# Conjugated Polymers with Geminal Trifluoromethyl Substituents Derived from Hexafluoroacetone

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ABSTRACT: Convenient syntheses of 9,9-bis(trifluoromethyl)fluorene and 6,6,12,12-tetrakis(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-dioctylfluorene).

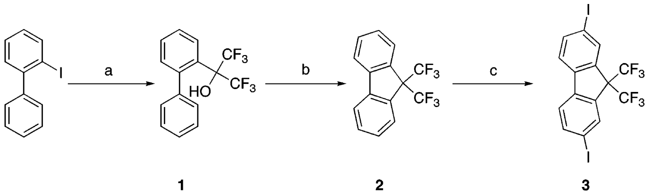
## Introduction

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 $\pi$-system of poly(fluorene)s. 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 interpolymer interactions.[5] This was achieved by a postpolymerization perfluoroalkylation of a fluorene/9,9-dialkylfluorene copolymer. Holmes et al. have reported that a $CF_3$-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)s that does not require any postpolymerization synthetic chemistry. We have prepared a new poly(fluorene) monomer, **3**, that presents geminal-trifluoromethyl (*gem*-$CF_3$) groups at the 9-position of fluorene. One motivation for the design of this monomer is that the *gem*-$CF_3$ 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 sensing[9] and in some electronics applications.[10]

**Scheme 1. Synthesis of Monomer 3**[a]



[a] (a) (i) *n*-BuLi, hexanes, −78 °C to RT, 0.5 h; (ii) hexafluoroacetone, −78 °C to RT, 3 h, 80%; (b) $SOCl_2$, pyridine, 100 °C, 48 h, 83%; (c) *N*-iodosuccinimide, AcOH, $H_2SO_4$, 65 °C, 18 h, 55%.

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 indenofluorene, **6**, and its 1:1 copolymer with 9,9-dioctylfluorene by a similar synthetic route. We demonstrate that the incorporation of the *gem*-$CF_3$ 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*-$CF_3$ substituents demonstrate enhanced stability toward photooxidation.

## Results and Discussion

**Monomer Synthesis.** The synthetic route to the desired 2,7-diiodo-9,9-bis(trifluoromethyl)fluorene monomer, **3**, is illustrated in Scheme 1. Lithiation of a commercially available 2-iodo-substitued 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

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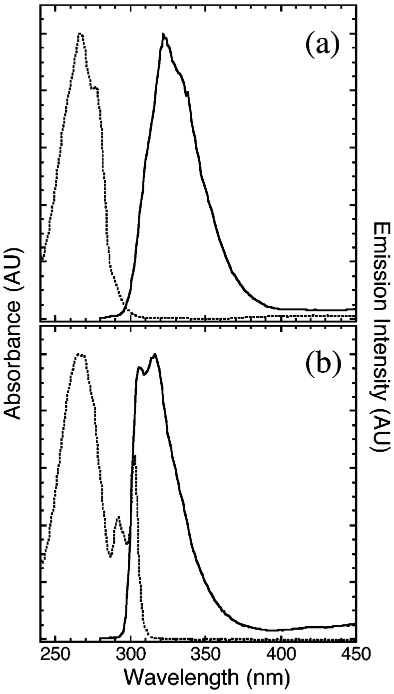
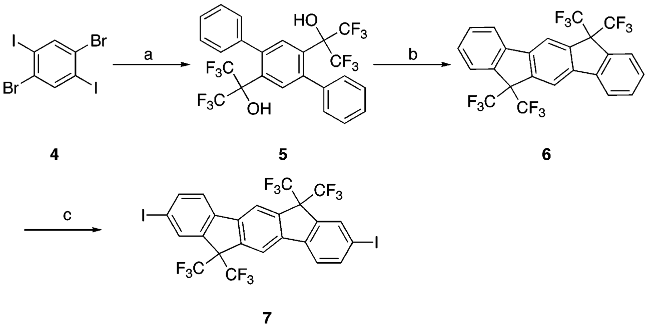


**Figure 1.** Absorption (dotted line) and fluorescence emission spectra (solid line) of (a) **2** and (b) 9,9-dimethylfluorene in chloroform solution.

not prove to be the case, as the generated carbocation underwent isomerization instead of the desired cyclization. Such isomerizations have been described elsewhere.[11] Initial investigations of the chemistry of the HFIP group by Cassidy and co-workers have reported their poor reactivity toward Friedel−Crafts reactions.[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*-$CF_3$ substituted fluorene, **2**.[13] One particularly attractive feature of this synthesis is that the *gem*-$CF_3$ 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 reported spectral changes and polymer degradation processes.[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.[15] From the data, we find that the presence of the *gem*-$CF_3$ 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,[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.[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*-$CF_3$ substituents.

