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Copolymers of 3,4-Ethylenedioxythiophene and of Pyridine Alternated with Fluorene or Phenylene Units: Synthesis, Optical Properties, and Devices

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ABSTRACT: We report the synthesis of four conjugated copolymers based on alkylated fluorene or phenylene units which band gap is tuned by the regular insertion of an electron-donating or electron-withdrawing unit, (3,4-ethylenedioxy)thiophene and pyridine, respectively. The $(AB)_n$ regular sequence is achieved by Suzuki polycondensation reactions. The characterization of the copolymers by size exclusion chromatography reveals chains lengths of about 20−30 repeat units (40−60 rings), leading to a good processability for potential optical applications. The 1:1 ratio between the two units improves the solubility of the material in common organic solvents, allowing for physicochemical characterizations. Raman and FT-IR experiments indicate that the electronic structure of the backbone is rather benzenic in the neutral (undoped) state, as opposed to a quinoic oxidized structure. All copolymers exhibit interesting electrochromic properties as attested by cyclic voltammetry and UV−vis experiments. They reversibly switch among the entire visible spectra, which is of particular importance for display applications. Moreover, the EDOT-based copolymers strongly absorb in the NIR window (1200 nm up to 3000 nm) with some potential electrochromic applications related to this spectral window. Light-emitting diodes were fabricated using these copolymers as active layer. To improve hole and electron injection, the active layer was sandwiched between a ITO/PEDOT:PSSA/copolymer/Ba/Al. The emitting properties were studied on the base of photoluminescence (PL) and electroluminescence (EL) experiments. The spectral emission varies from blue-green to yellow, depending on the composition of the copolymers.

Introduction

Since the discovery of polyacetylene electrical properties,[1] a great deal of interest has been devoted to the conjugated organic polymers with the expectation to develop these materials in all-plastic type devices, such as photovoltaics, polymer light-emitting diodes (PLEDs), electrochromics, and sensors.[2−4] In this way, wide families of polyanilines, polypyrroles, and polythiophenes semiconducting polymers were developed and studied.[5] With molecular design tools,[6] new monomers were synthesized with the goal to control and tune their optical and electrical properties. However, larger scale developments of these materials required more processability, especially water or organic solvents solubility. Our group is involved in the study of the structure−properties relationship of PLEDs based on PPV derivatives.[7] With the first demonstration of light-emitting properties of conjugated polymers published in the early 1990s,[8] large, flat, and flexible light emitting displays are expected for commercial development. If the optical properties are easily controlled with molecular design, only a few of the semiconducting polymers know commercial success. Poly(*p*-phenylenes)[9−11] (PPP) and poly(fluorenes)[12−14] (PF) are some suitable candidates as blue-light emitting materials; however, their fabrication at a larger scale is still limited by poor electroluminescence efficiencies and short lifetime. To overcome this problem, it is convenient to add charge carriers into the luminescent chromophore in order to get easier charge transfer at the interfaces and to obtain the radiative recombination into the polymer. 3,4-Ethylenedioxythiophene (EDOT) and pyridine units may act as hole and electron charge carriers, respectively. Therefore, the synthesis of alternated copolymers appears to be a common way to introduce these carriers into a PF and PPP material and to combine the properties of the respective homopolymers.

In this paper, we report the synthesis of two EDOT-based copolymers, poly[(3,4-ethylenedioxythiophene)-*alt*-(2,5-dioctyloxyphenylene)] (poly-**EP8**) and poly[(3,4-ethylenedioxythiophene)-*alt*-(9,9′dioctylfluorene)] (poly-**EF8**), in comparison with two pyridine-based copolymers, poly[2,5-pyridine-*alt*-(2,5-dioctyloxyphenylene)] (poly-**PyP8**) and poly[2,5-pyridine-*alt*-(9,9′dioctylfluorene)] (poly-**PyF8**). Some of the syntheses of similar copolymers were reported in the literature by our group[15] and others.[16] The optical properties were investigated, and the results show that these copolymers may be suitable materials for device developments such as electrochromics, PLEDs, and solar cells.

Experimental Section

Materials. Hydroxyquinone was recrystallized before use. EDOT was provided by the AGFA-Gevaert Research group. All other starting materials were purchased from Aldrich or

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Acros and used without purification. THF was dried on Na overnight before distillation and freshly used for synthesis. All syntheses are carried out under nitrogen flushing.

