Fluorene-Based Copolymers for Red-Light-Emitting Diodes**

By *Serge Beaupré* and *Mario Leclerc**

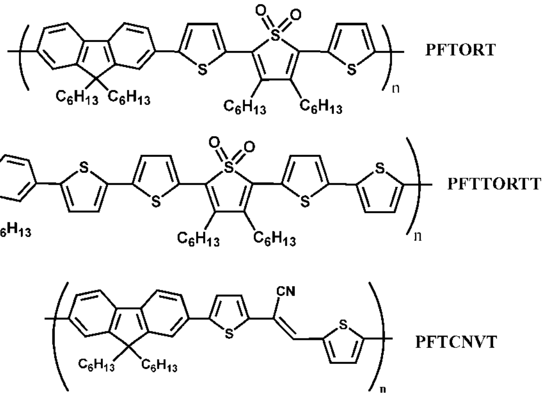
The syntheses of new fluorene-based π-conjugated copolymers; namely, poly((5,5″-(3′,4′-dihexyl-2,2′;5′,2″-terthiophene 1′,1′-dioxide))-*alt*-2,7-(9,9-dihexylfluorene)) (PFTORT), poly((5,5″″-(3″,4″-dihexyl-2,2′:5′,2′:5″,2‴:5‴,2″″-quinquethiophene 1″,1″-dioxide))-*alt*-2,7-(9,9-dihexylfluorene)) (PFTTORTT), and poly((5,5-*E*-α-(2-thienyl)methylene)-2-thiopheneacetonitrile)-*alt*-2,7-(9,9-dihexylfluorene)) (PFTCNVT), are reported. In the solid state, PFTORT and PFTCNVT present red–orange emission (with a maximum at 610 nm) while PFTTORTT shows a red emission with a maximum at 666 nm. In all cases, electrochemical measurements have revealed p- and n-dopable copolymers. All these copolymers have been successfully tested in simple light-emitting diodes and show promising results for orange- and red-light-emitting devices.

1. Introduction

Since the initial report 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. An important driving force for this research is the possibility of building ultrathin and flexible optical displays. The basic (and simplest) structure of a polymeric light-emitting diode consists of a positive hole-injecting electrode (usually transparent) with a high work function such as indium tin oxide (ITO) or a conducting polymer, a negative electron-injecting electrode with a low work function such as Al, Mg, or Ca, and the light-emitting polymer film sandwiched between these two electrodes. In this layered structure, the injected holes and electrons migrate across the polymeric layer and combine to form excitons, which then decay with photon emission. An optimized light-emitting diode requires therefore efficient and balanced charge injection, good and comparable mobilities for both holes and electrons, and high efficiency. Moreover, depending upon the chemical structure of the emissive polymer, different colors can be obtained.

In this regard, many π-conjugated polymers (e.g., poly(*p*-phenylene)s,[2] poly(phenylenevinylene)s,[1,3–5] poly(oxadiazole)s,[6] poly(2,7-(9,9-dialkylfluorene))s,[7–13] poly(3,6-carbazole)s,[14] and poly(2,7-carbazole)s[15] have been synthesized in order to obtain the three primary (RGB) colors. Among these polymers, polyfluorene derivatives have revealed particularly interesting optical and electrical properties since, up to now, this is the only family of conjugated polymers that emit colors spanning the entire visible range with high efficiency and low operating voltage.[16,17] Indeed, many blue-or green-light-emitting polyfluorene derivatives have been reported and, recently, red-light-emitting diodes, presumably made from random copolymers based on fluorenes and 4,7-bis(2-thienyl)-2,1,3-benzothiadiazole,[17] have been briefly described.[18] Other red-emitting materials have also been reported from energy transfer between emissive polymers and several dyes such as tetraphenylporphyrin or europium complexes.[19–21]

