Synthesis of Polyfluorenes with Pendant Silylcarboranes

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ABSTRACT: The synthesis of a novel silylcarborane-containing fluorene monomer is reported in the present paper. Homo- and copolymerization via microwave-assisted Ni(0)-mediated coupling are described, and the influence of sterically crowded silylcarboranes on the polymerization outcome is assessed. The fluorescence spectra and thermal characteristics of the resulting polymers are analyzed and compared to determine the impact of carborane cages. Pendant carboranes are shown to improve the stability of annealed thin films, and potential implications in sensing devices and neutron detection are discussed.

Introduction

For a little over 30 years, conjugated polymers have stimulated the imagination of chemists, physicists, and material scientists alike, and the desire to tailor properties through careful design has continued unabated.[1,2] Aside from the mere scientific curiosity, this desire has been fueled by the multitude of applications for which these compounds are used: antistatic coatings, electrochromic pannels, polymer light-emitting diodes (PLEDs), photovoltaic devices, etc.[3] However, one of the highly sought-after features of these materials, i.e., extended conjugation through aromatic moieties, is also one of their pitfalls. The rodlike nature of these systems contributes to the tendency of conjugated systems to bundle and π-stack. These phenomena are detrimental to the processability of such systems and pose subsequent problems in terms of their utilization in optoelectronic devices.[4,5] To circumvent these issues, chemists have devised synthetic strategies to confer solubility and stability to conjugated polymers while preserving their remarkable properties.

Notably, 9,9-disubstituted polyfluorenes (PFs) have emerged as a unique class of blue-emitting materials for PLEDs.[3,4] The planarization of the structure by the carbon bridge and the possibility for facile property tuning and solubility via functionalization at the 9-position as well as their remarkable quantum efficiency have made PFs a noticeable candidate in the field of optoelectronics.[6] Despite the presence of these solubilizing groups, commonly alkyl groups, it has been observed that upon applying a current or upon annealing the chains have a tendency to aggregate, and various groups have explored methodologies to efficiently thwart this phenomenon.[5,7] Notably, Klaerner et al. have successfully illustrated the possibility to use fourth-generation dendrons via end-capping as a means to efficiently contravene stacking.[8] Additionally, the utilization of dendrons has been demonstrated as a successful strategy to address this unwanted behavior.[5]

The utilization of boron in conjugated systems often stems from its Lewis acidic character, which makes the resulting compounds particularly attractive for sensor applications, and recently, copolymers of dibenzoborole and fluorene have been utilized as a route to detect anionic contaminants.[9] Another strategy to introduce boron in conjugated systems revolves around the utilization of carboranes. Several groups have utilized these inorganic clusters, both in the main chain or as side groups, to provide these systems with electrochemical stability and novel electronic properties, whether in small molecules or in polymers.[10−13] Particularly, seminal work by Vicente and co-workers on pyrroles and thiophene has underlined the advantage of introducing carboranes as a way to reinforce the thermo-oxidative resistance of electronic materials.[14,15]

In the present paper, we report the synthesis of a novel fluorene monomer **4** disubstituted with bulky silylcarborane clusters. The homopolymerization of **4** using microwave-assisted Yamamoto coupling and its copolymerization with 2,7-dibromo-9,9-dihexylfluorene (**5**) are described hereafter. Finally, the spectral properties of the homo- and copolymers are investigated, and practical applications are discussed.

Results and Discussion

In order to synthesize monomer **4**, a monofunctional silylcarborane moiety had to be obtained. On the basis of a procedure by Gomez et al., two of us have reported a reliable method to obtain [2-(*tert*-butyldimethylsilanyl)-1,2-dicarba-*closo*-dodecaboran(12)-1-yl]-propan-1-ol (**1**).[16] The conventional approach to obtain 9,9-disubstituted fluorenes involves deprotonating the benzylic bridge using two equivalents of a base and subsequently adding in excess of an electrophile, usually an alkyl bromide.[17] To emulate this strategy, the connectivity of **1** had to be reversed so as to obtain an electrophilic moiety, and this has been done using two routes (Figure 1). First, using *p*-toluenesulfonyl chloride, the alcohol was tosylated, affording compound **2**.[18] Alternatively, the connectivity reversal was undertaken by means of an Appel reaction in the presence of triphenylphosphine and carbon tetrabromide to obtain compound **3**.[19]

