photosynthetic system.[2] Great efforts have been devoted to the synthesis and property investigation of dendritic multiporphyrin arrays.[3] For example, porphyrins have been used as building blocks to construct dendrimers with porphyrins in the core, in the interior at every generation (repeat unit), and at the periphery.[2] The dendritic multiporphyrin arrays are of special interest, since the dendritic architecture allows for the maximum interactions between the porphyrin chromophores. The highly branched and globular features not only help to form amorphous films of good quality but also improve their light emitting efficiency. However, an efficient synthesis of multiporphyrin arrays remains a challenge. Until now, only low-generation dendritic porphyrins have been prepared.[4] Hyperbranched multiporphyrin arrays possess architectures and properties similar to those of dendritic multiporphyrin arrays, but their synthesis is much simpler.

[†] Chinese Academy of Sciences.

[‡] Jilin University.

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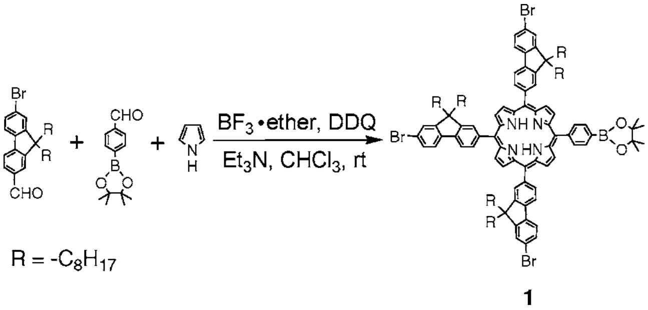
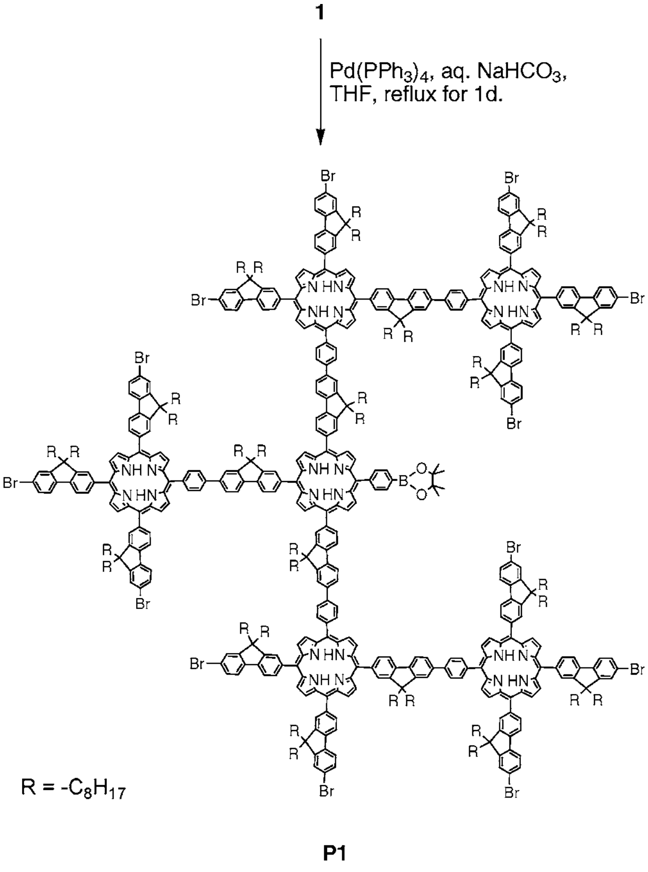
Scheme 1

