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New Well-Defined Poly(2,7-fluorene) Derivatives: Photoluminescence and Base Doping

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ABSTRACT: Well-defined poly(2,7-fluorene) derivatives have been prepared through palladium-catalyzed couplings between various 9,9-disubstituted or 9-monosubstituted 2,7-dibromofluorenes and 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene. Using this versatile synthetic method, processable polyfluorenes have been obtained in good yields. In solution, all these neutral yellow polymers exhibit blue emission (maximum of emission around 410 nm) with high quantum yields (up to 0.87). Moreover, novel acidic polyfluorene derivatives have been synthesized (i.e., poly[2,7′-(alkyl 9,9-dioctyl-7,2′-bifluorene-9′-carboxylate)]s) which show, upon base doping, electrical conductivities of 10^{-6}−10^{-5} S/cm. This new doping method for conjugated polymers could open the way to the preparation of air-stable electron-injecting electrodes. Both photophysical and electrical properties of these polymers are quite promising for the fabrication of efficient blue-light-emitting devices.

Introduction

Great interest has been devoted to conjugated polymers due to their unusual optical and electrical properties. Recently, these polymers have been used in the fabrication of light-emitting devices (LEDs and LECs).[1−5] It is believed that the next generation of flat panel displays could be fabricated from these polymeric light-emitting devices. Along these lines, there is a great interest to produce efficient and stable blue-light-emitting materials to get access to the three primary colors. In this regard, it has been shown that polyesters derived from bithiophenes or terthiophenes could give the desired color emission but their low fluorescence quantum yields put some limitations on their use in optical devices.[6] On the other hand, the utilization of large-band-gap, conjugated polymer materials can also give blue-light-emitting materials. Interesting results have been obtained with poly(paraphenylene)s,[7] but some of these materials show processing problems due to their limited solubility in common organic solvents.

Yoshino et al. reported another class of blue-emitting materials based on poly(9-alkylfluorene)s and poly(9,9-dialkylfluorene)s.[8] These polymers have been obtained from a simple chemical oxidation of the monomers using $FeCl_3$, a procedure similar to that developed for the preparation of poly(3-alkylthiophene)s.[9] However, this nonspecific oxidation reaction produces some partially cross-linked materials, and the soluble fraction of these polyfluorenes shows some evidence of irregular couplings along the backbone.[10] As shown with the preparation of well-defined polyacetylene[11] and polythiophene derivatives,[12] a more regular structure can involve a significant improvement in the performance of the materials and, therefore, it could be expected that the preparation of well-defined poly(2,7-fluorene) derivatives could yield better electrical and optical properties. In agreement with this assumption, efficient photoluminescence and electroluminescence have been recently reported, by Pei and Yang,[13] from a well-defined soluble polyfluorene derivative obtained from a nickel-catalyzed reductive polymerization of 2,7-dibromo-9,9-bis(3,6-dioxaheptyl)fluorene.

On the other hand, it could be useful to get access to another polymerization method, in particular, if one is interested in the preparation of polyfluorenes bearing reactive side chains toward a reducing agent (e.g., ester groups). Indeed, 9-monosubstituted polyfluorenes bearing strong electron-withdrawing groups such as ester or cyano moieties could become an important class of conjugated polymers since they should lead to acidic conjugated polymers.[14,15] It is then believed that the preparation of these new polyfluorene derivatives could give not only highly luminescent materials in the neutral state but also base-dopable conducting polymers. This novel base-doping approach is the counterpart of the acidic doping reported for polyanilines, where a simple protonation of the imine moieties (without the use of any external redox process) leads to an insulating-to-conducting transition.[16] For this purpose, we have recently reported the preparation of a novel acidic polyfluorene derivative[15] from palladium-catalyzed Suzuki couplings[17] between ethyl 2,7-dibromofluorene-9-carboxylate and 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene.[15] Using this versatile synthetic method, we report here the synthesis and characterization of various well-defined poly(2,7-fluorene) derivatives, namely, poly[(1,4-phenylene)-2,7-(9,9-dioctylfluorene)] (**P1**), poly[2,7′-(9,9-dioctyl-7,2′-bifluorene)] (**P2**), poly[2,7-(9,9-dioctylfluorene)] (**P3**), poly[2,7′-(diethyl 9,9-dioctyl-7,2′-bifluorene-9′,9′-dicarboxylate)] (**P4**), poly[2,7′-(ethyl 9,9-dioctyl-7,2′-bifluorene-9′-carboxylate)] (**P5**), and poly[2,7′-[(methoxyethoxy)ethyl 9,9-dioctyl-7,2′-bifluorene-9′-carboxylate]] (**P6**) (see Chart 1). As mentioned above, the luminescent and electrical (through base-doping) properties of these conjugated polymers could be very useful for the development of light-emitting devices.