Along these lines, we report here new orange- and red-light-emitting alternating polyfluorene derivatives. This work is mainly based on our previous results on alternating (donor–acceptor type) copolymers derived from fluorenes and thiophenes[11,13] and on the recent report of low-bandgap highly luminescent oligothiophenes by Barbarella and co-workers.[22] In a first step, we report the synthesis and characterization of these new, well-defined, fluorene-based, conjugated alternating copolymers; namely: poly((5,5″-(3′,4′-dihexyl-2,2′;5′,2″-terthiophene-1′,1′-dioxide))-*alt*-2,7-(9,9-dihexylfluorene)) (PFTORT), poly((5,5″″-(3″,4″-dihexyl-2,2′:5′,2′:5″,2‴:5‴,2″″-quinquethiophene-1″,1″-dioxide))-*alt*-2,7-(9,9-dihexylfluorene)) (PFTTORTT), and poly((5,5-*E*-α-((2-thienyl)methylene)-2-thiopheneacetonitrile)-*alt*-2,7-(9,9-dihexylfluorene)) (PFTCNVT) (see Scheme 1). In a second step, we present preliminary results on the fabrication and characterization of light-emitting diodes based on these copolymers.



Scheme 1.

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2. Results and Discussion

2.1. Synthesis of Polymers

Following previously published procedures,[11,23–25] all present alternating copolymers derived from fluorenes and thiophenes (see Scheme 1) were prepared from a palladium-catalyzed Suzuki coupling between 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dihexylfluorene and several α,ω-dihalogeno-oligothiophenes. This synthetic pathway has led to highly soluble polymers in common organic solvents (i.e., chloroform, toluene, tetrahydrofuran, THF) with number-average molecular weight (M_n) between 6000 and 13 000 and polydispersity indexes around 2 (see Table 1). In all cases, thin polymer films with good mechanical properties can be obtained by spin coating or simple casting. Moreover, it is worth noting that all these polymeric materials are amorphous with relatively high glass-transition temperatures (between 112 and 121 °C, see Table 1), which should lead to a good mechanical stability up to 100 °C. This parameter may become particularly important for their future utilization in light-emitting diodes.

Table 1. Physical properties of the fluorene-based copolymers.

Polymer	M_n	M_w/M_n	T_g [°C]
PFTORT	6000	1.4	112
PFTTORTT	9000	1.7	118
PFTCNVT	13000	2.4	121

2.2. Optical Properties

Obviously, UV-vis absorption and photoluminescence (PL) properties of these polymers have been investigated and are summarized in Table 2. The UV-vis spectrum of PFTTORTT shows two maxima at 394 nm and 548 nm, which correspond to a n,$\sigma^*_{S\text{–}O}$ and π–π^* transition, respectively. The optical properties of PFTTORTT are reported in Figure 1. All these red (maximum of absorption ranging from 500 to 547 nm in the solid state) polymers exhibit a maximum of emission over 600 nm leading to red–orange emission for PFTCNVT and PFTORT, and red emission for PFTTORTT. Despite relatively low fluorescence quantum yields in solution (ϕ_F = 0.03 to 0.05), these polymers seem highly fluorescent in solid state. These observations are surprising since it is known that the solid state generally favors the formation of aggregates, which often leads to a quenching of the fluorescence. However, this phenomenon has been already observed by Barbarella and co-workers[26] for similar thiophene S,S-dioxide derivatives. The solid-state PL quantum yields will be reported in a paper to follow.

Table 2. Optical properties of the fluorene-based copolymers. Absorption (A) and emission (PL, EL) wavelengths are taken at the maximum of the band. The subscript “sln” refers to the solution phase.

Polymer	$\lambda_{A\ sln}$ [nm]	$\lambda_{A\ film}$ [nm]	$\lambda_{PL\ sln}$ [nm]	$\lambda_{PL\ film}$ [nm]	λ_{EL} [nm]	$\phi_{F\ sln}$
PFTORT	510	509	602	610 (660)	610 (650)	0.05
PFTTORTT	394,548	394,547	662	666 (708)	668 (708)	0.04
PFTCNVT	500	500	556 (608)	610	582 (610)	0.03

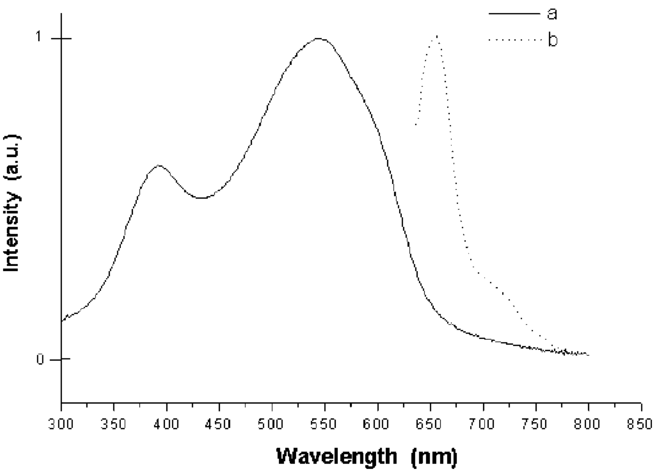

Fig. 1. a) UV-vis absorption spectrum and b) PL spectrum of a spin-coated film of PFTTORTT.