The next step was the coupling of 2,7-dibromofluorene with **2** or **3** to synthesize the desired monomer **4** (Figure 1). After several optimization steps, the solvent was chosen to be a 2:1 (v:v) mixture of benzene and diethyl ether. Remarkably, in spite of the steric hindrance of the silylcarborane, no monosubstituted fluorene was observed or recovered. Once the monomer was fully characterized, its polymerization was undertaken. In order to homo- and copolymerize **4**, microwave-assisted Yamamoto coupling was performed (Figure 2). This nickel-mediated coupling usually proceeds under mild conditions in excellent yields.[20] However, several groups have highlighted the interest of utilizing microwave-assisted aryl−aryl couplings to accelerate the screening process for novel polymeric semiconductors.[21] Additionally, through a significant reduction of the formation of side products, the yields of the reaction are often increased, making microwave heating an ideal candidate for the laboratory synthesis of libraries of optoelectronic materials.[22]

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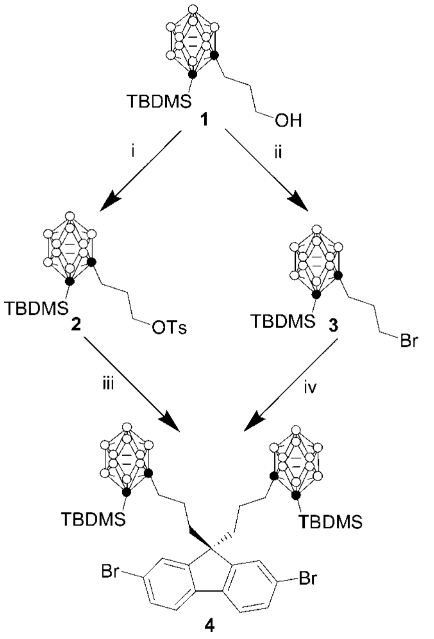

Figure 1. Synthesis strategies to attain monomer **4**: (i) CH_2Cl_2, TsCl, pyridine(dropwise); (ii) CH_2Cl_2, 0 °C, CBr_4, PPh_3; (iii) THF, *t*-BuOK, 2,7-dibromofluorene; (iv) PhH/Et_2O (2:1 v:v), *t*-BuOK, 2,7-dibromofluorene.

For the Yamamoto protocol, the reaction sequence is reported to proceed through an oxidative addition followed by disproportionation and finally reductive elimination to obtain the diaryl moiety. The last step is essential so as to understand some of the limitations that one can face while using sterically hindered molecules. Under the current conditions, the presence of bipyridine which binds to two adjacent coordination sites facilitates the elimination of the aryl to form the covalent C−C bond. While this step is crucial for the polymerization of **4**, one can easily understand that, as the polymer starts to grow, it becomes harder and harder for the aryl chains to approach each other, as the silylcarborane groups contribute to steric crowding of the chains. This phenomenon makes the likelihood of two aryl moieties being in two adjacent coordination sites less probable, as molecular weight increases, leading to an eventual plateau of molecular weight. This trend has been observed for the synthesis of **5**. The reaction temperature was varied from 100 to 150 °C without any observable increase of molecular weight. The number-average molecular weight was found to plateau at ~7000 g/mol, which, if the end of the polymers were to be brominated, corresponds to a degree of polymerization $DP_n = 8-9$. This number is obviously a crude approximation since the M_n are measured vs polystyrene standards and do not take into account the rigid nature of **5**, but they allow us to get a sense of how efficient the reaction was.

