Polymer Synthesis

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Hyperbranched: A Universal Conjugated Polymer Platform**

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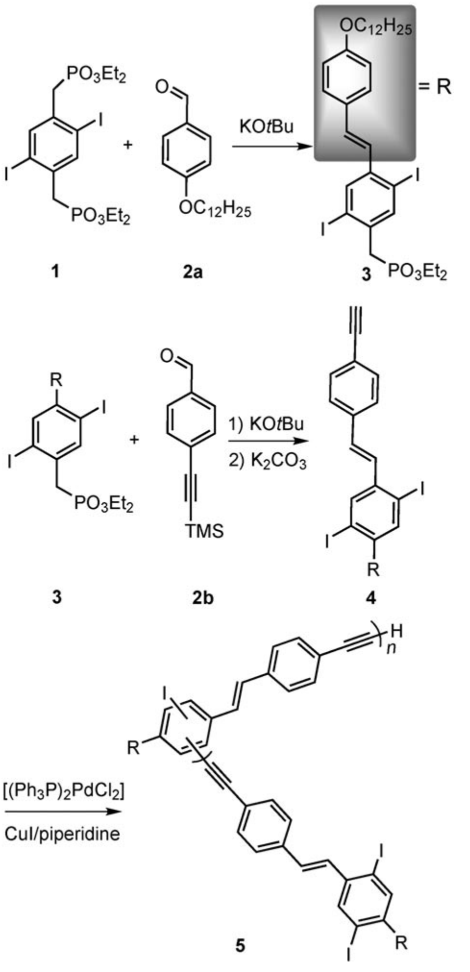
Post-functionalization strategies allow functional tuning late in a reaction sequence, but classic polymer chemistry operates on a different principle, as each polymer starts from its own monomer.[1] Weck's universal polymer backbone, by which a simple polynorbornene carrying a supramolecular attachment site is reversibly occupied by complementary species, is an important step towards post-functionalization strategies.[2] Another is the 1,3-dipolar cycloaddition of alkynes and azides that allows functionalities to be clicked onto a polymer backbone.[3]

In the case of conjugated polymers, post-functionalization schemes that allow the manipulation of the electronic structure by interposition of a suitable reagent are rare. End functionalization is possible, but problematic, owing to the low concentration of end groups. The synthesis of a hyperbranched conjugated polymer by polycondensation of an AB_2 monomer would circumvent this issue. Once formed, such a hyperbranched polymer would have one functional reactive B group per monomer. Such a polymer should—as long as the polycondensation reaction that forms the polymer is irreversible—allow the facile post-functionalization with any species that carries a complementary functional group.

Linear and hyperbranched[4] poly(phenyleneethynylene)s and dendrimeric[5] species based upon 1,2,4-trisubstituted benzenes have been made, but their potential with respect to postfunctionalization schemes that manipulate electronic structure and potential binding affinities to metal ions or other potential analytes of interest has been surprisingly rarely exploited.[6] The most thorough investigation of hyperbranched PPEs was performed by Moore et al.,[7] but their system, which is based on 1,3,5-triethynylbenzene units, was not designed nor intended to show enhanced electronic interactions, and they only reported post-functionalization of an insoluble hyperbranched polymer with 3,5-bis(*tert*-butyl)-phenylacetylene to obtain a soluble material. Weder et al.[8] prepared truly conjugated branched PPEs with interesting optical properties. Herein, we introduce a dodecyloxy group into the monomer **4**; the resulting polymers **5** and **9** are therefore soluble and processible, and **9** attains variable functionalities.

Starting from **1**, Horner reaction with **2a** furnishes **3**, which, after a second Horner reaction with **2b** and subsequent deprotection, gives the monomer **4**, which carries two iodine groups. Classic Sonogashira polymerization of **4** in a mixture of THF and piperidine with CuI as co-catalyst furnishes the hyperbranched polymer **5** in 87 % yield, with a molecular weight of 2.4×10^4 and a polydispersity index M_w/M_n of 2.0 (Scheme 1, Figure 1). In a similar fashion, the model compound **7** and the linear conjugated polymer **6** ($M_n = 2.5 \times 10^4$, $M_w/M_n = 2.5$, Scheme 2) were prepared (see the Supporting Information). By coincidence, both polymers had a similar molecular weight, which allowed a comparison of their intrinsic viscosity in chloroform, namely $[\eta] = 0.19\ \mathrm{dL\,g^{-1}}$ for **5** and $[\eta] = 0.32\ \mathrm{dL\,g^{-1}}$ for **6**.