2.3. Electrochemical Properties

As mentioned in the introduction, efficient injection and transport of both holes and electrons are important parameters for the rational design of optimized light-emitting diodes and in this regard, electrochemical data can lead to valuable information (Table 3). Interestingly, all these polymers are electroactive upon oxidation and reduction (as an example, see Fig. 2). However, it is clear that doping levels are much higher in the p-doped state for all copolymers. Furthermore, we have been able to calculate the value of the ionization potential (IP) and electron affinity (EA) of the three copolymers by the empirical relationship proposed by Brédas et al.[27] and already used for poly(9,9-dioctylfluorene).[28]

Table 3. Electrochemical properties of the fluorene-based copolymers.

Polymer	$E_{peak\ ox}$ ($E_{ox\ onset}$) V vs. SCE	$E_{peak\ red}$ ($E_{red\ onset}$) V vs. SCE	|IP| [eV]	|EA| [eV]	$E_{g\ electro}$ [eV]	$E_{g\ opt}$ [eV]
PFTORT	1.25; (1.09)	–1.43; (–1.15)	5.49	3.25	2.2	2.1
PFTTORTT	1.05; (0.91)	–1.37; (–1.09)	5.31	3.31	2.0	1.9
PFTCNVT	1.34; (1.07)	–1.50; (–1.10)	5.47	3.30	2.2	2.2

$$\text{IP} = (E'_{ox} + 4.4\ \text{eV})\ ;\ \text{EA} = (E'_{red} + 4.4\ \text{eV}) \quad (1)$$

where E'_{ox} and E'_{red} are the onset of the oxidation and reduction peak, respectively.

IP and EA are used to estimate the energy barrier for the injection of both holes and electrons into the polymer. Moreover, comparable bandgaps were obtained from electrochemical and

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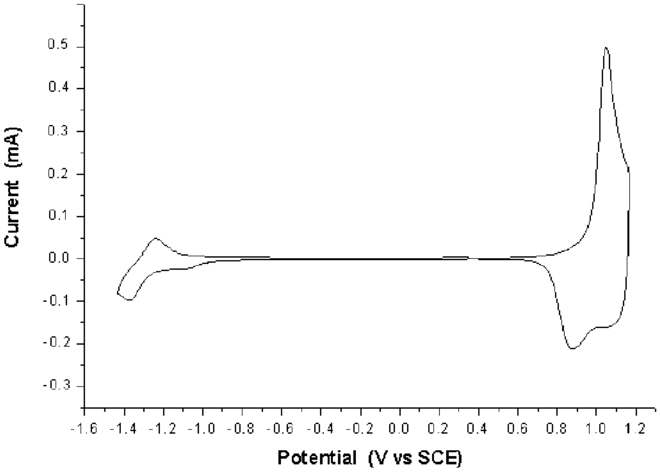

Fig. 2. Electrochemical properties of PFTTORTT in 0.1 M Bu_4NBF_4/MeCN solution at a scan rate of 50 mV/s.

optical measurements (Table 3). It is interesting to note that copolymers PFTORT and PFTTORTT present a lower bandgap than that reported for a similar alternating copolymer based on fluorene and thiophene *S*,*S*-dioxide.[29] These properties can be explained by the presence of more thiophene units in the repeat unit of the copolymers.