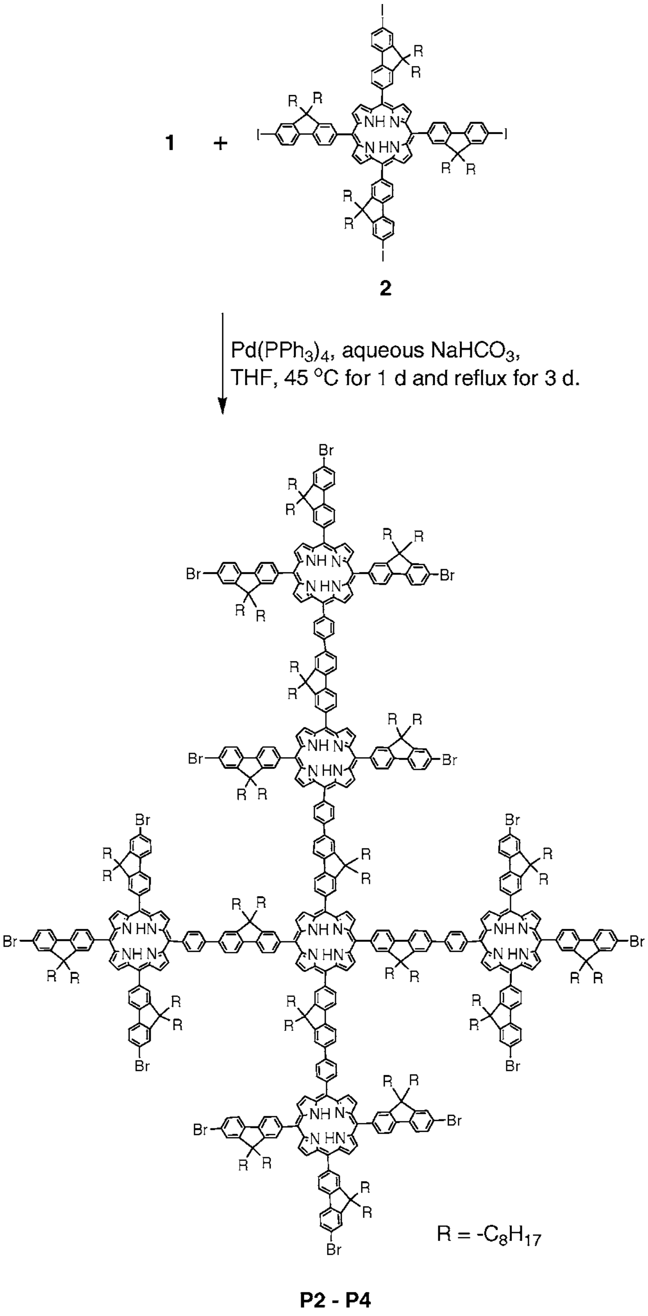


Here, we demonstrate that high molecular weight hyperbranched conjugated multiporphyrin arrays can be prepared by a one-pot reaction. The troublesome protection/deprotection processes, used in the synthesis of well-defined dendritic multiporphyrin arrays, can be avoided. It should be mentioned that the first elegant synthesis of hyperbranched porphyrins was achieved by Hecht and Fréchet through an $A_2 + B_3$ approach.[5]

Scheme 2



Scheme 3



In this paper, we describe the preparation of a novel kind of hyperbranched porphyrin arrays by one-pot Suzuki polycondensations (SPC) of AB_3 monomers or $AB_3 + C_4$ monomers. Fluorene-type porphyrins were used as monomers, which can form conjugated connections, and the octyl chains on fluorene units can help to increase their solubility.[6] The key AB_3 monomer **1** was prepared according to Scheme 1. Condensation of 7-bromo-9,9-diocylfluorene-2-aldehyde, 4-formylbenzeneboronic pinacol ester, and pyrrole with BF_3• ether complex as a catalyst afforded **1** in a yield of 15%. High purity (>98%) of **1** was confirmed by ^1H NMR spectroscopy and combustion analysis. SPC of the AB_3 monomer **1** was carried out in a biphasic system (THF/aqueous $NaHCO_3$) with freshly prepared $Pd(PPh_3)_4$ as a catalyst precursor (Scheme 2). After a standard treatment,

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hyperbranched porphyrin **P1** was obtained as a purple solid in a 85% yield. The molecular weight and the molecular weight distribution of the polymers were characterized by GPC with THF as an eluent and polystyrene as reference standard. The M_n was 33 400, the M_w up to 146 000, and the PD 4.3.

Recently, it has been proved by theoretical calculations, computer simulations, and experimental efforts that the introduction of multifunctional core molecules in the hyperbranched polymerization process can, to some extent, control the molecular weight and the molecular weight distribution.[7] We used 5,10,15,20-tetrakis(iodofluorene)porphyrin **2** (C_4) as a core molecule to copolymerize with the AB_3 monomer **1** to tailor the structures of the hyperbranched polymers (Scheme 3). Monomers **1** and **2** were fully soluble in THF, and the polymerization was done with different feed ratios between **1** and **2** under standard SPC conditions. It is well-known that the reaction of arylboronic acid (or ester), especially under mild conditions, proceeds at a higher rate with iodoaromatics than with bromoaromatics.[8] The polymerization should proceed in a core-first fashion. Standard workup afforded amorphous purple solids. The results are summarized in Table 1. As expected, the hyperbranched porphyrins exhibited good solubility in common organic solvents such as THF, chloroform, benzene, and methylene chloride. Compared with the hyperbranched homopolymers, the molecular weight of the porphyrin-cored, hyperbranched polymers was apparently lower, but their solubility in THF increased significantly. The molecular weights decreased upon increasing the ratio of the core porphyrin **2**. All polymers were unambiguously characterized with ^{1}H NMR spectroscopy and elemental analysis.

