Conjugated Polymers with Geminal Trifluoromethyl Substituents Derived from Hexafluoroacetone

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Received April 17, 2006; Revised Manuscript Received June 20, 2006

ABSTRACT: Convenient syntheses of 9,9-bis(trifluoromethyl)fluorene and 6,6,12,12-tetakis(trifluoromethyl)indenofluorene are reported. These compounds are readily prepared in two steps from simple halo-aromatics and hexafluoroacetone, which serves as the source of the geminal trifluoromethyl groups. Iodination yields polymerizable monomers that were used to prepare several conjugated polymers. The photophysical properties of these polymers are reported. The polymers demonstrate slightly blue-shifted UV−vis absorption and fluorescence emission spectra as well as high solution and solid-state fluorescence quantum efficiencies. Polymer photobleaching experiments reveal that poly(fluorene)s with geminal trifluoromethyl substituents demonstrate greater photooxidative stability than poly(9,9-dioctyfluorene).

Introduction

There is current interest in the development of highly emissive, conjugated polymer-based materials for display applications such as components of polymer light-emitting diodes (PLEDs).1 For these applications, it is important to have pure color emission, high charge-carrier mobility, stability to oxidizing environments, processability (solubility), and efficient photoluminescence (PL) and electroluminescence (EL). Poly-(fluorene)s have become prime candidates for blue PLED applications because they have demonstrated many of these characteristics.2 Unfortunately, poly(fluorene)s lack the high stability to oxidizing environments that is required for many commercial applications. Degradation of these polymers can result in the appearance of a blue-green emission that is undesirable for display applications.3 This spectral feature has been attributed to the formation of fluorenone defects in the polymer that serve as low-energy charge trapping sites for mobile excitons.3a The oxidative processes greatly reduce the polymer PL or EL yield; this can limit the operating lifetime of a poly(fluorene) in a PLED display.

To increase the stability of poly(fluorene)s to oxidation, many have investigated the incorporation of bulky groups into poly-(fluorene)s to minimize interpolymer aggregation or to impede the oxidation process.4 Substitution at the 9-position of fluorene does not interrupt conjugation along the extended aromatic π-system of poly(fluorene). Endo et al. have synthesized poly-(fluorene)s with perfluoroalkyl substituents at some of the 9-positions in an attempt to increase the stability of poly-(fluorene)s to spectral changes through minimization of inter-polymer interactions.5 This was achieved by a postpolymerization perfluoroalkylation of a fluorene/9,9-dialkylfluorene copolymer. Holmes et al. have reported that a CF3-substituted poly(phenylenevinylene) (PPV) shows increased stability to photooxidation than an unsubstituted PPV.6 Our group has also reported several highly electron-deficient conjugated polymers that demonstrate very high stability toward photooxidation processes.7

As part of an ongoing research effort in this area, we were interested in developing a route to poly(9,9-perfluoroalkylfluorene) that does not require any postpolymerization synthetic chemistry. We have prepared a new poly(fluorene) monomer, 3, that presents geminal-trifluoromethyl (gem-CF3) groups at the 9-position of fluorene. One motivation for the design of this monomer is that the gem- CF3 groups can be derived from hexafluoroacetone. This versatile reagent has a long history at DuPont,8 and its derivatives are finding utility in areas such as chemical sensing9 and in some electronics applications.10 Herein, we report an efficient synthetic route to 9,9-bis-(trifluoromethyl)fluorene, 2, and its incorporation into several new conjugated polymers. We also prepare the related indeno- fluorene, 6, and its 1:1 copolymer with 9,9-dioctyfluorene by a similar synthetic route. We demonstrate that the incorporation of the gem-CF3 substituents yields polymers with slightly blue-shifted UV−vis absorption and fluorescence emission spectra and high solution and solid-state fluorescence quantum yields. Poly(fluorene)s with gem-CF3 substituents demonstrate enhanced stability toward photooxidation.

