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ARTICLE

Hyperbranched Conjugated Polymers: Postfunctionalization

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ABSTRACT: In this contribution, the synthesis of two different hyperbranched poly(phenylene vinylene-phenylene ethynylene) (HB-PPV-PPE, **3a**−**b**) scaffolds are reported. The necessary AB_2 monomer **2** is obtained by an asymmetric Horner reaction and contains two iodine substituents and one ethynyl group. This AB_2 monomer provides, after Sonogashira polymerization, a hyperbranched conjugated polymer decorated with iodine groups, suitable to be further functionalized with terminal alkynes **4a**−**t** by a Pd-catalyzed coupling. Elemental analysis of the postfunctionalized polymers **5a**−**t** and **6a**−**q** reveals nearly complete substitution of the iodine groups. As a consequence of the replacement, substantial increases in fluorescence quantum yields as well as variation in the optical response of the new polymers are observed. The spectroscopic properties of the postfunctionalized polymers were investigated in solution and in the solid state. The emission of the formed hyperbranched polymers shows a strong dependence on the functional groups attached to the conjugated structure and ranges from 510 nm for **5a** to 602 nm for **6h**. In all cases, solid-state emission is surprisingly strong and red-shifted compared with emission observed in solution.

Introduction

From a general perspective of polymer chemistry, there are two ways to introduce functionalities into a polymeric structure: functionalization of the monomeric unit or postfunctionalization of an already formed polymer. The first method requires significantly more synthetic effort if libraries or “diversets” of polymers are desired because each polymer starts from its own monomer. Therefore, efficient postfunctionalization pathways are of great interest in terms of economy and versatility. Weck and coworkers[1] have used ring-opening metathesis polymerization (ROMP) of functionalized norbornenes and cyclooctenes to create a universal polymeric backbone containing a supramolecular connector. The addition of a molecule with a complementary functionality creates a host of new polymers in a mix-and-match approach.

In conjugated polymers, such as poly(*para*-phenylene ethynylene)s (PPEs),[2] an efficient postfunctionalization should also allow for manipulation of their electronic structure. Leclerc[3] and Holdcroft[4] have successfully postfunctionalized polythiophenes. Similar routes of postfunctionalization have been investigated in PPEs through 1,3-dipolar cylcoaddition of azides to alkynes.[5] However, in most cases, the modifications do not directly affect the conjugated backbone because the reaction occurs on nonconjugated side chains. Inherently, hyperbranched polymers[6] (HBPs) offer a possibility for postfunctionalization, as in a polymer formed from n AB_2 units, n reactive B groups will remain. Described from a theoretical point of view as an intermolecular condensation of AB_x monomers by Flory in 1952,[7] HBPs have been exploited over the last several years in live-cell imaging,[8] solar cells,[9] drug delivery systems,[10] and surface chemistry.[11]

Herein[12] we present polyfunctional and well-soluble conjugated HBPs prepared from the AB_2 monomers **2a** and **2b**. The properties of the formed HBPs (**3a** and **3b** in Scheme 1), accessible on a multigram scale, are tuned by a subsequent Pd-catalyzed alkynylation reaction. We have prepared 24 derivatives of these novel conjugated HBPs.

Results and Discussion

Scheme 1 displays the synthesis of polymers **3a** and **3b**. Following the same approach used for the preparation of asymmetrical cruciforms,[13] monomers **2a** and **2b** were constructed by monoalkenylation of the diphosphonate to furnish **1a** and **1b** in acceptable yields. After a second Horner reaction with 4-(trimethylsilylethynyl)benzaldehyde and subsequent deprotection with potassium carbonate, the desired monomers **2a** and **2b** were obtained. Sonogashira polymerization of **2a** and **2b** leads to the hyperbranched polymers **3a** and **3b** in 87 and 81% yield, respectively. These hyperbranched polymers are powdery orange solids soluble in common organic solvents. Both show expectedly low quantum yields (0.014 and 0.004, respectively) in solution because of the heavy atom effect of the iodine groups present in the polymeric skeleton. The molecular weight of **3a** is 2.4×10^4 with a polydispersity index M_w/M_n of 2.0 according to gel permeation gel (GPC). GPC measurements of **3b** show only peaks assigned to aggregated species. We attempted to disrupt the aggregation of the polymer **3b** by catalytic hydrogenation of the conjugated structure,[14] but again, only signals due to aggregated polymers were recorded. The incorporation of dialkylanilines into the structure seems to induce the aggregation of the polymer inside the column, hampering an accurate measurement of their molecular weight. Despite the lack of a measurement of the molecular weight of **3b**, the ^1H NMR spectra of **3a** and **3b** show broad signals compared with those of the corresponding

