Click Chemistry as a Powerful Tool for the Construction of Functional Poly(*p*-phenyleneethynylene)s: Comparison of Pre- and Postfunctionalization Schemes

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ABSTRACT: 1,3-Dipolar cycloadditions have been used to prepare a series of functionalized poly(*p*phenyleneethynylene)s (PPEs). This was accomplished by employing a PPE with pendent triisopropylsilylacetylene groups. The triisopropylsilyl groups can be removed in situ, exposing free alkynes in the side chains of the polymer to react with azides in a postpolymerization functionalization strategy in a 1,3-dipolar cycloaddition. The properties of these polymers were explored and compared to polymers of the same molecular structure but synthesized by a prepolymerization functionalization approach. Polymers of the same structure exhibit identical ¹H NMR, ¹³C NMR, and IR spectra regardless of whether they were obtained by a conventional route or by postfunctionalization of a suitable PPE. UV-vis and fluorescence spectra are similar in solution. Postmodification through click chemistry, when compared to premodification, is an excellent method to produce functionalized, defect-free PPEs. Reaction of the azides with the main chain alkyne units is not observed.

Introduction

The functionalization of an alkyne-appended poly(pphenyleneethynylene) (PPE 5 via 6) by 1,3-dipolar cycloaddition to organic azides 7 is described. The postpolymerization functionalization of conjugated polymers is a useful technique in which a specific polymer backbone is postsynthetically altered. Leclerc¹ has executed this concept elegantly in the polythiophene series by polymerization of an active-ester containing thiophene monomer, while Holdcroft² has developed postpolymerization halogenation of polythiophenes. These approaches allow introduction of molecular diversity late, in the final step, of the synthetic sequence and are therefore efficient compared to the introduction of functional elements during the synthesis of specific monomers. Additionally, postfunctionalization schemes allow the introduction of groups that might not be compatible with the polymerization conditions. Fast assembly of libraries of polymers and introduction of different and potentially sensitive functional groups are some of the advantages of postpolymerization functionalization. The caveat with postfunctionalization is the requirement of high yielding and specific reactions; errors in the functionalization of monomers can be corrected by the appropriate purification steps, while a polymer synthesized by postfunctionalization processes cannot be purified further.

Huisgen and Szeimies³ investigated the 1,3-dipolar cycloaddition of azides to alkynes. Triazoles are the only product of this reaction. Sharpless recognized the potential of this transformation and retooled the dipolar cycloaddition as "click chemistry" for the construction of biologically active molecules. The most effective variant uses terminal alkynes in combination with copper sulfate and sodium ascorbate. The sodium ascorbate reduces copper sulfate to Cu^+ , which will form a copper acetylide under these conditions. The copper

acetylide is considerably more reactive toward the azide so that a rate enhancement of the 1,3-dipolar cycloadditions results.⁴ The high yield and the specificity of this transformation make it appealing, not only for synthesis of small molecules but as well for the functionalization of polymers as reported recently by Hawker and Frechet⁵ in the attachment of dendrons to nonconjugated polymers.

Results and Discussion

PPEs are valuable due to their dramatic chromic responses.^{6–9} They have been utilized in sensory schemes and in semiconductor devices including to light-emitting diodes^{7a,b} and photodiodes.⁸ However, postfunctionalization schemes on PPEs have only sparsely been carried out.⁶ It is of significant interest to develop an efficient platform that could allow the manipulation of PPE's properties in a postpolymerization modification approach (Figure 1). In this contribution a PPE scaffold, 6, is introduced that allows to "click on" different functional groups by a 1,3-dipolar cycloaddition. The polymers 8 made by the postmodification approach were compared to those of the same structure but made by a conventional approach (Figure 1). This allowed the evaluation of the click process as tool to functionalized conjugated polymers. Important (specific) questions are if the postfunctionalization process selects the alkyne appendage over the backbone alkynes, if the conversion of the appended alkynes is complete, and if it occurs with a similar regiochemical 1,4-control as reported for the copper-catalyzed 1,3-dipolar cycloaddition (Figure 1).

Synthesis and Characterization of Polymers 5 and 6. Reaction of diiodohydroquinone (1) with the propargylic bromide 2 in the presence of excess potassium carbonate furnished 3 in 82% yield. The copolymerization of 3 with the diyne 4 under standard conditions with 0.7 mol % Pd-catalyst furnished polymer 5 in 87% yield as a yellow, reasonably soluble, fibrous material with a degree of polymerization (P_n) of 64 (gel



Figure 1. Post- and prepolymerization functionalization strategies.



permeation chromatography, $M_n = 65 \times 10^3$, $M_w/M_n = PDI = 4.4$). Polymer **5** is characterized by its ¹H NMR, ¹³C NMR, and IR spectra that are in excellent agreement with the proposed structure.

Reaction of the polymer **5** with tetrabutylammonium fluoride furnishes a considerably less soluble polymer (**6**) in almost quantitative (95%) yield as a deep yellow powder. Gel permeation chromatography (GPC) shows a decrease of P_n to 46 ($M_n = 24 \times 10^3$, PDI = 1.6). We believe that the decreased solubility of **6** as compared to that of **5** was due to a removal of higher molecular weight polymer chains during the filtration step that is necessary for the preparation of GPC samples. Aggregated and/or insoluble but finely suspended parts of the polymer are retained by the utilized GPC ultrafilters, yellowish in appearance after use and supporting our notion that significant amounts of **6** were retained.

We were able to obtain ¹H NMR and ¹³C NMR spectra of **6**. The proton NMR spectrum of **6** resembles that of **5** but (a) does not show a signal for the TIPS groups, (b) features an additional signal for the free alkyne groups at $\delta = 2.58$ ppm, and (c) displays a shift in the arene protons that are now spaced and resonate at 7.17 and 7.40 ppm. The IR spectrum of **6** shows a strong band at 3301 cm⁻¹, which is diagnostic for the presence of a terminal alkyne. Additionally, two bands at 2202 and 2122 cm⁻¹ can be attributed to the C=C stretch of the backbone and the free alkyne, respectively. It was possible to obtain a ¹³C NMR spectrum of **6** with a reasonable signal-to-noise ratio if chromium acetylacetonate (cracac) was added as relaxating agent.

The optical spectra of 5 and 6 in solution are similar and typical for PPEs (Figure 2 and Table 1). The solid-



Figure 2. UV-vis and emission spectra of polymer **5** (top) and polymer **6** (bottom) in chloroform solution and in the solid state (absorption and emission maxima, see Table 1).

