

Iptycene-Containing Poly(aryleneethynylene)s

V. E. Williams and T. M. Swager*

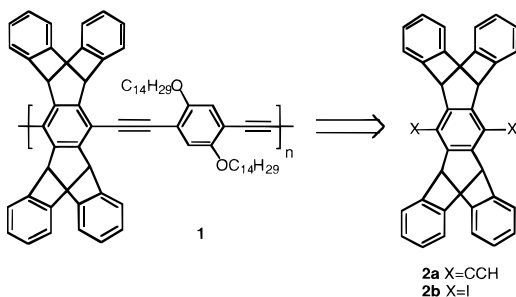
Department of Chemistry, Massachusetts Institute of Technology, 77 Massachusetts Ave., Cambridge, Massachusetts 02139

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ABSTRACT: The syntheses of two novel iptycene monomers, 1,4-diiodotriptycene (**5**) and 2,3-diiodo-4,9-dihydro-4,9-benzonaphtho[2,3,c]thiophene (**10**), are described herein. These monomers were subsequently copolymerized with a number of diethynylphenyl monomers via a Sonogashira–Hagihara coupling to afford both regiodefined polymers and random terpolymers. Terpolymers derived from coupling **5** and 2,5-dihexadecyloxy-1,4-diiodobenzene with a diethynylpentiptycene exhibit emission spectra that are only slightly perturbed from solution to the solid state, suggesting that polymer association is effectively inhibited in condensed phases. An “all-iptycene” polymer (**13**) derived from the copolymerization of **10** with a diethynylpentiptycene monomer is also notable in that it owes its solubility to a combination of its nonlinearity and the presence of rigid iptycene groups rather than to flexible side chains.

Introduction

The detection limits of a chemosensor that uses fluorescence quenching as a signal transduction mechanism is limited by the probability of a singlet excitation encountering a quenching analyte. In this context, the efficient energy migration characteristics of poly(aryleneethynylene)s allows these polymers to behave as “molecular wires” with greatly enhanced sensitivities to analytes such as paraquat¹ and TNT.² Unfortunately, the usefulness of these materials as solid-state sensors and electroluminescent devices is often severely limited by the low fluorescence quantum yields of conjugated polymers when cast as thin films. Maintaining the fluorescence of these polymers from solution to the solid state requires suppression of the stacking interactions that lead to self-quenching and excimer formation in condensed phases.³ We have shown that the incorporation of rigid, scaffold-like moieties into the polymer is an effective means of isolating the polymer backbones from each other.⁴ Thus, films of pentiptycene-containing poly(*p*-phenyleneethynylene)s such as **1** exhibit high fluorescent quantum yields and spectra that are shifted only slightly from solution to the solid state.^{2b}



The usefulness of iptycene functional groups motivated us to explore more general methods of incorporating them into conducting polymers. Specifically, we were interested in the possibility of creating polymers in which all the monomer subunits are derived from iptycenes. Synthesis of polymers of this type via palladium-catalyzed coupling reactions necessitates both diethynyl- and diiodoptycene monomers. While the diethynylpentiptycene, **2a**, was available from our

previous studies, there existed no established method for obtaining an analogous halogenated monomer such as the pentiptycene, **2b**, or the triptycene, **5**. We have therefore pursued the syntheses of these monomers as well as that of the diiodothiophene monomer **10**. An additional incentive for targeting such monomers is that, while acetylene compounds have limited synthetic scope, aryl iodides are useful in numerous cross-coupling methodologies including Suzuki, Stille, and Heck reactions.⁵ Thus, with halogenated monomers in hand, a broad range of iptycene-based conducting polymers potentially become accessible, including poly(*p*-phenylene)s and poly(*p*-phenylenevinylene)s.