In the case of copolymerization, polymer **6** was found to attain higher molecular weights, which can be explained by the diminution of steric hindrance with the introduction of linear *n*-hexyl side groups. The molar ratio of **4** to dihexylfluorene was set at 1:1 so as to simplify analysis. This increase in molecular weight is corroborated by the red shift in the emission spectrum of **6** with respect to **5** (Figure 4B). This displacement toward the high wavenumbers is consistent with the molecular weight of **5** being below the threshold (~10 units), after which conjugation length is no longer affected by the DP_n.[4] Additionally, the fluorescence emission and UV absorption sharpen with higher MW, consistent with studies of other oligomeric polyfluorenes.[23]

Similarly to the work by Shim, Wei, and Tang where polyhedral oligomeric silsesquioxane cages were added as a way to enhance thin film stability of PFs,[7,24,25] the present work is thought to provide an alternative approach to provide enhanced thermal resistance. DSC studies revealed that glass transition temperature (T_g) increases with carborane content (Table 1). Fluorescence emission of thin films before (Figure 4A) and after (Figure 4, inset) annealing for 3 h at 160 °C revealed that the characteristic green emission centered around 535 nm was reduced in intensity with increasing carborane content. The homopolymer, **5**, was subjected to 3 h of additional annealing at 200 °C under air and showed only a small increase in green emission. The green emission is characteristic of annealed polyfluorenes and is thought to be related to excimers and/or keto defects.[5,7] The carborane pendant groups raise T_g and hinder chain packing, increasing stability and color purity, essential qualities for display materials. More importantly, polymers **5** and **6** are thought to be interesting materials for neutron detection.[26] The high boron content coupled with the high

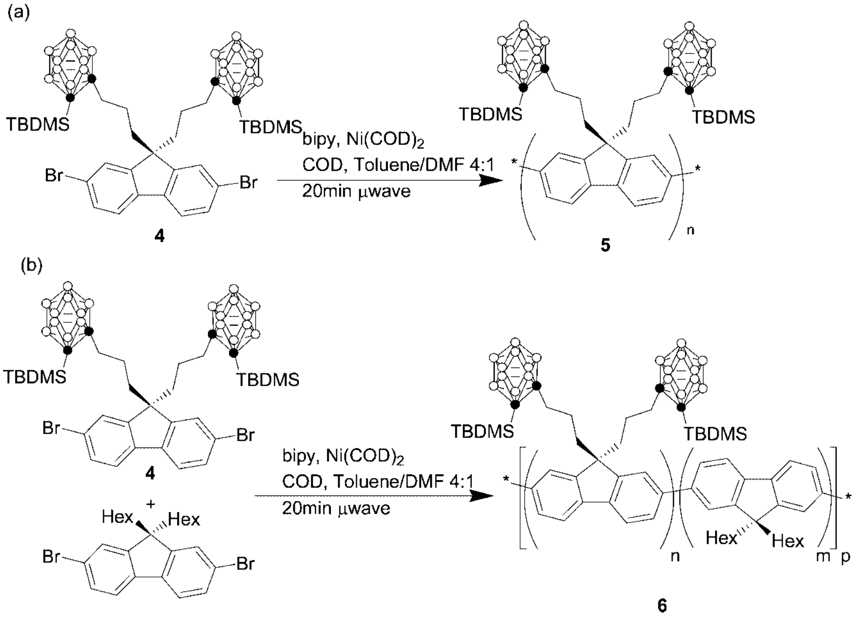

Figure 2. Microwave-assisted polymerization of **4**: (a) homo- and (b) copolymerizations with 2,7-dibromodihexylfluorene.

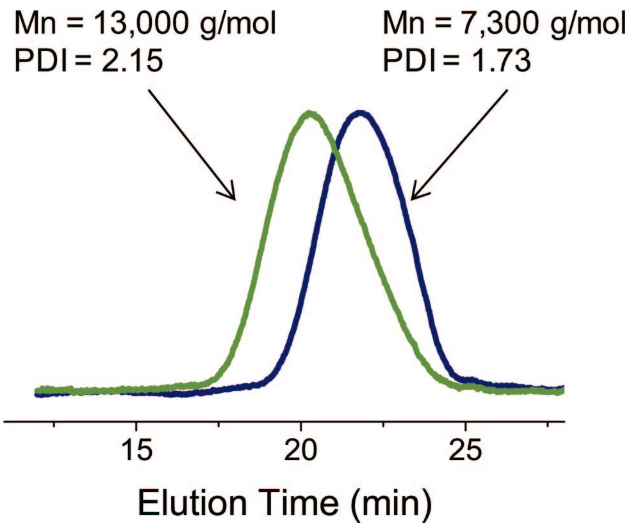

Figure 3. Gel permeation chromatograms for polymers **5** and **6**.