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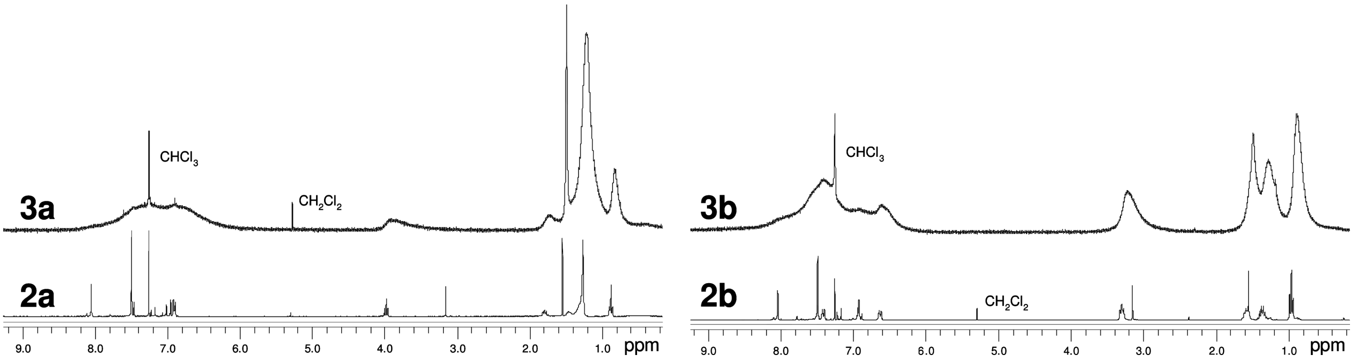
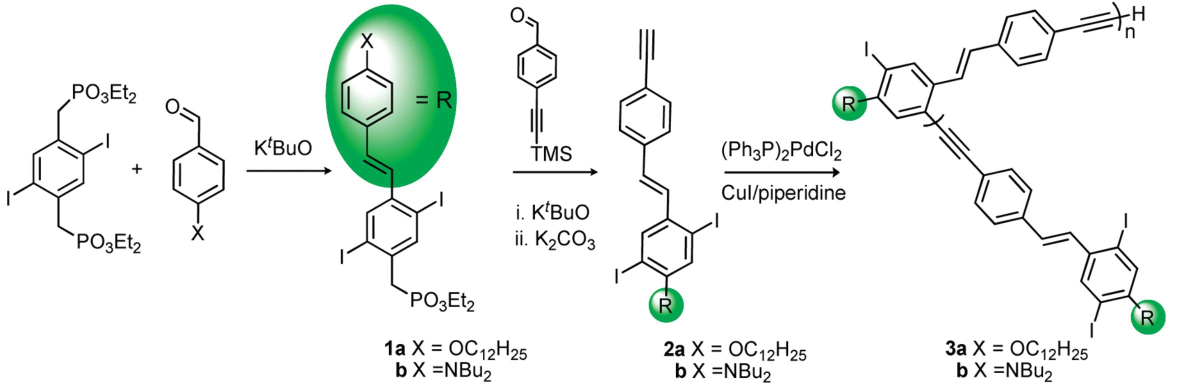


Figure 1. ^{1}H NMR spectra of monomers **2a** and **2b** (bottom) and polymers **3a** and **3b** prepared from them (top). Broad signals in **3a** and **3b** indicate a comparable degree of polymerization.

Scheme 1. Synthesis of Hyperbranched Iodinated Polymers by Pd-Catalyzed Coupling



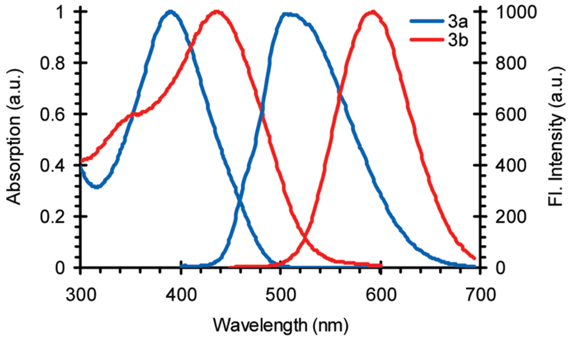


Figure 2. Normalized absorption and emission spectra of solutions of **3a** and **3b** in dichloromethane.