Results and Discussion

Monomer Synthesis. The synthetic route to the desired 2,7-diodo-9,9-bis(trifluoromethyl)fluorene monomer, 3, is illustrated in Scheme 1. Lithiation of a commercially available 2-iodo-substituted biphenyl with n-butyllithium and quenching of the generated organometallic species with hexafluoroacetone results in the formation of a 2-hexafluoro-2-propanol (HFIP)-substituted biphenyl, compound 1 (80% yield). It was initially suspected that treatment of 1 with a strong acid, a dehydrating agent, or a Lewis acid would result in facile Friedel−Crafts cyclization to yield the desired 9,9-bis(trifluoromethyl)fluorene, 2. This did
not prove to be the case, as the generated carbocation underwent isomerization instead of the desired cyclization. Such isomerizations have been described elsewhere.\textsuperscript{11} Initial investigations of the chemistry of the HFIP group by Cassidy and co-workers have reported their poor reactivity toward Friedel–Crafts reactions.\textsuperscript{12} After an attempt to prepare the chloride from alcohol 1, we discovered that treatment of 1 with an excess of thionyl chloride and pyridine as a base results in efficient cyclization (83\% yield) to the desired gem-CF\textsubscript{3} substituted fluorene, 2.\textsuperscript{13} One particularly attractive feature of this synthesis is that the gem-CF\textsubscript{3} substituents at the 9-position of the fluorene are not installed by the commonly employed fluorene deprotonation and alkylation strategy. The presence of 9-monoalkylfluorene contaminants in poly(9,9-dialkylfluorene)s contribute greatly to the alkylation strategy. The presence of 9-monoalkylfluorene contaminants in poly(9,9-dialkylfluorene)s contribute greatly to the reported spectral changes and polymer degradation processes.\textsuperscript{14} To prepare conjugated polymers derived from compound 2, it was necessary to install halogens at the 2,7-positions of the fluorene. Iodination of compound 2 with N-iodosuccinimide under acidic conditions afforded the 2,7-diiodo-substituted fluorene, 3, in good yield (55\%).

**Photophysical Properties of Compound 2.** Figure 1 presents the solution-state UV–vis absorption and fluorescence emission spectra of compound 2. For comparison, we also show the absorption and emission spectra of its hydrocarbon analogue, 9,9-dimethylfluorene.\textsuperscript{15} From the data, we find that the presence of the gem-CF\textsubscript{3} groups at the 9-position results in no major perturbation of UV–vis absorption \(\lambda_{max}\) (267 nm for 2, 265 nm for 9,9-dimethylfluorene) while there are some more significant differences in the fluorescence emission \(\lambda_{max}\) (322 nm for 2, 306 and 316 nm for 9,9-dimethylfluorene). We also find that 9,9-dimethylfluorene presents two peaks at 295 and 300 nm in its UV–vis absorption spectra,\textsuperscript{16} and the corresponding transitions are not apparent in the absorption spectra of 2. This observation is consistent with a previous report by Eaborn and Shaw, which reported that the intensity of the low-energy \(\pi-\pi^*\) transitions are greatly reduced in the ultraviolet absorption spectra of fluorenes with electron-withdrawing substituents located at the 9-position.\textsuperscript{17} In addition, the emission spectrum of 2 has a larger Stokes shift as well as less-resolved vibrational structure than that of 9,9-dimethylfluorene. The observed differences in the emission spectra of 2 may be attributed to excited-state interactions with the electron-withdrawing gem-CF\textsubscript{3} substituents.

**Synthesis of Indenofluorene Monomer 7.** The synthetic route to the 2,8-diiodo-6,6,12,12-tetrakis(trifluoromethyl)indenofluorene monomer, 7, is illustrated in Scheme 2. Treatment of 1,4-dibromo-2,5-diodobenzene (4) with phenylmagnesium bromide (5 equiv) results in the formation of a 2,5′-substituted p-terphenyl di-Grignard\textsuperscript{18} that is quenched with excess hexafluoroacetoacetone to afford compound 5 in 23\% yield. Heating compound 5 with an excess of thionyl chloride and pyridine provides the desired tetrakis(trifluoromethyl)-substituted indenofluorene, 6 (66\% yield). Iodination of compound 6 with N-iodosuccinimide under acidic conditions affords the 2,8-diiodo-substituted indenofluorene, 7, in 29\% yield.