**Scheme 2. Synthesis of Monomer 7**[a]



[a] (a) (i) PhMgBr, THF, 8 h; (ii) hexafluoroacetone, −78 °C to RT, 3 h, 23%; (b) $SOCl_2$, pyridine, 100 °C, 24 h, 66%; (c) *N*-iodosuccinimide, AcOH, $H_2SO_4$, 75 °C, 48 h, 29%.

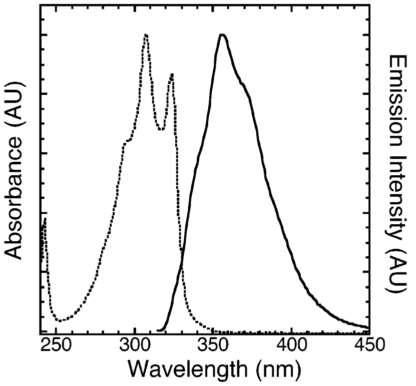
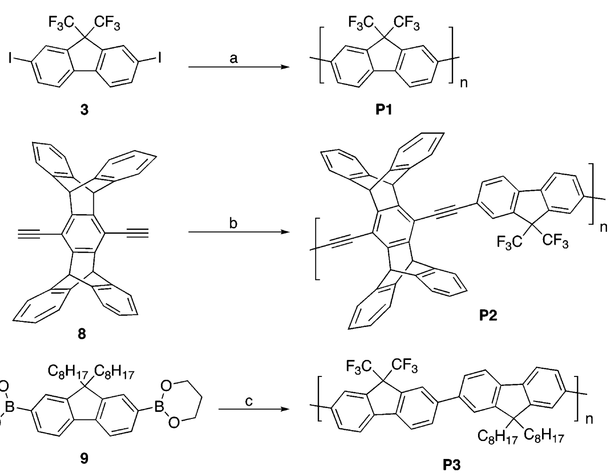


**Figure 2.** Absorption (dotted line) and fluorescence emission spectra (solid line) of **6** in chloroform solution.

**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[18] that is quenched with excess hexafluoroacetone 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.

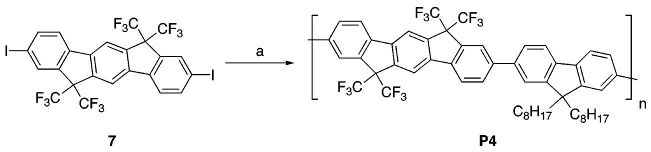
**Photophysical Properties of Compound 6.** Figure 2 presents the solution-state UV−vis absorption and fluorescence emission spectra of compound **6**. The absorption and fluorescence emission $\lambda_{max}$ of compound **6** (308 and 357 nm, respectively) are red-shifted with respect to fluorene **2**, 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.[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*-$CF_3$ substituents located at the 6- and 12-positions of indenofluorene **6**.

**Scheme 3. Synthesis of Conjugated Polymers with *gem*-$CF_3$ Substituents[a]**



[a] (a) $Ni(COD)_2$, 2,2′-bipyridyl, 1,5-cyclooctadiene (COD), DMF, toluene, 80 °C, 55% (polymer **P1**); (b) **3**, $Pd(PPh_3)_4$, CuI, toluene, $^iPr_2NH$, 65 °C, 35% (polymer **P2**); (c) **3**, $Pd(PPh_3)_4$, $K_2CO_3$, toluene, $H_2O$, Aliquat 336, 100 °C, 47% (polymer **P3**).

**Scheme 4. Synthesis of the Indenofluorene-Containing Polymer, P4[a]**



[a] (a) **9**, $Pd(PPh_3)_4$, $K_2CO_3$, toluene, $H_2O$, Aliquat 336, 100 °C, 39% (polymer **P4**).