Table 1. Optical Properties, Yields, Degree of Polymerization, and Degree of Functionalization of 5, 6, and 8

polymer	yield (%)	$M_{\rm n}({ m PDI})$	deg of post- functionalization (%)	absorption (CHCl ₃) [nm]	absorption (film) [nm]	emission (CHCl ₃) [nm]	emission (film) [nm]	$\begin{array}{c} quantum \\ yield \ (\Phi_{fl}) \end{array}$
5	87	$63.6 imes 10^3 (4.43)$	na	422	450, 426	448	462, 490, 512	0.99
6	95	$24.4 imes 10^3 (1.64)$	>95	420	462, 438	447	533	0.89
8a pre	91	$13.7 imes 10^3(5.24)$	na	415	434	448	463	0.98
8a post	92	$8.5 imes 10^3(3.20)$	>95	413	437	448	485	0.98
12	91	$25.5 imes 10^4 (4.25)$	>95	406	410	447	450	0.87
8b pre	82	$71.7 imes 10^3 (4.44)$	na	416	422	449	483	0.92
8b post	94	$25.4 imes 10^3(2.56)$	>95	418	435	448	479	0.97
8c pre	93	$24.5 imes 10^3 (1.01)$	na	421	433	454	470	0.94
8c post	76	$22.6 imes 10^3(2.39)$	>95	424	431	454	470, 523	0.98
8d pre	93	$16.2 imes 10^4 (7.70)$	na	408	416	452	470	0.96
8d post	82	$10.8 imes 10^4 (1.49)$	>95	412	426	450	452, 470	0.93
8e pre	75	$71.8 imes 10^3(2.10)$	na	416	428	450	460	0.97
8e post	96	$22.6 \times 10^3 (2.39)$	ca. 50	412	436	450	473	0.91

Scheme 2. In	n Situ	Generation	of 6 and	Its Reaction	n with	Azides 7	7а-е	Yielding 8a-	e and I	Prefuncti	onaliz	ation
Approach toward 8a-e												



state spectra of **5** and **6** are strikingly different. The removal of the TIPS groups leads to a 12 nm red shift (577 cm^{-1}) in absorption. This red shift could be a sign either of increased planarization or of interchromophore interaction that would give testimony to the formation of weak electronic aggregates between PPE chains on top of a significant contribution of chain planarization (1475 cm⁻¹). The solid-state emission of **6** shows an excimer band at 533 nm that is not present in the solid-state spectrum of **5**, reinforcing the notion of some interchain interactions existing in thin films of **6** in the excited state.⁹

Synthesis of Functionalized Polymers 8a-e. The successful formation of 6 allowed its reaction with different azides. In a first experiment, direct reaction of 6 with dodecyl azide 7a was performed under microwave irradiation, but the low solubility of polymer **6** in organic solvents led to material that was only to a moderate extent triazole-functionalized. It was found that an in situ deprotection of 5 with tetrabutylammonium fluoride (TBAF) and coupling procedure was a better way of obtaining the 1,3-dipolar cycloadducts. Reaction of 5 with the azides 7a-e in the presence of copper sulfate, TBAF, and sodium ascorbate in wet THF (5% water) as solvent gave the functionalized PPEs **8a-e** in yields of 75-96% after 48 h at 40-60 °C. Without the addition of copper sulfate and sodium ascorbate the reaction did not proceed as well. As a consequence, postmodification reactions were always executed in the presence of copper sulfate and sodium ascorbate. Workup is performed by 3-fold precipitation of the polymer into methanol to remove the starting azide reagent. The yields of the postfunctionalization reactions are high and shown in Table 1.

Reactions carried out with azides 7a-e afforded polymers 8a-e, of which 8a-d were fully and 8e mostly

functionalized, according to ¹H NMR, ¹³C NMR, and IR spectroscopies. This was confirmed by the synthesis of the same polymers 8a-d by a conventional approach (Scheme 2). These "premodified" polymers offer a standard the postmodified PPEs can be compared to. In completely postmodified polymers 8a-d, there were no peaks in the ¹H NMR at 2.55 for the terminal alkyne (Figure 3). Signals for the newly formed triazoles are present at 7.5–8.0 ppm. Signals from the carbons of the triazole nuclei are visible at 140-150 and 120-130 ppm in the ¹³C NMR spectrum of the functionalized polymers. The peak at 3294 cm⁻¹ has disappeared in the postfunctionalized 8. The excess of azide reagent 7 was removed completely by the 3-fold precipitation of the polymers 8 into methanol. According to IR spectroscopy the strong azide band at 2100 cm^{-1} (Figure 4) had disappeared. In situ deprotection and reaction of polymer 5 with azide dendron 7e afforded a polymer 8e which contained $\approx 10\%$ of unreacted terminal alkyne according to ¹H NMR spectroscopy and comparison of its spectral data to those of conventionally prepared 8e. Partial functionalization is not surprising, as Frechet and Hawker have observed similar results for the functionalization of nonconjugated polymeric systems.⁵

Reaction of 9 with azides 7a, c, d, and e afforded monomers 10a, c, d, and e. Reaction with diyne 4 under standard conditions furnished the polymers 8a,c-e in excellent yields (Table 1, Scheme 2). Monomer 10b was also obtained by this method. It is insoluble and could neither be characterized nor purified. An alternate approach employing the reaction of 3 with azide 7b under thermal conditions afforded monomer 11 (Scheme 3). Polymerization of 11 with 4 under standard conditions accessed 12 in almost quantitative yields. The presence of the triisopropylsilyl groups was confirmed by two signals recorded between $\delta = 10-20$ ppm in the



Figure 3. ¹H NMR of polymers 5, 6, 8a (post), and 8a (pre) (top to bottom).

¹³C NMR spectrum of **12**. Deprotection of **12** with TBAF yielded polymer **8b** as a moderately soluble yellow solid. Overall, the ¹³C NMR spectra of the polymers **5**, **6**, and **8a**-**e** are very similar and easily interpreted. The resonances due to the backbone carbon atoms and the triazoles are almost superimposable for all of the investigated polymers.

Regioisomers. At room temperature, the coppercatalyzed process is typically regioselective, favoring the 1,4-triazole. We opted to perform these copper-catalyzed reactions between 40 and 60 °C as we observed improved yields in monomers and higher degree of functionalization in polymeric systems. Under these conditions **10a** and **10c**-**e** were obtained as approximate 2:1 mixtures of the 1,4- and the 1,5-regioisomers as can be seen in the spectroscopic data for **10a** (Figure 5). The regioisomers were not separable by flash chromatography and therefore used as mixtures.

The ¹H NMR spectra of the conventionally prepared polymer **8a** and its twin made by the postfunctionalization of **5** are shown in Figure 3. The polymers are spectroscopically indistinguishable from each other. When one inspects the NMR spectra of the polymer **8a** (conventional), the spectral features of the regioisomers that are well resolved in the spectra of the monomer **10a** are not resolved at all in the spectra of the polymer **8a**. Because of this decrease in resolution, when going from monomer to polymer, we are not able to assess the regiochemistry of the triazole units in polymer **8** at all by NMR spectroscopy and cannot give any testimony with respect to the regioselectivity of the postfunctionalization process (Figure 5). In the formation of the sterically hindered monomer **11** high regioselectivity is observed, and only the 1,4-product is formed.

Characterization of Functionalized Polymers 8a-e. It was of interest to study the influence of postmodification on the molecular weight of 8. We find PPEs decrease in molecular weight (5, 63.6×10^3 ; 6, $25.4 \times 10^3 > 8 > 8.5 \times 10^3$) and polydispersity (5: 4.4 to between 3.2 > 8 > 1.5) when comparing 8 to platform polymer 5 (Table 1). This is possibly due to differences in solubility between 5 and the postfunctionalized polymers 8. Material is lost during the filtration step required for GPC due to aggregated and/or insoluble parts of 8, similarly to the case discussed for polymer 6. GPC ultrafilters are yellowish in appearance after filtration of solutions of 8a-e, and the decreased polydispersity is an excellent indication for the loss of high molecular weight fractions during filtration.