Instrumentation. Mass spectra (MS) were obtained from a Finnigan TSQ 70 fitted to a gas chromatograph using direct insertion probe mass spectroscopy (DIP-MS) analysis with the electronic impact method (70 eV). The average molecular weight and molecular weight distribution were determined relative to polystyrene standards (Polymer Labs) by size exclusion chromatography (SEC). Thermogravimetric analysis measurements (TGA) were performed on a TA Instrument 951 thermogravimetric analyzer with a continuous nitrogen flow and a heating rate of 10 °C/min; the copolymers (15 mg) were inserted in the solid state. FT-IR spectra of compounds and polymers were recorded using a Perkin-Elmer Spectrum One FT-IR spectrometer (nominal resolution 4 cm^{-1}) by acquisition and summation of 16 scans. The compounds and the polymers were solubilized in a CH_3Cl solution and drop-casted onto NaCl disks (diameter 25 mm and thickness 1 mm). Raman spectra were recorded on a Bruker IFS66 FT-IR spectrometer extended with a FRA106 Raman module. ^1H NMR spectra were recorded with a Varian VXR300 spectrometer operating at 300 MHz. $CDCl_3$ or DMSO-d_6 was used as deuterated solvent. Chemical shifts (δ) are given in ppm relative to tetramethylsilane (TMS) as internal standard. UV−vis−NIR spectra were obtained from a Cary Varian 500 UV−vis−NIR (Perkin-Elmer) spectrophotometer at 600 nm/min (resolution = 1 nm) with a continuous run from 2500 to 250 nm. The copolymers were diluted in THF solution at the concentration of 12 mg/L and spin-coated on a quartz glass (diameter = 25 mm and thickness = 3 mm). For spectroelectrochemistry, the polymers in solution were chemically oxidized using $NOBF_4$/THF as oxidizing agent. Fluorescence spectra were recorded on a Perkin-Elmer LS-5B luminescence spectrophotometer. The polymer were diluted in $CHCl_3$ or THF $c° = 12$ μg/L. The EL emission spectra were measured by an Avantes AVS-SD2000 spectrometer.

Device Fabrication. Polymer light-emitting diodes were prepared according to the following procedure: Glass substrates coated with ITO (resistance ∼ 90 ohms/sq) first were cleaned with 2-propanol in an ultrasonic bath for 20 min and dried in a nitrogen flow. The samples were brought into the glovebox under a nitrogen atmosphere. All the following steps are done inside the glovebox. A 100 nm layer of PEDOT/PSS (Pedot P from Bayer) was spin-coated on top of the ITO and heat-treated for 10 min at 100 °C on a hot plate. After the sample cooled to room temperature the polymer layer was spin-coated on top of the PEDOT from a 2 wt % chloroform solution for the EDOT-based copolymers and from a 1 wt % chloroform solution for the pyridine-based copolymers. The spin-coating of the active layer was a two-step procedure. Then, the top electrode Ba/Al was evaporated in a vacuum at 4×10^{-6} mbar. The active area of each diode is 6 mm^2. This device is a sandwich structure of ITO/PEDOT:PSSA/copolymer/Ba/Al.

Synthesis of 9,9-Dioctylfluorene (1). In a three-neck flask fitted with a 100 mL funnel are stirred 0.16 mol of *n*-butyllithium at −78 °C under a nitrogen atmosphere. 13.3 g (0.08 mol) of fluorene dissolved in degassed THF is introduced in the funnel and dropwise added under vigorous stirring. The solution rapidly turns to orange color to finally reach intense red toward the end of addition. Then, the crude reaction mixture is allowed to reach RT for 15 min. The solution is cooled again to −78 °C, and 30.8 g of octyl bromide is slowly introduced by the funnel under stirring. After 15 min of stirring at RT, the pale red-brown solution is poured into 200 mL of water and the organic phase is separated. Then, it is washed twice with brine and dried over magnesium sulfate. The solvent is removed under reduced pressure, and 30.8 g of **1** is obtained. **1** is used without any purification in the bromination step. GC-MS: M* at 390.