**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 solublizing 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 $\lambda_{max}$ 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 *gem*-$CF_3$ 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 $\lambda_{max}$ of **P4** are slightly red-shifted due to the indenofluorene framework. These photophysical results indicate that the incorporation of the *gem*-$CF_3$ substituted fluorene has only a minimal effect on the polymer UV−vis solution absorption and fluorescence emission characteristics.

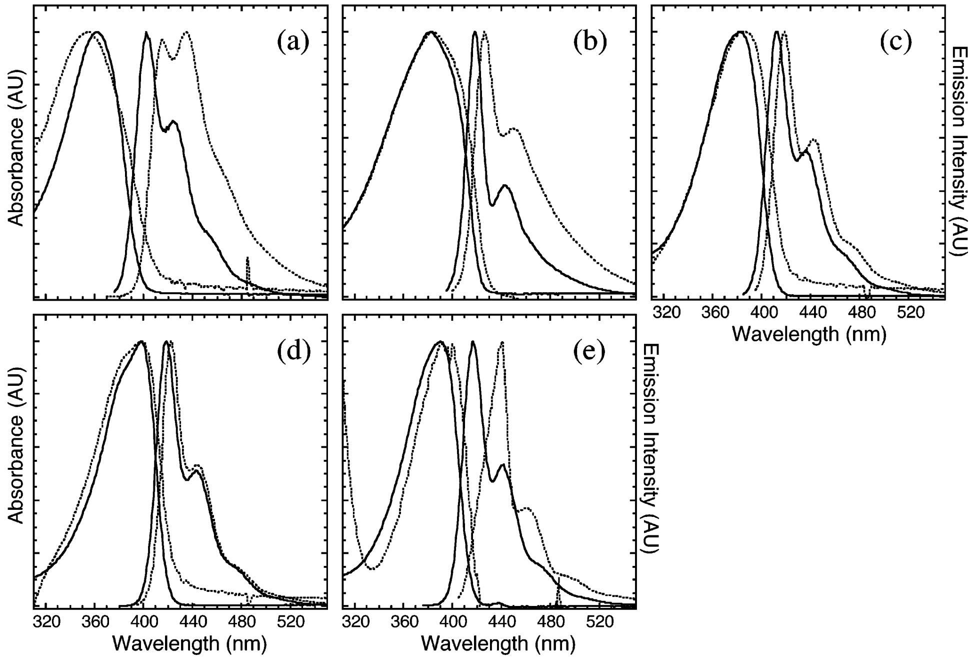


**Figure 3.** UV−vis absorption and fluorescence emission spectra of polymers (a) **P1**, (b) **P2**, (c) **P3**, (d) **P4**, and (e) **P5** in chloroform solution (solid lines) and as thin films (dotted lines).

**Table 1. Polymer Molecular Weight and Photophysical Data**

| | | | | solution | | film | | | |
|---|---|---|---|---|---|---|---|---|---|
| poly | $M_n$/kDa (PDI) | DP | $E_g$/eV[a] | $\lambda_{max,abs}$/ nm,<br>$\lambda_{max,em}$/nm | Stokes shift/ $cm^{-1}$ [b] | $\lambda_{max,abs}$/nm,<br>$\lambda_{max,em}$/nm | Stokes shift/ $cm^{-1}$ | $\Phi_F$[c] ($CHCl_3$) | $\Phi_{rel}$[d] (film) |
| **P1** | 4 (1.2) | 13 | 3.06 | 362<br>402, 424 | 2700 | 355<br>415, 435 | 4100 | 0.99 ± 0.07 | 0.88 ± 0.14 |
| **P2** | 10 (4.0) | 13 | 2.88 | 382<br>418, 443 | 2300 | 384<br>426, 450 | 2500 | 0.79 ± 0.03 | 0.15 ± 0.02 |
| **P3** | 12 (1.8) | 17 | 2.95 | 382<br>412, 436 | 1900 | 386<br>419, 443 | 2000 | 0.97 ± 0.06 | 1.18 ± 0.05 |
| **P4** | 14 (1.8) | 15 | 2.90 | 398<br>419, 443 | 1200 | 399<br>423, 444 | 1400 | 0.96 ± 0.04 | 1.07 ± 0.13 |
| **P5** | 15 (3.4) | 40 | 2.82 | 390<br>417, 442 | 1600 | 392<br>440, 461 | 2800 | 0.97 ± 0.09 | 1.00 |