To rule out the possibility of diyne formation, i.e., cross-linking, as a reason for observed insolubility, we treated polymer **6** with TBAF, copper sulfate, and sodium ascorbate in wet THF (5% water) in the presence of air. Only after heating to reflux for 24 h did we



Figure 4. IR of polymers 5, 6, 8a (post), and 8a (pre) (top to bottom). The blue arrows point to the bands of the terminal alkynes.



Scheme 3. Synthesis of Polymer 8b via a Prefunctionalized Strategy Starting from Monomer 3

observe a material containing some diyne linkages. The material was still soluble, and the amount of crosslinking must have been moderate. The signals of the diyne groups are however visible the in ¹³C NMR due to their shorter relaxation time as compared to the signals attributed to the alkyne carbons of the main chain. Signals assignable to diyne formation were not observed in any of the postfunctionalized polymers 8a-e because those were synthesized in a nitrogen atmosphere, under scrupulous exclusion of oxygen.

The possibility of incorporation of triazole groups into the backbone of the PPEs as a cause for the decreased solubility was also considered. Control experiments were performed in which didodecyl-PPE was treated at 40 °C for 16 h with an excess of dodecyl azide under standard postfunctionalization conditions. After pre-



Figure 6. UV-vis and emission spectra of polymer **8b** (conventional) and polymer **12** in chloroform (left) and in the solid state (right). The only difference is the TIPS group attached to the triazole units.

350

400

450

500

550

600

cipitation into methanol only unfunctionalized PPE was isolated according to ¹H NMR, ¹³C NMR, and UV–vis spectroscopy. Attack on the backbone-ynes is not favored under those reaction conditions.

450

500

550

600

350

400

There is precedence for decreased solubility of clickfunctionalized polymers: Kluger et al. performed postfunctionalization of poly(oxynorbornenes)¹⁰ and noted dramatic differences in solubility between polymers functionalized with 1,4-triazoles and those not. In some cases, GPC data for these polymers could not be obtained due to limited solubility. Matyjaszewski et al. have recently modified polymers of acrylonitrile with click-type chemistry to form tetrazoles and also noted marked differences in solubility between polymers modified by click chemistry and their unmodified precursors.¹¹ It is, however, surprising that the attachment of dodecyl chains or Frechet-type dendrons leads to a decrease in solubility of 8 in our case. A possible explanation is that the presence/incorporation of the triazole group per se reduces the solubility of any polymer.

Optical Properties of Functionalized Polymers 8a-e. The optical properties of polymers 8a-e were examined and compared with those of their premodified counterparts. In solution, absorption and fluorescence maxima of structurally identical polymers 8a-e occur at similar wavelengths $(\pm 2 \text{ nm})$. The largest difference in absorption is found when comparing platform polymer 6 to functionalized polymers 8 and 12. For all polymers 8, both pre- and postfunctionalized, blue shifts in absorption are observed when compared to 6 (Table 1). Polymer 12 with TIPS groups attached to the pendant triazole moieties is an extreme case and has a solution absorption maximum of 406 nm, which is blueshifted by 6-24 nm of the absorption maxima of polymers 8a - e (Figure 6). The solid-state emission of 12 is almost unchanged to that obtained in solution. We assume that the increased steric demand of the TIPS groups forces the backbone of this PPE into a nonplanar ground state.^{12,13}

All of the investigated polymers 5, 6, 8, and 12 have the same backbone. In the solid state, i.e., in thin films, their absorption spectra vary considerably. Polymer **6** shows an absorption maximum at 462 nm, while the TIPS-substituted **12** has a solid-state absorption maximum located at 410 nm. All of the other triazole-functionalized polymers, **8**, show absorption maxima ranging from 416 to 436 nm. The red shift in the absorption spectra of **8a**-**e**, when going from solution into the solid state is quite small, only 6–17 nm. That is unusual because the precursor polymer **6** shows a shift of 42 nm when going from solution into the solid state. The differences in the thin film UV spectra between pre- and postfunctionalized polymers **8a**-**e** of identical structure are small, and as a rule the absorption of the postfunctionalized samples is 8–13 nm red-shifted.

The introduction of the triazole unit into the side chains of the PPEs 8 and the PPE 12 influences their absorption insofar as a more twisted conformation of the main chain must be assumed. In the case of 12 the large TIPS substituent will probably lead to an additional twist of the main chain, and the conformations of 12's backbone in solution and in the solid state will be very similar. The subtle differences between the absorption of the pre- vs the postfunctionalized triazolesubstituted PPEs 8a-e is possibly due to difficult-tobe-detected differences in the ratio of 1,4- and 1,5isomers.

We examined the fluorescence quantum yields of 5, 6, and 8a-e in solution (Table 1). There are no significant differences between the quantum yields of the conventional and the click-functionalized PPEs. The deprotected polymer 6 and the polymer 12 have the lowest quantum yields (0.89 and 0.87). The postfunctionalization therefore does not seem to disturb the backbone of the PPE.

DSC of Functionalized Polymers 8a-e. The thermal behavior of polymers 8a-e was investigated between 0 and 250 °C by differential scanning calorimetry (DSC). Polymers 5, 6, 8b, 8c, 8d, and 8e show slow decomposition and no phase transitions. Polymer 8a, obtained by a premodification strategy, shows an endothermic transition beginning at 66 °C and ending at 126 °C.^{5b} A reproducible isotropic transition at 200 °C upon heating and cooling was also observed. Polymer 8a synthesized by a postmodification strategy showed only slow decomposition. When comparing polymers synthesized by a post- and premodification strategy, it is important to note that the conventional and the click polymers 8 often have different degrees of polymerization but identical substitutents and are therefore expected to behave differently. Longer polymer chains would melt at higher temperatures. As discussed above, slightly differing polymer structures such as the presence of 1,5-triazoles would also be expected to cause differences in the solid-state properties of these polymers.

Conclusions

We have produced a series of PPEs (8a-e) by employing click chemistry in both pre- and postpolymerization functionalization approaches. In examples where the structural repeat unit of the polymer was the same, the optical properties of these polymers in solution proved to be identical. Differing thin-film optical and thermal properties result from differening degrees of polymerization and perhaps a different distribution of triazole regioisomers. Click chemistry provided a means

to completely functionalize PPE **6** via a postmodification strategy into **8a-d**. In the case of azide **7e**, this approach provided a polymer **8e**, which was up to 90% functionalized. While all of these triazole-functionalized polymers aggregate, their absorption spectra are quite insensitive to this aggregation process, which suggests that water-soluble triazole-functionalized PPEs may find attractive applications in biological sensing schemes.¹⁴

Experimental Section

Instrumentation. The ¹H and ¹³C NMR spectra were taken on a Varian 300 MHz or a Bruker 400 MHz spectrometer using a broadband probe. The ¹H chemical shifts are referenced to the residual proton peaks of CDCl3 at δ 7.24 and DMSO at δ 2.49. The ¹³C resonances are referenced to the central peak of $CDCl_3$ at δ 77.0 and DMSO at δ 39.5. Chromium(III) acetylacetonate was used when obtaining ¹³C NMR data for all polymers. UV-vis measurements were made with a Shimadzu UV-2401PC recording spectrophotometer. Fluorescence data were obtained with a Shimadzu RF-5301PC spectrofluorophotometer. A Headway Research model PWM32 instrument was used to spin-coat dilute chloroform solutions of polymers onto quartz slides for thin film experiments. 1,4-Diiodo-2,5-dihydroquinone,¹³ 1,4-diethynyl-2,5-bis(2-ethylhexyl)benzene (4),¹³ dodecyl azide (7a),¹⁰ and 9¹² were prepared and characterized in accordance with published procedures.