Table 1. Feed Ratios, Molecular Weights, and Polydispersity (PD) of Hyperbranched Porphyrins **P1**−**P4**

polymers	feed ratio (**1**/**2**)	M_n	M_w	PD
P1	1:0	33 400	146 000	4.3
P2	8:1	10 600	17 000	1.6
P3	12:1	11 200	17 300	1.5
P4	18:1	14 300	25 000	1.8

All hyperbranched porphyrins exhibited good thermal stability. They showed less than 5% decomposition up to 400 °C under nitrogen but lost about 50% of their weight at about 550 °C. No distinct glass transition was observed for all polymers in the DSC curves of the second heating (10 °C/min). The UV−vis absorption spectra of tetraphenylporphyrin (**TPP**), **1**, **P1**, and **P3** in dilute THF solution are shown in Figure 1. Monomer **1** exhibited an intense Soret band with an absorption maximum at $\lambda = 423$ nm together with four weak Q-bands between 517 and 651 nm. The Soret band was red-shifted compared with that of **TPP**. All polymers exhibited an intense and broad Soret band with an absorption maximum at $\lambda = 428$ nm together with four weak Q-bands between 515 and 652 nm. For all polymers, the Soret bands were remarkably red-shifted compared with that of monomer **1**.

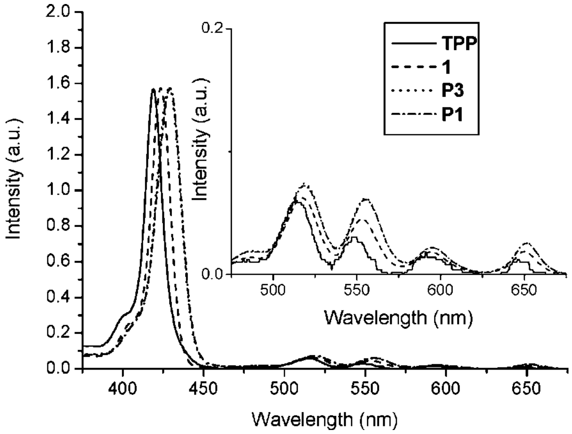

Figure 1. Electronic absorption spectra of **TPP**, **1**, **P1**, and **P3** in THF solution.

The emission spectra of **TPP**, **1**, and the polymers in THF solution are shown in Figure 2. All polymers exhibited an intense red emission peak at around 655 nm and a shoulder at 713 nm. Solid films on quartz plates used for UV−vis and fluorescence characterization were prepared by spin coating with 1% toluene solution at 1500 rpm. The emission spectra of the spin-coated films (**1** and **P1**−**P4**) are shown in Figure S2 (see the Supporting Information). All polymer films (**P1**−**P4**) exhibited an intense red emission peak at around 659 nm and a shoulder at 716 nm, while **TPP** showed

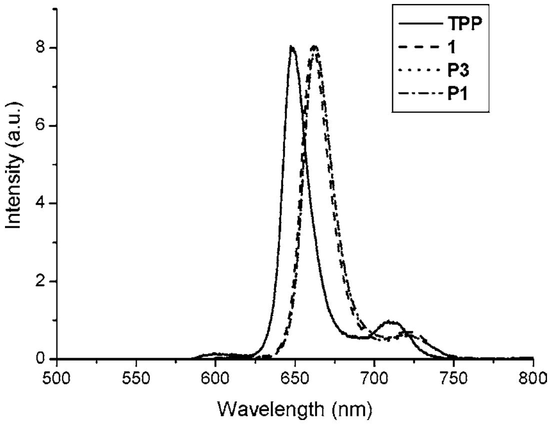

Figure 2. Fluorescence spectra of **TPP**, monomer **1**, **P1**, and **P3** in THF solution.

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two relatively weak emission peaks at around 662 and 722 nm. From the efficiency gain and the blue shift in the emission, we concluded that the degree of aggregation of the porphyrin polymers was significantly reduced. All emission peaks as films were slightly red-shifted compared with those in solution. The quantum yields (Φ_F) of the hyperbranched porphyrins in toluene were measured to be around 0.15 in comparison to **TPP** ($\Phi_F = 0.11$).

In conclusion, we have developed a highly efficient method to synthesize conjugated hyperbranched porphyrins by one-pot SPC of AB_3 or $AB_3 + C_4$ monomers. The hyperbranched porphyrin polymers obtained are of high molecular weight and good solubility in common organic solvents.

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Supporting Information Available: Detailed experimental procedures and characterization of the key compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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