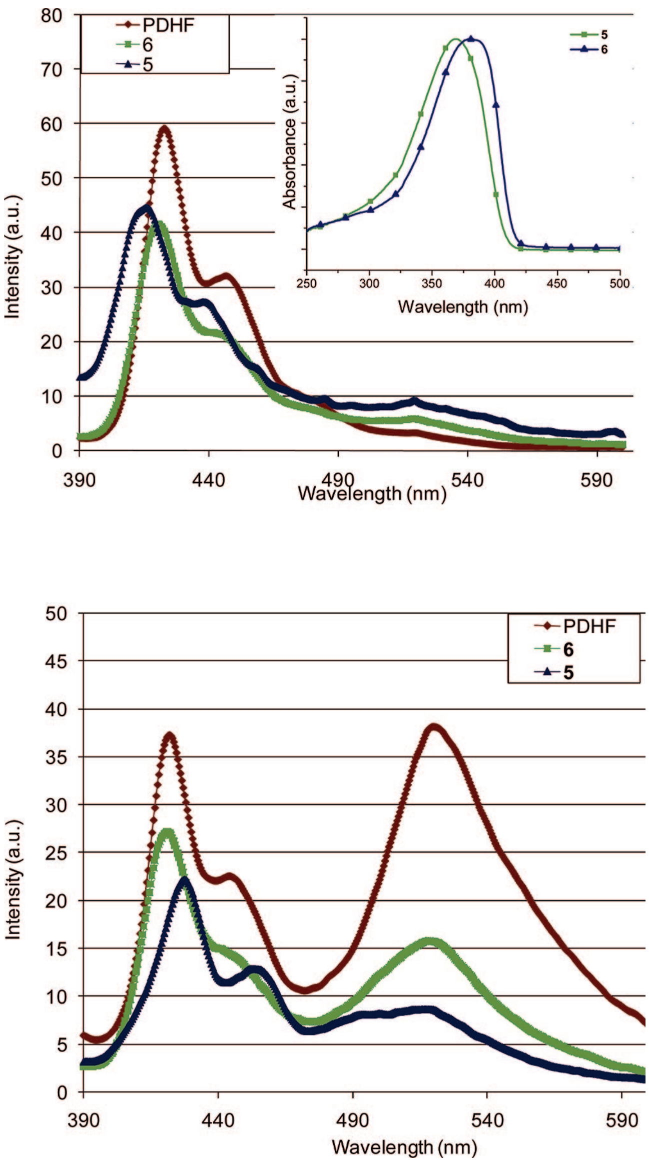

Figure 4. Thin film emission spectra for **5**, **6**, and poly(dihexylfluorene) (PDHF) before annealing (A, top) and thin film emission spectra for **5**, **6**, and poly(dihexylfluorene) (PDHF) after annealing (B, bottom). UV absorption of **5** and **6** (top inset).

Table 1. Molecular Weights and Glass Transition Temperatures

sample	M_n (g/mol)	T_g (°C)
PDHF	50K	102
copolymer **6**	13K	132
homopolymer **5**	7.3K	181

neutron capture area of ^{10}B could potentially lead to a pathway for the detection of fissile materials.

