8986 *Macromolecules* **2003,** *36,* 8986−8991

Optical and Electrical Properties of π-Conjugated Polymers Based on Electron-Rich 3,6-Dimethoxy-9,9-dihexylfluorene Unit

Serge Beaupré and Mario Leclerc*

Canada Research Chair in Polymer Chemistry, Département de Chimie, Université Laval, Quebec City, Quebec, Canada G1K 7P4

Received July 23, 2003; Revised Manuscript Received September 15, 2003

ABSTRACT: A new family of π-conjugated polymers has been developed using 3,6-dimethoxy-9,9-dihexylfluorene as an electron-rich unit. These electroactive and photoactive polymers have been prepared from nickel(0)-mediated coupling or by palladium-catalyzed Suzuki coupling. These new 3,6-dimethoxy-9,9-dihexylfluorene-based copolymers have demonstrated emission spanning the entire visible spectrum. Moreover, all of these polymers show reversible electroactivity upon reduction and oxidation, and as expected, the presence of methoxy groups onto the fluorene moiety increases the ionization potential of the resulting copolymers by about 0.2 eV when compared with some 9,9-dihexylfluorene-based copolymers. The reduction of the energy barrier for the injection of holes in related polymeric light-emitting devices should contribute to the enhancement of their performances.

Introduction

Since the discovery of polymeric light-emitting diodes based on poly(*p*-phenylenevinylene) by the Cambridge group,[1] the search for new photoactive and electroactive conjugated polymers has expanded rapidly, including new poly(phenylenevinylene)s,[1−3] poly(*p*-phenylene)s,[4,5] poly(thiophene)s,[6] poly(2,7-(*N*-alkylcarbazole))s,[7,8] and poly(fluorene)s.[9−15] Among these polymers, polyfluorene derivatives have revealed particularly interesting optical and electrical properties and emit colors spanning the entire visible range. It is known that an optimized light-emitting diode requires efficient and balanced charge injection, good and comparable mobilities for both holes and electrons, and high luminescence quantum yield. One of the drawbacks for light-emitting diodes based on polyfluorene derivatives is the injection of holes from the anode due to the low ionization potential (IP) of most derivatives. The control of the ionization potential becomes important for the optimization of PLED's made from this class of polymers. Many ways have been used to modulate the ionization potential (IP), electron affinity (EA), and band gap of polyfluorenes derivatives.[13,15−18] We report here a new synthetic strategy to modulate the IP of polyfluorenes derivatives by using two new monomers: 2,7-dibromo-3,6-dimethoxy-9,9-dihexylfluorene and 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,6-dimethoxy-9,9-dihexylfluorene. Here, we report the synthesis, the optical properties, and the electrochemical properties of a series of well-defined copolymers having 3,6-dimethoxy-9,9-dihexylfluorene moiety.

Experimental Part

General. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX300 in deuterated chloroform solutions at 298 K. Number-average (M_n) and weight-average (M_w) molecular weight were determined by size exclusion chromatography (SEC) with HPLC Pump using a Waters 515 differential refractometer. The calibration curve was made with a series of monodispersed polystyrene standards in THF (HPLC grade, Aldrich).

UV−vis absorption spectra were recorded on a Hewlett-Packard diode-array spectrophotometer (model 8452A), and fluorescence measurements were carried out with a Carry Eclipse spectrometer. For solution fluorescence analyses, the polymer concentration was about 10^{-6} M, giving an absorbance always less than 0.06 to avoid any inner filter effect. The quantum yield of fluorescence was determined by the relative method by comparing the areas of the fluorescence spectra of the standard and the sample. As reference substances, we used 9,10-diphenylanthracene ($\phi_F = 0.90 \pm 0.02$; cyclohexane),[19] PQC10 ($\phi_F = 0.11$; chloroform),[20] 2,2-bipyridylruthenium chloride ($\phi_F = 0.28$; water),[21] and rhodamine 101 (0.89 ± 0.02; acidified ethanol).[22] For the fluorescence spectrum in the solid state, a thin film of polymer was applied on a triangular cell. The cell was put at 45° of the incident beam.

Thermogravimetric analysis (TGA) was performed on a Mettler Toledo TG50 under heating rate of 20 °C/min and a nitrogen flow rate of 200 mL/min. Differential scanning calorimetry (DSC) was performed on Perkin-Elmer DSC7 module in conjunction with the Perkin-Elmer thermal analysis controller TAC7/DX at a heating rate of 20 °C/min.

Cyclic voltammetry was carried out in a two-compartment cell with a Solartron potentiostat (model 1287) with platinum electrodes at a scan rate of 50 mV/s against an Ag/Ag^+ (0.1 M $AgNO_3$ in acetonitrile) reference electrode in an anhydrous and argon-saturated solution of 0.1 M Bu_4NBF_4 in acetonitrile.

Synthesis. *3,6-Dimethoxy-9-fluorenone* (**1**).[23,24] 2,5⁗-Diiodo-3,3′,4‴,3⁗-tetramethyl-3″,4″-dihexyl-2,2′:5′,2″:5″,2‴:5‴,2⁗-quinquethiophene-1″,1″dioxide,[15,21] 2,5-bis(octyloxy)-1,4-benzenedicarboxaldehyde,[25] 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dihexylfluorene[26] (monomer A), and tetrakis(triphenylphosphine)palladium(0)[27] were synthesized following procedures reported in the literature. 1,4-Dibromobenzene, 2,5-dibromothiophene, and 2-thiopheneacetonitrile were purchased from Aldrich and used without further purification. Acetonitrile (Aldrich) was dried over CaH_2 under an inert atmosphere (nitrogen) for 24 h. Tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) was recrystallized three times in a 50/50 mixture of methanol/water and dried at 100 °C under reduced pressure, as reported in the literature.[28]

3,6-Dimethoxyfluorene (**2**). In a 250 mL round-bottom flask, 3,6-dimethoxy-9-fluorenone (10.0 g, 41.6 mmol) was dissolved in dichloromethane (165 mL) and cooled to 0 °C. The solution was treated under stirring with $TiCl_4$, which was added by syringe through a septum. A solution of dimethylamine−borane complex (4.90 g, 83.2 mmol) in dichloromethane (21 mL) was added to the cold solution, and the mixture was

---

* To whom correspondence should be addressed.