Experimental Part

Instrumentation. ^1H and ^{13}C NMR spectra were recorded on Bruker AMX300 and AMX400 spectrometers in deuterated chloroform solutions at 298 K. Number-average (M_n) and weight-average (M_w) molecular weights were determined by size-exclusion chromatography (SEC) with a HPLC Waters 510 pump using a Waters 410 differential refractometer. The calibration was made with a series of monodispersed polystyrene standards in THF (HPLC grade, Aldrich) at 308 K. Fluorescence measurements were carried out with a Spex Fluorolog 1681 spectrometer. In all cases, the polymer con-

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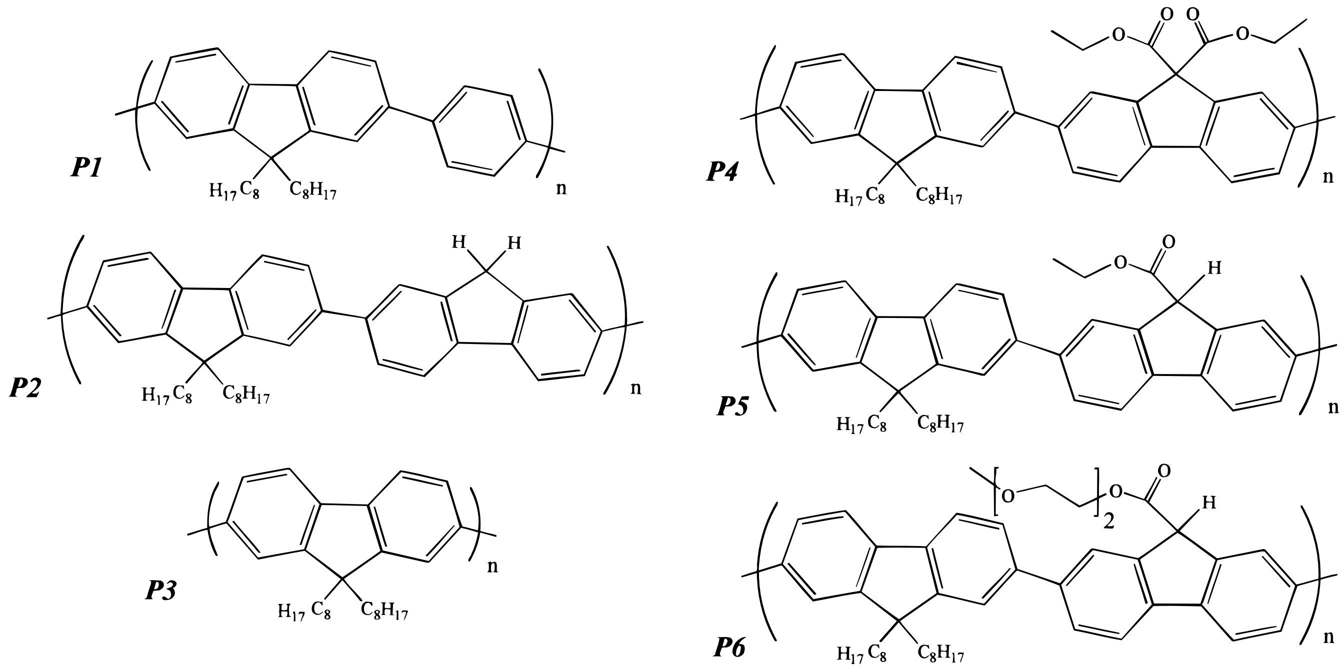
Chart 1



centration was about 10^{-6} M (on the basis of one repeat unit), giving absorbances always less than 0.06 to avoid any inner filter effect. The quantum yields of fluorescence were determined in argon-saturated solutions at 298 K in chloroform against 9,10-diphenylanthracene (Aldrich) in cyclohexane ($\phi_F = 0.90$) as the standard.[18] All corrected fluorescence excitation spectra were found to be equivalent to their respective absorption spectra. UV−visible absorption spectra were recorded on a Hewlett-Packard diode-array spectrophotometer (Model 8452A).

Materials. Fluorene and 1,4-dibromobenzene were obtained from Aldrich.

Synthesis. 9,9-Dioctylfluorene (1).[9] To a solution of 8.48 g (51.1 mmol) of fluorene (Aldrich) in THF (120 mL) at −78 °C was added dropwise, 42.92 mL (107.31 mmol) of *n*-butyllithium (2.5 M in hexane; Aldrich). The mixture was stirred at −78 °C for 45 min, and 22.70 g (117.53 mmol) of octyl bromide (Aldrich) in THF (25 mL) was added dropwise to the mixture. The solution was allowed to warm to room temperature and was stirred for 3 h. The mixture was poured into water and extracted with ether. The organic extracts were washed with brine and dried over magnesium sulfate. The solvent was removed under reduced pressure. The excess of octyl bromide was removed by distillation (44 °C/0.3 mmHg) to give 19.75 g of 9,9-dioctylfluorene (pale-brown powder) R_f: 0.87 (silica TLC in hexane). Mp: 34−37 °C. ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 150.63, 141.15, 126.98, 126.70, 122.78, 119.64, 55.01, 40.46, 31.84, 30.11, 29.26, 29.05, 23.77, 22.64, 14.09. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.82 (dd, 2H, J = 4.3 Hz), 7.42 (m, 6H), 2.12 (m, 4H, J = 3.8 Hz), 1.35−1.24 (m, 20H), 0.96 (t, 6H, J = 7.1 Hz), 0.79 (m, 4H, J = 3.8 Hz). HRMS. Calcd for $C_{29}H_{42}$: 390.651. Found: 390.598.