**Photophysical Properties of Compound 6.** Figure 2 presents the solution-state UV–vis absorption and fluorescence emission spectra of compound 6. The absorption and fluorescence emission \(\lambda_{max}\) of compound 6 (308 and 357 nm, respectively) are red-shifted with respect to fluorene 2, as is expected from an extended conjugated system. Similar to the case of 2, the absorption spectrum of 6 shows a reduction in the intensity of the lowest energy \(\pi-\pi^*\) transition (324 nm) when compared to reported spectra for an unsubstituted indenofluorene.\textsuperscript{19} The fluorescence emission spectrum of compound 6 also shows a larger Stokes shift as well as less-resolved vibrational structure than an unsubstituted indenofluorene. These spectral changes are consistent with those observed for compound 2 and are attributed to the effect of the electron-withdrawing gem-CF\textsubscript{3} substituents located at the 6- and 12-positions of indenofluorene 6.
Polymer Synthesis. The 2,7-diiodo-substituted fluorene monomer 3 was incorporated into several conjugated polymers (Scheme 3). Poly(fluorene) P1 was prepared by the method of Yamamoto using a zerovalent nickel complex. 20 Perhaps not surprisingly, this polymer demonstrates fairly poor solubility due to the lack of solubilizing side chains. The only soluble material from the polymerization were oligomers with a number-average molecular weight ($M_n$) of 4000 Da (degree of polymerization: 13). Polymer P2, a poly(phenylene ethynylene) (PPE), was prepared by a palladium-catalyzed Sonogashira—Hagihara cross-coupling polymerization of monomer 3 with a dialkynyl-substituted pentiptycene. 8,21 Similar PPEs have been studied extensively in our research group. In an effort to prepare a more soluble poly(fluorene) with higher molecular weight, polymer P3 was prepared by a Suzuki-type cross-coupling polymerization between monomer 3 and a commercially available 9,9-dioctylfluorene diboronate ester, 9. As expected, the incorporation of alkyl side chains increased the solubility of the polymer, and polymer P3 was isolated with higher molecular weight ($M_n = 12 000$ Da) than polymer P1.

The indenofluorene monomer 7 was polymerized by a Suzuki-type cross-coupling polymerization with monomer 9 to yield polymer P4 (Scheme 4). Although monomer 7 is sparingly soluble in organic solvents, P4 is soluble and was obtained with relatively high molecular weight ($M_n = 14 000$ Da).

Polymer Photophysical Properties. The polymer molecular weight data and photophysical properties are summarized in Figure 3 and Table 1. For comparison, we also report data for poly(9,9-dioctylfluorene) (P5) purchased from H.W. Sands Corp. Polymers P1 and P3 demonstrate blue-shifted UV—vis absorption and fluorescence emission spectra relative to polymer P5 as well as comparable solution and solid-state fluorescence quantum yields. We find that the low molecular weight polymer P1 demonstrates the bluest UV—vis absorption and fluorescence emission maxima of all of the polymers. The thin-film fluorescence emission spectrum from polymer P1 demonstrates some aggregate emission near 435 nm that could be due to its low molecular weight and poor film-forming properties. Polymer P3, which contains 50% of the $\text{gem}$-$\text{CF}_3$ substituted fluorene monomer, has absorption and emission spectra that lie in between those of P1 and P5. Polymer P4 presents very similar absorption and emission spectral features to polymer P3. The absorption and emission $\lambda_{\text{max}}$ of P4 are slightly red-shifted due to the indenofluorene framework. These photophysical results indicate that the incorporation of the $\text{gem}$-$\text{CF}_3$ substituted fluorene has only a minimal effect on the polymer UV—vis solution absorption and fluorescence emission characteristics.