[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 $\Delta = \lambda_{max,em} - \lambda_{max,abs}$. [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.[23] [d] Thin-film fluorescence quantum yields of **P1**, **P2**, **P3**, and **P4** are reported relative to **P5**; $\Phi_{rel} = 1.00$ (lit. $\Phi_F = 0.55$).[24]

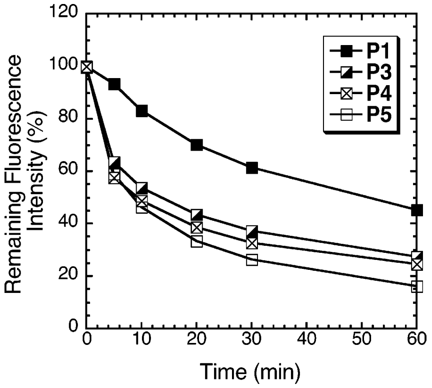


**Figure 4.** Time dependence of the fluorescence emission intensity of thin films of **P1**, **P3**, **P4**, and **P5** under UV irradiation at 380 nm. The optical density of all of the polymer films at the irradiation wavelength was 0.10 ± 0.01.

This trend is also evident in the optical band gap data where an increase in *gem*-$CF_3$ substituted fluorene content corresponds with a slight widening of the band gap. The *gem*-$CF_3$ groups also appear to limit $\beta$-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 $\beta$-phase formation.[2b,22]

**Polymer Photobleaching.** To determine whether the incorporation of the *gem*-$CF_3$ groups could impart increased photooxidative stability 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 $\lambda_{max}$. 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*-$CF_3$-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*-$CF_3$-containing polymers **P1**, **P3**, and **P4** demonstrate greater stability than the parent poly(9,9-dioctylfluorene), **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*-$CF_3$ 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*-$CF_3$ 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*-$CF_3$-substituted fluorenes demonstrate blue-shifted UV−vis absorption and fluorescence emission spectra and slightly wider band gaps than a 9,9-dialkyl-substituted poly(fluorene). Overall, perturbations to the polymer electronics due to the *gem*-$CF_3$ substituents at the 9-position of fluorene were minimal. Photobleaching experiments revealed that the *gem*-$CF_3$ groups significantly enhance the photostability of poly(fluorene)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 $\mu$m silica gel. All organic extracts were dried over $MgSO_4$ and filtered prior to removal with a rotary evaporator. Compounds **4**[18] and **8**[21] can be prepared by literature procedures.

$^1H$ NMR, $^{13}C$ NMR, and $^{19}F$ 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 $CHCl_3$/TMS (7.27 ppm for $^1H$, 77.23 ppm for $^{13}C$). For $^{19}F$ 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 $CF_3$ groups and proximal quaternary centers were not reported in the $^{13}C$ 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 Transform 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 $\mu$m 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-$\tau^3$ fluorometer (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** ($\Phi_{rel} = 1.00$) 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 5.60 g (20.0 mmol) of 2-iodobiphenyl 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 a heavy flow of argon. Both the reaction mixture and the condenser were then cooled to −78 °C. An excess of anhydrous hexafluoroacetone was admitted to the flask by means of a tube connected to the stopcock. The reaction mixture was allowed to warm to room temperature, and the hexafluoroacetone was allowed to reflux for 3 h. Excess hexafluoroacetone was removed by flushing the apparatus 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 (50 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, $CDCl_3$): $\delta$ 7.79 (m, 1H), 7.47 (m, 5H), 7.38 (m, 2H), 7.19 (m, 1H), 3.48 (s, 1H). $^{13}C$ NMR (125 MHz, $CDCl_3$): $\delta$ 141.5, 140.0, 135.5, 129.4, 129.3, 129.0, 128.9, 128.2, 128.1, 126.7, 124.0, 121.7. $^{19}F$ NMR (282 MHz, $CDCl_3$): $\delta$ −75.3. FT-IR (KBr): $\nu$/cm$^{-1}$: 3506, 3065, 1597, 1574, 1483, 1444, 1366, 1196, 1150, 1111, 1057, 1010, 966, 951, 926, 763, 709, 661, 538. HRMS (EI): calcd for $C_{15}H_{10}F_6O$ ($M^+$), 320.0630; found 320.0626. $C_{15}H_{10}F_6O$ (320.1): calcd C 56.26, H 3.15; found C 56.21, H 3.03%.