monomers **2a** and **2b** (Figure 1), suggesting a similar degree of polymerization for both polymers. Polymers **3a** and **3b** contain one iodine substituent per repeat unit, however, different from linear or truly dendritic polymers, these iodine groups are statistically distributed over terminal and linear modules in the formed hyperbranched polymers. The donor character of the amino groups in **3b** destabilizes its HOMO. As a result, a strong bathochromic effect compared with **3a** is observed in its absorption and fluorescent response (Figure 2).

We obtained a diverset of hyperbranched polymers **5** and **6** by coupling **3a** and **3b** to the alkynes **4a**−**t** (Scheme 2) using Sonogashira conditions. The set of alkynes **4a**−**t** includes donor and acceptor species with different heteroatoms, aliphatic and aromatic substituents, heterocycles, and complex structures such as **4r**, a T-shaped alkyne featuring two dibutylamino groups, or **4t**, a flavin derivative potentially useful in supramolecular chemistry.[15] All reactions were followed by a simple workup consisting of the precipitation of the polymers into methanol. The yields are generally >85%, with all products isolated as yellow-to-red powders (**5a**−**t** from **3a** and **6a**−**q** from **3b**). In most cases, NMR spectroscopy was not very useful to elucidate the functionalization of the polymer because of the broad signals in the aromatic region of the spectrum. Therefore, combustion analyses were performed to assess the remaining amount of iodine present in the polymer after the reaction and to have a handle on the degree of the postfunctionalization (Table 1). In all cases but **5n** and **5f**, the iodine content is < 1%. These values indicate that >95% of iodine groups have been replaced by the corresponding alkyne. A graphic of the number-average molecular weight of the new polymers, as measured by gel permeation chromatography (GPC), compared with their theoretical values, if complete substitution of the iodines in **3a** is assumed, also confirms the high degree of functionalization (Figure 3). A linear regression of these values shows a gradient ($M_{n_{exp}}/M_{n_{th}}$) near the expected 1 ($y = 1.1x$).

To elucidate the effect of the substituents on the electronic properties of polymers, we recorded their UV−vis and emission spectra in solution and in the solid state. Figure 4 displays photographs of solutions of the polymers **5** and **6** in dichloromethane as well as a selection of them in their solid state. The pictures were taken under black light illumination at λ = 366 nm. Qualitatively, we observe that emission of the polymers varies from blue-green for **5a** to orange-red for **6h**. The strong solid-state emission of the polymers shows bathocromically shifted features compared with their spectra in solution, ranging from yellow (**5l**) to red (**6h**), depending on the substitution. The principal spectroscopic properties of **3a**−**b** and the postfunctionalized polymers **5a**−**t** and **6a**−**q** are shown in Table 1. Without much changes in the absorption spectra, the incorporation of different functional groups into the polymeric structure leads to a general increase in the quantum yields up to a factor of 20, as a consequence of the removal of the iodine groups. The derivatives

Scheme 2. Postfunctionalization of the Hyperbranched Polymer 3 by Pd-Catalyzed Couplings to Different Alkynes 4