General Procedure for Conversion of Halide to Azide. In a round-bottom flask the corresponding organic halide was dissolved in acetone; 10 equiv of sodium azide was added, and the mixture was heated to reflux for 24 h and cooled to room temperature, and the solvent was removed under vacuum. Following aqueous work-up, the crude products were purified by column chromatography on silica gel with dichloromethane: hexane as an eluent.

Synthesis of 3. 1,4-Hydroxy-2,5-diiodobenzene (4.73 g, 13.1 mmol), potassium carbonate (18.1 g, 131 mmol), and 2 (9.00 g, 32.7 mmol) were dissolved in acetone (150 mL). The mixture was heated to reflux for 24 h, allowed to cool to room temperature, then diluted with dichloromethane, and washed with 1 N HCl (2 × 150 mL). The solvent was removed under vacuum. The crude solid was purified by chromatography on silica gel (1:1, dichloromethane:hexane) to yield **3** as a colorless crystalline solid (8.05 g, 82%). ¹H NMR (CDCl₃): δ 7.47 (m 2H), 4.73 (m, 4H), 1.20 (m, 6H), 1.03 (m, 36H). ¹³C NMR (CDCl₃): δ 152.2, 124.6, 101.2, 90.8, 86.4, 59.0, 18.9, 11.4. IR: ν 2953, 2735, 2610, 2461, 2183, 2081, 1999, 1901, 1821, 1469, 1372, 1272, 1217, 1068, 1003, 915; mp 80–82 °C. Calcd: C, 48.00; H, 6.44. Found: C, 48.07; H, 6.52.

Synthesis of Polymer 5. Monomer 3 (10.0 g, 13.3 mmol) and 2,5-ethylhexyl-1,4-diethynylbenzene (4) (4.72 g, 13.5 mmol) were dissolved in tetrahydrofuran (26 mL) and piperidine (26 mL) in an oven-dried Schlenk flask. The flask was flushed with nitrogen, frozen, and evacuated three times after which $(Ph_3P)_2PdCl_2$ (65 mg, 93 μ mol) and CuI (10 mg, 53 μ mol) were added. The mixture was allowed to stir at room temperature for 48 h, after which the solvent was removed and the mixture was dissolved in dichloromethane and washed with 1 N HCl, 1 N NH₄OH, and water. The organic layer was dried over MgSO₄ and the solvent removed. The resulting polymer was redissolved in dichloromethane and precipitated out of methanol (three times 1 L) to yield 6 (9.81 g, 87%) as a yellow solid. ¹H NMR (CDCl₃): δ 7.29 (m, 2H), 7.24 (m, 2H), 4.79 (m, 4H), 2.74 (m, 2H), 1.75 (m, 2H), 1.52 (m, 16H), 1.25 (m, 6H), 1.02 (m, 36H), 0.82 (m, 6H). ¹³C NMR (CDCl₃): δ 152.4, 141.2, 133.2, 123.1, 118.6, 114.5, 101.7, 94.7, 90.1, 58.0, 40.3, 38.4, 32.4, 28.8, 25.6, 23.0, 22.2, 20.5, 18.4, 16,4, 13.9, 11.1, 10,7. IR: v 2957, 2943, 2920, 2911, 2883, 2860, 2846, 2361, 2159, 1507, 1498, 1489, 1481, 1464, 1457, 1442, 1415, 1344, 1280, 1251, 1196, 1185, 1038, 1032, 1023, 1015, 1008, 983, 879, 665, 647. GPC (polystyrene standards): $M_{\rm n} = 63.6 \times 10^3$, PDI = 4.42. Calcd: C, 79.56; H, 10.01. Found: C, 79.03; H, 9.94.

Synthesis of Polymer 6. Polymer **5** (0.250 g, 0.296 mmol) was dissolved in THF (50 mL) under nitrogen purge in an

oven-dried Schlenk flask. Under nitrogen tetrabutylammonium fluoride (1 mL, 1 M solution in THF, containing ca. 5% water) was added slowly over 5 min. The mixture was allowed to stir at room temperature for 12 h. The solvent was removed, and the mixture was dissolved in dichloromethane and washed with 1 N HCl, 1 N NH4OH, and water. The organic layer was dried over MgSO₄ and the solvent removed. The product was dissolved in dichloromethane and precipitated out of methanol (200 mL) to yield polymer 6 (0.149 g, 95%) as a deep yellow solid. ¹H NMR (CDCl₃): δ 7.38 (m, 2H), 7.19 (m, 2H), 4.80 (m, 4H), 2.75 (m, 4H), 2.55 (m, 2H), 1.76 (m, 2H), 1.55 (m, 16H), 1.28 (m, 6H), 0.84 (m, 6H). ¹³C NMR (TCE): δ 152.8, 141.5, 133.4, 123.2, 118.3, 114.9, 95.2, 89.9, 57.4, 40.4, 38.4, 32.5, 28.8,25.7, 23.1, 14.0, 10.8. IR: v 3752, 3663, 3309, 2960, 2921, 2864, 2200, 2135, 1545, 1507, 1455, 1416, 1371, 1262, 1202, 1033, 924, 892, 854, 674, 632. GPC (polystyrene standards) $M_{\rm n} =$ 24.4×10^3 , PDI = 1.64. Calcd: C, 85.67; H, 8.32. Found: C, 85.73; H.8.46.

Synthesis of Polymer 8a (Postpolymerization Functionalization). Polymer 5 (0.100 g, 0.118 mmol) and azide 7a (62 mg, 0.295 mmol) were dissolved in THF (15 mL) under a nitrogen purge in an oven-dried Schlenk flask. The flask was flushed with nitrogen and frozen and evacuated three times, after which $CuSO_4$ (0.5 mg, 1.9 μ mol), sodium ascorbate (4 mg, 19 μ mol), and tetrabutylammonium fluoride (0.25 mL, 1 M solution in THF, containing ca. 5% water) were added. The mixture was allowed to stir at 40 °C for 48 h. The THF was removed under vacuum, and the mixture was dissolved in dichloromethane and washed with 1 N HCl, 1 N NH₄OH, and water. The organic layer was dried over MgSO₄ and the solvent removed. The resulting polymer was dissolved in dichloromethane and precipitated out of methanol to yield 8a (0.104 g, 92%) as a yellow solid. ¹H NMR (CDCl₃): δ 7.58 (m, 2H), 7.28 (m, 4H), 5.33 (m, 4H), 4.31 (m, 4H), 2.72 (m, 4H), 1.87 (m, 12H), 1.58 (m, 46H), 0.86 (m, 18H). ¹³C NMR (CDCl₃): δ 152.8, 143.9, 141.2, 133.2, 123.1, 122.0, 118.1, 114.9, 94.7, 89.9, 64.1, 50.2, 40.2, 38.3, 32.3, 31.7, 30.0, 29.2, 26.3, 25.5, 22.7, 13.8, 10.6. IR: v 3136, 2948, 2851, 2729, 2673, 2418, 2201, 2094, 1599, 1507, 1461, 1446, 1418, 1378, 1334, 1277, 1212, 1007, 861, 722. GPC (polystyrene standards) $M_{\rm n} = 8463$, PDI = 3.20