Scheme 1. Synthesis of the hyperbranched polymer **5**. TMS = trimethylsilyl.

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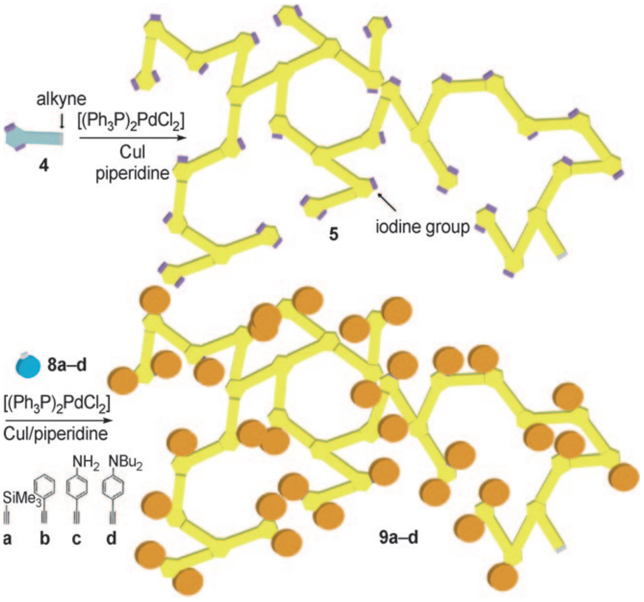
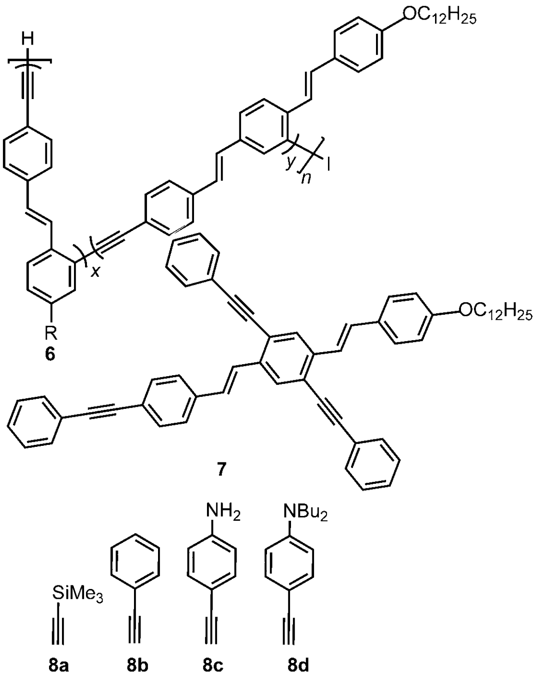


Figure 1. Synthesis and palladium-catalyzed post-functionalization of **5**.



Scheme 2. Linear polymer **6** and model compound **7** along with alkynes **8a**–**8d** used for post-functionalization.

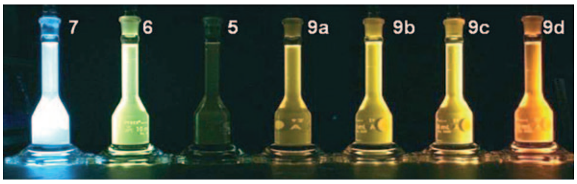


Figure 2. Solutions of **5**–**7** and **9a**–**9d** in dichloromethane under a black light (λ_{max} = 365 nm) at a concentration of 10^{-5} mol L^{-1}.

Table 1: Optical properties of **5**–**7** and **9a**–**9d**.

	λ_{max} abs[a]	λ_{max} em[a]	Φ [%]	ε[b]	Yield [%]
7	337, 389	472	87	39800	na
6	380	500	30	66450	na
5	392	510	3	84000	na
9a	397	513	25	43600	97
9b	397	519	19	32600	84
9c	386	528	13	60700	89
9d	392	553	6	65600	85

[a] Maximum wavelength for absorption and emission in nm; all measurements carried out in dichloromethane. [b] ε in L mol^{-1} cm^{-1} per repeat unit for the polymers.