2,7-Dibromo-9,9-dioctylfluorene (2).[19] To a solution of 9,9-dioctylfluorene (**1**) (15.01 g, 38.42 mmol) in $CHCl_3$ (58 mL) at 0 °C were added 96 mg (0.59 mmol) of ferric chloride and 4.14 mL (80.52 mmol) of bromine. It is important that the reaction proceeds in the dark to avoid any bromination of the aliphatic part of the molecule. The solution was warmed to room temperature and was stirred for 3 h. The resulting slurry was poured into water and washed with sodium thiosulfate until the red color disappeared. The aqueous layer was extracted with $CHCl_3$ (two times), and the combined organic layers were dried over magnesium sulfate to afford 21.07 g (>99%) of the title product as a pale-brown solid. R_f: 0.85 (silica TLC in hexane). Mp: 44−47 °C. ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 152.44, 138.94, 130.04, 126.07, 121.38, 120.96, 55.56, 40.02, 31.63, 29.78, 29.04, 29.01, 23.51, 22.47, 13.94. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.53 (d, 2H, J = 7.7 Hz), 7.46 (d, 2H, J = 1.8 Hz), 7.44 (d, 2H, J = 1.1 Hz), 1.91 (m, 4H, J = 3.7 Hz), 1.26−1.05 (m, 20H), 0.83 (t, 6H, J = 3.6 Hz), 0.58 (m, 4H, J = 3.5 Hz). HRMS. Calcd for $C_{29}H_{40}\cdot 79Br_2$: 546.150. Found: 546.149.

Preparation of $CuBr_2$ on Alumina (3).[20] To a solution of copper(II) bromide (10 g, 44.8 mmol; Aldrich) in distilled water (100 mL) was added 20 g of neutral alumina (∼150 mesh; Brockmann I Aldrich). The water was removed under reduced pressure, and the dry mixture gave a brown powder. The solid is dried at 90 °C below a pressure of 1 mmHg for 4 h.

2,7-Dibromofluorene (4).[20] To a solution of fluorene (1.5 g, 9.0 mmol; Aldrich) in CCl_4 (80 mL) was added 30 g of copper(II) bromide on alumina (**3**). The mixture was stirred at reflux for 5 h. Then, the solution was cooled to room temperature, and the solid material was filtered and washed with CCl_4 (50 mL). The organic solution was dried over magnesium sulfate. Removal of solvent gave 2.87 g (98%) of the title product as yellow crystals. Recrystallization was made in a mixture of ethyl acetate/ hexane (5:95 v/v). Mp: 159−160 °C (lit. mp 160−161 °C). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 144.65, 139.55, 130.01, 128.16, 121.04, 120.82, 36.43. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.67 (2H, d, J = 1 Hz), 7.61 (2H, d, J = 8 Hz), 7.51 (2H, dd, J = 8 Hz), 3.87 (2H, s). HRMS. Calcd for $C_{13}H_8\cdot 79Br_2$: 321.898. Found: 321.899.

Diethyl 2,7-Dibromofluorene-9,9-dicarboxylate (5). To a solution of diisopropylamine (1.54 g, 15.1 mmol; Aldrich) in THF (7 mL) at −78 °C was added dropwise 5.63 mL (14.07 mmol) of *n*-butyllithium (2.5 M in hexane; Aldrich). The mixture was stirred at −78 °C for 20 min and at 0 °C for 15 min and cooled again at −78 °C. 2,7-Dibromofluorene (**4**; 2.165 g, 6.7 mmol) in THF (70 mL) was added dropwise to the lithium diisopropylamide (LDA) solution and stirred for 30 min at this temperature. Ethyl chloroformate (3.43 g, 31.55 mmol; Aldrich), previously distilled on $CaCl_2$, was added to the mixture. The solution was allowed to warm to room temperature and was stirred for 3 h. The mixture was poured into water and extracted with ether. The organic extracts were washed with brine and dried over magnesium sulfate. The solvent was removed, and the residue was purified by column chromatography (silica gel, 7% ethyl acetate in hexane, R_f 0.15) to provide 2.99 g (95%) of the title product as a pale-white solid. Mp: 131−133 °C. ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 167.06, 141.38, 149.11, 132.35, 130.06, 121.63, 121.16, 68.68, 62.2, 13.83. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.93 (d, 2H, J = 1.7 Hz), 7.58 (dd, 2H, J = 1.5 and 8.2 Hz), 7.53 (d, 2H, J = 8.2

Hz), 4.27 (q, 4H, $J = 7.1$ Hz), 1.29 (t, 6H, $J = 7.1$ Hz). HRMS. Calcd for $C_{19}H_{16}O_4\cdot 79Br_2$: 466.951. Found: 466.949.