**Compound 2.** Into a 250 mL heavy walled glass tube with a magnetic stirring bar and a Teflon screwcap closure were added 3.00 g (9.4 mmol) of **1**, 21 mL (290 mmol) of thionyl chloride, and 4 mL (50 mmol) of pyridine. The reaction mixture was heated to 100 °C for 48 h. The reaction mixture was evaporated to dryness. The residue was purified by column chromatography (hexanes) to yield 2.36 g (83%) of a colorless powder; mp 75−76 °C. $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ 7.81 (m, 4H), 7.58 (td, 2H, $J = 1$, 8 Hz), 7.43 (td, 2H, $J = 1$, 8 Hz). $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ 142.7, 134.8, 131.0, 128.5, 126.6, 120.8. $^{19}F$ NMR (282 MHz, $CDCl_3$): $\delta$ −68.8. FT-IR (KBr): $\nu$/cm$^{-1}$: 3069, 1477, 1453, 1305, 1271, 1187, 1160, 1143, 1115, 979, 964, 944, 930, 763, 738, 695, 677, 669. HRMS (EI): calcd for $C_{15}H_8F_6$ ($M^+$), 302.0525; found 302.0518. $C_{15}H_8F_6$ (302.1): calcd C 59.61, H 2.67; found C 59.75, H 2.79%.

**Compound 3.** Into a 50 mL Schlenk tube with a magnetic stirring bar were added 0.15 g (0.5 mmol) of **2**, 0.24 g (1.1 mmol) of *N*-iodosuccinimide, and 5 mL of a 5:1 acetic acid/concentrated sulfuric acid solution. The reaction mixture was heated to 65 °C for 18 h. After cooling to room temperature, the reaction mixture was poured into a 10% NaOH(aq) solution and extracted with dichloromethane (150 mL). The organic extract was washed with 10% NaOH (100 mL), water (100 mL), and brine (100 mL) and dried. The residue was purified by column chromatography (hexanes). Recrystallization with hexanes afforded 0.15 g (55%) of colorless needles; mp 228−230 °C. $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ 8.09 (s, 2H), 7.91 (dd, 2H, $J = 2$, 8 Hz), 7.51 (d, 2H, $J = 8$ Hz). $^{13}C$ NMR (125 MHz, $CDCl_3$): $\delta$ 141.3, 140.4, 136.1, 135.5, 122.4, 93.9. $^{19}F$ NMR (282 MHz, $CDCl_3$): $\delta$ −68.4. FT-IR (KBr): $\nu$/cm$^{-1}$: 1559, 1456, 1396, 1289, 1263, 1221, 1179, 1134, 1063, 969, 950, 884, 813, 742, 683, 525, 426. HRMS (EI): calcd for $C_{15}H_6F_6I_2$ ($M^+$), 553.8458; found 553.8446. $C_{15}H_6F_6I_2$ (553.8): calcd C 32.52, H 1.09; found C 32.46, H 0.85%.