![Figure 3](image-url)

**Figure 3.** UV—vis absorption and fluorescence emission spectra of polymers (a) P1, (b) P2, (c) P3, (d) P4, and (e) P5 in chloroform solution (solid lines) and as thin films (dotted lines).
Table 1. Polymer Molecular Weight and Photophysical Data

<table>
<thead>
<tr>
<th>poly</th>
<th>( M_n/\text{kDa} ) (PDI)</th>
<th>DP</th>
<th>( E_g/\text{eV}^a )</th>
<th>( \lambda_{\text{max,abs}}/\text{nm}, \lambda_{\text{max,em}}/\text{nm} )</th>
<th>Stokes shift/ ( \text{cm}^{-1} )</th>
<th>( \lambda_{\text{max,abs}}/\text{nm}, \lambda_{\text{max,em}}/\text{nm} )</th>
<th>Stokes shift/ ( \text{cm}^{-1} )</th>
<th>( \Phi_f^\text{C} (\text{CHCl}_3) )</th>
<th>( \Phi_f^d ) (film)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>4 (1.2)</td>
<td>13</td>
<td>3.06</td>
<td>362, 402, 424</td>
<td>2700</td>
<td>355, 410, 415, 435</td>
<td>0.99 ± 0.07</td>
<td>0.88 ± 0.14</td>
<td></td>
</tr>
<tr>
<td>P2</td>
<td>10 (4.0)</td>
<td>13</td>
<td>2.88</td>
<td>382, 418, 443</td>
<td>2300</td>
<td>384, 426, 450, 490</td>
<td>0.79 ± 0.03</td>
<td>0.15 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>P3</td>
<td>12 (1.8)</td>
<td>17</td>
<td>2.95</td>
<td>382, 410, 436</td>
<td>1900</td>
<td>386, 200, 419, 443</td>
<td>0.97 ± 0.06</td>
<td>1.18 ± 0.05</td>
<td></td>
</tr>
<tr>
<td>P4</td>
<td>14 (1.8)</td>
<td>15</td>
<td>2.90</td>
<td>398, 419, 443</td>
<td>1200</td>
<td>399, 423, 444, 449</td>
<td>0.96 ± 0.04</td>
<td>1.07 ± 0.13</td>
<td></td>
</tr>
<tr>
<td>P5</td>
<td>15 (3.4)</td>
<td>40</td>
<td>2.82</td>
<td>390, 417, 447</td>
<td>1600</td>
<td>392, 2800, 440, 461</td>
<td>0.97 ± 0.09</td>
<td>1.00</td>
<td></td>
</tr>
</tbody>
</table>

\( ^a \) The optical HOMO–LUMO energy gap is based on the low-energy onset in the solution-state UV–vis spectra. \( ^b \) The magnitude of the Stokes shift was calculated by \( \Delta = \lambda_{\text{max,em}} - \lambda_{\text{max,abs}} \). \( ^c \) Solution-state fluorescence quantum yields were determined using quinine sulfate in 0.1 N sulfuric acid (\( \Phi_f = 0.53 \)) as the fluorescence standard. \( ^d \) Thin-film fluorescence quantum yields of P1, P2, P3, and P4 are reported relative to P5; \( \Phi_f = 1.00 \) (lit. \( \Phi_f = 0.55 \)).

**Figure 4.** Time dependence of the fluorescence emission intensity of thin films of P1, P3, P4, and P5 under UV irradiation at 380 nm. The optical density of all of the polymer films at the irradiation wavelength was 0.10 ± 0.01.