Synthesis of 2,7-Dibromo-9,9-dioctylfluorene (2). Compound **1** is dissolved in 100 mL of $CHCl_3$ in a round-bottom flask with 0.2 g of $FeCl_3$. Then, the flask is embedded into a aluminum foil so that to proceed the bromination in the dark. 26.85 g of dibromine is droopily added at 0 °C to the mixture. The reaction is allowed to reach RT for 3 h. The resulting slurry is poured into water and washed with sodium thiosulfate until the red color is disappeared. The aqueous layer is extracted with 100 mL of $CHCl_3$, and the combined organic phases are washed twice with water and then dried over magnesium sulfate to afford 39.3 g of 2,9-dibromo-9,9-dioctylfluorene. Recrystallization proceeded into boiling ethanol gives a pale yellow powder. Yield: 90%. GC MS: M* at 548. ^1H NMR ($CDCl_3$, δ ppm): 0.40−0.60 (m, 4p) $-CH_2-$, 0.70−0.92 (t, 6p) $-CH_3$, 1.02−1.25 (m, 20p) $-CH_2-$, 1.85−1.91 (m, 4p) $-CH_2-$, 7.41−7.48 (3 dd, 6p) Ar−H.

Synthesis of 2,7-Bis[4,4,5,5-tetramethyl-(1,3,2)-dioxaborolan-2-yl]-9,9-dioctylfluorene (3). In a three-neck flask are dissolved 12.60 g of **2** in dry THF. The mixture is cooled at −78 °C before adding 30 mL of *n*-butyllithium (1.6 M) via a syringe. The mixture is allowed to warm to RT for 15 min and cooled again at −78 °C. 2-Isopropoxy-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (9.16 g in 50 mL of THF) is added droopwise via a funnel. The reaction is kept at RT for 24 h. Then, the mixture is poured into water, and the organic phase is extracted with diethyl ether and washed with brine two times. The solvent is evaporated under vacuum. ^1H NMR ($CDCl_3$, δ ppm): 0.75 (t, 6p, $J = 6.83$ Hz), 0.90−1.21, (m, 12p) CH_3, 1.96 (m, $J = 4.10$ Hz, 4p), 2.10 (m, $J = 5.35$ Hz, 4p), 4.10−4.20 (t, $J = 5.36$ Hz, 8p), 7.70 (d, $J = 7.50$ Hz, 2p), 7.74 (s, 2p), 7.80 (d, $J = 7.50$ Hz, 2p). FT-IR (ν cm^{-1}): 996, 1211, 1359, 1458, 1499, 2846, and 2916.

Synthesis of 1,4-Dioctyloxyphenylene (4). In a three-neck flask, 6.40 g (58 mmol) of hydroquinone, 6.84 g (2.1 equiv) of KOH, 1.74 g (0.2 equiv) of NaI, and 22.45 g (2.0 equiv) of octyl bromide are mixed in 50 mL of EtOH and bring to reflux for 48 h under stirring. Then, the solution is cooled to RT. Solvent is distilled off, and the residual product is taken up with 200 mL of 10% NaOH/H_2O. It is extracted twice with 100 mL of CH_2Cl_2. The organic phases are combined and washed with water and dried with $MgSO_4$. The solvent is distilled off. The obtained dark brown oil precipitates on cooling, and the crude product is recrystallized using 10 mL of EtOH. Yield 85%; mp 55−58.5 °C. GC MS: M* at 334. ^1H NMR ($CDCl_3$, δ ppm): 0.70−0.85 (t, 6p) $-CH_3$, 1.20−1.80 (m, 24p) $-CH_2-$, 3.90 (t, 4p), $-O-CH_2-$, 6.90 (4p, s), Ar−H.

Synthesis of 1,4-Dibromo-2,5-dioctyloxyphenylene (5). In a three-neck flask is dissolved 3.0 g (8.9 mmol) of **4** in a mixture of 50 mL of CH_2Cl_2/glac CH_3COOH (1:1). Then, 3.30 g (2.0 equiv) of *N*-bromosuccinimide is added. The brown-orange mixture is stirred at reflux for 24 h and poured into 200 mL of water. The organic layer is separated and extracted using 4 times 100 mL of saturated Na_2SO_3. Finally, it is dried over $MgSO_4$ and the solvent is distilled off. The obtained yellow oil crystallized on cooling. The crystals are filtered and washed using a large amount of MeOH. Yield: 75%. GC MS: M* at 492. ^1H NMR ($CDCl_3$, δ ppm): 0.70−0.85 (t, 6p) $-CH_3$, 1.20−1.80 (m, 24p) $-CH_2-$, 3.92 (t, 4p), $-O-CH_2-$, 7.06 (s, 2p) Ar−H.