2.4. Electroluminescence Properties

For these preliminary studies in light-emitting devices, a multilayer configuration was utilized, similar to the one we have reported for polyfluorene derivatives[30] (Fig. 3). The use of a LiF/Al cathode is based on previous studies, which have shown that a thin layer of LiF reduces the interface barrier for electron injection at the cathode in organic light-emitting diodes.[31,32] Moreover, Salaneck and co-workers[33] have studied the interfaces between LiF and some polyfluorenes. They have shown that the inclusion of a thin layer of LiF between the polyfluorene film and the Al cathode decreases Al–polymer interactions that lead to the degradation of the π-conjugated polymers. Moreover, they suggest that the utilization of a thin layer of LiF can act as a protecting shield for the polymer layer during the evaporation of the cathode. This shield contributes to reduce the number of quenching sites at the interface. Moreover, a thin layer of LiF has been deposited onto the anode. Here, LiF acts as an insulating layer that builds up a potential between the ITO and the polymer, which enhances the injection of holes into the emissive layer.[13] Preliminary results of electroluminescence (EL) are reported in Table 4 and Figure 4. Once again, it is interesting to note that PFTTORTT presents a red emission (λ_{max} = 668 nm), which is significantly red-shifted when compared to the orange emission for the copolymer containing only one thiophene *S*,*S*-dioxide unit (λ_{max} = 604 nm) recently reported by Charas and co-workers.[34]

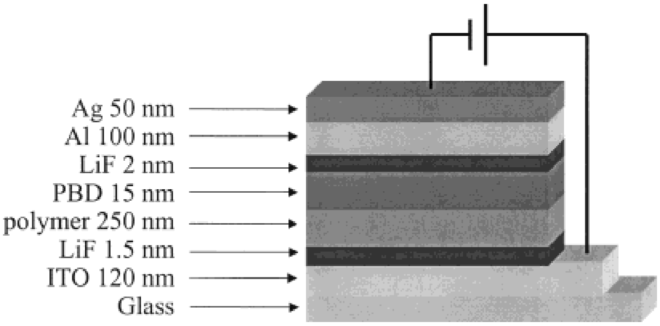

Fig. 3. Schematic description of the light-emitting diodes.

Table 4. EL properties of the fluorene-based copolymers.

Polymer	Turn-on voltage [V]	Luminance	Color
PFTORT	4	120 cd/m^2 at 7V	Red–orange
PFTTORTT	4	15 cd/m^2 at 8V	Red
PFTCNVT	5	45 cd/m^2 at 10V	Red–orange

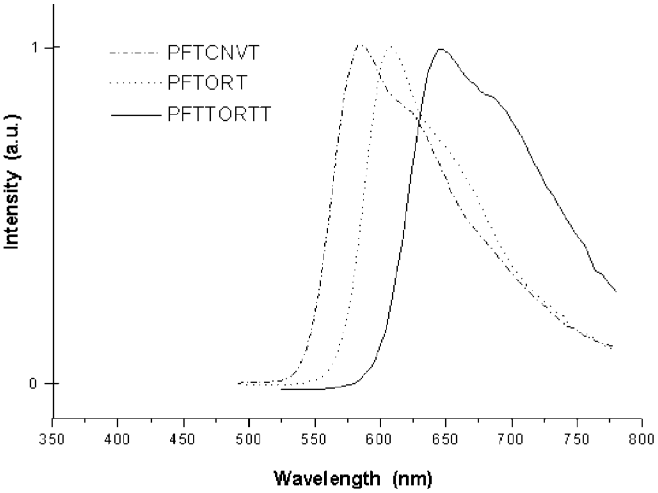

Fig. 4. EL spectra of the fluorene-based copolymers.

It is well known that EL efficiency strongly depends on the charge injection into the emitter. In the present case, the injection of both holes and electrons should be difficult due to the mismatch between the work function of electrodes and the highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO–LUMO) energy levels of the emissive polymers. For instance, neglecting the effect of LiF on the cathode and the anode, PFTORT has an energy barrier for the injection of electrons from the aluminum cathode (ϕ = 4.2 eV) of about 0.9 eV and 0.6 eV for the injection of holes from ITO (ϕ = 4.9 eV). In these conditions, the injection of both charges (holes and electrons) is difficult. Similar phenomena are observed for PFTTORTT and PFTCNVT. In order to improve the device efficiency, we have first used a thin layer of hole-blocking/electron-transporting layer of Bu-PBD (2-(4-biphenylyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole) to improve the injection and transport of electrons into the emissive layer.[30] However, many other approaches can be taken to enhance the injection of charges. For instance, the utilization of calcium (ϕ = 2.9 eV) as cathode instead of aluminum

(ϕ = 4.2 eV) should lead to a better injection of electrons and to higher luminance values. Furthermore, the injection of holes can be improved by the deposition of a thin layer of poly(3,4-ethylenedioxythiophene) (PEDOT) derivatives onto the anode. Indeed, it has been suggested that the presence of PEDOT derivatives enhances the injection of holes, reduces the roughness of the anode, and reduces the diffusion of oxygen from ITO into the polymer.[35] All these parameters should lead to more efficient light-emitting devices and will be tested in the near future.