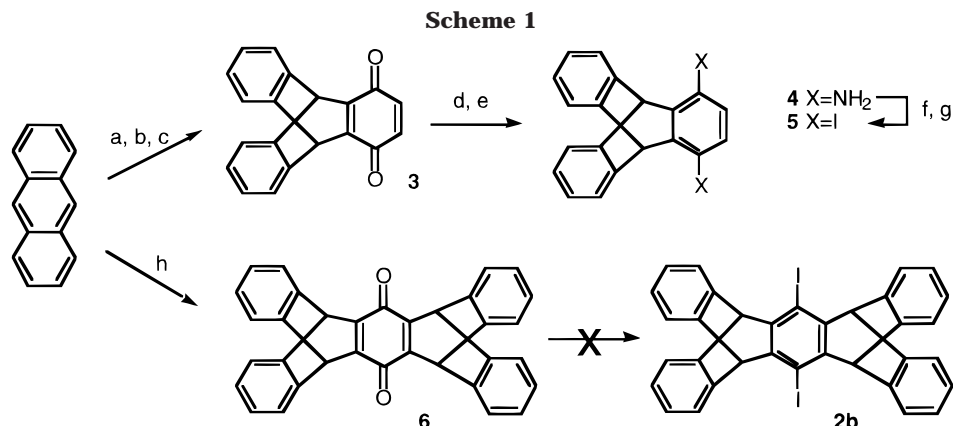
Results and Discussion

The synthesis of monomer **5** is outlined in Scheme 1. The triptycene quinone, **3**, was obtained by the reaction of benzoquinone with anthracene in xylenes, followed by tautomerization and oxidation. The conversion of the quinone, **3**, via the corresponding dioxime to the diaminoptycene, **4**, and the subsequent tetraazotization of this product were carried out according to the method of Bartlett.⁶ Reaction of the tetraazonium intermediate with potassium iodide yielded **5** in 38% yield.

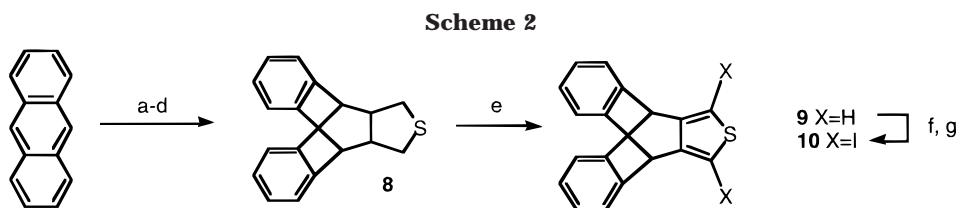
The pentiptycene dione, **6**, was obtained in 84% yield via a one-pot reaction of anthracene and benzoquinone in refluxing acetic acid. This method is a considerable improvement over our previously reported two-step synthesis,^{2b} which gave **6** in only 39% yield and required a difficult separation of **3** and **6**. Unfortunately, efforts to obtain the diiodo monomer **2b** from **6** using the approach outlined for the triptycene, **5**, were unsuccessful due to the lower reactivity of the pentiptycene dione.

The synthesis of the diiodothiophene analogue **10** is shown in Scheme 2. The tetrahydrothiophene **8** was prepared according to literature procedures in three steps from the Diels–Alder adduct of anthracene and maleic anhydride.⁷ Oxidation of **8** with DDQ in refluxing toluene yields the thiophene, **9**, which was then converted to **10** in 82% yield by sequential treatment with mercury(II) acetate and I₂.

The utility of **5** as a precursor to poly(aryleneethynylene)s was demonstrated by its copolymerization with a number of 2,5-dialkoxy-1,4-diethynylbenzenes.

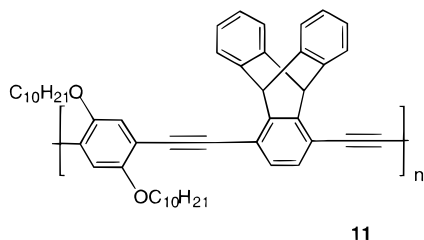


^a Benzoquinone, xylenes. ^b AcOH, HBr (cat.). ^c KBrO₃. ^d NH₂OH·HCl, EtOH. ^e SnCl₂, HCl/EtOH. ^f NaNO₂, AcOH, H₂SO₄, H₂O. ^g KI. ^h Benzoquinone, AcOH.



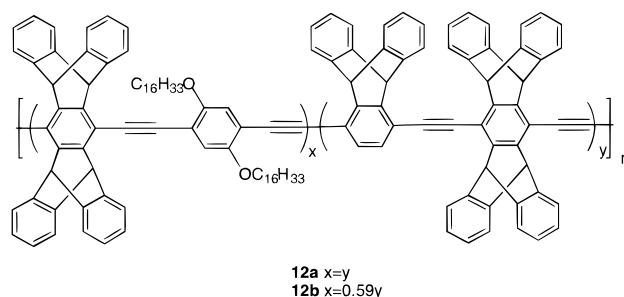
^a Maleic anhydride, dioxane. ^b LiAlH₄, THF. ^c TsCl, pyridine. ^d Na₂S·9H₂O, DMSO. ^e DDQ, toluene. ^f Hg(OAc)₂, CH₂Cl₂. ^g I₂.