Synthesis of 1,4-Bis[4,4,5,5-tetramethyl-(1,3,2)-dioxaborolan-2-yl]-2,5-dioctyloxyphenylene 6a. In a three-neck flask is dissolved 10.0 g (20.0 mmol) of **5** in 100 mL of dry THF. Then, 27 mL of *n*-butyllithium (1.6 M in hexanes) is slowly added via a syringe at −78 °C. The mixture is allowed to reach RT for 1 h. Then it is cooled again to −78 °C, and 8.0 g of 2-isopropoxy-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane dissolved in 50 mL of THF is droopwise added via a 100 mL funnel. The mixture is let to reach RT and stirred for 24 h. The organic phase is extracted with diethyl ether, washed twice with brine, and dried over magnesium sulfate. The solvent is distilled off, and the crude product is dissolved again in 25 mL of THF. Reprecipitation with *n*-hexanes gives 9.0 g of compound **6** that is recrystallized in ethyl acetate. Yield: 75%. GC MS: M* at 586. ^1H NMR ($CDCl_3$, δ ppm): 0.79 (s, 6p) $-CH_3$, 1.05−1.95 (24p) $-(CH_2)_n-$, 4.01 (s, 4p), $-O-CH_2-$, 4.35 (s, 4p) $-O-CH_2-CH_2-O-$, 7.66 (s, 2p) Ar−H. FTIR (ν cm^{-1}): 2909, 2853, 1494, 1421, 1384, 1351, 1294, 1197, 1046.

Synthesis of 1,4-Bis(dihydroxyborolan)-2,5-dioctyloxyphenylene (6b). In a three-neck flask is dissolved 2.0 g (4.0 mmol) of **5** in 20 mL of dry THF. Then, 3.2 mL of *n*-

butyllithium (2.5 M in hexane) is slowly added via a syringe at −78 °C. The mixture is allowed to reach RT for 1 h. Then it is cooled again to −78 °C, and 1.10 g of $B(OCH_3)_3$ is dropwise added. The mixture is allowed to reach RT for 24 h. Finally, the diboronic ester is hydrolyzed in a 2 M HCl aqueous solution, giving the desired diboronic acid compound. Recrystallization from ethyl acetate gives compound **6b** with a yield of 32%. ^{1}H NMR (DMSO-d_6, δ ppm): 0.70−0.85 (t, 6p) $-CH_3$, 1.20−1.80 (m, 24p) $-CH_2-$, 3.87 (t, 4p), $-O-CH_2-$, 7.17 (s, 2p) Ar−H, 7.81 (s, 4p) −B−OH. FTIR (ν cm^{-1}): 725, 1049, 1204, 1298, 1386, 1425, 1491, 2845, 2899, 3338.

Synthesis of 2,5-Dibromoethylenedioxythiophene (7). 5.10 g (0.036 mol) is dissolved in mixture of 40 mL of THF/glac CH_3COOH (1:1). Then, 13.0 g (0.072 mol) of *N*-bromosuccinimide (NBS) is added in small portions under stirring at RT. After 2 h stirring, the deep-blue solution is poured into 100 mL of water. The precipitate is filtered off and washed with water until pH reaches 6.0. Finally, **7** is recrystillized twice from 10 mL of MeOH and washed with freeze MeOH until white needles are obtained. When blue-gray crystals are obtained, the purification is realized by column chromatography on silica gel using diethyl ether as eluent. Yield: 85%; mp 95.3−97.0 °C. GCMS: M* at 296. ^{1}H NMR ($CDCl_3$, δ ppm): 4.13, (s, 4p), $-CH_2-O-$. FTIR (ν cm^{-1}): 457, 939, 1081, 1357, 1412, 1508, 2875, 2945.

Synthesis of Copoly(2,5-ethylenedioxythiophene-*alt*-2,5-dioctyloxyphenylene), Poly-EP8. *Procedure 1.* In a 50 mL round flask fitted by a thermometer and a condenser are added 0.142 g (0.47 mmol) of **7**, 200 mg of **6a**, and 4 mL of K_2CO_3 (2 M in H_2O) in 20 mL of THF under a nitrogen atmosphere. $Pd^0(PPh_3)_4$ (0.6% mol) is then added, and the mixture is allowed to reflux at 60 °C for 24 h. The polymer is precipitated in 200 mL of MeOH and filtered. The precipitate is washed with a large amount of water followed by MeOH. The polymer is dissolved in 20 mL of $CHCl_3$ and reprecipitated three times in 200 mL of MeOH, filtered, and dried under vacuum. Yield: 65% (according $(AB)_n$). ^{1}H NMR (DMSO-d_6, δ ppm): 0.79 (s, 6p) $-CH_3$, 1.1−1.9 (24p) $-CH_2-$, 4.01 (s, 4p), $-O-CH_2-$, 4.35 (s, 4p) $-O-CH_2-CH_2-O-$, 7.66 (s, 2p) Ar−H. FTIR (ν cm^{-1}): 1083, 1360, 1429, 1461, 1490, 2853, 2909.