3. Conclusion

Suzuki coupling between functionalized fluorenes and oligothiophenes have successfully led to new processable alternating copolymers with relatively high glass-transition temperatures and interesting optical and electrochemical properties. For instance, these polymers are p- and n-dopable with bandgaps ranging from 2.0 to 2.2 eV. PFTORT and PFTCNVT emit a red–orange light whereas PFTTORTT seems to be a promising candidate for the fabrication of red-light-emitting diodes.

4. Experimental

Synthesis of Monomers: 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dihexylfluorene [11,12], *E*-α-((2-thienyl)methylene)-2-thiopheneacetonitrile [36], 3,4′-dihexyl-2,2′;5′,2″-terthiophene 1′,1′-dioxide, 2,5⁗diiodo-3″,4″-dihexyl-2,2′:5′,2′:5″,2‴:5‴,2⁗-quinquethiophene-1″,1″-dioxide [37], and tetrakis(triphenylphosphine) palladium(0) [38] were synthesized following procedures reported in the literature.

5,5-Dibromo-E-α-((2-thienyl)methylene)-2-thiopheneacetonitrile: To a solution of 1.00 g (4.60 mmol) of *E*-α-((2-thienyl)methylene)-2-thiopheneacetonitrile in chloroform (15 mL) at 0 °C, 1.51 g (9.43 mmol) of bromine was added. The solution was maintained at 0 °C for 2 h and then the precipitate was filtered off and washed with chloroform and 10 % $NaHCO_3$. The product was dried under vacuum to afford 1.30 g of the title product as a yellow powder (yield: 75 %), melting point, m.p. 199–201 °C.

^{1}H nuclear magnetic resonance (NMR) (300 MHz, dimethylsulfoxide, DMSO) δ [ppm]: 7.98 (s, 1H); 7.56 (d, J = 3.9 Hz, 1H); 7.42 (d, J = 4.0 Hz, 1H); 7.31 (d, J = 3.9 Hz, 1H); 7.22 (d, J = 3.9 Hz, 1H).

^{13}C NMR (75 MHz, DMSO) δ [ppm]: 135.6; 133.3; 131.9; 131.6; 127.3; 125.7; 123.7; 122.1; 118.0; 116.4; 112.6.

High-resolution mass spectrometry (HRMS): Calc. for $C_{11}H_7NS_2$: 372.8239. Found: 372.8240.

5,5″-Dibromo-3′,4′-dihexyl-2,2′;5′,2″-terthiophene 1′,1′-dioxide: To a solution of 1.30 g (2.90 mmol) of 3,4′-dihexyl-2,2′;5′,2″-terthiophene 1′,1′-dioxide in dimethylformamide (DMF) (30 mL) at room temperature, 1.06 g (5.60 mmol) of *N*-bromosuccinimide was added slowly. The solution was warmed up to 80 °C and stirred at this temperature for 42 h. The solution was cooled to room temperature and then quenched with a saturated solution of ammonium chloride and extracted several times with diethyl ether. The product was purified by column chromatography using 10 % ethyl acetate/hexane as eluent (R_f = 0.59) to afford 1.32 g of a red crystalline product (yield: 75 %). m.p. 72–74 °C.

^{1}H NMR (300 MHz, $CHCl_3$) δ [ppm]: 7.44 (d, J = 4.2 Hz, 2H); 7.14 (d, J = 3.9 Hz, 2H); 2.58 (t, J = 6.8 Hz, 4H); 1.53 (m, 8H); 1.35 (m, 8H); 0.92 (t, J = 6.8 Hz, 6H).

^{13}C NMR (75 MHz, $CHCl_3$) δ [ppm]: 137.6; 130.8; 129.6; 129.6; 129.2; 115.8; 31.1; 29.4; 28.4; 26.9; 22.3; 13.8.