This diiodide was observed to react rapidly with dialkynes under standard conditions² to yield polymers with degrees of polymerization up to 85.^{8,9} For example, coupling of **5** with 1,4-diethynyl-2,5-dihexadecyloxybenzene afforded polymer **11** ($M_n = 25\,000$, $M_w = 83\,000$).¹² It is instructive to compare the properties of this triptycene-containing polymer with its pentiptycene analogue **1**. A useful measure of the ability of different functional groups to prevent association is to compare the changes in the emission and absorption spectra of the polymers on going from solution to the solid state (Figure 1a). While the emission maximum of thin films¹³ of **1** is red-shifted by only 3 nm relative to the maximum in solution, the fluorescence of **11** undergoes a shift of 14 nm in the solid state. This most likely reflects the lower efficiency of triptycene groups at sequestering polymer chains than the sterically more demanding pentiptycene group. The spectra of structurally analogous poly(*p*-phenyleneethynylene)s that lack iptycene functional groups show a somewhat larger red shift (18 nm) and greater broadening when the polymers are cast as films.



Attempts to synthesize "all-iptycene" polymers were hampered by the low solubility of the coupled products. Thus, despite our previous observation that iptycene groups increase the solubility of polymers such as **1**, reaction of **2a** with **5** yielded only sparingly soluble oligomers. Although we were unable to produce soluble all-iptycene polymers of this kind, it was possible to synthesize random terpolymers in which iptycene groups

accounted for considerably more than 50% of the monomer units. For example, polymerization of **2a**, **5**, and 1,4-diiodo-2,5-dihexadecyloxybenzene in 2:1:1 and 2.7:1.7:1 ratios yielded polymers **12a** ($M_n = 54\,000$, $M_w = 283\,000$) and **12b** ($M_n = 44\,000$, $M_w = 312\,000$), respectively.¹³ These polymers represent a compromise between the advantageous spectroscopic features derived from maximizing the iptycene content of the polymers and the solubilizing ability of flexible side chains.



The solid-state and solution absorption and emission spectra of polymers **1**, **12a**, and **12b** are shown in Figure 1.¹⁴ The absorption spectra of these polymers show significant changes relative to one another and between solution and the solid state. The sensitivity of the absorption spectra to polymer composition is particularly striking in the case of the lowest energy band at 441 nm. This band appears as the principal absorption in polymer **1** and shrinks successively in **12a** and **12b** as the number of chromophores associated with dialkoxybenzene groups decreases in the polymers. This result is consistent with the dialkoxybenzene groups producing a lower local band gap than the iptycene monomers.

In contrast, the solution emission spectra of the terpolymers are remarkably similar both to each other and to that of the parent polymer **1**. The relative insensitivity of the fluorescence to polymer structure