Synthesis of 10a. Diiodo compound 9 (1.00 g, 2.28 mmol) and azide 7a (1.93 g, 9.13 mmol) were dissolved in THF under nitrogen purge in an oven-dried Schlenk flask. The flask was flushed with nitrogen, frozen, and evacuated three times, after which $CuSO_4$ (6 mg, 22.8 μ mol) and sodium ascorbate (45 mg, 228 μ mol) were added. The mixture was allowed to stir at 50 °C for 48 h. The solvent was removed, and the mixture dissolved in dichloromethane and washed with 1 N HCl, 1 N NH₄OH, and water. The organic layer was dried over MgSO₄. The solvent was removed under vacuum, and the crude product was purified by chromatography on silica gel (1:1, ethyl acetate:hexane) to yield 10a as a light yellow crystalline solid (1.74 g, 89%). ¹H NMR (CDCl₃): δ 7.66 (s, 2H), 7.35 (s, 2H), 5.19 (s, 4H), 4.34 (t, 8H), 3.89 (m, 4H), 1.91 (m, 4H), 1.24 (m, 36H), 0.84 (t, 6H). ¹³C NMR (CDCl₃): δ 152.7, 143.7, 135.3, 125.1, 123.9, 122.8, 86.8, 65.0, 50.8, 32.5, 32.2, 30.6, 29.9, 29.8, 29.7, 29.6, 29.3, 26.8, 26.7, 23.7, 23.0, 14.5. IR: v 3179, 2947, 2844, 2428, 2121, 1900, 1650, 1573, 1485, 1409, 1341, 1204, 1142, 1072, 1038, 892, 840, 802, 723, 647. MS calcd for [C₃₆H₅₈I₂N₆O₂]: 860.69; found: 860.3; mp 113-115 °C.

Synthesis of Polymer 8a (Prepolymerization Functionalization). Monomer 10a (0.500 g, 0.581 mmol) and 2,5ethylhexyl-1,4-diethynylbenzene (4) (0.205 g, 0.586 mmol) were dissolved in dichloromethane (2 mL) and piperidine (2 mL) in an oven-dried Schlenk flask. The flask was flushed with nitrogen, frozen, and evacuated three times, after which (Ph₃P)₂PdCl₂ (4 mg, 6 μ mol) and CuI (1 mg, 6 μ mol) were added. The mixture was allowed to stir at room temperature for 48 h. The solvent was removed, and the mixture was dissolved in dichloromethane and washed with 1 N HCl, 1 N NH₄OH, and water. The organic layer was dried over MgSO₄ and the solvent removed. The resulting polymer was dissolved in dichloromethane and precipitated out of methanol three times to yield 8a (0.511 g, 91%) as a yellow solid. ¹H NMR (CDCl₃): δ 7.57 (m, 2H), 7.26 (m, 4H), 5.31 (m, 4H), 4.30 (m, 4H), 2.72 (m, 4H), 1.85 (m, 12H), 1.56 (m, 46H), 0.82 (m, 18H). ¹³C NMR (CDCl₃): δ 153.0, 143.82, 141.1, 133.0, 124.8, 121.9, 117.8, 114.5, 94.4, 89.7, 89.7, 63.9, 50.0, 40.0, 38.1, 32.0, 29.0, 26.0, 22.6, 13.6, 10.4. IR: v 3602, 3083, 2954, 2841, 2434, 2196, 2028, 1688, 1529, 1499, 1361, 1212, 890, 824, 777, 600. GPC (polystyrene standards) $M_n = 13.7 \times 10^3$, PDI = 5.24.

Synthesis of Polymer 8b (Postpolymerization Functionalization). Polymer 5 (0.100 g, 0.118 mmol) and azide 7b (0.231 g, 0.471 mmol) were dissolved in THF (15 mL) under nitrogen purge in an oven-dried Schlenk flask. The flask was flushed with nitrogen, frozen, and evacuated three times, after which CuSO₄ (0.5 mg, 2 μ mol), sodium ascorbate (4 mg, 19 μ mol), and tetrabutylammonium fluoride (0.25 mL, 1 M solution in THF, containing ca. 5% water) were added. The mixture was allowed to stir at 60 °C for 48 h. The solvent was removed under vacuum. The mixture was redissolved in dichloromethane and washed with 1 N HCl, 1 N NH₄OH, and water. The organic layer was dried over MgSO₄, and the solvent was removed. The resulting polymer was dissolved in dichloromethane and precipitated out of methanol to yield 8b (0.168 g, 94%) as a yellow solid. ¹H NMR (CDCl₃): δ 7.64 (m, 2H), 7.26 (m, 2H), 7.17 (m, 2H), 5.34 (m, 4H), 4.64 (m, 4H), 2.82 (m, 4H), 1.25 (m, 20H), 0.84 (m, 12H). ¹³C NMR (CDCl₃): δ 153.0, 144.5, 141.2, 133.2, 122.2, 118.2, 114.9, 110.6, 94.8, 90.1, 63.8, 57.9, 42.3, 40.3, 38.3, 32.3, 31.7, 29.7, 28.6, 25.5, 22.9, 18.3, 13.8, 11.0, 10.6. IR: v 3311, 3259, 2961, 2443, 2204, $1702,\,1592,\,1505,\,1456,\,1415,\,1356,\,1316,\,1258,\,1076,\,1015,$ 887, 799, 752, 707, 658. GPC (polystyrene standards) $M_{\rm n} =$ 25.4×10^3 , PDI = 2.56.

Synthesis of 11. Diiodo compound **3** (1.00 g, 1.33 mmol) and azide **7b** (2.93 g, 5.99 mmol) were dissolved in *o*-xylene under nitrogen purge in an oven-dried Schlenk flask. The mixture was allowed to stir at reflux for 48 h. The solvent was removed under vacuum, and the crude product was purified by chromatography on silica gel (1:3, ethyl acetate:hexane) to yield **11** as a colorless solid and single regioisomer (2.01 g, 86%). ¹H NMR (CDCl₃): δ 7.25 (s, 2H), 5.06 (s, 4H), 4.74 (t, 4H), 3.04 (m, 4H), 1.43 (m, 6H), 1.09 (m, 36H). ¹³C NMR (CDCl₃): δ 152.4, 142.3, 137.0, 123.0, 85.8, 60.8, 40.7, 31.8, 18.8, 18.5, 11.5, 1.1. ¹⁹F NMR (CDCl₃): -82.1, -115.4, -123.0, -123.2, -124.1, -124.5, -127.5. IR: *v* 3090, 2947, 2867, 2725, 2464, 2363, 2105, 2002, 1692, 1467, 1458, 1375, 1352, 1233, 1207, 1150, 1055, 1000, 883, 848, 711, 647. MS calcd for [C₅₀H₅₆F₃₄L₂N₆O₂Si₂], 1728.9; found: 1729.4; mp 146-150 °C. Calcd: C, 34.73; H, 3.26. Found: C, 34.24; H, 3.25.