10.1021/ma035064j CCC: $25.00

allowed to warm to room temperature. Stirring was continued for 30 min. Thereafter, the solution was poured in 200 mL of aqueous 1 N HCl for the destruction of excess reductant and hydrolysis. Phases were separated, and the aqueous layer was extracted three times with dichloromethane. The combined extracts were washed with brine and dried with sodium sulfate. The solvent was removed under reduced pressure, and the crude product was purified by recrystallization from ethanol to afford the title product as white needles (7.05 g, 75%); mp 89−91 °C. ^{13}C NMR (75 MHz, CDCl$_3$, ppm): 159.22; 142.99; 136.52; 125.59; 113.37; 104.85; 55.58; 35.43. ^{1}H NMR (300 MHz, CDCl$_3$, ppm): 7.42 (d, 2H, $J = 8.2$ Hz); 7.29 (d, 2H, $J = 2.2$ Hz); 6.89 (dd, 2H, $J = 2.2$ and 8.2 Hz); 3.91 (s, 6H); 3.76 (s, 2H). HRMS: Calculated for $C_{15}H_{14}O_2$: 226.0994. Found: 226.0998.

3,6-Dimethoxy-9,9-dihexylfluorene (**3**). To a solution of 3,6-dimethoxyfluorene (10.0 g 44.2 mmol) in anhydrous THF (220 mL) at −78 °C, *n*-butyllithium (38.0 mL; 95 mmol; 2.5 M in hexane) was added dropwise. The mixture was stirred at −78 °C for 45 min, and 1-bromohexane (14.9 mL, 106.1 mmol) was added dropwise to the mixture. The solution was allowed to warm to room temperature and stirred for 5 h. The mixture was poured into water and extracted several times with diethyl ether. The organic extracts were washed with brine and dried over magnesium sulfate. The solvent was removed under reduced pressure, and the excess of 1-bromohexane was removed by distillation under reduced pressure to afford the 3,6-dimethoxy-9,9-dihexylfluorene as a viscous oil (16.3 g, 93%). ^{13}C NMR (75 MHz, CDCl$_3$, ppm): 159.20; 143.89; 142.28; 123.53; 113.49; 104.78; 55.57; 53.86; 40.62; 31.71; 29.91; 23.93; 22.74; 14.16. ^{1}H NMR (300 MHz, CDCl$_3$, ppm): 7.19 (m, 4H); 6.84 (dd, 2H, $J = 2.2$ Hz and $J = 6.1$ Hz); 3.89 (s, 6H); 1.88 (m, 4H); 1.12−1.03 (m, 12H); 0.75 (t, 6H, $J = 6.7$ Hz); 0.63 (m, 4H). HRMS: calculated for $C_{27}H_{38}O_2$: 394.2872. Found: 394.2878.

2,7-Dibromo-3,6-dimethoxy-9,9-dihexylfluorene (**4**). To a solution of 3,6-dimethoxy-9,9-dihexylfluorene (16.3 g, 41.3 mmol) in chloroform (65 mL) at 0 °C, ferric chloride (5% mol) and bromine (4.4 mL, 86 mmol) were added. The solution was allowed to warm to room temperature and stirred for 24 h. The resulting slurry was poured into water and washed several times with a sodium thiosulfate aqueous solution. The aqueous layers were extracted with chloroform, and the organic layers were combined and dried over magnesium sulfate. The solvent was removed under reduced pressure, and the crude product was purified by recrystallization from a mixture of ethanol/tetrahydrofuran to afford the title product as white needles (15.0 g, 66%); mp 171−173 °C. ^{13}C NMR (75 MHz, CDCl$_3$, ppm): 155.35; 144.58; 140.81; 127.70; 111.28; 103.28; 56.61; 54.63; 40.29; 31.67; 29.73; 23.83; 22.72; 14.14. ^{1}H NMR (300 MHz, CDCl$_3$, ppm): 7.44 (s, 2H); 7.18 (s, 2H); 4.00 (s, 6H); 1.86 (m, 4H); 1.15−1.04 (m, 12H); 0.77 (t, 6H, $J = 6.6$ Hz); 0.56 (m, 4H). HRMS: calculated for $C_{27}H_{36}O_2Br_2$: 550.1082. Found: 550.1076.

*2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,6-dimethoxy-9,9-dihexylfluorene (Monomer B)***.** To a solution of 2,7-dibromo-3,6-dimethoxy-9,9-dihexylfluorene (5.00 g, 9.1 mmol) in anhydrous THF (90 mL) at −78 °C was added TMEDA (2.8 mL, 19.1 mmol) and *n*-butyllithium (7.6 mL, 19.1 mmol, 2.5 *m* in hexane). The mixture was stirred at −78 °C for 45 min. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5.5 mL, 27.2 mmol) was added rapidly to the solution. The mixture was allowed to warm to room temperature and stirred overnight. The mixture was poured into water and extracted with diethyl ether. The organic extracts were combined and washed with brine. The solvent was removed under reduced pressure, and the crude product was purified by recrystallization from an EtOH/THF mixture to afford the title as white powder (2.26 g, 39%); mp 165−166 °C. ^{13}C NMR (75 MHz, CDCl$_3$, ppm): 164.04; 144.98; 143.46; 130.43; 102.05; 83.32; 56.14; 53.90; 39.96; 31.46; 29.59; 24.85; 23.56; 22.52; 14.03. ^{1}H NMR (300 MHz, CDCl$_3$, ppm): 7.54 (s, 2H); 7.15 (s, 2H); 3.93 (s, 6H); 1,91 (m, 4H); 1.38 (s, 24H); 1.10−1.01 (m, 12H); 0.75 (t, 6H, $J = 6.6$ Hz); 0.58 (m, 4H). HRMS: Calculated for $C_{39}H_{60}B_2O_6$: 646.4576. Found: 646.4565.