HRMS: Calc. for $C_{24}H_{30}Br_2O_2S_3$: 603.9775. Found: 603.9781.

3″,4″-Dihexyl-2,2′:5′,2′:5″,2‴:5‴,2⁗-quinquethiophene 1″,1″-dioxide: To a solution of 500 mg (0.82 mmol) of 5,5″-dibromo-3,4′-dihexyl-2,2′;5′,2″-terthiophene 1′,1′-dioxide in anhydrous THF (17 mL) at room temperature, 0.92 g (2.47 mmol) of 2-(tributylstannyl)-thiophene (Aldrich) and 46 mg (2 mol-%) of $PdCl_2(PPH_3)_2$ were added. The solution was stirred at reflux for 24 h and then evaporated. The crude product was purified by column chromatography over silica gel using 10 % ethyl acetate/hexane as eluent (R_f = 0.62) to afford 330 mg of a red crystalline product (yield = 66 %), m.p. 112 °C.

^{1}H NMR (300 MHz, CD_3COCD_3, ppm): 7.63 (d, J = 4.0 Hz, 2H); 7.53 (d, J = 4.9 Hz, 2H); 7.43 (d, J = 3.7 Hz, 4H); 7.14 (q, J = 3.9 and 5.1 Hz, 2H); 2.80 (m, 4H); 1.60 (m, 8H); 1.40 (m, 8H); 0.92 (m, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ [ppm]: 140.1; 137.0; 136.4; 130.3; 129.8; 128.1; 125.7; 124.6; 31.4; 29.7; 28.6; 27.2; 22.6; 14.1.

PFTORT: Carefully purified 5,5″-dibromo-3′,4′-dihexyl-2,2′;5′,2″-terthiophene 1′,1′-dioxide (500.0 mg; 0.8244 mmol) and 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dihexylfluorene (483.5 mg; 0.8244 mmol) and freshly prepared $Pd(PPh_3)_4$ (5 mol-%) were dissolved in a mixture of THF ([monomer] = 0.1 M) and aqueous 2 M K_2CO_3 (1.5:1). Solvents were purged with dry argon. The solution was put under argon atmosphere and was heated at 80 °C for 48 h. The solution was then poured into methanol (50 mL). The precipitated material was recovered by filtration. The polymer was then dissolved in a small amount of $CHCl_3$ and poured again in methanol to remove impurities. This operation was repeated several times. The polymer was washed for 24 h in a Soxhlet apparatus using acetone to remove catalyst residues and oligomers. The resulting polymer (454.0 mg ; Y = 35 %) was soluble in $CHCl_3$ and THF.

^{1}H NMR (300 MHz, $CHCl_3$) δ [ppm]: 7.75 (m, 4H); 7.64 (m, 4H); 7.48 (m, 2H); 2.77 (m, 4H); 2.04 (m, 4H); 1.69-1.59 (m, 16H); 1.4 (m, 6H); 1.08 (m, 6H); 0.96 (m, 6H); 0.79 (m, 10H).

PFTTORTT: Carefully purified 2,5⁗-diiodo-3″,4″-dihexyl-2,2′:5′,2′:5″,2‴:5‴,2⁗-quinquethiophene-1″,1″-dioxide (200.0 mg; 0.2313 mmol) and 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dihexylfluorene (135.6 mg; 0.2313 mmol) and freshly prepared $Pd(PPh_3)_4$ (5 mol-%) were dissolved in a mixture of THF ([monomer] = 0.05 M) and aqueous 2 M K_2CO_3 (1.5:1). Solvents were purged with dry argon. The solution was put under argon atmosphere and was heated at 80 °C for 48 h. The solution was then poured into methanol (50 mL). The precipitated material was recovered by filtration. The polymer was then dissolved in a small amount of $CHCl_3$ and poured again in methanol to remove impurities. This operation was repeated several times. The polymer was washed for 24 h in a Soxhlet apparatus using acetone to remove catalyst residues and oligomers. The resulting polymer (175.0 mg; Y = 42 %) was soluble in $CHCl_3$ and THF.

^{1}H NMR (300 MHz, $CHCl_3$) δ [ppm]: 7.63 (m); 7.30 (m); 2.70 (m); 2.04 (m); 1.56 (m); 1.42 (m); 1.08 (m); 0.90 (m); 0.77 (m).