Ethyl 2,7-Dibromofluorene-9-carboxylate (6). The same procedure as that described for diethyl 2,7-dibromofluorene-9,9-dicarboxylate (**5**) was used, but with just 1 equiv of ethyl chloroformate. It is necessary to use 2 equiv of LDA to avoid the production of diethyl 2,7-dibromofluorene-9,9-dicarboxylate. Yield: 96% of yellow solid after purification by column chromatography (silica gel, 7% ethyl acetate in hexane, R_f 0.23). Mp: 98−100 °C. ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 169.16, 142.01, 139.19, 131.31, 128.93, 121.29, 121.14, 61.78, 52.81, 14.05. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.81 (d, 2H, $J = 0.7$ Hz), 7.57 (d, 4H), 7.55 (d, 2H), 4.82 (s, 1H), 4.27 (q, 2H, $J = 7.2$ Hz), 1.32 (t, 3H, $J = 7.2$ Hz). HRMS. Calcd for $C_{16}H_{12}O_2\cdot 79Br_2$: 394.928. Found: 394.929.

(Methoxyethoxy)ethyl 2,7-Dibromofluorene-9-carboxylate (7). To a solution of (diethylene glycol) methyl ether, $CH_3(OCH_2CH_2)_2OH$ (25 mL; Aldrich), were added 3.85 g (9.7 mmol) of ethyl 2,7-dibromofluorene-9-carboxylate (**6**) and concentrated H_2SO_4 (10 mol %). The solution was stirred and heated to 60 °C at about 10 mmHg. At this low pressure, ethanol was easily removed. The product (viscous limpid oil, 4.29 g) was purified by column chromatography (silica gel, 15% ethyl acetate in hexane, R_f 0.12). Yield: 94%. ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 168.96, 141.75, 139.07, 131.23, 128.91, 121.19, 121.03, 71.71, 70.34, 68.68, 64.56, 58.84, 52.58. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.80 (d, 2H, $J = 0.9$ Hz), 7.49 (m, 4H), 4.81 (s, 1H), 4.35 (q, 2H, $J = 4.5$ Hz), 3.72 (q, 2H, $J = 3.3$ Hz), 3.60 (m, 4H), 3.39 (s, 3H). HRMS. Calcd for $C_{19}H_{18}O_4\cdot 79Br_2$: 468.965. Found: 468.964.

2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (8).[21] To a solution of 2,7-dibromo-9,9-dioctylfluorene (**2**; 5 g, 9.1 mmol) in THF (70 mL) at −78 °C was added, by syringe, 7.64 mL (19.11 mmol) of *n*-butyllithium (2.5 M in hexane; Aldrich). The mixture was stirred at −78 °C, warmed to 0 °C for 15 min, and cooled again at −78 °C for 15 min. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4.00 g, 21.5 mmol; Aldrich) was added rapidly to the solution, and the resulting mixture was warmed to room temperature and stirred for 24 h. The mixture was poured into water and extracted with ether. The organic extracts were washed with brine and dried over magnesium sulfate. The solvent was removed by rotary evaporation, and the residue was purified by column chromatography (silica gel, 7% ethyl acetate in hexane, R_f 0.20) to provide 3.80 g (65%) of the title product as a pale-yellow solid. ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 150.31, 143.78, 133.54, 128.77, 119.23, 83.54, 55.03, 39.36, 31.65, 29.79, 29.05, 29.00, 24.80, 23.44, 22.45, 13.94. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.84 (d, 2H, $J = 7.6$ Hz), 7.78 (s, 2H), 7.75 (d, 2H, $J = 7.6$ Hz), 2.03 (m, 4H, $J = 3.4$ Hz), 1.43 (s, 24H), 1.26−1.04 (m, 20H), 0.83 (t, 6H, $J = 6.6$ Hz), 0.58 (m, 4H). HRMS. Calcd for $C_{41}H_{64}O_4\cdot 11B_2$: 642.499. Found: 642.497.

Preparation of Tetrakis(triphenylphosphine)palladium(0) $(PPh_3)_4Pd(0)$.[22] To a solution of palladium dichloride (0.25 g, 1.41 mmol; Aldrich) in dimethyl sulfoxide (DMSO, 17 mL; Aldrich) was added 1.85 g (7.06 mmol) of triphenylphosphine (Aldrich). The system was kept under an argon atmosphere. The mixture was heated at 140 °C until complete solubilization occurred. The heated bath was then taken away, and the solution was rapidly stirred for approximately 15 min. Hydrazine hydrate (0.28 mL; Aldrich) was added over 1 min. A vigorous reaction took place with evolution of nitrogen. The dark solution was immediately cooled with a water bath; crystallization began to occur at ∼125 °C. At this point the mixture is allowed to cool without the use of the water bath. After the mixture reached room temperature, it was filtered under argon on a coarse, sintered-glass funnel. The solid was washed successively with two 15 mL portions of ethanol and two 15 mL portions of diethyl ether. The product (yellow crystalline solid, 1.53 g) was stored under an inert atmosphere. Yield: 94%.

Polymerization.[17] Carefully purified 2,7-dibromofluorene derivative (1 equiv), 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (1 equiv), and $(PPh_3)_4Pd(0)$ (1.5−0.5 mol %) were dissolved in a mixture of toluene ([monomer] = 0.5 M) and aqueous 2 M Na_2CO_3 (or K_2CO_3) (1:1.5 toluene). The solution was first put under a nitrogen atmosphere and was refluxed with vigorous stirring for 48 h. The whole mixture was then poured into methanol (150 mL). The precipitated material was recovered by filtration through a Büchner funnel and washed with dilute HCl. The solid material was washed for 24 h in a Soxhlet apparatus using acetone to remove oligomers and catalyst residues. The resulting polymers were soluble in THF and $CHCl_3$. Yields: ∼65−90%.