2-Thiophene-(1-cyano)vinylene-2,5-dioctyloxy)-1,4-phenylene-(2-cyano)vinylene-5-thiophene (**5**). In a 100 mL round-bottom flask, 50 mL of methanol is added to a mixture of 1.75 g of 2,5-bis(octyloxy)-1,4-benzenedicarboxaldehyde and 1.15 mL of 2-thiopheneacetonitrile (2.4 equiv). Once the monomers were in solution, potassium *tert*-butoxide was added in catalytic amount. The mixture was stirred for 3 h at room temperature. The solid was filtered and washed with a large amount of methanol to afford the title product as an orange powder (85%); mp 120−122 °C. ^{13}C NMR (75 MHz, CDCl$_3$, ppm): 151.51; 139.92; 133.28; 128.16; 127.21; 126.46; 125.44; 117.23; 110.88; 106.01; 69.40; 31.80; 29.37; 29.29; 29.22; 26.22; 22.70; 14.12. ^{1}H NMR (300 MHz, CDCl$_3$, ppm): 7.87 (s, 2H); 7.83 (s, 2H); 7.39 (d, 2H, $J = 3.5$ Hz); 7.32 (d, 2H, $J = 5.1$ Hz); 7.08 (m, 2H); 4.10 (t, 4H, $J = 6.2$ Hz); 1.84 (qt, 4H, $J = 6.7$ Hz); 1.53 (m, 4H); 1.37−1.26 (m, 16H); 0.88 (t, 6H, $J = 6.2$ Hz). HRMS: Calculated for $C_{36}H_{44}N_2O_2S_2$: 600.2844. Found: 600.2840.

2-Bromothiophene-(1-cyano)vinylene-2,5-dioctyloxy)-1,4-phenylene-(2-cyano)vinylene-5-bromothiophene (**6**). In a 100 mL round-bottom flask, 40 mL of DMF was added to monomer **5**. The flask was put in the dark, and then 724 mg (2.1 equiv) of NBS was added in one step. The solution was warmed to 80 °C and stirred for 24 h. The mixture was allowed to cool to room temperature and poured in 30 mL of water. The red solid was filtered and washed with methanol. The crude product was purified by recrystallization from chloroform to afford the title product as red needles (73%); mp 162−164 °C. ^{1}H NMR (300 MHz, CDCl$_3$, ppm): 7.77 (s, 2H); 7.71 (s, 2H); 7.12 (d, 2H, $J = 3.9$ Hz); 7.02 (d, 2H, $J = 4.0$ Hz); 4.07 (t, 4H, $J = 6.2$ Hz); 1.84 (qt, 4H, $J = 6.7$ Hz); 1.53 (m, 4H); 1.37−1.26 (m, 16H); 0.88 (t, 6H, $J = 6.2$ Hz). HRMS: Calculated for $C_{36}H_{42}N_2O_2S_2Br_2$: 756.1054. Found: 756.1064.

General Procedure of Polymerization. The synthesis of all copolymers are shown in Schemes 2−4. Poly(2,7-(3,6-dimethoxy-9,9-dihexylfluorene) (**P1**) was synthesized by nickel(0)-mediated polymerization.[29] All others copolymers (**P2**−**P6**) were synthesized by palladium-catalyzed Suzuki couplings.[10,15] Here is a typical procedure for the synthesis of the copolymers. To a mixture of carefully purified 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,6-dimethoxy-9,9-dihexylfluorene (monomer B) or 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dihexylfluorene (monomer A), dihalide compound (1.00 equiv), and freshly prepared Pd(0)(PPh$_3$)$_4$ was added a degassed mixture of THF ([monomer = 0.25 M]) and aqueous 2 M K_2CO_3 (3/2 in volume). The mixture was vigorously stirred at 85−90 °C for 48−72 h. The whole mixture was then poured slowly into cold methanol. The precipitate material was collected by filtration and washed with methanol. The solid 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$_3$.

Poly(2,7-(3,6-dimethoxy-9,9-dihexylfluorene)) (**P1**). ^{1}H NMR (300 MHz, CDCl$_3$, ppm): 7.37 (m, 4H); 3.94 (s, 6H); 1.98 (m, 4H); 1.17 (m,12H); 0.97 (m, 4H); 0.82 (m, 6H).

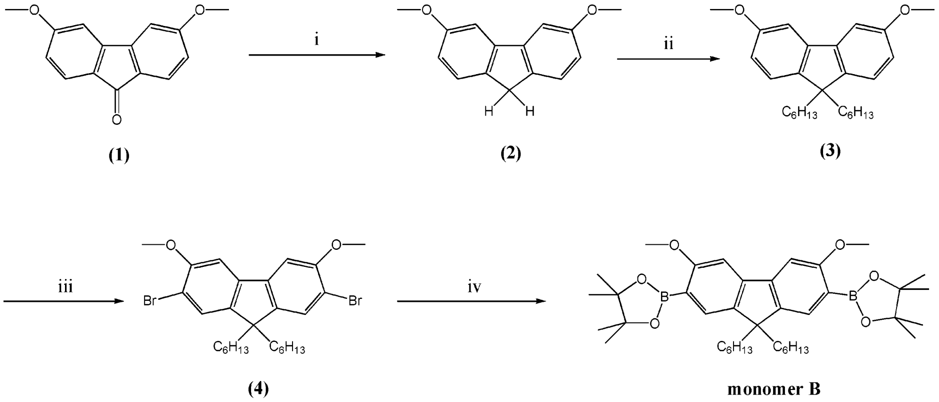
Poly[2,7-(3,6-dimethoxy-9,9-dihexylfluorene)-co-alt-2,7-(9,9-dihexylfluorene)] **(P2).** ^{1}H NMR (300 MHz, CDCl$_3$, ppm): 7.83 (m, 2H); 7.69 (m, 2H); 7.60 (m, 2H); 7.39 (m, 4H); 4.01 (s, 6H); 2.06 (m, 8H); 1.18 (m, 24H); 0.85 (m, 20H).