This trend is also evident in the optical band gap data where an increase in gem-CF₃ substituted fluorene content corresponds with a slight widening of the band gap. The gem-CF₃ groups also appear to limit β-phase formation, as the thin-film absorption and emission spectra of polymers P3 and P4 are minimally red-shifted with respect to their solution-state spectra while a thin film of polymer P5 demonstrates the appearance of a small feature near 400 nm (3.1 eV) in the absorption spectrum as well as a significantly red-shifted emission spectrum with a well-resolved vibronic progression that can be attributed to β-phase formation.²⁰,²²

**Polymer Photobleaching.** To determine whether the incorporation of the gem-CF₃ groups could impart increased photostability for display applications, photobleaching experiments on thin films of the polymers were performed. Figure 4 compares the photooxidation of thin films of polymers P1, P3, P4, and P5. In these experiments, the polymer films were subjected to UV irradiation at 380 nm for extended periods under aerobic conditions. A 450 W xenon lamp was used as the irradiation source (excitation band-pass = 10 nm). The optical density of all of the polymer films were matched at 0.10 ± 0.01 at the irradiation wavelength (380 nm). The percent fluorescence intensity is calculated on the basis of the emission intensity at the emission \( \lambda_{\text{max}} \). From the data, we find that polymer P1 demonstrates the greatest photostability, maintaining ~65% of the initial fluorescence intensity after 30 min of irradiation. Polymer P5 demonstrates the most rapid photooxidative bleaching, with less than 30% of the initial intensity remaining after 30 min of irradiation. Polymer P3, the 1:1 copolymer of the gem-CF₃-substituted fluorene and 9,9-dioctyl-substituted fluorene monomers, is much less stable to photooxidation than P1 but displays slightly greater photostability than P5. Approximately 40% of the initial fluorescence intensity remains after 30 min of UV irradiation of this polymer. Polymer P4 demonstrates photobleaching behavior similar to that of polymer P3. The indenofluorene framework does not appear to impart any additional photooxidative stability to the polymer. In summary, the photobleaching experiments revealed that the gem-CF₃-containing polymers P1, P3, and P4 demonstrate greater stability than the parent poly(9,9-dioctyfluorene), P5. The homopolymer P1 demonstrates by far the highest stability toward photooxidation, while the copolymers P3 and P4 demonstrate only modest improvements in stability when compared to P5. These results indicate that although gem-CF₃ substitution at the 9-position of fluorene results in only minimal perturbations to the polymer spectral features, it does significantly increase the stability of the polymers to photooxidation.

Poly(9,9-dialkylfluorene)s are known to undergo oxidation at the 9-position of fluorene to form fluorenone defect sites that result in the appearance of an undesired blue-green emission in PLED devices. We observe the appearance of a broad, featureless, red-shifted emission from all four polymer films upon UV irradiation in the area-normalized fluorescence emission spectra (see Supporting Information). We suspect that the rate of photooxidation is perturbed by substitution of gem-CF₃ groups at this site. Interestingly, we find that during the first 5 min of irradiation the rate of photobleaching of polymers P3, P4, and P5 appears to be much more rapid than in the case of P1. The rate appears to slow after longer irradiation exposures, likely due to restricted oxygen transport to deeper levels in the films.

**Conclusion.** We have developed efficient synthetic routes to 9,9-bis(trifluoromethyl)fluorene and 6,6,12,12-tetrakis(trifluoromethyl)indenofluorene and have investigated their incorporation into several different conjugated polymers. We find that conjugated polymers which contain gem-CF₃-substituted fluorenes demonstrate blue-shifted UV–vis absorption and fluorescence emission spectra and slightly wider band gaps than a 9,9-dialkyl-substituted polyfluorene. Overall, perturbations to the polymer electronics due to the gem-CF₃ substituents at the 9-position of fluorene were minimal. Photobleaching experiments revealed that the gem-CF₃ groups significantly enhance the photostability of polyfluorene(s) to photooxidation. We are interested in the development of these new materials for highly stable PLED applications.