Poly[(1,4-phenylene)-2,7-(9,9-dioctylfluorene)] (P1). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.85 (2H, d), 7.65−7.5 (4H, m), 2.1 (4H, m), 1.15 (24H, m), 0.85 (6H, t).

Poly[2,7′-(9,9-dioctyl-2′,7-bifluorene)] (P2). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.1−8.0 (12H, m), 4.0 (2H, s), 2.1 (4H, m), 1.1 (24H, m), 0.8 (6H, t).

Poly[2,7-(9,9-dioctylfluorene)] (P3). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.85 (2H, d), 7.68 (4H, m), 2.15 (4H, m), 1.2 (24H, m), 0.8 (6H, t).

Poly-2,7′-(diethyl 9,9-dioctyl-2,7′-bifluorene-9′,9′-dicarboxylate)] (P4). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.2 (2H, s), 7.75 (5H, m), 7.65 (5H, m), 4.45−4.2 (4H, m), 2.1 (4H, m), 1.7 (1.5H, m), 1.4−1.0 (24H, m), 0.9−0.6 (6H, 2t).

Poly[2,7′-(ethyl 9,9-dioctyl-2,7′-bifluorene-9′-carboxylate)] (P5). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.2 (s, 2H), 7−7.8 (m, 10H), 4.7 (1H, s), 4−4.4 (2H, m), 1.8−2.2 (4H, m), 1.6 (3H, m), 0.5−1.4 (30H, m).

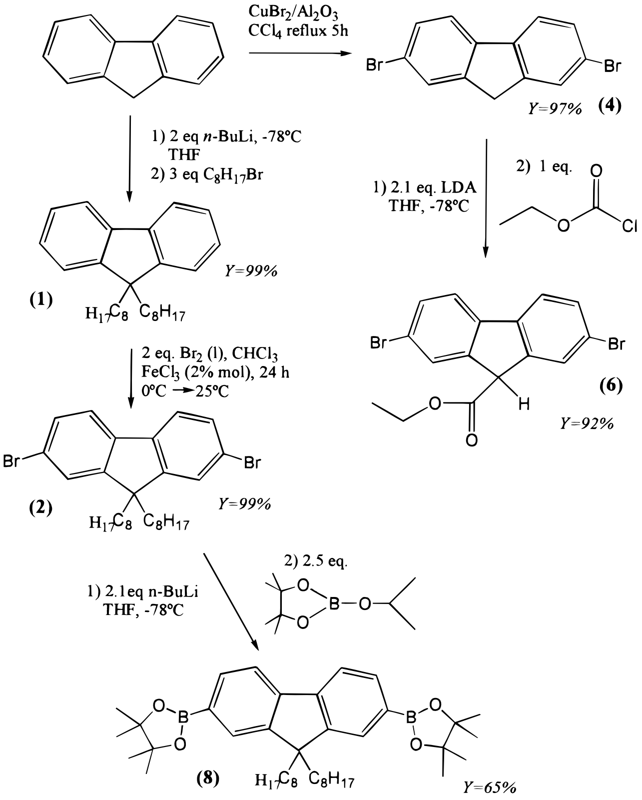
Poly[2,7′-[(methoxyethoxy)ethyl 9,9-dioctyl-2′,7-bifluorene-9′-carboxylate]] (P6). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.9−7.6 (12H, m), 4.7 (1H, s), 4.45 (2H, m), 3.7 (6H, d), 3.4−3.1 (3H, m), 2.1 (4H, m), 1.4−1.0 (24H, m), 0.9−0.6 (6H, m).

Base Doping. Polymer P5 was solubilized in a solution of THF (Aldrich). To this solution were added 2 equiv of potassium *tert*-butoxide, and the mixture was warmed slightly for activation of the base. The precipitated polymer was filtered on nylon filters (0.45 μm) under vacuum and was washed with cooled THF. Before electrical measurements on pressed pellets, polymers were dried under reduced pressure (25 °C/0.1 mmHg).