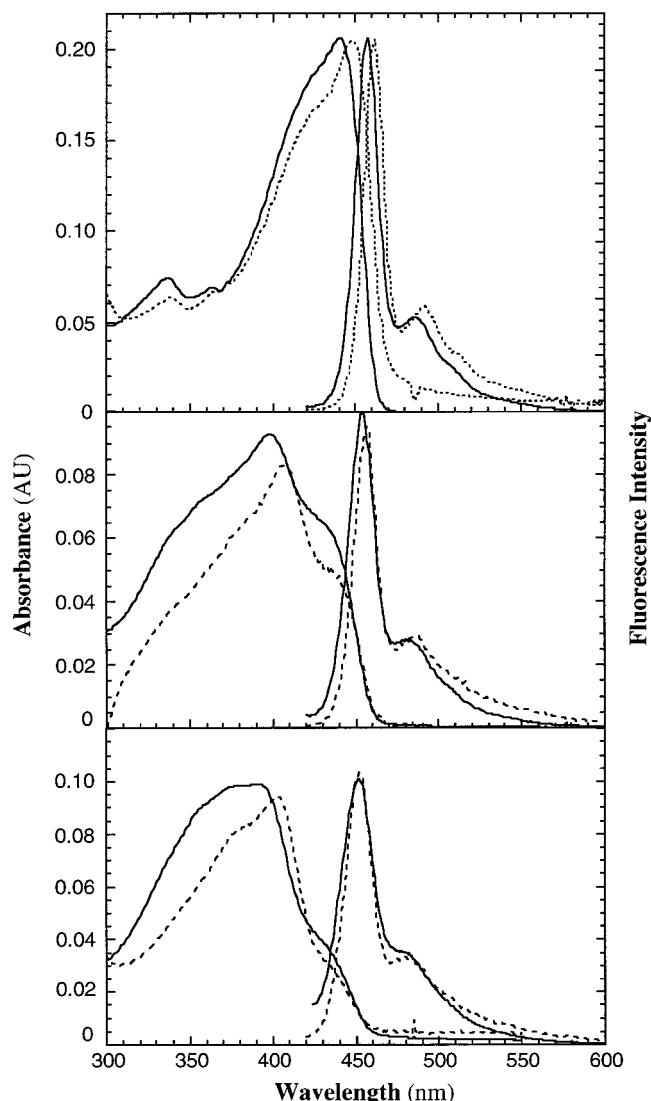


Figure 1. Absorption and emission spectra of (A) **1**, (B) **12a**, and (C) **12b** in dichloromethane (solid lines) and in spin-cast films (broken lines).

suggests that emission takes place from similar chromophore units within the polymers. In all cases, there is only a small (<2 nm) shift between the solution and thin film maxima. The largest perturbation is observed for **1**, which conforms to the expectation that decreasing the iptycene content (relative to **12a** or **12b**) increases the interaction of the polymer chains in the solid state.

The thin film fluorescence quantum yields of these polymers also reflect the varying degrees of chromophore interactions in the solid state. Thus, while $\phi_F = 0.09 \pm 0.03$ for **11**, the pentiptycene-containing polymers **12a** and **12b** exhibited fluorescence quantum yields of 0.22 ± 0.05 and 0.30 ± 0.04 , respectively.¹⁵

In contrast to the results obtained from monomers **2b** and **5**, Sonogashira–Hagihara coupling of the diiodothiophene monomer **10** with **2a** in dichloromethane¹⁶ afforded polymer **13** ($M_n = 22\,000$, $M_w = 37\,000$), which was slightly soluble in chloroform, toluene, and THF but exceedingly soluble in dichloromethane. This represents the first example of a soluble poly(aryleneethynylene) composed entirely of iptycene monomer units. The solubility of **13** is unusual in that it does not arise from flexible side chains, as is typically the case for conjugated polymers; rather, its solubility appears to derive

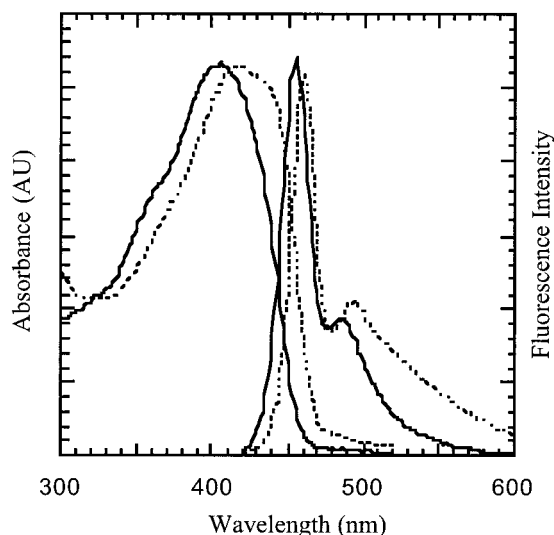
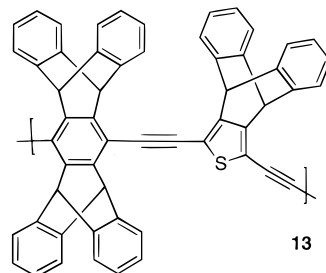


Figure 2. Absorption and emission spectra of polymer **13** in dichloromethane (solid lines) and spin-cast films (broken lines).

from both its nonlinearity and the high concentration of iptycene groups.¹⁷ That nonlinearity¹⁸ is a necessary feature is suggested by the relative insolubility of the coupling products of **5** with the analogous triptycene, **2a** (vide supra). It also seems likely that the possibility for syn–anti conformational isomerism with respect to thiophene groups on adjacent repeat units may provide crucial disorder that prevents **13** from crystallizing. However, these factors, which derive from the geometry of thiophene monomer, are insufficient by themselves to create a soluble polymer, since reaction of **2a** with 2,5-diiodothiophene yielded only insoluble products. Hence, the ability of iptycene groups to inhibit chain interactions also appears to be an integral feature of the solubility of **13**.