**Compound 5.** Into a 250 mL three-necked, round-bottom flask with a magnetic stirring bar and a 125 mL addition funnel were added a solution of phenylmagnesium bromide (51.0 mmol) in 100 mL of THF. A solution of 5.00 g (10.2 mmol) of 1,4-dibromo-2,5-diiodobenzene (**4**) in 50 mL of THF was added slowly dropwise over 1.5 h. After the addition was complete, the solution was stirred at room temperature for 8 h. The addition funnel was quickly replaced with a Dewar-type condenser under a heavy flow of argon. The reaction mixture was cooled to 0 °C, and the Dewar-type condenser was cooled to −78 °C. An excess of anhydrous hexafluoroacetone was admitted to the flask by means of a long needle. The reaction mixture was allowed to warm to room temperature, and the hexafluoroacetone was allowed to reflux for 3 h. Excess hexafluoroacetone was removed by flushing the apparatus 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 (150 mL) and extracted with diethyl ether (300 mL). The organic extracts were washed with a 5% HCl solution (100 mL), water (150 mL), and brine (100 mL) and dried. The residue was purified by column chromatography (0−20% ethyl acetate in hexanes) to yield an oily paste. This residue was triturated with a small amount of hexanes and filtered to yield 1.33 g (23%) of a colorless powder; mp 220−222 °C. $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ 7.56 (s, 2H), 7.54−7.50 (m, 6H), 7.42−7.38 (m, 4H), 3.41 (s, 2H). $^{13}C$ NMR (125 MHz, $CDCl_3$): $\delta$ 141.3, 138.7, 133.0, 129.4, 129.2, 129.1, 128.1, 123.6, 121.3. $^{19}F$ NMR (282 MHz, $CDCl_3$): $\delta$ −74.9. FT-IR (KBr): $\nu$/cm$^{-1}$: 3431, 3069, 1207, 1141, 965, 764, 732, 714. HRMS (EI): calcd for $C_{24}H_{14}F_{12}O_2$ ($M^+$), 562.0797; found 562.0812. $C_{24}H_{14}F_{12}O_2$ (562.1): calcd C 51.26, H 2.51; found C 51.08, H 2.63%.

**Compound 6.** Into a 50 mL heavy walled glass tube with a magnetic stirring bar and a Teflon screwcap closure were added

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). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 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). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 143.2, 141.7, 137.8, 135.0, 131.3, 129.1, 126.7, 121.2, 118.9. $^{19}$F NMR (282 MHz, CDCl$_3$): $\delta$ −68.4. FT-IR (KBr): $\nu$/cm$^{-1}$: 1255, 1187, 980, 761, 727. HRMS (EI): calcd for $C_{24}H_{10}F_{12}$ (M$^+$), 526.0585; found 526.0597. $C_{24}H_{10}F_{12}$ (526.1): calcd C 54.77, H 1.92; found C 54.70, H 1.68%.

**Compound 7.** Into a 50 mL round-bottom flask with a magnetic stirring bar were added 0.14 g (0.3 mmol) of **6**, 0.26 g (1.2 mmol) of *N*-iodosuccinimide, and 15 mL of a 4:1 acetic acid/concentrated sulfuric acid solution. The reaction mixture was heated to 75 °C for 48 h. After cooling to room temperature, the reaction mixture was poured into water (200 mL). The precipitate was isolated by vacuum filtration and was rinsed with water (100 mL) and methanol (50 mL) and dried. The poorly soluble residue was triturated with hot ethyl acetate three times to afford 0.06 g (29%) of a colorless powder; mp >350 °C. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.13 (s, 2H), 8.09 (s, 2H), 7.97 (dd, 2H, $J = 2$, 8 Hz), 7.63 (d, 2H, $J = 8$ Hz). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 140.6, 122.7 (partial).[25] $^{19}$F NMR (282 MHz, CDCl$_3$): $\delta$ −68.3. FT-IR (KBr): $\nu$/cm$^{-1}$: 1572, 1463, 1428, 1302, 1256, 1181, 1156, 1141, 1125, 1059, 1029, 979, 964, 887, 822, 752, 730, 684, 531. HRMS (EI): calcd for $C_{24}H_8F_{12}I_2$ (M$^+$), 777.8518; found 777.8523.

**Polymer P1.** Into a 50 mL Schlenk tube with a magnetic stirring bar were added 7 mg (0.04 mmol) of 2,2′-bipyridyl, 11 mg (0.04 mmol) of bis(1,5-cyclooctadiene)nickel(0), 20 mg (0.20 mmol) of 1,5-cyclooctadiene, and 0.30 mL of a deoxygenated[26] 2:5 dimethylformamide:toluene solution. The reaction mixture was heated to 80 °C for 30 min. A solution of 10 mg (0.02 mmol) of compound **3** in 0.15 mL of toluene was then added. The reaction mixture was heated at 80 °C for 72 h. After cooling to room temperature, the polymer was precipitated into 15 mL of methanol. The precipitate was isolated by centrifugation and decantation of the supernatant. The precipitate was washed with another 20 mL portion of methanol. The material was dried under vacuum to yield a lightly colored solid (3 mg, 55%). **P1**: GPC (THF): $M_n = 4$K Da, $M_w = 5$K Da. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.09−8.02 (aromatic C−H), 8.00−7.82 (aromatic C−H). $^{19}$F NMR (282 MHz, CDCl$_3$): $\delta$ −68.4. FT-IR (KBr): $\nu$/cm$^{-1}$: 2925, 1284, 1256, 1198, 1180, 1144, 979, 893, 815, 745, 699, 668.