Several routes could contribute to the detection of neutrons. First, the ionizing particles emitted upon capture of a thermal neutron can cause ionization of the conjugated backbone, leading to changes in its emission. Alternatively, one could utilize the secondary γ-radiation to detect the presence of a neutron. Zhao et al. have demonstrated the use of PFs blends with dyes and γ-sensitizers for the detection of γ-rays.[27] Inspired by this methodology, the utilization of carborane-containing PFs could offer an interesting alternative to costly gas chamber detectors. Finally, studies to introduce the carborane in the backbone are underway. This last approach is thought to be even more promising for neutron detection, in that the conjugation of the polymer would be directly modified by the loss of σ-aromaticity upon neutron capture. Moreover, the electronics of the subsequent polymers might lead to electrochemically stable PFs with unique emission spectra.

Conclusions

We have successfully developed a new monomer, **4**, that allowed for the synthesis of polyfluorenes **5** and **6** with bulky silylcarborane side chains. It was observed that the molecular weight of the homopolymers was constrained by steric limitations and that its fluorescence maximum was blue-shifted with respect to conventional fluorenes. To remediate this phenomenon, copolymerization with 2,7-dibromo-9,9-dihexylfluorene was undertaken, leading to a significant increase in molecular weight. Both homo- and copolymerizations studies were performed using microwave-assisted Yamamoto couplings. Increasing carborane content was found to increase T_g and effectively reduce the intensity of green emission during annealing, yielding improved stability. Finally, we have alluded to some of the potential applications of such materials, including device stability and efficiency as well as utilization in neutron detection, and alternative strategies incorporating carboranes in the main chain have been depicted and are currently being investigated.

Experimental Section

Materials. All organic reactants and reagents were purchased from Aldrich Chemical Co. and used as received unless specified otherwise. Anhydrous benzene and diethyl ether were dried over sodium with benzophenone as an indicator. Dichloromethane (DCM) was obtained through Fisher, distilled over calcium hydride, and degassed with freeze−pump−thaw cycles. *o*-Carborane was supplied by KatChem.

Instrumentation. Gel permeation chromatography (GPC) measurements for the polymers were performed in tetrahydrofuran (THF) at 1.0 mL/min using a Knauer K-501 pump with a K-2301 refractive index detector and a K-2600 UV detector and a column bank consisting of two Polymer Laboratories PLGel Mixed D columns at 40 °C. All other measurements were performed using a similar system with a column banks consisiting of three Polymer Laboratories PLGel Mixed D columns at 40 °C. Molecular weights are reported relative to polystyrene standards.

^{1}H, ^{11}B, and ^{13}C NMR were recorded at 300, 128, and 100 MHz, respectively, on a Bruker NMR spectrometer at room temperature in deuterated chloroform. The individual NMR spectral assignments do not list the carborane B−H resonances. Because of the quadrupolar nature of boron, the resonances for the 10 B−H are observed as broad multiplets ($\delta = 3.20−1.01$ ppm). The integration of these multiplets accounts for 10 H. Melting points were measured with a melting point apparatus Electrochemical Mel-Temp in a capillary tube.

Differential scanning calorimetry was performed on a TA Q2000 DSC with refrigerated cooling system using a heat−cool−heat program at 10 °C/min. T_g was taken to be the onset T_g during the second heating cycle.

Fluorescence emission spectra of thin films on quartz slides were recorded on a Perkin-Elmer LS-50B using an excitation wavelength of 365 nm.