Poly[2,7-(3,6-dimethoxy-9,9-dihexylfluorene)-co-alt-2,5-thiophene] (**P3**). ^{1}H NMR (300 MHz, CDCl$_3$, ppm): 7.62 (m, 4H); 7.31 (m, 2H); 4.11 (s, 6H); 2.01 (m, 4H); 1.10 (m, 12H); 0.79 (m, 10H).

Poly[2,7-(3,6-dimethoxy-9,9-dihexylfluorene)-co-alt-p-phenylene] (**P4**). ^{1}H NMR (300 MHz, CDCl$_3$, ppm): 7.75 (m, 4H); 7.38 (m, 4H); 4.03 (s, 6H); 1.98 (m, 4H); 1.14 (m, 12H); 0.83 (m, 10H).

Poly[2,7-(3,6-dimethoxy-9,9-dihexylfluorene)-co-alt-2,5-(3,3′,-4‴,3⁗-tetramethyl-3″,4″-dihexyl-2,2′:5′,2″:5″,2‴:5‴,2⁗-quinquethiophene-1″,1″dioxide) (**P5**). ^{1}H NMR (300 MHz, CDCl$_3$, ppm): 7.66 (m, 2H); 7.61 (m, 2H); 7.47 (m, 2H); 7.29 (m, 2H); 4.09 (m, 6H); 2.70 (m, 4H); 2.33 (m, 12H); 2.00 (m, 4H); 1.62−1.56 (m, 8H); 1.36 (m, 8H); 1.08 (m, 12H); 0.92 (m, 6H); 0.78−0.69 (m, 10H).

Scheme 1. Synthesis of 3,6-Dimethoxy-9,9-dihexylfluorene Units[a]



[a] Reagents and conditions: (i) $TiCl_4$–dimethylamine–borane complex/CH_2Cl_2; (ii) *n*-BuLi/1-bromohexane/THF; (iii) Br_2/$FeCl_3$/$CHCl_3$; (iv) *n*-BuLi/2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane/THF.

Scheme 2. Synthesis of Polymers P1 and P2

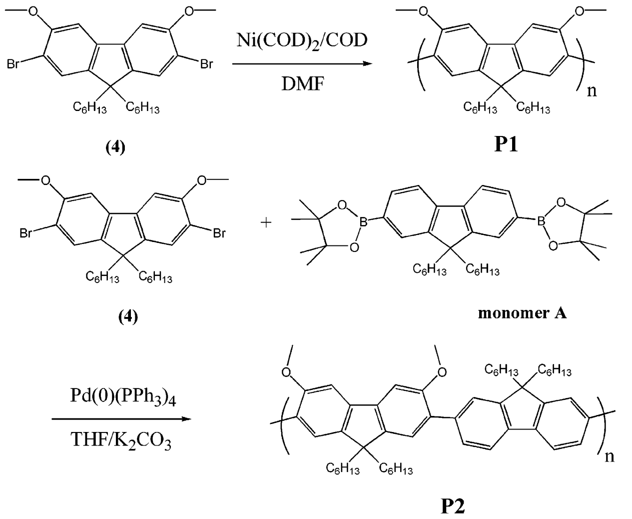


Table 1. Molecular Weights and Thermal Analysis Data of P1–P6

polymer	M_n	M_w	M_w/M_n	T_g (°C)	T_d (°C)
P1	5600	9200	1.6	130	407
P2	41 200	176 000	4.3	128	412
P3	2400	3100	1.3	65	399
P4	2700	3700	1.4	60	224
P5	2500	3600	1.4	111	260
P6	13 300	41 000	3.0		388

Poly[2,7-(3,6-dimethoxy-9,9-dihexylfluorene)-co-alt-2,5-bis(2-thienyl-2-cyanovinyl)-1-(2′-octyloxy)-5′-octyloxybenzene) (**P6**). ^1H NMR (300 MHz, $CDCl_3$, ppm): 7.95 (m, 4H); 7.60 (m, 2H); 7.43 (m, 4H); 7.31 (m, 2H); 4.14 (m, 10H); 1.92 (m, 8H); 1.59 (m, 4H); 1.37–1.10 (m, 24H); 0.85–0.78 (m, 20H).