Synthesis of Polymer 12 (Prepolymerization Functionalization). Monomer 11 (single regioisomer) (1.00 g, 0.574 mmol) and 2,5-ethylhexyl-1,4-diethynylbenzene (4) (0.203 g, 0.579 mmol) were dissolved in dichloromethane (2 mL) and piperidine (2 mL) in an oven-dried Schlenk flask. The flask was flushed with nitrogen, frozen, and evacuated three times, after which $(Ph_3P)_2PdCl_2$ (20 mg, 29 μ mol) and CuI (6 mg, 29 μ mol) were added. The mixture was allowed to stir at room temperature for 48 h. The solvent was removed, and the mixture was dissolved in dichloromethane and washed with 1 N HCl, 1 N NH₄OH, and water. The organic layer was dried over MgSO₄ and the solvent removed. The resulting polymer 12 was dissolved in dichloromethane and precipitated out of methanol three times to yield a yellow solid (1.42 g, 91%). ^{1}H NMR (CDCl₃): δ 7.26 (m, 4H), 7.18 (m, 2H), 5.35 (m, 4H), 4.66 (m, 4H), 2.80 (m, 4H), 1.24 (m, 18H), 1.01 (m, 42H) 0.82 (m, 12H). ¹³C NMR (CDCl₃): δ 152.7, 141.9, 141.4, 137.4, 133.2, 122.5, 117.3, 114.7, 113.2, 110.5, 95.6, 88.8, 60.4, 44.8, 40.4, 38.1, 32.2, 31.6, 28.6, 25.4, 22.8, 18.3, 13.7, 11.3, 10.5. IR: v 2962, 2867, 2726, 2357, 2205, 1506, 1460, 1412, 1367, 1259, 1092, 1018, 872, 797, 658. GPC (polystyrene standards): $M_{\rm n}$ $= 25.5 \times 10^4$, PDI = 4.25.

Synthesis of Polymer 8b (Prepolymerization Functionalization). Polymer 12 (0.500 g, 0.331 mmol) was dissolved in THF (50 mL) under nitrogen purge in an oven-dried Schlenk flask. Under nitrogen, tetrabutylammonium fluoride (3 mL, 1 M solution in THF, containing ca. 5% water) was added slowly over 5 min. The mixture was stirred for 24 h. The solvent was removed under vacuum, and the resulting solid was dissolved in dichloromethane and washed with water. The organic layer was dried under MgSO₄ and filtered, and the solvent was removed to afford **8b** as a yellow solid (0.398 g, 96%). ¹H NMR (CDCl₃): δ 7.65–7.51 (m, 2H), 7.25 (m, 2H), 7.18 (m, 2H), 5.32 (m, 4H), 4.63 (m, 4H), 2.82 (m, 4H), 1.24 (m, 20H), 0.83 (m, 12H). 13 C NMR (CDCl₃): δ 152.7, 140.8, 132.9, 122.8, 117.1, 114.3, 112.7, 100.7, 94.5, 89.6, 67.5, 63.1, 42.0, 40.0, 37.8, 31.8, 28.2, 25.0, 22.5, 17.9, 13.5, 10.2. IR: ν 2959, 2863, 2206, 1691, 1614, 1463, 1223, 1027, 883, 744, 709, 652. GPC (polystyrene standards): $M_{\rm n}$ 71.7 \times 10³, PDI = 4.44.

Synthesis of Polymer 8c (Postpolymerization Functionalization). Polymer 5 (0.100 g, 0.118 mmol) and azide 7c (88.4 mg, 0.355 mmol) were dissolved in THF (15 mL) under nitrogen purge in an oven-dried Schlenk flask. The flask was flushed with nitrogen and frozen and evacuated three times, after which $CuSO_4$ (0.5 mg, 2 μ mol), sodium ascorbate (4 mg, 19 μ mol), and tetrabutylammonium fluoride (0.25 mL, 1 M solution in THF, containing ca. 5% water) were added. The mixture was stirred at 50 °C for 48 h. The solvent was removed, and the mixture was dissolved in dichloromethane and washed with 1 N HCl, 1 N NH₄OH, and water. The organic layer was dried over MgSO₄, and the solvent was removed under vacuum. The resulting polymer was dissolved in hot DMSO and precipitated out of methanol (three times) to yield **8c** (0.093 g, 76%) as a yellow solid. ¹H NMR (DMSO): δ 7.56– 7.50 (m, 4H), 7.41 (m, 2H), 5.73 (m, 2H), 4.92 (m, 2H), 4.59 (m, 6H), 4.01 (m, 12H), 3.18 (m, 12H), 1.91 (m, 32H), 1.73 (m, 6H), 1.55 (m, 16H), 1.25 (m, 6H), 0.84 (m, 12H). ¹³C NMR (TCE): δ 152.6, 141.7, 132.6, 124.6, 117.5, 102.8, 93.9, 90.3, 76.4, 72.9, 69.8, 67.0, 60.8, 57.3, 48.1, 30.1, 27.8, 24.8, 22.6, 18.7, 13.2, 10.3. IR: v 3544, 3309, 2948, 2866, 2528, 2200, 2102, 1730, 1625, 1436, 1382, 1203, 1118, 1076, 1041, 862, 740, 555, 453, 412. GPC (polystyrene standards): $M_{\rm n} = 22.6 \times 10^3$, PDI = 2.39

Synthesis of 10c. Diiodo compound 9 (1.00 g, 2.28 mmol) and azide 7c (2.00 g, 4.79 mmol) were dissolved in THF under nitrogen purge in an oven-dried Schlenk flask. The flask was flushed with nitrogen, frozen, and evacuated three times, after which $CuSO_4$ (6 mg, 22.8 μ mol) and sodium ascorbate (45 mg, 228 μ mol) were added. The mixture was allowed to stir at 50 °C for 48 h. The solvent was removed, and the mixture was dissolved in dichloromethane and washed with 1 N HCl, 1 N NH₄OH, and water. The organic layer was dried over MgSO₄. The solvent was removed under vacuum, and the crude product was purified by chromatography on silica gel (1:1, ethyl acetate: dichloromethane) to yield ${\bf 10c}$ as a colorless crystalline solid (1.81 g, 62%). ¹H NMR (CDCl₃): δ 7.78 (s, 2H), 7.41 (s, 2H), 7.24 (s, 2H), 5.15 (m, 6H), 4.49 (m, 12H), 3.95 (m, 4H), 3.68 (m, 4H), 1.97 (m, 24H). ¹³C NMR (CDCl₃): δ 170.3, 169.8, 169.1, 169.0, 152.5, 143.1, 124.2, 123.7, 100.4, 86.5, 72.3, 71.8, 70.8, 68.1, 67.6, 64.4, 61.6, 50.1, 20.7, 20.5. IR: v 3557, 3479, 3454, 3086, 2955, 2876, 2739, 2450, 2419, 2109, 2028, 1961, 1916, 1732, 1645.17, 1482, 1320, 1172, 993, 952, 907, 854, 795, 753, 696, 649, 602. MS calcd for $[C_{44}H_{54}I_2N_6O_{22}]$: 1272.74; found: 1273.1; mp 156-160 °C.