**Polymer P2.** Into a 25 mL Schlenk tube with a magnetic stirring bar were added 10 mg (0.02 mmol) of compound **3**, 9 mg (0.02 mmol) of compound **8**, copper iodide (<1 mg), and Pd(PPh$_3$)$_4$ (<1 mg). 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 72 h. After cooling to room temperature, the reaction mixture was precipitated by slow addition to 20 mL of methanol. The precipitate was isolated by centrifugation and decantation of the supernatant. The precipitate was washed with several 20 mL portions of methanol to remove any short oligomers. The material was then dissolved in dichloromethane and filtered through a 0.2 $\mu$M syringe filter. The material was dried under vacuum to yield a yellow solid (5 mg, 35%). **P2**: GPC (THF): $M_n = 10$K Da, $M_w = 40$K Da. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.30−8.25 (aromatic C−H), 8.12−8.08 (aromatic C−H), 7.52−7.43 (aromatic C−H), 7.08−6.99 (aromatic C−H), 6.01−5.94 (aliphatic C−H). $^{19}$F NMR (282 MHz, CDCl$_3$): $\delta$ −68.1. FT-IR (KBr): $\nu$/cm$^{-1}$: 2926, 1459, 1381, 1297, 1260, 1203, 1150, 980, 898, 828, 753, 668, 566.

**Polymers P3 and P4.** A general procedure is illustrated by the synthesis of polymer **P3**. Into a 25 mL Schlenk tube with a magnetic stirring bar were added 10 mg (0.02 mmol) of compound **3**, 10 mg (0.02 mmol) of 9,9-dioctylfluorene-2,7-bistrimethyleneborate (**9**), and Pd(PPh$_3$)$_4$ (<3 mg). A deoxygenated aqueous 2 M K$_2$CO$_3$ solution (1 mL), deoxygenated toluene (1 mL), and ~30 mg of Aliquat 336 were added. The reaction mixture was heated to 100 °C for 48 h. After cooling to room temperature, the polymer was precipitated into 15 mL of methanol. The precipitate was isolated by centrifugation and decantation of the supernatant. The precipitate was dissolved in diethyl ether (2 mL) and precipitated into 15 mL of methanol. The precipitate was isolated by centrifugation and decantation of the supernatant. The material was then dissolved in dichloromethane and filtered through a 0.2 $\mu$M syringe filter. The material was dried under vacuum to yield a yellow solid (6 mg, 47%).

**P3**: GPC (THF): $M_n = 12$K Da, $M_w = 21$K Da. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.14−8.06 (aromatic C−H), 7.96−7.82 (aromatic C−H), 7.74−7.60 (aromatic C−H), 2.22−1.98 (aliphatic C−H), 1.36−0.94 (aliphatic C−H), 0.92−0.68 (aliphatic C−H). $^{19}$F NMR (282 MHz, CDCl$_3$): $\delta$ −68.4. FT-IR (KBr): $\nu$/cm$^{-1}$: 2927, 2855, 1459, 1259, 1199, 1166, 1146, 979, 889, 816, 745, 668.

**P4**: (39%) GPC (THF): $M_n = 14$K Da, $M_w = 25$K Da. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.25−8.16 (aromatic C−H), 8.14−8.06 (aromatic C−H), 8.04−7.82 (aromatic C−H), 7.74−7.58 (aromatic C−H), 2.22−1.94 (aliphatic C−H), 1.38−0.96 (aliphatic C−H), 0.95−0.64 (aliphatic C−H). $^{19}$F NMR (282 MHz, CDCl$_3$): $\delta$ −68.2. FT-IR (KBr): $\nu$/cm$^{-1}$: 2929, 2856, 1463, 1437, 1258, 1201, 1176, 1150, 981, 953, 890, 819, 751, 732, 668.

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**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.

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