Procedure 2. In a 50 mL round flask fitted by a thermometer and a condenser are added 0.142 g (0.47 mmol) of **7**, 277 mg of **6b**, and 4 mL of K_2CO_3 (2 M in H_2O) in 20 mL of THF under a nitrogen atmosphere. $Pd^0(PPh_3)_4$ (0.6% mol) is then added, and the mixture is allowed to reflux at 60 °C for 24 h.The polymer is precipitated in MeOH and filtered. The polymer is dissolved in 20 mL of $CHCl_3$ and reprecipitated three times in 200 mL of MeOH, filtered, and dried under vacuum. Yield: 65% (according $(AB)_n$). ^{1}H NMR (DMSO-d_6, δ ppm): 0.79 (s, 6p) $-CH_3$, 1.05−1.95 (24p) $-CH_2-$, 4.01 (s, 4p), $-O-CH_2-$, 4.35 (s, 4p) $-O-CH_2-CH_2-O-$, 7.65 (s, 2p) Ar−H.

Synthesis of Copoly(2,5-ethylenedioxythiophene-*alt*-9,9-dioctylfluorene), Poly-EF8. In a 100 mL round flask fitted by a thermometer and a condenser are added 420 mg (1.401 mmol) of **7**, 900 mg of **3**, and 10 mL of K_2CO_3 (2 M in H_2O) in 50 mL of dry THF under N_2. $Pd^0(PPh_3)_4$ (0.6% mol) is added, and the mixture is allowed to reflux for 24 h. The polymers is end-capped by the use of small amounts (0.1% mol) of phenylboronic acid and bromobenzene and 0.05% of catalyst. The precipitate is washed by a large amount of water followed by MeOH. It is dissolved in 20 mL of $CHCl_3$, reprecipitated three times in 200 mL of MeOH, filtered, and dried under vacuum. Yield: 86% (according $(AB)_n$). ^{1}H NMR ($CDCl_3$, δ ppm): 0.76−0.81 (t, 6p) $-CH_3$, 0.90−1.24 (m, aliphatic proton), 1.55 (s, 2p) $-CH_2-$, 1.80−2.1 (s, 4p) $-CH_2-$, 4.49 (s, 4p) $-O-CH_2-CH_2-O$-, 7.67 (d, $J = 6$ Hz, 4p) Ar−H, 7.81 (d, $J = 6$ Hz, 2p) Ar−H.

Synthesis of Copoly(2,5-pyridine-*alt*-2,5-dioctyloxyphenylene), Poly-PyP8. In a 100 mL round flask fitted by a thermometer and a condenser are added 363 mg (1.535 mmol) of 2,5-dibromopyridine (**8**) (Aldrich, 98%), 900 mg of **6**, and 10 mL of K_2CO_3 (2 M in H_2O) in 50 mL of THF under N_2. Then, $Pd^0(PPh_3)_4$ (0.6 mol %) is added, and the mixture is allowed to reflux at 60 °C for 24 h. The polymer is precipitated in MeOH and filtered and washed with a large amount of water followed by MeOH. The polymer is dissolved in 20 mL of $CHCl_3$ and reprecipitated three times in MeOH, filtered, and dried under vacuum. Yield: 87% (according $(AB)_n$). ^{1}H NMR (δ ppm, $CDCl_3$): 0.84 (s, 6p) $-CH_3$, 1.0−2.0 (m, alliphatic protons), 3.93−4.20 (m, 4p) $Ar-O-CH_2-$, 7.80−8.20 (m, 2p) Pyr-H, 8.96 (s, 1p) Pyr-H. FTIR (ν cm^{-1}): 845, 1205, 1221, 1463, 1505, 2855, 2924.