Synthesis of Polymer 8c (Prepolymerization Functionalization). Monomer 10c (0.230 g, 0.251 mmol) and 2,5ethylhexyl-1,4-diethynylbenzene (4) (0.088 g, 0.251 mmol) were dissolved in dichloromethane (2 mL) and piperidine (2 mL) in an oven-dried Schlenk flask. The flask was flushed with nitrogen, frozen, and evacuated three times, after which $(Ph_3P)_2PdCl_2$ (3 mg, 5 µmol) and CuI (1 mg, 5 µmol) were added. The mixture was allowed to stir at room temperature for 48 h. The solvent was removed, and the mixture was dissolved in dichloromethane and washed with 1 N HCl, 1 N $\rm NH_4OH,$ and water. The organic layer was dried over $\rm MgSO_4$ and the solvent removed. The solvent was concentrated and the polymer precipitated out of H_2O (50:50) twice to yield 13 (0.241 g, 93%). ¹H NMR (DMSO): δ 7.56 (m, 2H), 7.50 (m, 2H), 7.41 (m, 2H), 5.72 (m, 2H), 4.91 (m, 2H), 4.59 (m, 6H), 4.01 (m, 12H), 3.18 (m, 12H), 1.91 (m, 32H), 1.70 (m, 6H), 1.54 (m, 16H), 1.26 (m, 6H), 0.87 (m, 6H). ¹³C NMR (DMSO): δ 152.7, 141.9, 140.7, 132.6, 124.5, 122.3, 117.7, 113.7, 111.9, 102.7, 93.8, 85.9, 76.48, 73.0, 69.9, 66.6, 61.0, 58.1, 49.4, 31.5, 27.8, 24.9, 21.9, 13.2, 10.2. IR: v 3577, 3454, 3258, 3126, 2956, 2924, 2806, 2710, 2201, 1960, 1644, 1598, 1513, 1466, 1401, 1279, 1213, 1163, 1023, 991, 870, 804. GPC (polystyrene standards): $M_{\rm n}=24.5\times10^4, {\rm PDI}=1.01.$

Synthesis of Polymer 8d (Postpolymerization Functionalization). Polymer 5 (0.100 g, 0.188 mmol) and azide 7d (0.116 g, 0.375 mmol) were dissolved in THF under nitrogen purge in an oven-dried Schlenk flask. The flask was flushed with nitrogen, frozen, and evacuated three times, after which $CuSO_4$ (0.5 mg, 1.9 μ mol), sodium ascorbate (4 mg, 18.7 μ mol), and tetrabutylammonium fluoride (0.25 mL, 1 M solution in THF, containing ca. 5% water) were added. The mixture was allowed to stir at 40 $^{\circ}\mathrm{C}$ for 48 h. The solvent was concentrated, and the polymer precipitated out of methanol: $H_2O(50:50)$ twice to yield 8d (0.149 g, 82%). ¹H NMR (CDCl₃): δ 8.01 (m, 1H), 7.63 (m, 1H), 7.38 (m, 2H), 6.86 (m, 2H), 4.80 (m, 4H), 4.13 (m, 8H), 3.89 (m, 8H), 3.73 (m, 16H), 2.75 (m, 4H), 2.55 (m, 2H), 1.76 (m, 2H), 1.55 (m, 16H), 1.28 (m, 6H), 0.84 (m, 6H). ¹³C NMR (TCE): δ 153.5, 150.0, 144.9, 141.7, 133.6, 130.6, 120.7, 118.1, 114.3, 112.5, 107.1, 94.9, 90.1, 70.4, 69.6, 64.5, 53.23, 40.4, 38.5, 32.4, 28.8, 25.6, 22.6, 14.0, 10.9. IR: v 3642, 3561, 3515, 3412, 2930, 2857, 2351, 2205, 1644, 1592, 1504, 1445, 1263, 1138, 1130. GPC (polystyrene standards): $M_n =$ 108.4×10^3 , PDI = 1.49.

Synthesis of 10d. Diiodo compound 9 (0.500 g, 1.14 mmol) and azide 7d (1.05 g, 3.39 mmol) were dissolved in THF under nitrogen purge in an oven-dried Schlenk flask. The flask was flushed with nitrogen, frozen, and evacuated three times, after which $CuSO_4$ (3 mg, 11 μ mol) and sodium ascorbate (23 mg, 114 μ mol) were added. The mixture was allowed to stir at 50 °C for 48 h. The solvent was removed, and the mixture was dissolved in dichloromethane and washed with 1 N HCl, 1 N NH₄OH, and water. The organic layer was dried over MgSO₄. The solvent was removed under vacuum, and the crude product was purified by chromatography on silica gel (10:1, ethyl acetate:hexane) to yield 10d as a colorless crystalline solid (0.651 g, 53%). ¹H NMR (CDCl₃): δ 7.77 (m, 2H), 7.23 (m, 2H), 7.56 (m, 4H), 6.78 (t, 2H), 5.14 (m, 4H), 4.11 (m, 8H), 3.87 (m, 8H), 3.61 (m, 16H). ¹³C NMR (CDCl₃): δ 152.9, 135.5, $130.1,\,124.8,\,124.4,\,118.5,\,114.8,\,111.4,\,107.4,\,86.8,\,78.9,\,71.9,$ 71.0, 69.9, 61.1, 58.2. IR: v 3259, 2954, 2871, 2360, 2115, 1734, 1600, 1518, 1455, 1349, 1223, 1021, 801. MS calcd for [C₄₀H₄₆I₂N₆O₁₂]: 1056.6; found: 1057.2; mp 162-164 °C.

Synthesis of Polymer 8d (Prepolymerization Functionalization). Monomer 10d (0.301 g, 0.280 mmol) and 2,5ethylhexyl-1,4-diethynylbenzene (4) (99.2 mg, 0.283 mmol) were dissolved in dichloromethane (2 mL) and piperidine (2 mL) in an oven-dried Schlenk flask. The flask was flushed with nitrogen, frozen, and evacuated three times, after which $(Ph_3P)_2PdCl_2$ (10 mg, 14 μ mol) and CuI (3 mg, 14 μ mol) were added. The mixture was allowed to stir at room temperature for 48 h. The solvent was removed; and the mixture was dissolved in dichloromethane and washed with 1 N HCl, 1 N NH₄OH, and water. The organic layer was dried over MgSO₄ and the solvent removed. The resulting polymer was dissolved in dichloromethane and precipitated out of methanol three times to yield $8d~(0.309~g,\,93\%)$ as a yellow solid. ¹H NMR (CDCl₃): δ 8.01 (m, 2H), 7.26 (m, 10H), 5.39 (m, 4H), 4.14 (m, 16H), 3.75 (m, 16H), 2.68 (m, 4H), 1.24 (m, 16H), 0.84 (m, 12H). ¹³C NMR (CDCl₃): δ 153.0, 144.4, 142.6, 141.2, 135.0, 133.0, 131.7, 130.3, 120.4, 117.2, 113.2, 112.0, 106.3, 95.0, 89.8, 70.7, 70.7, 68.8, 63.7, 40.1, 38.0, 32.1, 30.5, 28.4, 25.2, 22.7, 13.8, 10.5. IR: v 2958, 2207, 1604, 1510, 1453, 1261, 1101, 1018, 933, 802. GPC (polystyrene standards): $M_{\rm n} = 16.2 \times 10^4$, PDI = 7.70.