Preparation of 3-[2-(*tert*-Butyldimethylsilanyl)-1,2-dicarba-*closo*-dodecaboran(12)-1-yl]-propan-1-*p*-toluenesulfonate (2). [2-(*tert*-Butyldimethylsilanyl)-1,2-dicarba-*closo*-dodecaboran(12)-1-yl]-propan-1-ol (**1**) (0.500 g, 1.5 mmol, 1 equiv) was placed into a 50 mL two neck round-bottom flask and flushed with nitrogen. DCM (1.5 mL, freshly distilled from CaH_2) was added, and the solution was cooled to 0 °C. *p*-Toluenesulfonyl chloride (0.451 g, 2.3 mmol, 1.5 equiv) was added during a slight nitrogen overpressure. Pyridine (0.25 mL, 0.248 g, 3.6 mmol, 2 equiv) was subsequently added. The reaction mixture was stirred at 0 °C for 4 h, and the course of reaction was followed by TLC (hexane/ethyl acetate, 3:1). After completion of the reaction, ether (40 mL) were added, and the organic layer was washed with 40 mL of each water, 1 M HCl, and a 5% $NaHCO_3$ solution. The ether phase was then dried over $MgSO_4$ and concentrated in vacuo to give 0.504 g of a white powder (71% yield). Recrystallization from acetonitrile afforded 0.411 g of pure product **2** (68% yield). High-resolution MS (FAB-): *m/z* calcd 471.3296; found 471.3257. ^1H ($CDCl_3$): δ (ppm) = 7.76 (d, J = 8.35, 2H), 7.36 (d, J = 7.36, 2H), 3.99 (t, J_1 = 5.63, 2H, CH_2OTs), 2.29 (m, 2H, CH_2CH_2OTs), 1.85 (m, 2H, CH_2−cage), 1.03 (s, 9H, CCH_3), 0.31 (s, 6H, $SiCH_3$). ^{13}C NMR ($CDCl_3$): δ (ppm) = 145.25, 132.63, 130.06, 127.85, 80.07, 77.47, 76.54, 68.80, 34.14, 29.37, 27.51, 21.67, 20.32, −2.52; mp 101 °C.

Preparation of 1-Bromo-3-[2-(*tert*-butyldimethylsilanyl)-1,2-dicarba-*closo*-dodecaboran(12)-1-yl]propane (3). [2-(*tert*-Butyldimethylsilanyl)-1,2-dicarba-*closo*-dodecaboran(12)-1-yl]-propan-1-ol (**1**) (500 mg, 1.58 mmol, 1 equiv) and carbon tetrabromide CBr_4 (785 mg, 2.37 mmol, 1.5 equiv) were placed into a 50 mL two-neck round-bottom flask and flushed with nitrogen. DCM (6 mL) was added, and after cooling the mixture to 0 °C, triphenylphosphine (621 mg, 2.37 mmol, 1.1 equiv) was added to the solution with an slight nitrogen overpressure. After 3 h of stirring, the reaction solution was concentrated in vacuo, and EtOH was added in order to crystallize. After filtration, 474 mg of a white powder was obtained (yield 80%). High-resolution MS (FAB-): *m/z* calcd 379.2374; found 379.2380. ^1H ($CDCl_3$): δ (ppm) = 3.38 (t, 2H, CH_2Br, J = 6 Hz), 2.39 (m, 2H, $CH_2CH_2CH_2$), 2.08 (m, 2H, CH_2−cage), 1.10 (s, 9H, CH_3C), 0.36 (s, 6H, CH_3Si). ^{13}C NMR ($CDCl_3$): δ (ppm) = 80.31, 76.36, 36.90, 32.54, 32.43, 27.78, 20.55, −2.23; mp 91 °C.

Preparation of 2,7-Dibromo-9,9-di{3-[2-(*tert*-butyldimethylsilanyl)-1,2-dicarba-*closo*-dodecaboran(12)-1-yl]propane}-fluorene from Compound 3 (4). In a 50 mL round-bottom flask flushed with nitrogen, 2,7-dibromofluorene (0.137 g, 0.425 mmol, 1 equiv) and [2-(*tert*-butyldimethylsilanyl)-1,2-dicarba-*closo*-dodecaboran(12)-1-yl]-propan-1-*p*-toluenesulfonate (0.5 g, 1.062 mmol, 2.5 equiv) were dissolved in freshly distilled THF and cooled to 0 °C. *t*-BuOK (1.3 mL of 1 M solution in THF, 3 equiv) was introduced dropwise with a syringe over a period of 30 min. The solution was then heated to 40 °C, and the solution turned purple. After 1 day, the reaction was stopped by adding water (20 mL), and the product was extracted with 3 × 20 mL of DCM. The organic phases were gathered and dried in vacuo to afford a sticky yellow solid which was recrystallized in methanol (yield 30%).