**Experimental Section**

**General Methods and Instrumentation.** All chemicals were of reagent grade from Aldrich Chemical Co. (St. Louis, MO), Strem Chemicals, Inc. (Newburyport, MA), or H.W. Sands Corp. (Jupiter,
FL) and used as received. All synthetic manipulations were performed under an argon atmosphere using standard Schlenk line or drybox techniques unless otherwise noted. Dimethylformamide (DMF) was distilled under reduced pressure over calcium hydride before use. Glassware was oven dried before use. Column chromatography was performed using Baker 40 μm silica gel. All organic extracts were dried over MgSO₄ and filtered prior to removal with a rotary evaporator. Compounds 4⁻⁸ and 8⁻¹ can be prepared by literature procedures.

¹H NMR, ¹³C NMR, and ¹⁹F NMR spectra were obtained on Varian Mercury (300 MHz), Bruker Avance-400 (400 MHz), and Varian Inova (500 MHz) instruments. NMR chemical shifts are referenced to CHCl₃/CDMS (7.27 ppm for ¹H, 77.23 ppm for ¹³C). For ¹⁹F NMR spectra, trichlorofluoromethane was used as an external standard (0 ppm), and upfield shifts are reported as negative values. In some cases, signals associated with the CF₃ groups and proximal quaternary centers were not reported in the ¹³C NMR spectra due to C–F coupling and low signal-to-noise ratios. High-resolution mass spectra (HRMS) were obtained at the MIT Department of Chemistry Instrumentation Facility (DCIF) using a peak-matching protocol to determine the mass and error range of the molecular ion. Fourier Transformed infrared (FT-IR) spectroscopy was performed on a Perkin-Elmer model 2000 FT-IR spectrophotometer using the Spectrum v. 2.00 software package.

All polymer solutions were filtered through 0.2 μm syringe filters prior to use. Polymer molecular weights were determined at room temperature on a HP series 1100 GPC system in THF at 1.0 mL/min (1 mg/mL sample concentrations) equipped with a diode array detector (254 and 450 nm) and a refractive index detector. Polymer molecular weights are reported relative to polystyrene standards. Polymer thin films were spin-cast from chloroform solution onto microscope coverslips (18 × 18 mm).

UV/vis spectra were recorded on an Agilent 8453 diode-array spectrophotometer and corrected for background signal with either a solvent-filled cuvette (for solution measurements) or a clean glass coverslip (for thin-film measurements). Emission spectra were acquired on a SPEX Fluorolog-r² fluorescence spectrometer (model FL-321, 450 W xenon lamp) using either right-angle detection (solution measurements) or front-face detection (thin-film measurements). Fluorescence quantum yields of solutions were determined by comparison to appropriate standards and are corrected for solvent refractive index and absorption differences at the excitation wavelength (366 nm). Fluorescence quantum yields of thin films are reported relative to polymer P5 (Φrel = 1.00) and are corrected for differences in absorbance at the excitation wavelength (380 nm).

Melting points were measured with a Meltemp II apparatus and are reported uncorrected.