Synthesis of 7e. 3,4-Dibenzyloxybenzyl chloride (0.500 g, 1.48 mmol) and sodium azide (0.959 g, 14.8 mmol) were dissolved in acetone in an oven-dried Schlenk flask. The mixture was allowed to stir at reflux for 48 h. The solvent was removed, and the mixture was dissolved in dichloromethane and washed with water. The organic layer was dried over MgSO₄. The solvent was removed under vacuum, and the crude product was purified by chromatography on silica gel (2:1, dichloromethane:hexane) to yield **7e** as a light yellow crystalline solid (0.430 g, 84%). ¹H NMR (CDCl₃): δ 7.39 (m,

10H), 6.85 (m, 3H), 5.19 (s, 4H), 4.23 (s, 2H). ¹³C NMR (CDCl₃): δ 149.3, 149.2, 137.4, 134.3, 128.7, 128.1, 128.1, 127.6, 127.5, 121.8, 115., 3, 115.1, 71.6, 71.5, 54.9. IR: v 3337, 3027, 2897, 2838, 2445, 2079, 1599, 1413, 1304, 1248, 1201, 1057, 988, 940, 839, 767, 670, 633. MS calcd for [C₂₁H₁₉N₃O₂]: 345.39; found: fragmentation; mp 82-85 °C. Calcd: C, 57.46; H, 4.11. Found: C, 57.29; H, 4.62.

Synthesis of Polymer 8e (Postpolymerization Functionalization). Polymer 5 (0.100 g, 0.118 mmol) and azide $\mathbf{7e}\,(163\text{ mg},0.471\text{ mmol})$ were dissolved in THF (10 mL) under nitrogen purge in an oven-dried Schlenk flask. The flask was flushed with nitrogen, frozen, and evacuated three times, after which CuSO₄ (0.5 mg, 2 μ mol), sodium ascorbate (4 mg, 19 μ mol), and tetrabutylammonium fluoride (0.25 mL, 1 M solution in THF, containing ca. 5% water) were added. The mixture was stirred at 60 °C for 48 h. The solvent was removed, and the mixture was dissolved in dichloromethane and washed with 1 N HCl, 1 N NH₄OH, and water. The organic layer was dried over MgSO₄, and the solvent was removed under vacuum. The resulting polymer was dissolved in dichloromethane and precipitated out of methanol (three times) to yield **8e** (0.139 g, 96%) as a yellow solid. ¹H NMR (CDCl₃): δ 7.37 (m, 2H), 7.25 (m, 28H), 4.79 (m, 16H), 2.74 (m, 4H), 2.54 (m, 2H), 1.74 (m, 2H), 1.54 (m, 16H), 1.29 (m, 6H), 0.84 (m, 6H). ¹³C NMR (TCE): δ 152.3, 141.4, 133.4, 132.0, 128.4, 127.8, 127.3, 123.1, 118.2, 115.2, 94.2, 89.5, 71.3, 57.4, 40.4, 38.4, 32.4, 28.7, 25.7, 23.0, 14.0, 10.8. IR: v 3306, 2957, 2918, 2864, 2200, 2122, 1948, 1638, 1599, 1505, 1456, 1419, 1259, 1204, 1025, 804. GPC (polystyrene standards): $M_{\rm n} = 22.6 \times 10^3$, PDI = 2.39.

Synthesis of 10e: Diiodo compound 9 (0.400 g, 0.913 mmol) and azide 7e (1.26 g, 3.65 mmol) were dissolved in THF under nitrogen purge in an oven-dried Schlenk flask. The flask was flushed with nitrogen, frozen, and evacuated three times, after which $CuSO_4$ (2 mg, 9 μ mol) and sodium ascorbate (18 mg, 97.3 μ mol) were added. The mixture was allowed to stir at 50 °C for 48 h. The solvent was removed, and the mixture was dissolved in dichloromethane and washed with 1 N HCl, 1 N NH₄OH, and water. The organic layer was dried over MgSO₄. The solvent was removed under vacuum, and the crude product was purified by chromatography on silica gel (1:1, ethyl acetate:dichloromethane) to yield 10e as a colorless solid (0.830 g, 80%). ¹H NMR (CDCl₃): δ 7.56 (s, 2H), 7.46 (m, 22H), 7.12 (m, 6H), 5.64 (d, 4H), 5.39 (m, 4H), 5.10 (d, 8H). ¹³C NMR $(CDCl_3): \delta 152.5, 149.2, 149.0, 138.7, 136.7, 136.6, 128.4, 127.8,$ 127.2, 127.0, 123.7, 122.5, 121.3, 114.7, 114.7, 86.6, 71.2, 64.6, 54.0. IR: v 3060, 3031, 2927, 2867, 2088, 1953, 1753, 1728, 1595, 1513, 1348, 1263, 1217, 1135, 1054, 1021, 846, 698, 616. MS calcd for [C₅₂H₄₂I₂N₆O₆]: 1100.74; found: fragmentation; mp 155-157 °C.

Synthesis of Polymer 8e (Prepolymerization Functionalization). Monomer 10e (0.600 g, 0.532 mmol) and 2,5ethylhexyl-1,4-diethynylbenzene (4) (0.188 g, 0.537 mmol) were dissolved in THF (2 mL) and piperidine (2 mL) in an ovendried Schlenk flask. The flask was flushed with nitrogen, frozen, and evacuated three times, after which (Ph₃P)₂PdCl₂ (19 mg, 27 $\mu mol)$ and CuI (5 mg, 27 $\mu mol)$ were added. The mixture was allowed to stir at room temperature for 48 h. The solvent was removed, and the mixture was dissolved in dichloromethane and washed with 1 N HCl, 1 N NH₄OH, and water. The organic layer was dried over MgSO4 and the solvent removed. The resulting polymer was dissolved in dichloromethane and precipitated out of methanol three times to yield 8a (0.493 g, 75%) as a yellow solid. ¹H NMR (CDCl₃): δ 7.36 (m, 2H), 7.23 (m, 28H), 4.80 (m, 16H), 2.74 (m, 4H), 2.54 (m, 2H), 1.74 (m, 2H), 1.54 (m, 16H), 1.29 (m, 6H), 0.83 (m, $\,$ 6H). ¹³C NMR (CDCl₃): δ 160.6, 152.8, 148.8, 143.9, 141.1, 136.4, 133.0, 131.1, 128.1, 127.5, 127.0, 123.9, 122.3, 121.0, 117.5, 114.4, 94.6, 89.9, 70.8, 63.5, 53.6, 45.7, 40.0, 38.0, 31.9, 31.4, 30.6, 29.0, 28.3, 27.3, 25.1, 24.5, 23.3, 22.7, 20.3, 13.7, 10.4. IR: v 2944, 2938, 2723, 2597, 2396, 2204, 1955, 1602, 1445, 1268, 1125, 1004, 803. GPC (polystyrene standards): $M_{\rm n}$ $= 71.8 \times 10^3$, PDI = 2.10.

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Supporting Information Available: ¹³C NMR of polymers 5, 6, 8a (post), and 8a (pre) and bar chart of ¹³C NMR spectra of polymers 5, 6, and 8a-e. This material is available free of charge via the Internet at http://pubs.acs.org.

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