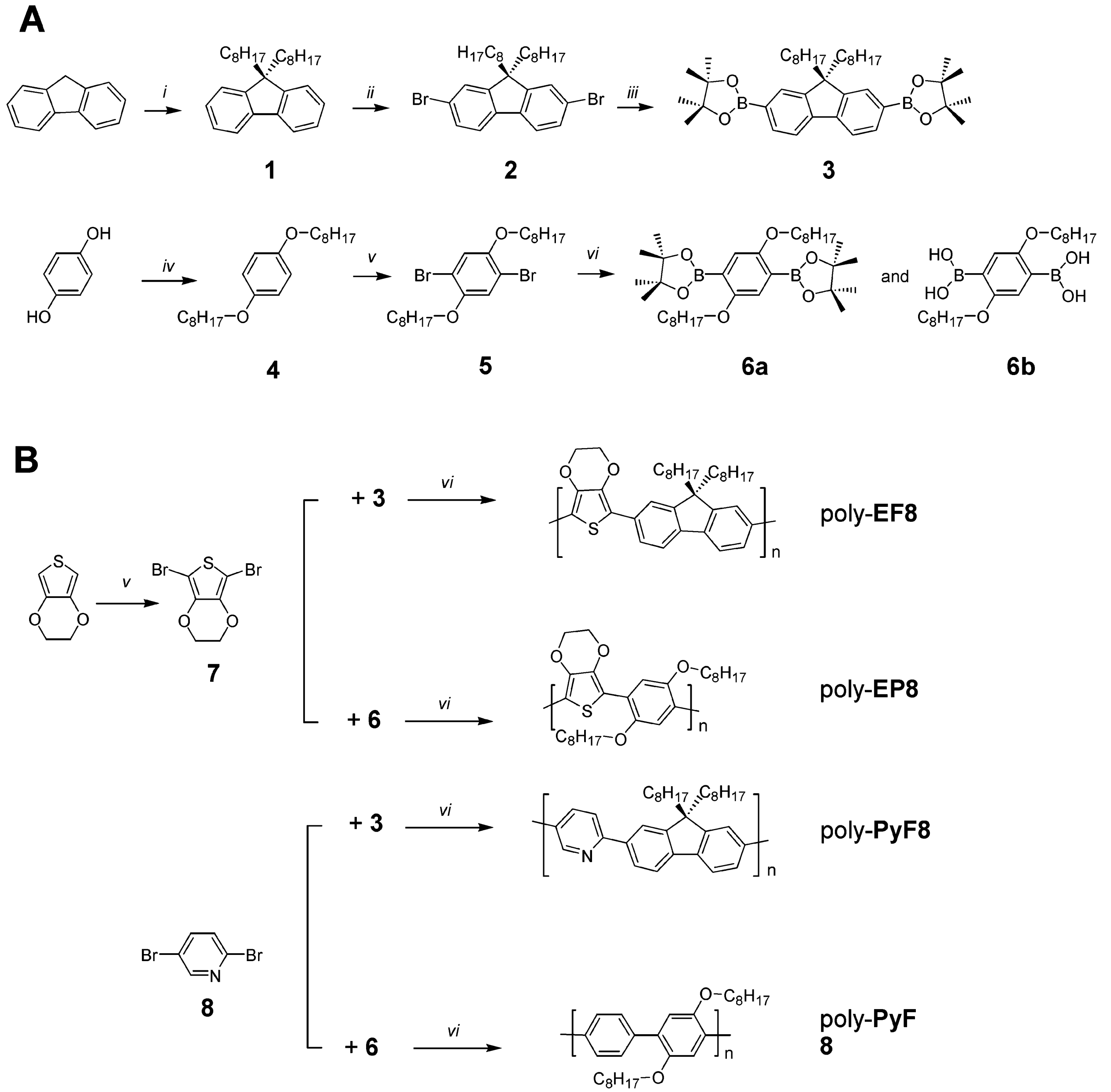
Synthesis of Copoly(2,5-pyridine-*alt*-9,9-dioctylfluorene), Poly-PyF8. In a 100 mL round flask are added 363 mg (1.535 mmol) of 2,5-dibromopyridine (**8**), 900 mg of **3**, and 10 mL of K_2CO_3 (2 M in H_2O) in 50 mL of THF under N_2. $Pd^0(PPh_3)_4$ (0.6% mol) is then added, and the mixture is allowed to reflux for 24−48 h. The polymer is precipitated in MeOH, filtered, and washed with a large amount of water followed by MeOH. The polymer is dissolved in 20 mL of $CHCl_3$ and reprecipitated three times in 200 mL of MeOH, filtered, and dried under vacuum. Yield: 82%. ^{1}H NMR ($CDCl_3$, δ ppm): 0.75−0.85 (t, 6p) $-CH_3$, 0.90−1.25 (m, aliphatic proton), 1.80−2.1 (s, 4p) $-CH_2-$, 7.67 (d, $J = 6$ Hz, 4p) Ar−H, 7.81 (d, $J = 6$ Hz, 2p) Ar−H, 7.85−8.20 (m, 2p) Pyr-H, 8.96 (s, 1p) Pyr-H. FTIR (ν cm^{-1}): 815, 1017, 1098, 1260, 1456, 1589, 2853, 2926.