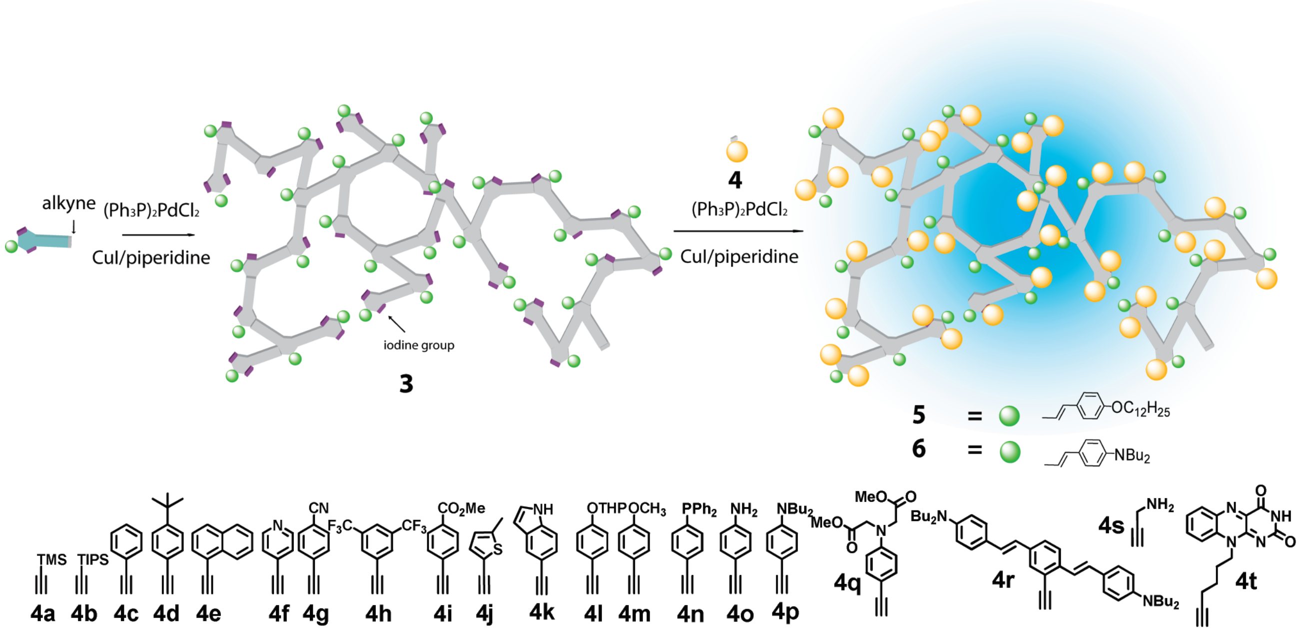


Table 1. Chemical and Spectroscopic Data of Polymers 5 and 6

	λ_{max} absorption (nm)[a]	λ_{max} emission (nm)	Φ (%)[c]	ε (L cm^{-1} mol^{-1})	yield (%)	% iodo
3a	392	510 (553)[b]	1.4	84 000		17.5
5a	397	513 (558)	24	43 600	97	0.8
5b	397	513 (557)	25	58 400	59	0.1
5c	397	522 (565)	11	32 000	84	0.2
5d	397	523 (560)	13	42 600	95	0.4
5e	375	533 (570)	15	59 000	95	0.1
5f	396	505	2.1	51 600	62	1.8
5g	395	519 (578)	7.2	45 000	90	0.2
5h	396	527 (582)	10	54 200	52	0.5
5i	395	528 (568)	16	44 500	77	0.3
5j	395	523 (571)	14	32 300	51	0.1
5k	389	524 (559)	5.9	32 300	89	1.1
5l	396	527 (562)	24	51 900	86	0.1
5n	386	519 (560)	4.3	25 400	90	3.8
5o	386	528 (565)	13	60 700	89	0.2
5p	392	553 (569)	2.1	65 600	85	0.3
5r	407	517, 595[d] (612)	0.7	N/A	83	0.1
5s	378	502 (581)	2.6	8400	88	0.7
5t	394	504 (559)	1.7	57 200	70	N/A
3b	437	586 (613)	0.4	66 200		21.8
6a	441	593 (605)	9.2	58 700	88	0.3
6b	442	587 (597)	15	60 200	93	0.2
6c	354, 442	593 (618)	6.0	64 200	91	0.8
6h	357, 438	602 (629)	5.1	57 900	98	0.4
6m	362, 440	593 (616)	8.9	66 500	94	0.3
6q	382, 441	592 (622)	13	70 100	71	0.3

[a] Fluorescence measurements were performed in dichloromethane solutions of the polymers. [b] Wavelength of maximum emission of the polymers in the solid state in parentheses. [c] Quinine sulfate was used as standard in quantum yield measurements. [d] **5r** presents a significant shoulder around 595 nm.

5f, **5r**, and **5t** are exceptions to this behavior. The presence of pyridinic nitrogen leads to an almost quenched emission in **5f** and **5t**. The fluorescence of **5r** in dichloromethane shows a dual emission with a main band centered at 515 nm and a shoulder around 595 nm corresponding to **4r** (Figure 5). The emissive lifetimes of the two bands are significantly different (τ_{515} = 1.2 ns and τ_{595} = 2.0 ns).[16] According to the longer lifetime of the red-shifted band, we postulate an inefficient energy transfer from the polymeric backbone to the bis(dibutylaminostyryl) moiety in solution to explain the low quantum yields of **5r**. The energy transfer is more efficient in the solid state, and this secondary band appears to be the only one observed in solid state (λ_{max} = 612 nm). We also note from Figure 4 that **5r** is brightly fluorescent in the solid state but almost nonfluorescent in solution, reinforcing our assumption of the efficient energy transfer.