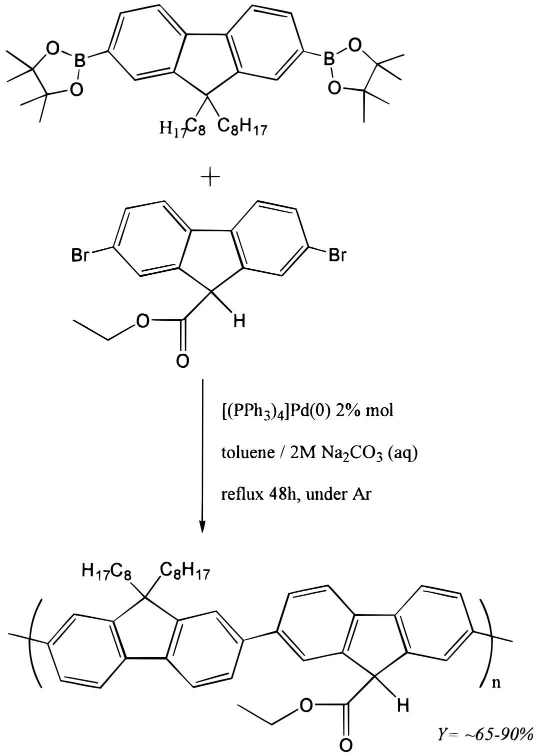
Results and Discussion

Synthesis and Structural Characterization. As shown in Scheme 1, all monomers have been easily prepared from fluorene. In the synthesis of ethyl 2,7-dibromofluorene-9-carboxylate, it was necessary to use 2 equiv of lithium diisopropylamide (LDA) since the pK_a of this fluorene derivative is about 10 while fluorene has a pK_a of 22.[23] With 1 equiv of LDA, the lithium moieties migrated to the formed monosubstituted derivative to yield almost exclusively the 9,9-disubstituted fluorene. Suzuki couplings[17] between 2,7-dibromofluorene derivatives and fluorene derivatives bearing diboronic moieties (see Scheme 2) allowed the preparation of all polymers shown in Chart 1, including the novel acidic conjugated polymers. Because of the use of organolithium compounds in the synthesis of the boronic derivatives, it was impossible to prepare the homopolymers with ester substituents. Therefore, with the exception of poly[2,7-(9,9-dioctylfluorene)] (**P3**), this synthetic procedure gives alternating polyfluorene derivatives. This alternating structure can be, however, very useful for the preparation of well-defined amphiphilic conjugated polymers. For instance, assuming an anti conformation for polymer **P6** (as shown in Chart 1), it is quite evident that this structure should give access to amphiphilic properties (and, possibly, **P4** and **P5**) where one side of the molecules has a hydrophobic nature whereas the other one can exhibit some hydrophilic properties. These interesting properties could be particularly useful for the preparation of well-defined polymeric Langmuir−

Scheme 1



Scheme 2



Blodgett films and should be tested in the near future in different electrical and optical devices.

On the basis of SEC measurements (with a calibration using polystyrene standards), this versatile synthesis allows the preparation of polyfluorene derivatives with good molecular weights (Table 1). Indexes of polydispersity (M_w/M_n) around 2 have been calculated, which is consistent with a polycondensation reaction. On the basis of these results, it seems that the presence of flexible and solubilizing side chains is required to get high molecular weights. Indeed, polymers without substituents on the 2,7-dibromofluorenes (or 1,4-dibromobenzene) show systematically lower molecular weights.

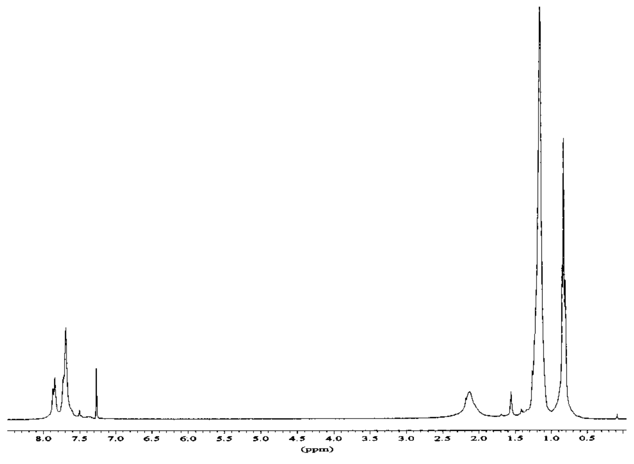


Figure 1. ^{1}H-NMR spectrum of poly[2,7-(9,9-dioctylfluorene)] in CDCl$_3$ at 298 K.

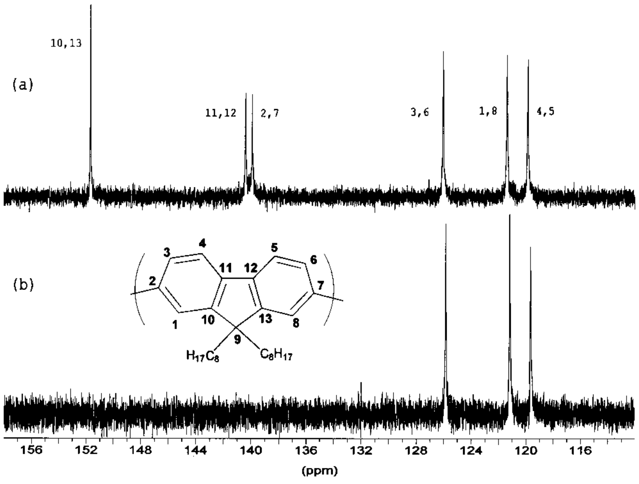


Figure 2. Aromatic region of the (a) ^{13}C NMR and (b) DEPT135 NMR spectra of poly[2,7-(9,9-dioctylfluorene)] in CDCl$_3$ at 298 K.