Results and Discussion

Synthesis of the Precursors. 9,9-Dioctylfluorene (**1**), 2,7-dibromo-9,9-dioctylfluorene (**2**), 2,7-bis[4,4,5,5-tetramethyl-(1,3,2)-dioxaborolan-2-yl]-9,9-dioctylfluorene (**3**), 1,4-dioctyloxybenzene (**4**), 1,4-dibromo-2,5-dioctyloxybenzene (**5**), 1,4-bis[4,4,5,5-tetramethyl-(1,3,2)-dioxaborolan-2-yl]-2,5-dioctyloxyphenylene (**6**), and 2,5-dibromo-3,4-ethylenedioxythiophene (**7**) are synthesized according to literature with some necessary modifications.[17−19] A general description is given in Scheme 1A. The synthesis of fluorene and phenylene boronic esters **3** and **6a,b** are achieved in three steps: grafting alkyl chains,[20] bromination,[18,19,21−24] and then boronation. The phenylene compound was brominated by NBS according to the same conditions as in previous cited references while the fluorene derivative **1** was substituted by bromine[18,19] in the presence of $FeCl_3$. The use of diboronic ester precursors vs the diacid ones is found to be interesting given that literature reports a possible self-dehydration of boronic acid thiophene derivatives into anhydride trimers.[25,26] For example, compound **6b** was surprisingly insoluble in THF and $CHCl_3$ after recrystallization, resulting in inefficient ^{1}H NMR (in $CDCl_3$) and GC-MS characterizations. The dehydration of a disubstituted compound can lead to an insoluble polymeric network. This suggestion was attested by GPC experiments, indicating that this compound may be an aggregate of 6−8 phenylene units. For these reasons, **2** and **5** were preferably disubstituted by 2-isopropoxy-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane. The boronation occurs subsequently after *n*-butyllithium treatment, generally from trimethylborolan or 2-isopropyloxy-4,4,5,5-tetramethyl-(1,3,2)-dioxaborolan. The bromation of EDOT[17] occurs easily on α,α′ positions by the use of 2.1 equiv of NBS. Successive recrystallizations are not sufficient to purify **7** since the pure **7** precipitates with insoluble oligomers giving a slight blue-gray coloration to the crystals. We found that **7** is better purified (white crystals) on silica gel column using diethyl ether as eluent.

Synthesis of the Polymers. The Suzuki, the Stille cross-couplings, and the McCullough reaction are interesting routes to synthesized conjugated copoly(arylenes). Reynolds et al.[27] synthesized poly[3,4-(ethylenedioxy)thiophene-*alt*-2,5-didodecyloxyben-zene] via the McCullough reaction starting from a Br−Ar−Ar′−MgBr precursor. Bao et al.[28] synthesized poly[thiophene-

Scheme 1. General Scope of Synthesis of Precursors and Their Copolymerization[a]



[a] (i) n-BuLi (−78 °C) then $C_8H_{17}Br$. (ii) $Br_2/CHCl_3$, 0 °C, N_2, dark, 3 h. (iii) n-BuLi (−78 °C), N_2, then 2-isopropoxy-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane, 24 h. (iv) KOH/NaI_{cat} in EtOH, then $C_8H_{17}Br$, reflux 48 h. (v) 2.1 equiv of NBS in CH_2Cl_2/CH_3COOH glac., reflux 48 h, (vi) compound **6a**: n-BuLi (−78 °C), N_2, then 2-isopropoxy-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane, 24 h, compound **6b**: n-BuLi (−78 °C), N_2, then $B(OMe)_3$, 24 h, then H_2O/HCl, 24 h.