PFTCNVT: Carefully purified 5,5-dibromo-*E*-α-((2-thienyl)methylene)-2-thiopheneacetonitrile (500.0 mg; 0.8525 mmol) and 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dihexylfluorene (319.8 mg; 0.8525 mmol) and freshly prepared $Pd(PPh_3)_4$ (5 mol-%) were dissolved in a mixture of THF and aqueous 2 M K_2CO_3 (1.5:1). Solvents were purged with dry argon. The solution was put under argon atmosphere and was heated at 80 °C for 48 h. The solution was then poured into methanol (50 mL). The precipitated material was recovered by filtration. The polymer was then dissolved in a small amount of $CHCl_3$ and poured again in methanol to remove impurities. This operation was repeated several times. The polymer was washed for 24 h in a Soxhlet apparatus using acetone to remove catalyst residues and oligomers. The resulting polymer (672.0 g; Y = 72 %) was soluble in $CHCl_3$ and THF.

^{1}H NMR (300 MHz, $CHCl_3$) δ [ppm]: 7.62–7.36 (m, 11H); 2.06 (m, 4H); 1.09 (m, 12H); 0.77 (m, 10H).

Instrumentation: ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX300 in deuterated chloroform, methyl sulfoxide, or acetone solutions, at 298 K. Number-average (M_n) and weight-average (M_w) molecular weight were determined by size-exclusion chromatography (SEC) with high-pressure liquid chromatography (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). Differential scanning calorimetry (DSC) analyses were performed on a Perkin-Elmer (DSC-7) instrument at 20 °C/min under argon flow.

UV-vis absorption spectra were recorded on a Hewlett-Packard diode-array spectrophotometer (model 8452A) and fluorescence measurements were carried out on an Aminco Bowman Spectrometer or on a Spex Fluorolog 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 in argon-saturated solutions at 298 K in chloroform, against 1,3,5,7,8-pentamethyl-2,6-diethylpyrromethene-BF_2 in ethanol ($\phi_F = 0.83 \pm 0.02$) as standard [39]. For solid-state fluorescence spectra, a thin polymer film was spin-coated on glass plate and placed at 30° with respect to the incident beam.

Cyclic voltammetry was carried out in a two-compartment cell with a Solartron potentiostat (model 1287), using platinum electrodes, at a scan rate of 50 mV s^{-1} against Ag/Ag^+ (0.1 M of $AgNO_3$ in acetonitrile) reference electrode in an anhydrous and argon-saturated solution of 0.1 M Bu_4NBF_4 in acetonitrile. Acetonitrile (Aldrich) was dried over CaH_2 under inert atmosphere (argon) during 24 h. Tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) was recrystallized 3 times in 50:50 mixture of methanol/water and dried at 100 °C under reduced pressure, as reported in the literature [40]. In these conditions, the half-wave potential ($E_{1/2}$) of ferrocene was 0.045 V vs. $Ag/AgNO_3$ (0.1 M Bu_4NBF_4 in MeCN), whereas $E_{1/2}$ of ferrocene was 0.413 V vs. saturated calomel electrode (SCE) in 0.1 M Bu_4NBF_4/MeCN solution.

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The polymer light-emitting diodes were prepared on patterned ITO-coated (120 nm) glass substrates with a sheet resistance of 15 Ω/□ (Applied Films Corp.). The substrates were 5 cm × 5 cm with ten segments as active device areas of 5.0 × 6.0 mm^2. The substrates were treated in a UV-ozone oven for 10 min prior to coating or evaporating. All materials except polymers were deposited by thermal evaporation and the depositions were performed at high vacuum (2×10^{-7} torr), at room temperature. The typical growth rate was 2 Å/s, except for LiF (0–1 Å/s). An ultrathin layer of LiF (15 Å) was deposited on ITO, and the polymer was spin coated on the substrate. Spin coating was achieved at 1500 rpm during 50 s, from a polymer solution of 6 mg/mL in chloroform. Subsequent layers of Bu-PBD, lithium fluoride, aluminum, and silver were then deposited under vacuum, and the device was encapsulated under nitrogen before being characterized in air. The EL spectra and luminance were measured by using a PhotoResearch-650 SpectraColorimeter and Keithley 236 voltage source measurement unit.

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