Table 1. Number-Average (M_n) and Weight-Average (M_w) Molecular Weights of the Polyfluorene Derivatives

polymer	M_n	M_w	M_w/M_n
P1	4600	7600	1.7
P2	2400	2900	1.2
P3	24000	40000	1.7
P4	14000	32000	2.2
P5	5600	7800	1.4
P6	6300	8900	1.4

NMR analyses indicate clearly that well-defined poly(2,7-fluorene) derivatives have been indeed obtained. As an example and because of its simple repeating unit, we show here the ^{1}H (Figure 1) and ^{13}C NMR (Figure 2) spectra of poly[2,7-(9,9-dioctylfluorene)] (**P3**). Moreover, a similar analysis had been previously reported by Yoshino et al.[10] for FeCl$_3$-polymerized poly(9,9-dialkylfluorene)s and could serve for comparison purposes. As shown in Figure 1, the ^{1}H NMR spectrum of P3 is consistent with a well-defined structure. The only major difference from that published by Yoshino et al. is the lower intensity of the 7.5 ppm peak which had been attributed to the terminal units.[10] This result is in agreement with the higher molecular weight of the

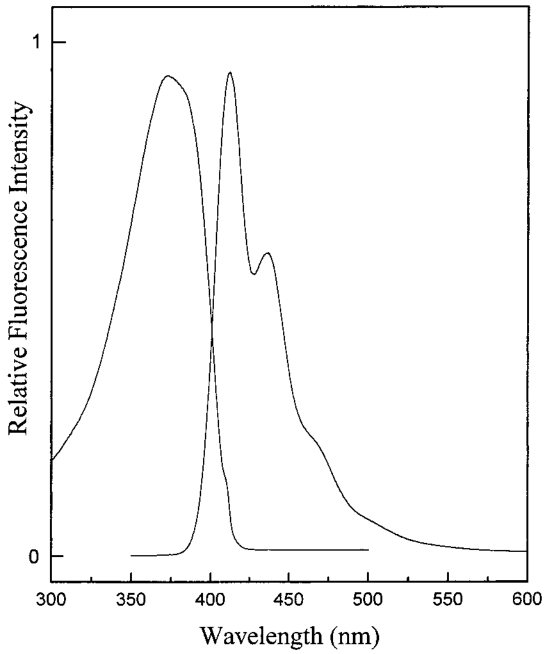


Figure 3. Excitation and emission spectra of fluorescence poly[(1,4-phenylene)-2,7-(9,9-dioctylfluorene)] in chloroform at 298 K.

Table 2. Maximum Excitation Wavelength, Maximum Emission Wavelength, and Fluorescence Quantum Yield for the Polyfluorene Derivatives in Chloroform at 298 K

polymer	λ_{exc} (nm)	λ_{em} (nm)	ϕ_{fl}
P1	362	407	0.87
P2	372	415	0.71
P3	373	412	0.79
P4	367	408	0.36
P5	368	413	0.50
P6	371	415	0.16

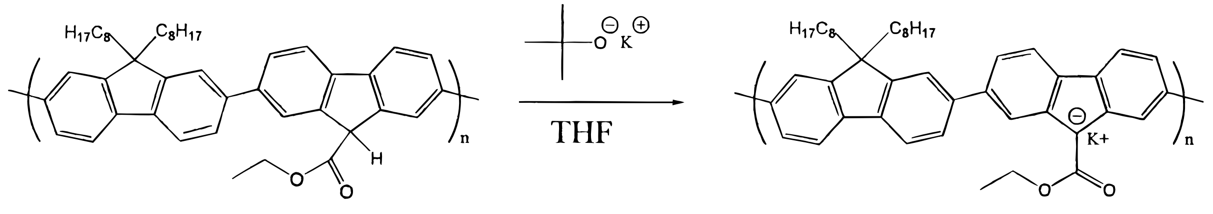
polymer obtained with the palladium-catalyzed polymerization reaction. On the other hand, the aromatic region of the ^{13}C NMR spectrum of poly[2,7-(9,9-dioctylfluorene)] gives more precise information about the regiochemical structure of the polymer. As reported in Figure 2, only six peaks appear in the aromatic region, related to the 12 aromatic carbon atoms of the symmetric repeating unit (Chart 1). Once again, this ^{13}C NMR spectrum is in agreement with that reported by Yoshino et al., with the difference that their ^{13}C NMR spectrum shows many additional peaks related to cross-linking or misslinking reactions.[10] Moreover, distortionless enhanced by polarization transfer (at 135°) (DEPT135) NMR analyses show only three peaks related to the aromatic carbon atoms bearing a hydrogen atom. This information confirms that the polymer prepared from a palladium-catalyzed polymerization reaction is regioregular (2,7-linked).

Fluorescence Properties. All these polyfluorene derivatives have been prepared for their potentially interesting luminescent properties. These polymers possess a rigid structure and a large band gap; all these properties should favor good blue-light-emitting properties.[7,24] All polymers of this study show similar absorption and emission spectra; all these polyfluorene derivatives emit in the blue region with a maximum around 410 nm (Table 2). All emission spectra exhibit also the same vibronic structure which is associated with a coupled C=C stretching mode (1550−1600 cm^{-1}) (Figure 3). In general, the presence of a well-defined vibronic structure in the emission spectra indicates that the polymers have a rigid and well-defined backbone.[2,7] In addition to interesting blue emission, some fluorescence quantum yields are very high (up to 0.87; see Table 2). However, it is worth noting that the presence of the carbonyl function in **P4**, **P5**, and **P6** reduces strongly the fluorescence quantum yield. It is well-known that the carbonyl moieties are good fluorescence quenchers since an intercrossing process is favored by their n−π* transition.