Preparation of 2,7-Dibromo-9,9-di{3-[2-(*tert*-butyldimethylsilanyl)-1,2-dicarba-*closo*-dodecaboran(12)-1-yl]propane}-fluorene from Compound 3 (4). In a 25 mL two-neck round-bottom flask, 2,7-dibromofluorene (0.5 g, 1.54 mmol, 1 equiv) and tBuOK (415 mg, 3.70 mmol, 2.4 equiv) were dissolved in 15 mL of a 4:1 mixture (v:v) of benzene and diethyl ether. Upon addition of the solvent mixture, the solution turned deep purple. To the solution, **3** (1.46 g, 3.86 mmol, 2.5 equiv) was added. The mixture was allowed to react overnight and turned dark orange. To terminate the reaction, ethyl acetate (10 mL) and water (20 mL) were added to the reaction. A slurry formed and was filtered. The filtrate was washed with additional water (10 mL), and the solid was set aside. The organic phase was dried over magnesium suflate and concentrated in vacuo to afford a yellow solid. The solid was rinsed with methanol to remove any remaining bromide. The solid resulting from the filtration of the slurry was dissolved in dichloromethane (5 mL) and methanol (20 mL), and the solution was concentrated in vacuo to give a yellow solid. Both solids were combined and identified as monomer **4** (yield = 65%). High-resolution MS (FAB-): *m/z* calcd 921.5210, found 920.5282. ^1H ($CDCl_3$): δ (ppm) = 7.6 (d, 2H, J_{ortho} = 8.1 Hz), 7.53 (dd, 2H, J_{ortho} = 8.1 Hz, J_{meta} = 1.5 Hz), 7.33 (d, 2H, J_{meta} = 1.5 Hz), 1.91 (t, 4H, J = 8.4 Hz), 1.82 (t, 4H, 7.8 Hz), 1.00 (s, 18H, CCH_3), 0.80 (bm, 4H, $CH_2CH_2CH_2$), 0.17 (s, 12H, $SiCH_3$). ^{13}C NMR ($CDCl_3$): δ (ppm) = 150.28, 139.09, 131.41, 125.93, 122.13, 122.04, 81.18, 76.12, 54.86, 39.30, 37.69, 37.60, 24.42, 20.44, −2.65; mp 235 °C.

Microwave-Assisted Homo- and Copolymerization: 5 and 6. In a microwave tube equipped with a stir bar, the monomer (1 equiv) was introduced as well as bipyridine (2.2 equiv). The tube was then pumped into a glovebox, and Ni(COD)2 (2.3 equiv) was added. The tube was sealed and taken out of the glovebox. Additional COD (2.7 equiv) was added, and the reagents were dissolved in 4 mL of a toluene:DMF (4:1) mixture. The tube was quickly degassed and filled with nitrogen twice. The tube was then introduced in a microwave apparatus, and the solution was allowed to react for 20 min at 130 °C. The solution was then filtered using a syringe mounted with filter paper as well as a 0.2 nm anodizc filter and precipitated in 20 mL of a solution of acidified methanol (0.5 M HCl). A yellowish solid was recovered and identified as the desired polymer. The yield of **5** was 49% and that of **6** was 56%; the synthesis of poly(dihexylfluorene) was achieved in 71% by using a similar coupling protocol.

Preparation of Thin Films. Solutions of **5**, **6**, and poly(dihexylfluorene) were prepared by dissolving 2.0 mg/mL of polymer in a 2:1 mixture of toluene/THF. Quartz slides were cleaned in a solution of concentrated H_2SO_4 and 30% hydrogen peroxide (5:1 by volume) at 100 °C for 30 min, rinsed with DI water and ethanol, and dried under a stream of N_2. The polymer solutions were spun onto the slides at 2000 rpm for 30 s and dried in a vacuum oven for 1 h at room temperature.

Annealing Study. Fluorescence emission of the thin films was taken after drying and the slides were placed on a temperature-controlled aluminum plate heated to 160 °C and covered with a Petri dish under air for 3 h. The slides were then cooled to room temperature, and fluorescence emission was retaken.

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Supporting Information Available: NMR spectra of **5** and **6** as well as TGA and SCS traces. This material is available free of charge via the Internet at http://pubs.acs.org.

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