**Compound 1.** Into a 250 mL round-bottom flask with a sidearm stopcock, a magnetic stirring bar, and a 50 mL addition funnel were added 5.6 g (20.0 mmol) of 2-isodioiphosphine and 50 mL of hexanes. The mixture was cooled to −78 °C, and 14 mL of a 1.6 M solution (22.4 mmol) of n-butyllithium in hexanes was added slowly dropwise over 1 h. After the addition was complete, the solution was allowed to warm to room temperature for 30 min. The addition funnel was quickly replaced with a Dewar-type condenser under nitrogen atmosphere with argon for several hours. A bubbler filled with 10% aqueous NaOH solution was used to trap the reactive vapor. The reaction mixture was treated with a 5% HCl solution (100 mL) and extracted with diethyl ether (300 mL). The organic extracts were washed with a 5% HCl solution (100 mL), water (300 mL), and brine (100 mL) and dried. The residue was purified by column chromatography (0⁻−20% ethyl acetate in hexanes) to yield 5.15 g (80%) of a crystalline solid; mp 52–53 °C. ¹H NMR (500 MHz, CDCl₃): δ 7.79 (m, 1H), 7.47 (m, 5H), 7.38 (m, 2H), 7.19 (m, 1H), 3.48 (s, 1H). ¹³C NMR (125 MHz, CDCl₃): δ 141.5, 140.0, 135.5, 129.4, 129.3, 129.0, 128.9, 128.2, 128.1, 126.7, 124.0, 121.7, 101.0, 966, 925, 763, 709, 661, 538. HRMS (EI): calcd for C₁₅H₁₄F₆O₂ (M⁺): 350.0630; found 350.0626. C₁₅H₁₄F₆O₂ (320.1): calcd C 56.26, H 3.15; found C 56.21, H 3.03%.
0.50 g (1.0 mmol) of 5, 4.0 mL (55 mmol) of thionyl chloride, and 0.9 mL (11 mmol) of pyridine. The reaction mixture was heated to 100 °C for 24 h. The reaction mixture was evaporated to dryness. The residue was purified by column chromatography (0–5% ethyl acetate in hexanes) to yield 0.31 g (66%) of a colorless powder; mp 283–284 °C (sublimes). 1H NMR (500 MHz, CDCl3): δ 8.14 (s, 2H), 7.89 (m, 2H), 7.83 (m, 2H), 7.63 (td, 2H, J = 1, 8 Hz), 7.48 (td, 2H, J = 1, 8 Hz). 13C NMR (125 MHz, CDCl3): δ 143.2, 141.7, 138.5, 130.5, 131.3, 129.1, 126.7, 121.7, 121.8, 118.9. 19F NMR (282 MHz, CDCl3): δ −68.4. FT-IR (KBr): w/cm−1: 1572, 1463, 1428, 1302, 1256, 1181, 1156, 1141, 1125, 1059, 1029, 979, 964, 887, 882, 722, 730, 684, 531. HRMS (EI): calcd for C2H4F2I2 (M+): 526.0585; found 526.0597. C12H10I2F2 (526.1): calcd C 45.70, H 1.68%. 

A general procedure is illustrated by the synthesis of polymer P3. Into a 25 mL Schlenk tube with a magnetic stirring bar were added 0.14 g (0.3 mmol) of Compound 7. A deoxygenated solution of 3:2 (v/v) toluene/diisopropylamine (0.60 mL) was then added. The tube was sealed and heated to 65 °C for 30 min. A solution of 10 mg (0.02 mmol) of compound 4 into 15 mL of methanol to remove any short oligomers. The material was then dissolved in dichloromethane and filtered through a 0.2 μm syringe filter. The material was dried under vacuum to yield a yellow solid (282 MHz, CDCl3): δ 6.99 (aromatic C–H), 6.01 (aromatic C–H), 8.08 (aromatic C–H), 8.14–8.06 (aromatic C–H), 8.04–7.82 (aromatic C–H), 7.74–7.60 (aromatic C–H), 2.22–1.94 (aliphatic C–H), 1.38–0.96 (aliphatic C–H), 0.95–0.64 (aliphatic C–H). 19F NMR (282 MHz, CDCl3): δ −68.2. FT-IR (KBr): w/cm−1: 2929, 2856, 1436, 1437, 1258, 1201, 1176, 1150, 981, 953, 890, 819, 751, 732, 668.

Acknowledgment. The authors thank the DuPont-MIT alliance for funding.

Supporting Information Available: Fluorescence emission spectra from polymer photobleaching experiments. This material is available free of charge via the Internet at http://pubs.acs.org.
We suggest that both the ready availability and low cost of the reagents (thionyl chloride and pyridine) make large-scale production of compound 2 feasible.


(a) Yang, J.-S.; Swager, T. M. J. Am. Chem. Soc. 1998, 120, 11864–11873. (b) Compound 8 was purchased from Nomadics Inc. (Stillwater, OK).


The complete 13C NMR spectrum was not obtained for compound 7 due to its very poor solubility.

Solvents were deoxygenated by vigorous argon bubbling for 20 min.