From **5a** to **5e**, an extension of the conjugation causes a red shift of the fluorescence. Naphthyl-substituted **5e** is slightly stronger bathochromically shifted than the indole-substituted polymer **5k**. The presence of electron-withdrawing groups also induces a red shift, as is observed in **5g**–**i** and especially in **6h**, a donor–acceptor system, which shows an emission maximum at 602 nm. Electron-donating substituents in the polymers prepared from **3a** cause a red shift of the fluorescence. On the other hand, no significant effect is observed in those prepared from **3b**, because a strong donor is already present in the structure. Polymer **5p** shows the strongest bathochromic effect upon the emission in solution, whereas **5r** is the most red-shifted polymer of its family in the solid state. Sterics also have a significant influence on the fluorescence of the polymers; **6a** and **6b**, TMS- and TIPS-substituted polymers, respectively, show a different fluorescence response both in solution and in solid state. In the solid state, the bulkier substituent in **6b** increases the quantum yield and induces a blue shift in fluorescence compared with **6a**. This behavior is surprisingly not observed for **5b** and **5a**.

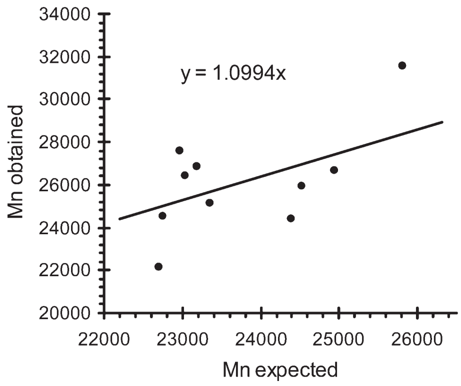


Figure 3. Number-average molecular weight by GPC and theoretical molecular weight-average number in postfunctionalization reactions for derivatives of **5**.

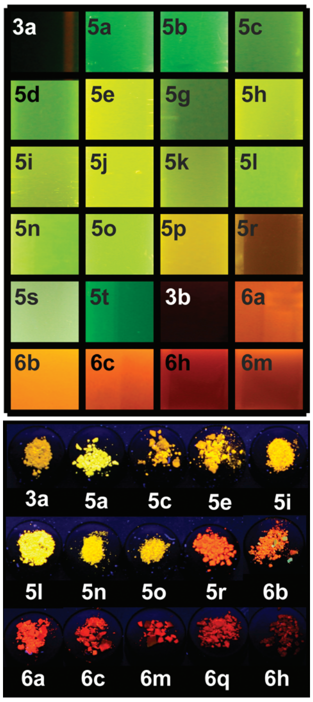


Figure 4. Photographs of fluorescence emission of polymers **5** and **6** in dichloromethane solutions (top) and in the solid state (bottom) under illumination using a hand-held blacklight (λ_{em} = 366 nm).

In **5p** and **6m**, the pre- and postfunctional groups are similar but switched. The amino groups in **6m** seem to have a stronger influence on the electronic structure of the polymer than in **5p**, with a significant red shift in both absorption (48 nm) and emission (40 nm) of **6m** compared with **5p**. The difference in the spectroscopic properties of **6m** and **5p** might be due to the difference in connection of the dialkylamino functionalities to the conjugated backbone. A recent study of the electronic characteristics of substituted distyrylbenzenes and bisarylethynylbenzenes reveals a general red shift of the fluorescence of distyrylbenzene derivatives compared with their corresponding bisarylethynylbenzene pairs because of the vinylic connection.[17] However, the significant change observed in the fluorescence of **6m** and **5p** has not been recorded in small molecules; as a consequence, we assume that other factors might play a role. An examination of the polymer structure shows that in **6m**, the dialkylamino groups are present in each monomeric unit of the polymer, whereas in **5p**, the amines are located only where there were iodine groups in **3a**, that is, not necessarily on each monomer because the position of the iodine groups depends on the degree of branching of the hyperbranched polymers (Figure 6). Only in an ideal linear polymer will every monomeric unit contain an amine, whereas in a purely dendritic system, only the peripheral units will carry two iodine substituents each. If we assume the theoretical 50% degree of branching calculated for this type of monomer by Frechet et al.,[18] then the number of amino groups situated in the inner part of the backbone will be much lower in **5p** than in **6m**. This difference in the distribution of amino groups might play a critical role in the different optical gaps of these two pseudoisomeric polymers.