As expected, the hyperbranched polymer **5** is less viscous than a linear polymer with the same molecular weight. As **5** contains one iodine atom per repeat unit (17.5% iodine by combustion analysis), its fluorescence is quenched by the heavy atom effect (Figure 2), but **5** is freely soluble in dichloromethane and chloroform. We performed a Sonogashira coupling of **5** with **8a**–**8d** (Figure 1) to obtain **9a**–**9d** smoothly as yellow or orange powders after standard workup, in yields that ranged from 84–97% (Table 1). From combustion analysis, the polymers that formed had an iodine content between 0.2 and 0.5 wt%, indicating efficient substitution. For **9a**–**9d**, the quantum yields of emission were increased by a factor of 3–10 (Table 1) as a consequence of the removal of the iodine groups. The emission wavelength changed from 510 nm in **5** to 553 nm in **9d**, documenting a significant red shift of emission upon functionalization. The addition of a donor group, as represented by the dibutylaniline unit in **9d**, has the strongest bathochromic effect upon the emission. The position of the absorption maxima of **5** and **9a**–**9d** are almost unaffected and vary from 386 to 397 nm. Figure 2 shows representative solutions of the model compound **7**, the linear polymer **6**, **5**, and **9a**–**9d** (corresponding spectra are given in the Supporting Information). It is important to note that all of the hyperbranched polymers show a red-shifted absorption and emission relative to **6** and to the model **7**.

It was of interest to establish whether **9** could also support blue-shifted emission. Upon protonation of **9d**, a material with green emission (λ_{max} (em) = 487 nm) and an absorption maximum (λ_{max} (abs) = 346 nm) results, suggesting that the optical properties of hyperbranched PAEs **9** can be engineered not only to be more red-emissive, but also into blue- or green-emissive materials. Protonation is not only an excellent way to shift the electronic properties of the prepared hyperbranched polymers, but it also indicates that the introduction of electronegative residues into the hyperbranched polymers should lead to hypsochromically shifted derivatives of **9**.

An attractive aspect of hyperbranched conjugated polymers is their branched character, which should increase the rate of energy transfer, as a general matter of structural principle.[9] A useful tool to test these polymers for increased energy transfer through branching is the quenching of their fluorescence by paraquat. Swager et al.[10] demonstrated that quenching of conjugated polymers of the PPE type by paraquat displays an approximately 80-fold increased efficiency in comparison to that of small molecules, which is a result of the molecular-wire effect. The factor of 80 is the maximum number of monomer units that is sampled by a single exciton in a linear chain. Branching should increase the efficiency of an exciton to sample polymer chains. Figure 3 shows the quenching of **9b** and linear polymer **6** by paraquat. The Stern–Volmer equation is used, with $F_0/F_{[Q]} = K_{sv}[Q] + 1$, where F_0 denotes the fluorescence intensity without added quencher Q, $F_{[Q]}$ is the fluorescence intensity of the solution in the presence of the concentration [Q] of the quencher Q, and K_{sv} is the Stern–Volmer constant.[11] In this equation, the easily measured total concentration of quencher [Q] is used as an approximation for its free concentration; for the condition [fluorophore][K_{sv}] < 1, this approximation holds well, and K_{sv} values of 2.0×10^2 and 4.1×10^2 result. These K_{sv} values are low, as there is no binding element engineered into either **9b** nor **6**. However, the hyperbranched polymer **9b** is more efficiently quenched by paraquat than **6** by a factor of about two. We can compare the two values, as the molecular weights of the two polymers are approximately equal and their degree of polymerization is considerably below $P_n < 80$. In hyperbranched polymers of higher molecular weight, this effect should be even more distinctive. The immediate application for hyperbranched polymers would be in sensors, where efficient quenching is desired but the simple molecular-wire effect, even if combined with multivalent interactions, is not sufficient to obtain enough sensitivity.[12] Hyperbranching should give a sensitivity boost to such systems.

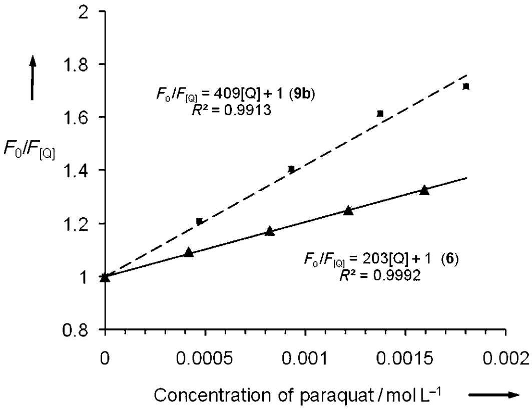


Figure 3. Quenching of **9b** (–––) and **6** (——) by paraquat. See text for details.

In conclusion, **5** is easily functionalized into **9a–d** in a proof-of-concept study, making **5** and its derivatives **9** an attractive proposition and competition for the more traditional conjugated polymers in sensory applications, but also potentially in organic electronics, as the fluorescent polymers **9** are amorphous and form free-standing films of excellent quality.

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