The absorption and emission spectra of **13** are shown in Figure 2. Somewhat surprisingly, this polymer shows a larger perturbation from solution to the solid state than **12a** or **12b**, despite its higher iptycene content. The red shift observed for both thin film spectra of **13** suggests that there are significant polymer interactions in the solid state (vide supra). This feature, coupled with the low luminescence of **13**, may limit the usefulness of this polymer in sensory applications.



The results reported herein demonstrate the utility of monomers **5** and **10** as precursors to arylenethynylene polymers. For the first time, we have been able to synthesize soluble polymers that are composed primarily (75–100%) from iptycene monomer units. We are currently undertaking the detailed investigation of the photophysical properties of these polymers, as well as exploring the chemistry of other conducting polymers derived from diiodoptycene monomers.

Experimental Section

General Methods. NMR (^1H and ^{13}C) spectra were recorded on a Varian 300 MHz spectrometer, and chemical shifts are reported in ppm relative to TMS (^1H spectra) or to CHCl_3 (^{13}C spectra). The molecular weights of polymers were determined using a Plgel 5 mm Mixed-C (300×7.5 mm) column and a diode array detector at 254 nm at a flow rate of 1.0 mL/min. Molecular weights are reported relative to polystyrene standards purchased from Polysciences, Inc. Spin casting was carried out on a Lavall Technologies WS-400-6NPP\Lite spin coater. Polymer films were cast on microscope cover glass (18×18 mm) at 3000 rpm from 0.5 mg/mL solutions of polymer in toluene, chloroform, or dichloromethane. Mass spectra were determined with a Finnigan MAT 8200 system using sector double focus and an electron impact source with an ionizing voltage of 70 V. Fluorescence studies were carried out with a SPEX Fluorolog-t2 fluorometer (model FL112, 450 W xenon lamp). Polymer thin film spectra were recorded by front-face (22.5°) detection. Thin film fluorescence quantum yields were determined relative to $\sim 10^{-3}$ M films of 9,10-diphenylanthracene in poly(methyl methacrylate) (PMMA) ($\phi_F = 0.83$).^{3b} Monochromators were corrected by lamp output and a water Raman scan. UV spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer.

Materials. All solvents were spectral grade unless otherwise noted. Silica gel (40 mm) was obtained from J. T. Baker. Anhydrous toluene, THF, dichloromethane, and diisopropylamine were purchased from Aldrich Chemical Co., Inc. 2,3-Dichloro-4,5-dicyanobenzoquinone (DDQ), obtained from Aldrich, was recrystallized from chloroform before use. $\text{Pd}(\text{PPh}_3)_4$ was obtained from Strem Chemicals, Inc. All other reagents were obtained from Aldrich and used without further purification.

1,4-Diiodotriptycene (5). To a suspension of the hydrochloride salt of **4** (0.45 g, 1.26 mmol) in 30 mL of glacial acetic acid cooled to 5°C was added a similarly cooled mixture of 20 mL of concentrated sulfuric acid, 20 mL of acetic acid, and 14 mL of water. Sodium nitrite (0.45 g) was slowly added to this solution, with care being taken to maintain the temperature below 10°C . The resulting red solution was stirred at 5°C for 1 h and then poured into an aqueous solution of potassium iodide (1 g in 100 mL). This mixture was stirred at room temperature overnight. The solid product was collected via filtration, washed with hot water, and purified by column chromatography on silica with an eluent gradient of 100% hexanes to 100% dichloromethane. The product was then recrystallized from ethanol to yield 0.24 g of white solid (38% yield). ^1H NMR (300 MHz, CDCl_3): δ 7.50 (dd, $J = 3.0$ Hz, 5.1 Hz, 4H), 7.13 (s, 2H), 7.08 (dd, $J = 3.0$ Hz, 5.1 Hz, 4H), 5.80 (s, 2H). ^{13}C NMR (75 MHz, CDCl_3): δ 59.0, 94.3, 124.2, 125.9, 136.5, 144.3, 150.0. MS (EI): m/z 508 ($\text{M}^+ + 2$, 2), 507 ($\text{M}^+ + 1$, 22), 506 (M^+ , 100), 252 ($\text{M}^+ - \text{I}_2$, 96). HRMS calcd for $\text{C}_{20}\text{H}_{12}\text{I}_2$ (M^+), 505.9029; found, 505.9024; mp $253.5\text{--}255^\circ\text{C}$. Anal. Calcd for $\text{C}_{20}\text{H}_{12}\text{I}_2$: C, 47.46; H, 2.39; I, 50.15. Found: C, 47.63; H, 2.21; I, 50.15.