We attempted to confer water solubility to **5** by hydrolysis of **5i** to the corresponding carboxylate and by the deprotection of the phenol group from **5l**. Although the results are promising and both **5i** and **5l** dissolve in mixtures of methanol/water and THF/water, they are not completely soluble in water. In the future we will use alkynes that carry more than one carboxylate group to imbue water solubility to these polymers.

Because the frontier molecular orbitals of the polymer are influenced by electron pairs such as those in dialkylamino groups, their optical properties should vary upon metal complexation or protonation. To explore this response, the effect of protonation upon the photophysics of **5f**, **5n**, **5o**, **5p**, **5r**, and **5t** as well as upon

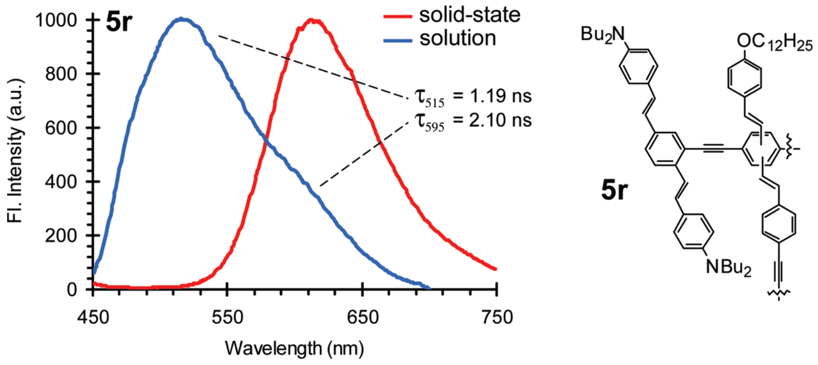


Figure 5. Emission spectra of **5r** in dichloromethane solution (blue) and in solid state (red). Fluorescence lifetimes of the two bands observed in the emission of **5r** in dichloromethane are presented.

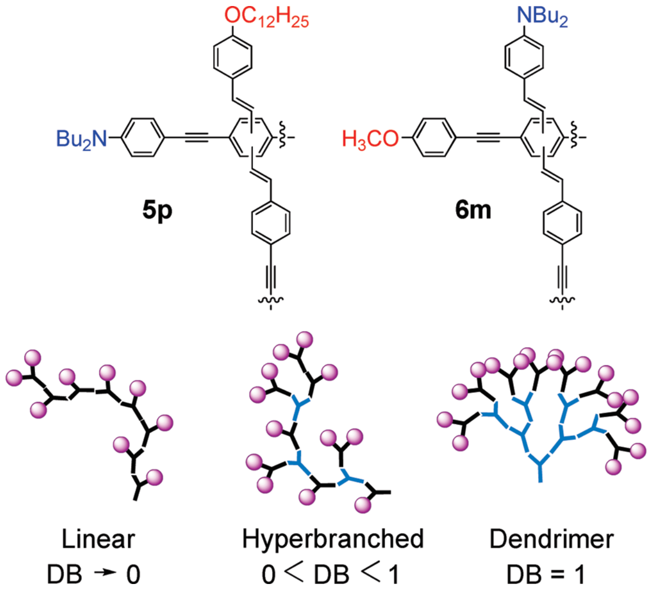


Figure 6. Simplified representation of the pseudoisomers **5p** and **6m** showing the different connectivities of the functional groups to the polymer (top). Schematic view of the distribution of the alkynes after postfunctionalization (purple spheres) depending on the degree of branching (DB). Branching units (blue) do not bear postfunctional groups (bottom).

Table 2. Absorption and Emission of the polymers upon addition of TFA in dichloromethane

	λ_{max} absorption (nm)[a]	λ_{max} emission (nm)	Φ (%)
5f	396/396	505/quench	2.1/quench
5n	386/355	519/498	4.3/0.9
5o	386/395	528/494	13/0.4
5p	392/358	553/494	2.1/5.8
5r	407/368	595/499	0.7/10.8
5t	394/389	504/501	1.7/0.5
6a	441/388	593/498	9.2/62
6b	442/384	587/485	15/66
6c	442/388	593/496	6.0/32
6h	438/388	602/495	5.1/28
6m	440/386	593/498	8.9/66
6q	441/378	592/510	13/19

[a] Values on the right correspond to the protonated species.