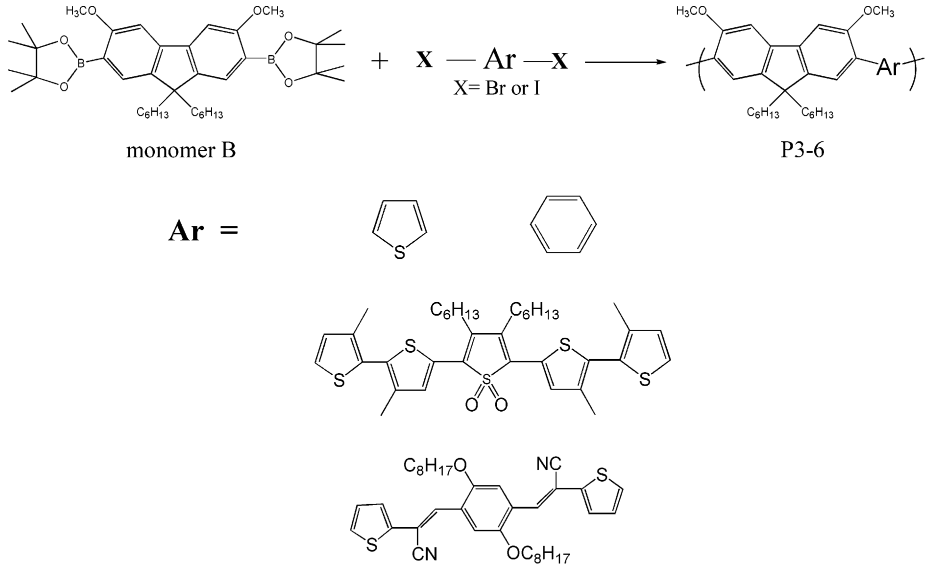
Results and Discussion

Synthesis of Monomers. The synthesis of the fluorene derivatives is shown in Scheme 1. 3,6-Dimethoxy-9-fluorenone (**1**) was prepared in a good yield following a multiple-step synthesis.[23,24] In our first attempts to obtain 3,6-dimethoxyfluorene (**2**), an 1,2-ethanedithiol/$FeCl_3$–SiO_2/Raney nickel[30,31] treatment was utilized, but low yields were obtained. We found an efficient one-step reaction to obtain, in a high yield, compound **2**: 3,6-dimethoxy-9-fluorenone is treated with titanium tetrachloride in the presence of a dimethylamine–borane complex.[32] This mild and fast deoxygenation reaction is useful to reduce diaryl ketone to methylene in the presence of methoxy groups and is more efficient than other reduction reactions such as Wolf–Kishner or Clemmensen reaction. This direct reduction of (**1**) afforded 3,6-dimethoxyfluorene (**2**) in 75% yield. Alkylation of **2** with *n*-BuLi/Br–$CH_2(CH_2)_4CH_3$ afforded compound **3** in 93% yield. Direct bromination of 3,6-dimethoxy-9,9-dihexylfluorene (**3**) with bromine and catalytic amount of ferric chloride afforded monomer **4** in 66% yield. Monomer B, 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,6-dimethoxy-9,9-dihexylfluorene, was obtained by treating **4** with *n*-BuLi/2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. 2-Bromothiophene-(1-cyano)vinylene-2,5-dioctyloxy)-1,4-phenylene-(2-cyano)vinylene-5-bromothiophene (**6**) was prepared in good yield from 2-thiopheneacetonitrile and 2,5-bis(octyloxy)-1,4-benzenedicarboxaldehyde through a Knoevanegel reaction followed by direct bromination with NBS. Monomer A was synthesized using an already published procedure.[26]

Synthesis and Characterization of Polymers. All copolymers were prepared in good yields (45–75%, see Schemes 2–4) and are highly soluble in most common organic solvents such as chloroform, tetrahydrofuran, and toluene. The number-average molecular weight (M_n) and weight-average molecular weigth (M_w) of the copolymers ranged from 2400 to 41 200 and 3100 to 176 000, respectively, with a polydispersity indexes ranging from 1.3 to 4.3. These data are summarized in Table 1. We have observed that the copolymers (**P3**–**P6**) obtained from monomer B present lower molecular weight than the one obtained by monomer A. We can attribute this effect to a lower reactivity of the monomer B due to the fluorene ring bearing two electron-donating groups. It seems that polymerization via Suzuki couplings of some electron-rich monomers tend to give low molecular weight polymers.[33]

The thermal stability of the polymers was evaluated by thermogravimetric analyses (TGA) under a nitrogen atmosphere. The data are summarized in Table 1. All copolymers, except **P4** and **P5**, exhibit very good thermal stabilities up to 350–400 °C. Differential scanning calorimetry (DSC) measurements were also performed on all copolymers. The DSC data are also reported in Table 1. It is interesting to note that **P1**, **P2**, and **P5** present a glass transition temperature higher than poly(2,7-(9,9-dihexylfluorene), a well-studied polymer.[34] Moreover, it is worth noting that all these polymeric materials are amorphous, which should lead to a good mechanical stability up to 100 °C. This parameter may become particularly important for their future utiliza-