4,9-Dihydro-4,9-benzonaphtho[2,3,c]thiophene (9). A solution of **8** (1.0 g, mmol) and 2,3-dichloro-4,5-dicyanobenzoquinone (2.5 g, 9.47 mmol) in 50 mL of toluene was stirred at reflux for 2 h. The solution was then cooled and filtered through silica gel. The solvent was removed under reduced pressure, and the black residue was purified on a silica column of 15% dichloromethane/hexanes to yield 1.77 g of white solid (72% yield). ^1H NMR (300 MHz, CDCl_3): δ 7.34 (dd, $J = 3.0$ Hz, 5.4 Hz, 4H), 7.02 (dd, $J = 3.0$ Hz, 5.4 Hz, 2H), 6.88 (s, 2H), 5.32 (s, 2H). ^{13}C NMR (75 MHz, CDCl_3): δ 147.1, 145.3, 125.6, 123.9, 114.6, 50.3. MS (EI): m/z 262 ($\text{M}^+ + 2$, 6.5), 261 ($\text{M}^+ + 1$, 22), 260 (M^+ , 99), 252 ($\text{M}^+ - 1$, 100); mp 286°C (lit.: 268°C).¹⁹

2,3-Diiodo-4,9-dihydro-4,9-benzonaphtho[2,3,c]thiophene (10). To a solution of **9** (0.1 g, 0.38 mmol) in 6 mL of dichloromethane was added 0.375 g of $\text{Hg}(\text{O}_2\text{CCF}_3)_2$. The resulting solution was stirred at room temperature (RT) for 2 h, then 1.0 g of I_2 (3.9 mmol) was added, and the solution was stirred at RT overnight. The mixture was then poured into a 40 mL of aqueous potassium iodide solution (10 wt %), which was

extracted with 3×20 mL of dichloromethane. The combined organic extracts were washed with 30 mL of $\text{KOH}_{(\text{aq})}$ and 20 mL of brine, dried (MgSO_4), and evaporated to yield a white solid. This product was further purified on a silica column with 10% dichloromethane/hexanes to yield 0.161 g of white solid (82% yield). ^1H NMR (300 MHz, CDCl_3): δ 7.39 (dd, $J = 3.3$ Hz, 4.4 Hz, 4H), 7.06 (dd, $J = 3.3$ Hz, 4.4 Hz, 4H), 5.15 (s, 2H). ^{13}C NMR (75 MHz, CDCl_3): δ 153.2, 144.1, 126.1, 124.3, 68.2, 51.7. MS (EI): m/z 514 ($\text{M}^+ + 2$, 1.7), 513 ($\text{M}^+ + 1$, 14), 512 (M^+ , 38), 385 ($\text{M}^+ - \text{I}$, 27), 258 ($\text{M}^+ - \text{I}_2$, 100). HRMS calcd for $\text{C}_{18}\text{H}_{10}\text{I}_2\text{S}$ (M^+), 511.8590; found, 505.8593; mp $256\text{--}257.5^\circ\text{C}$.