6a−q was examined. The results are shown in Table 2. (All spectra are presented in the Supporting Information.) Upon the addition of an excess of trifluoreacetic acid (TFA) to solutions of the polymers in dichloromethane, a strong blue shift in the absorption is observed for the dialkylamino-substituted polymers as well as for the triphenylphosphine-substituted derivative **5n**. These shifts are mirrored in their emission spectra, where hypsochromic shifts are also measured upon protonation. These shifts are significant in **6a−q** (the polymers prepared from **3b**) and are accompanied by a large increase in their quantum yields. Polymers **5p** and **5r** also experience a modest increase in their quantum yields upon protonation of their amino groups. It is important to note that all of the emission maxima of the protonated species of the dialkylamino-containing polymers converge at around 495−500 nm regardless of the relative position of the amino group in the polymer (Figure 7). Because the electron pairs of the amino groups are no longer available, the fluorescence originates from the "naked" conjugated backbone. In the case of **5f** and **5t**, pyridine- and flavin-substituted derivatives, respectively, the effects of protonation are almost imperceptible in absorption. Regarding the fluorescence, quenching of **5f** is observed, whereas **5t** does not experience any change in either emission wavelength or quantum yields.

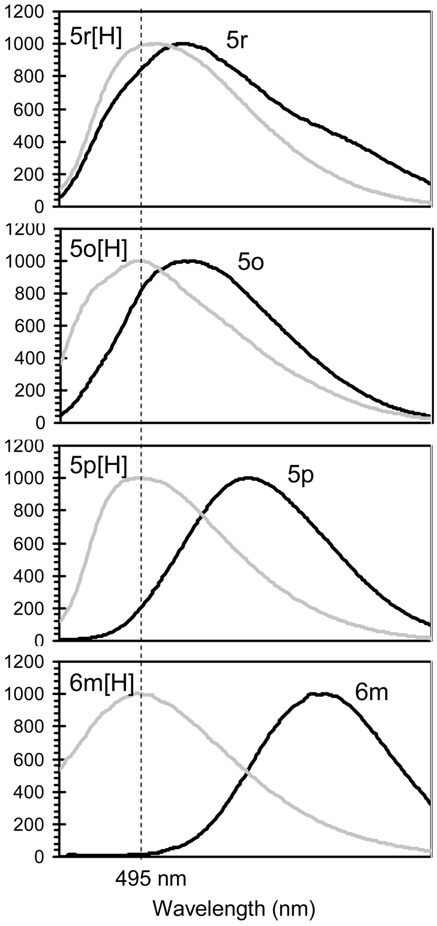


Figure 7. Selected fluorescence emission of some of the dialkylamino containing polymers (**5o**, **5p**, **5r**, and **6m**) in dichloromethane (black traces) and upon addition of TFA (gray traces).

Conclusions

In summary, we have prepared the iodinated hyperbranched polymers **3a** and **3b**. The facile modification of these polymers was achieved by Sonogashira coupling; a wide set of alkynes was incorporated into the structure. We have demonstrated that the functionalization of the polymers occurs to near completion. We have also shown that the position and distribution of the electron-donating dibutylamino groups change the optical properties of these hyperbranched polymers. The styryl groups introduced in the first step of the synthesis have a strong influence on the electronic properties of the polymers. In this regard, it would be of great interest to introduce this functionality likewise in a latter synthetic step to gain control of the styryl functionality once the polymerization reaction is completed.

The demonstrated simplicity and versatility of the synthetic strategy involved in the preparation of these hyperbranched conjugated polymers is attractive. The use of novel methods of functionalization as well as a better understanding of their behavior will allow us to pursue further uses for these structures in organic electronics, sensory applications, supramolecular chemistry and for the synthesis of organic and inorganic hyperbranched structures. Particularly attractive is the generation of diversity in the last step; that is, starting from a common precursor, a diverset of new and different polymers can be obtained.

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Supporting Information Available: Experimental details are provided for the synthesis of the polymers and alkynes reported in this work as well as details for the photophysical experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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