Base-Doping and Electrical Properties. Polymers **P5** and **P6** possess an acidic proton in the 9-position which should have, on the basis of studies performed on the monomers,[14,23] a pK_a of about 10 in DMSO and of about 14 in water. These polymers could then be deprotonated (base-doped) and, in principle, this novel doping method could generate n-type charge carriers which could lead to some interesting electrical properties. Since these polymers are soluble in organic solvents such as tetrahydrofuran and chloroform, the base-doping reaction was carried out in these solvents with potassium *tert*-butoxide (see Scheme 3). As shown in Figure 4, the neutral form of **P5** exhibits a strong absorption band at 368 nm, whereas, upon base doping, the deprotonated form exhibits an additional peak near 430 nm. A similar absorption band around 400 nm was reported for the deprotonated monomeric analog.[14] This base-doping reaction induces a yellow-to-orange color change. This phenomenon is reversible, and the polymer recovers its initial color upon protonation. It is important to note here that, due to its alternating structure, only 50% of the fluorene units can be deprotonated. Nevertheless, this feature can be an advantage since fully protonated polyanilines are less conducting than 50% acid-doped polyanilines.[25]

As expected, four-probe measurements on dried pressed pellets of the base-doped form show electrical conductivities of 10^{-6}−10^{-5} S/cm, while neutral polyfluorene derivatives exhibit conductivities lower than 10^{-9} S/cm. However, at this conductivity level, it is difficult to distinguish ionic from electronic contribution. More extensive electrical characterization will be performed to determine the nature of the charge carriers and the mechanisms involved in the electrical transport. Nevertheless, it must be mentioned that this electrical conductivity level is excellent for an n-doped polymer considering that all doping processes and electrical measurements have been carried out in air. Moreover, it is possible that the enolate form of the ester substituent decreases the mobility of the charge carrriers due to a partial localization of the negative charge onto the

Scheme 3



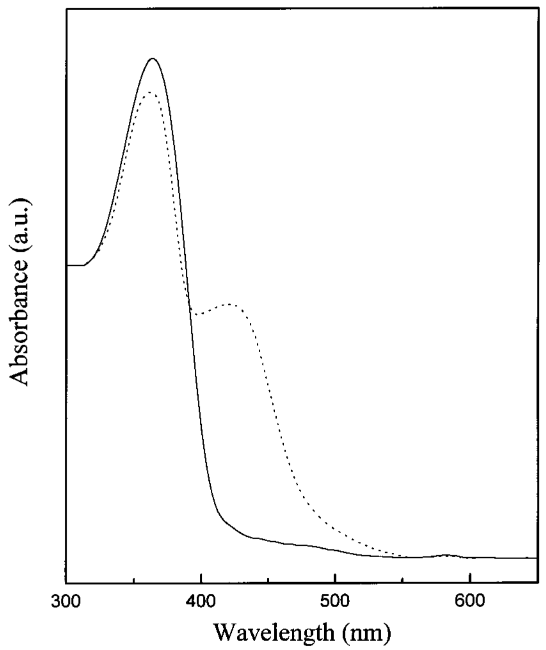


Figure 4. UV-visible spectra of the poly[2,7′-(ethyl 9,9-dioctyl-7,2′-bifluorene-9-carboxylate)] in the neutral state (—) and in the base-doped state (- - -). These spectra were obtained in THF at 298 K. Base doping was carried out with the use of potassium *tert*-butoxide.

oxygen atom.[14] This assumption is in agreement with some results reported by Pei et al.[26] on poly(2-hydroxy-1,4-phenylene) that have shown that the generation of anions, even directly connected to a conjugated polymer chain, leads to electrical conductivities of only 5×10^{-9} S/cm. For all these reasons, it is expected that the synthesis of monosubstituted polyfluorenes bearing a cyano group at the 9-position should allow the preparation of base-dopable highly conducting polymers.

Conclusions

This study has shown that palladium-catalyzed Suzuki couplings can give easy access to a large number of well-defined processable poly(2,7-fluorene) derivatives. In particular, this synthetic method allowed the preparation, for the first time, of acidic conjugated polymers (e.g., poly[2,7-(alkyl 9,9-dioctyl-7,2′-bifluorene-9′-carboxylate)]) which, upon base doping, shows electrical conductivities of 10^{-6}–10^{-5} S/cm. Moreover, all polyfluorene derivatives investigated in this study have exhibited strong fluorescence in the blue region (emission maximum around 410 nm). All these interesting electrical and photophysical properties make these materials quite promising for applications in blue-light-emitting devices as emitting units as well as novel air-stable electron-injecting electrodes. It is even expected that some of these polyfluorene derivatives could be processed by the Langmuir–Blodgett technique, permitting the fabrication of well-organized molecular devices.

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