Polymers 12a, 12b, and 13. A general procedure is illustrated by the synthesis of polymer **12a**. Under an atmosphere of argon, diisopropylamine/toluene (0.5 mL/1 mL) was added to a 10 mL Schlenk flask containing compound **2a** (20 mg, 0.0404 mmol), **5** (10.5 mg, 0.020 mmol), 2,5-diiodo-1,4-dihexadecyloxybenzene (16.1 mg, 0.020 mmol), CuI (2 mg, 0.01 mmol), and $\text{Pd}(\text{PPh}_3)_4$ (3 mg, 0.0026 mmol). This mixture was heated at 65°C for 3 days and cooled, and the solvent was removed. The solid was redissolved in chloroform, washed with an aqueous solution of ammonium chloride, and dried (MgSO_4), and the solvent was removed in vacuo. The residue was reprecipitated from chloroform into methanol and then from chloroform into acetone. The yellow solid was then washed thoroughly with hot acetone. **11:** Yield 53%. ^1H NMR (300 MHz, CDCl_3): δ 7.53 (br, 4H), 7.20 (br, 4H), 7.06 (br, 4H), d 6.20 (br, 2H), 4.26 (br, 4H), 2.10 (br, 4H), 1.64 (br, 4H), 1.41 (br, 4H), 1.21 (br, 20H), 0.85 (br, 6H). $M_n = 25\,000$, $M_w = 83\,000$. Anal. Calcd for $\text{C}_{50}\text{H}_{54}\text{O}_2$: C, 87.42; H, 7.92. Found: C, 81.92; H, 8.01. **12a:** Yield 78%. ^1H NMR (300 MHz, CDCl_3): δ 7.78 (br, 4H), 7.55 (br, 22 H), 7.2 (br, 2H), 7.08 (br, 16 H), 6.60 (br, 2H), 6.20 (br, 8H), 4.5 (br, 4H), 2.28 (br, 4H), 1.80 (br, 4H), 1.50 (br, 4H), 1.25 (br, 44H), 0.88 (br, 6H). $M_n = 99$ kDa, $M_w = 337$ kDa. Anal. Calcd for $\text{C}_{134}\text{H}_{120}\text{O}_2$: C, 91.32; H, 6.86. Found: C, 85.10; H, 6.82. **12b:** Yield 79%. ^1H NMR (300 MHz, CDCl_3): δ 7.75 (br, 8H), 7.55 (br, 44 H), 7.20 (br, 2H), 7.08 (br, 26 H), 6.58 (br, 4H), 6.2 (br, 12H), 4.5 (br, 4H), 2.28 (br, 4H), 1.8 (br, 4H), 1.5 (br, 4H), 1.25 (br, 44H), 0.88 (br, 6H). $M_n = 33$ kDa, $M_w = 99$ kDa. Anal. Calcd for $\text{C}_{175}\text{H}_{142}\text{O}_2$: C, 92.31; H, 6.29. Found: C, 83.50; H 6.13. **13:** Yield 62%. ^1H NMR (300 MHz, CD_2Cl_2): δ 7.68 (br, 4H), 7.50 (br, 8H), 7.22 (br, 4H), 7.05 (br, 8H), 6.05 (br, 4H), 5.89 (br, 2H). $M_n = 14.5$ kDa, $M_w = 49$ kDa. Anal. Calcd for $\text{C}_{56}\text{H}_{30}\text{S}$: C, 91.52; H, 4.12; S, 4.36. Found: C, 84.50; H, 4.08; S, 3.07.

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Supporting Information Available: ^1H NMR spectra of polymers **11–14**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (8) All polymer molecular weights reported herein were determined by GPC analysis calibrated against polystyrene standards.
- (9) GPC analysis of poly(*p*-phenyleneethynylene)s generally overestimates the molecular weights of these rigid-rod polymers at low degrees of polymerization.¹⁰ At higher molecular weights ($>5 \times 10^4$), however, weights determined by GPC have been shown to be in good agreement with values obtained by light scattering experiments.¹¹ ¹H NMR analyses of these polymers show no evidence of end groups, suggesting degrees of polymerization greater than ~ 20 .
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- (12) The polydispersities of polymers **11**, **12a**, and **12b** are all extremely high (i.e. >3), presumably due to heterogeneous conditions during the course of the polymerization reactions. In all cases, at least partial precipitation of the polymer from the reaction mixture was observed during the polymerization.
- (13) Analysis of the ¹H NMR spectra of **12a** and **12b** did not provide significant insight into the regioregularity of these polymers. However, given that similar kinetics were observed for polymerization of either dialkoxy-diodobenzene monomers or **5** with diethynylbenzenes, it seems likely that the polymers will be largely regiorandom.
- (14) The data shown for polymer **1** were initially published in ref 2a.
- (15) Reported errors in quantum yields correspond to one standard deviation of values obtained from 3 to 4 trials.
- (16) Attempts to obtain polymer **12** in solvents such as THF or toluene led to smaller oligomeric materials, presumably due to the lower solubility of the coupled products in these solvents.
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