Scheme 3. Synthesis of Copolymers from Suzuki Cross-Coupling Reaction



Scheme 4. Polymers from 3,6-Dimethoxy-9,9-dihexylfluorene Unit

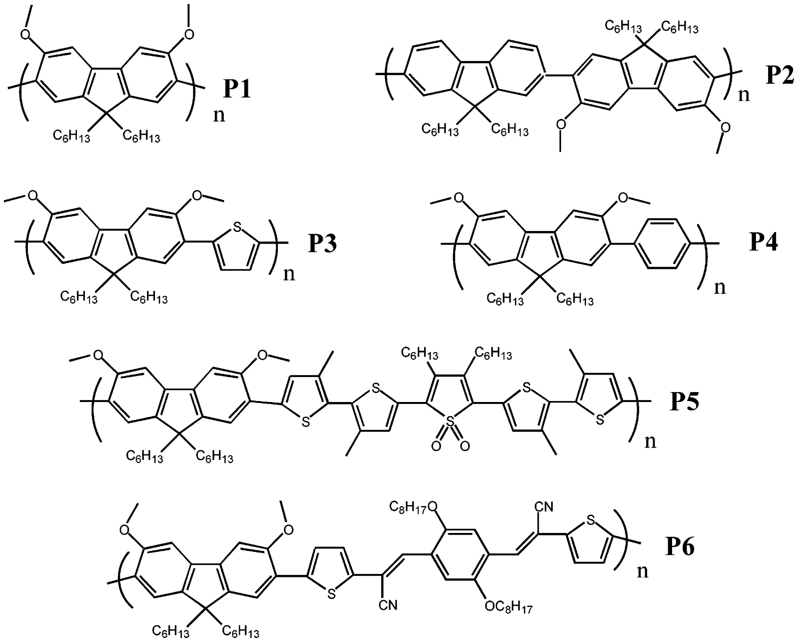


Table 2. Optical Data and the Fluorescence Quantum Yield

	absorption λ_{max} (nm)[a]		fluorescence λ_{max} (nm)[a]		PL efficiency solution
polymer	solution	film	solution	film	ϕ_F
P1	374	366	412 (436)	430	0.48
P2	388	380	420 (445)	434	0.93
P3	444	446	498 (530)	510	0.30
P4	374	366	415 (438)	424	0.85
P5	482 (388)	478 (392)	645 (702)	662	0.21
P6	538	563 (601)	616	656 (702)	0.32

[a] The data in parentheses are the wavelengths of shoulders and subpeaks.

tion in light-emitting diodes. For **P3** and **P4**, the low glass transition temperature observed is mainly due to the low molecular weight of the copolymers. In the case of **P6**, no glass transition temperature has been observed.

Optical Properties. Obviously, UV−vis absorption and photoluminescence properties of these polymers have been investigated and are summarized in Table 2. All spectroscopic properties were measured both in solution (chloroform) and as thin film. Absorption and fluorescence spectra of all copolymers in solution are shown in Figure 1 and Figure 2. It is important to note that all polymers were fluorescent both in solution and as thin film. Furthermore, we have been able to modulate the maximum emission wavelength in order to obtain the three primary colors (blue, green, and red). Moreover, it is interesting to compare the absorption and emission spectra of **P1**, **P3**, and **P4** with their

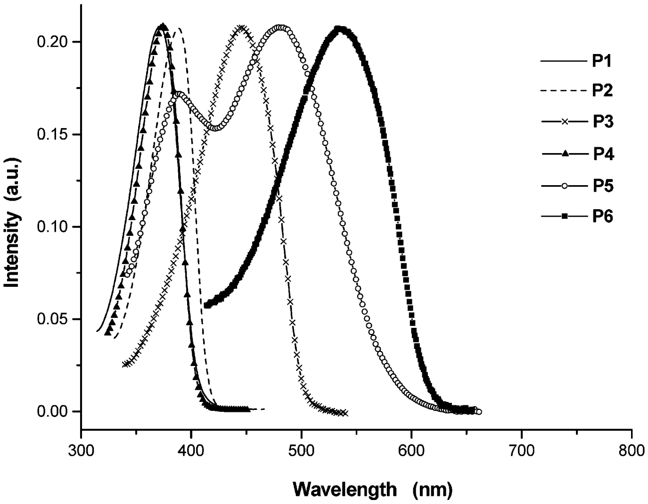


Figure 1. UV−vis absorption spectra of **P1**−**P6** in solution.

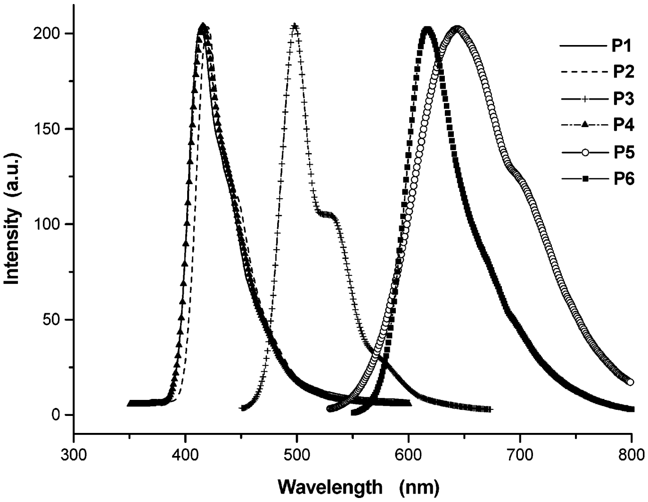


Figure 2. Fluorescence spectra of **P1**−**P6** in solution.

similar copolymers but that are not bearing methoxy groups at the 3,6-positions. For instance, Liu et al.[34] have reported for poly(2,7-(9,9-dihexylfluorene) (PDHF) an absorption maximum at 379 nm and an emission maximum at 415 (438, 469) nm. For **P1** we have obtained almost the same values—374 nm for the absorption maximum and 412 (436) nm for the emission maximum. In this case, the substitution by methoxy groups at the 3,6-positions of the fluorene ring does not affect the absorption or emission spectra. However, a decrease of the quantum yield of fluorescence (ϕ_F) from 0.82 for PDHF to 0.48 for **P1** observed. On the other hand, Ranger and Leclerc[35] have reported for poly(2,7-(9,9-dioctylfluorene)-*alt*-(2,5-thiophene) (PFT) an absorption maximum at 431 nm and an emission maximum at 496 nm, in solution. We report a red shift of 15 nm between **P3** and PFT for the absorption maximum.

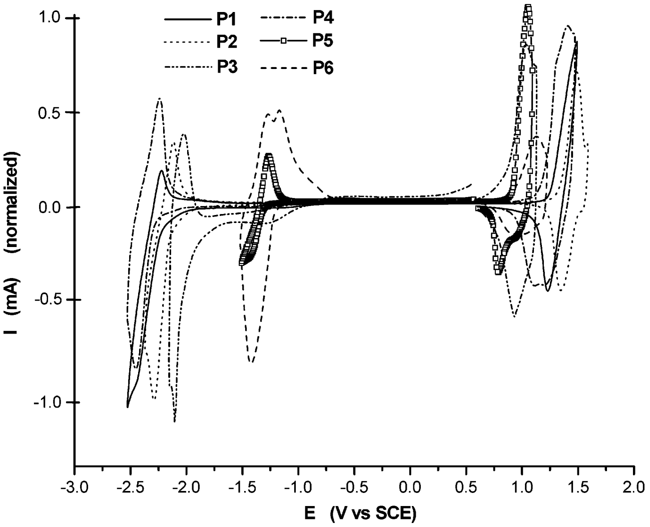


Figure 3. Cyclic voltammograms of **P1**−**P6**.

This red shift can be attributed to a stronger push−pull effect between the fluorene ring and the thiophene ring, or it may also be explained by a more planar conformation of the ground state of **P3** due to an anomeric effect between the methoxy group and the hydrogen atom of the thiophene ring. However, there is no difference between **P3** and PTF in their emission spectra. We can suppose that these two polymers adopt the same molecular geometry in the excited state, and there is no significant effect from the methoxy groups on the fluorene moiety. However, the quantum yield of fluorescence for **P3** is lower than for PFT, 0.30 for the former and 0.49 for the latter. Finally, Liu et al.[34] have reported for poly(2,7-(9,9-dihexylfluorene)-*alt*-(1,4-phenylene) (PFP) an absorption maximum at 370 nm and an emission maximum at 408 (431) nm. We observed almost the same results for **P4** that is 374 nm for the absorption maximum and 415 (438) nm for the emission maximum. Unlike **P1** and **P3**, the fluorescence quantum yield is not affected by the methoxy group and ϕ_F remains quite high at 0.85.

Electrochemical Properties. As shown in Figure 3 and summarized in Table 3, all copolymers synthesized from 3,6-dimethoxy-9,9-dihexylfluorene exhibit quasi-reversible oxidation and reduction electrochemical processes. **P1**−**P6** show good reversibility during the p-doping process as well as in the n-doping process; this is an advantage for polymeric light-emitting devices. The goal of this work was to investigate the influence of the substitution of the fluorene ring with two electron-donating groups on the ionization potential (IP). We have been able to estimate, by using a well-established electrochemical method,[15] the HOMO−LUMO energy levels, and the results are summarized in Table 3. To appreciate the modulation of the ionization potential, we will compare **P1**, **P3,** and **P4** with similar copolymers

Table 3. Electrochemical Properties of P1−P6

	n-doping (V vs SCE)[a]			p-doping (V vs SCE)[a]			energy levels (eV)		
polymer	E_{onset}	E_{pc}	E_{pa}	E_{onset}	E_{pa}	E_{pc}	HOMO	LUMO	E_g[b]
P1	−2.02	−2.47	−2.21	1.25	1.49	1.24	5.65	2.38	3.27
P2	−2.10	−2.29	−2.11	1.28	1.48	1.34	5.67	2.30	3.37
P3	−1.87	−2.11	−2.11	0.81	1.03	0.93	5.21	2.53	2.68
P4	−2.17	−2.44	−2.23	1.16	1.42	1.21	5.56	2.23	3.33
P5	−1.31	−1.51	−1.27	0.88	1.04	0.78	5.28	3.09	2.19
P6	−1.08	−1.42	−1.27	0.92	1.13	1.00	5.32	3.32	2.00

[a] E_{pa} and E_{pc} stand for anodic peak potential and cathodic peak potential. [b] E_g stands for the band gap energy.

reported in the literature (PDOF, PFT, and PFP) that are not bearing a methoxy group at the 3,6-positions. First of all, Janietz et al.[36] have reported values of the ionization potential (IP) and the electron affinity (EA) for poly(2,7-(9,9-dioctylfluorene) (PDOF). They have reported an IP = 5.80 eV and an EA = 2.12 eV. We have obtained for **P1** IP = 5.65 eV/EA = 2.38 eV. Moreover, Charas et al.[18] have reported values of IP and EA for two copolymers: PFT and PFP. For PFT, they have found an IP = 5.49 eV and an EA = 2.84 eV whereas we have obtained for **P3** IP = 5.21 eV/EA = 2.53 eV. Finally, Charas and co-workers[18] have reported for PFP an IP = 5.79 eV and EA = 2.61 eV. For **P4**, we have obtained IP = 5.56 eV and EA = 2.23 eV. It is clear now from these results that the 3,6-dimethoxy-9,9-dihexylfluorene unit allows the modulation of the ionization potential. This should be useful to enhance the injection of holes from anode in light-emitting diodes. For instance, the performances of these polymers in light-emitting devices are under investigation, and the results will be reported in a forthcoming publication.

Conclusion

Six copolymers containing the 3,6-dimethoxy-9,9-dihexylfluorene moiety have been prepared. All copolymers are highly soluble in organic solvents. All copolymers exhibit good thermal stability and relatively high glass transition temperature. **P1**, **P2**, and **P4** emit blue light and **P3** is a green emitting material, whereas **P5** and **P6** are red-light emitters. With this new family of polyfluorenes derivatives we have obtained the three primary colors (RGB). Moreover, we have been able to demonstrate the influence of the electron-rich unit on the electrochemical properties of the conjugated polymers by comparing these new copolymers (**P1**, **P3**, and **P4**) with their similar copolymers that are not bearing the methoxy group. For these three polymers, the ionization potential have been significantly modified. The increase of the ionization potential should lead to a better injection of holes from the anode, reducing the turn-on voltage and enhancing the performance of light-emitting diode made from this new family of π-conjugated polymers.

Acknowledgment. This work was supported by operating and strategic grants from the Natural Sciences and Engineering Research Council of Canada (NSERC). We thank Jean-François Morin for the synthesis of 2-thiophene-(1-cyano)vinylene-2,5-dioctyloxy)-1,4-phenylene-(2-cyano)vinylene-5-thiophene and 2-bromothiophene-(1-cyano)vinylene-2,5-dioctyloxy)-1,4-phenylene-(2-cyano)vinylene-5-bromothiophene.

References and Notes

(1) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burn, P. L.; Holmes, A. B. *Nature (London)* **1990**, *347*, 539.

(2) Brown, A. R.; Bradley, D. D. C.; Burroughes, J. H.; Friend, R. H.; Greenham, N. C.; Burn, P. L.; Holmes, A. B.; Kraft, A. *Appl. Phys. Lett.* **1992**, *7*, 2.

(3) Braun, D.; Heeger, A. J. *Appl. Phys. Lett.* **1991**, *58*, 1982.

(4) Yang, Y.; Pei, Q. *Synth. Met.* **1994**, *67*, 161.

(5) Grem, G.; Paar, C.; Stampfl, J.; Leising, G. *Chem. Mater.* **1995**, *7*, 2.

(6) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed.* **1998**, *37*, 402.

(7) Morin, J.-F.; Leclerc, M. *Macromolecules* **2001**, *34*, 4680.

(8) Morin, J.-F.; Beaupré, S.; Leclerc, M.; Lévesque, I.; D'Iorio, M. *Appl. Phys. Lett.* **2002**, *80*, 341.

(9) Ohmori, Y.; Uchida, M.; Muro, K.; Yoshino, K. *Jpn. J. Appl. Phys.* **1991**, *20*, L1941.

(10) Ranger, M.; Rondeau, D.; Leclerc, M. *Macromolecules* **1997**, *30*, 7686.

(11) Pei, Q.; Yang, Y. *J. Am. Chem. Soc.* **1996**, *118*, 7416.

(12) Bernius, H.; Inbasekaran, M.; Woo, E.; Wu, W.; Wujkowski, L. *J. Mater. Sci.* **2000**, *11*, 111.

(13) Donat-Bouillud, A.; Lévesque, I.; Tao, Y.; D'Iorio, M.; Beaupré, S.; Blondin, P.; Ranger, M.; Bouchard, J.; Leclerc, M. *Chem. Mater.* **2000**, *12*, 1931.

(14) Leclerc, M. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 2867.

(15) Beaupré, S.; Leclerc, M. *Adv. Funct. Mater.* **2002**, *12*, 192.

(16) Lévesque, I.; Donat-Bouillud, A.; Tao, Y.; D'iorio, M.; Beaupré, S.; Blondin, P.; Ranger, M.; Bouchard, J.; Leclerc, M. *Synth. Met.* **2001**, *122*, 79.

(17) Lee, J.-I.; Klaerner, G.; Davey, M. H.; Miller, R. D. *Synth. Met.* **1999**, *102*, 1087.

(18) Charas, A.; Barbagallo, N.; Morgado, J.; Alcacer, L. *Synth. Met.* **2001**, *122*, 23.

(19) Eaton, D. F. *Pure Appl. Chem.* **1988**, *60*, 1107.

(20) Donat-Bouillud, A.; Mazerolle, L.; Gagnon, P.; Goldenberg, L.; Petty, M. C.; Leclerc, M. *Chem. Mater.* **1997**, *9*, 2815.

(21) Barbarella, G.; Favaretto, L.; Sotgiu, G.; Zambianchi, M.; Fattori, V.; Cocchi, M.; Cacialli, F.; Gigli, G.; Cingolani, R. *Adv. Mater.* **1999**, *11*, 1375.

(22) Pereira, E. J. N.; Berberan-Santos, M. N.; Federov, A.; Vincent, M.; Gallay, J.; Martinho, J. M. G. *J. Chem. Phys.* **1999**, *110*, 1600.

(23) Meyers, A. I.; Gabel, R.; Milhelich, E. *J. Org. Chem.* **1978**, *43*, 1372.

(24) Chuang, C.; Lapin, S. C.; Schrock, A. K.; Schuster, G. B. *J. Am. Chem. Soc.* **1985**, *107*, 4238.

(25) Sarker, A. M.; Ding, L.; Lahti, P. M.; Karasz, F. E. *Macromolecules* **2002**, *35*, 223.

(26) Beaupré, S.; Ranger, M.; Leclerc, M. *Macromol. Rapid Commun.* **2000**, *21*, 1013.

(27) Coulson, D. R. *Inorg. Synth.* **1972**, *13*, 121.

(28) Rault-Berthelot, J.; Angely, L.; Delaunay, J.; Simonet, J. *New J. Chem.* **1987**, *11*, 487.

(29) Klaerner, G.; Miller, R. D. *Macromolecules* **1998**, *31*, 2007.

(30) Patney, H. K. *Tetrahedron Lett.* **1991**, *32*, 2259.

(31) Bull, J. R.; Sickle, E. S. *J. Chem. Soc., Perkin Trans. 1* **2000**, 4476.

(32) Dehmlow, E. V.; Niemann, T.; Kraft, A. *Synth. Commun.* **1996**, *26*, 1467.

(33) Jayakannan, M.; Dongen, J. L. J. V.; Janssen, R. A. J. *Macromolecules* **2001**, *34*, 5386.

(34) Liu, B.; Yu, W.-L.; Lai, Y.-H.; Huang, W. *Chem. Mater.* **2001**, *13*, 1984.

(35) Ranger, M.; Leclerc, M. *Can. J. Chem.* **1998**, *76*, 1571.

(36) Janietz, S.; Bradley, D. D. C.; Grell, M.; Giebeler, C.; Inbasekaran, M.; Woo, E. P. *Appl. Phys. Lett.* **1998**, *73*, 2453.

MA035064J