alt-2,5-dialkoxybenzene] via the Stille coupling. Our synthetic approach favors the Suzuki cross-coupling as described in Scheme 1B considering that (i) the McCullough route requires the synthesis of a unique precursor, X−Ar−Ar′−MgX (−X = halogen), containing the two different arylenes. The possibility to generalize this multistep synthesis to further conjuguated systems seems to us somewhat more difficult. (ii) The Stille coupling requires to synthesize 2,5-bis(tributylstannyl)-EDOT precursor. Although stable, the distannylation reaction is not quantitative, and the separation of the precursor from the monostannyl compound is unsuccessful. We point out here that any presence of monofunctional precursors would lead to stop the growth of the polymer chains. The polycondensations via palladium cross-coupling are very sensitive to purity of the precursors[26] with the consequence that the molecular weights may drastically drop. Also, a lot of parameters may influence the Suzuki cross-coupling reaction and therefore the polymers characteristics,[29] such as the choice of the palladium source and its associated base, the solvent, the nature of the boronic substituent, and the temperature during the reaction. The Suzuki cross-coupling polycondensations involving phenylene or fluorene with EDOT or pyridine were carried out in THF/H_2O under nitrogen using $Pd^0(PPh_3)_4$, a weak base (sodium acetate or hydrogenocarbonate), and either the acid or ester form of the boronic-based monomer. Extreme attention was paid to the absolute oxygen-free conditions and to the strict stoichiometry of the comonomers engaged, the first one poisoning the Pd complex and the second one decreasing dramatically the molecular weight of the resulting polymers.

Table 1. Physicochemical Properties of All Polymers

entry	catalyst (%)	vol[a]	reaction time (h)	end-capping	yield (%)	M_w	PD	T_c (°C)	T_g (°C)	n[b]
poly-**PyP8**	1.5	2V1	24	yes	67	5765	1.55	447		15
poly-**PyF8**	1.5	2V1	24	yes	65	8047	2.17	482		22
poly-**EP8**[c]										
1	1.5	V1	24	no	65	13489	2.64			28
2	0.2	4V1	72	no	70	8482	1.59			20
3	1.5	2V1	288	yes	84	6939	1.48			17
4	1.5	2V1	24	yes	65	7851	1.59			18
poly-**EP8**	1.5	2V1	24	yes	65	7851	1.44	426	160/192	18
poly-**EF8**	0.5	V1	24	yes	70	9686	2.108	458	98/101	18

[a] For 0.5 mmol of reagents, volumes are 4 mL of water and 10 mL of THF. [b] According $-(AB)_n-$. [c] Prepared with boronic acid.

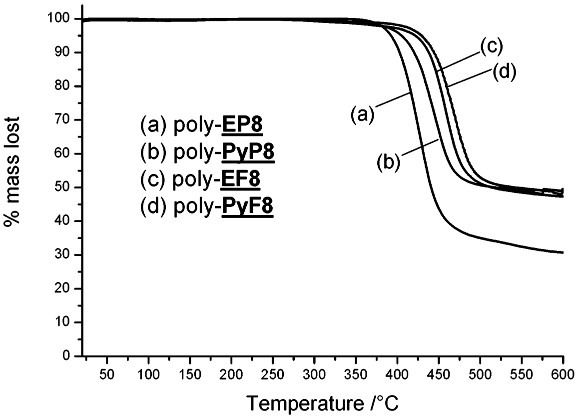


Figure 1. Thermal gravimetric analysis results of the copolymers poly-**EP8**, poly-**EF8**, poly-**PyP8**, and poly-**PyF8**.

Characterizations of the Copolymers. Compared to the $(A_2B)_n$ type copolymers,[42,43] poly-**EP8**, poly-**EF8**, poly-**PyP8**, and poly-**PyF8** exhibit more solubility in common organic solvents such as methylene chloride, chloroform, THF, dichloroethane, and chlorobenzene. This result is of importance given that processablility is required for the electronic device applications. This behavior is provided by the alkyl side chains grafted on the phenylene and on the fluorene rings and by the 1:1 ratio between the two different units along the polymeric chain. Table 1 gives the results of SEC performed in THF using polystyrene. Poly-**EP8** is the single example in this study of a copolymer prepared from an acid and an ester diboronic derivative. Even if the chain lengths are small (n < 30), the polymerization leads to a monomodal distribution of M_w and a M_w/M_n around 2, what is consistent with a polycondensation reaction.[25] Furthermore, these results are analogous with some results published in the literature, involving alternated thiophene and phenylene copolymers.[28,30] Thermal stability was determined by TGA. All four copolymers are thermally stable up to 325−375 °C as shown in Figure 1. This point suggests also that these copolymers can be incorporated into devices. The dioctyloxy-substituted polymers, poly-**EP8** and poly-**PyP8,** are the less stable materials compared to their fluorene homologues with a degradation starting around 325 °C and completed before 500 °C. The percentage of mass lost during heating is consistent with the dealkylation of the backbone.

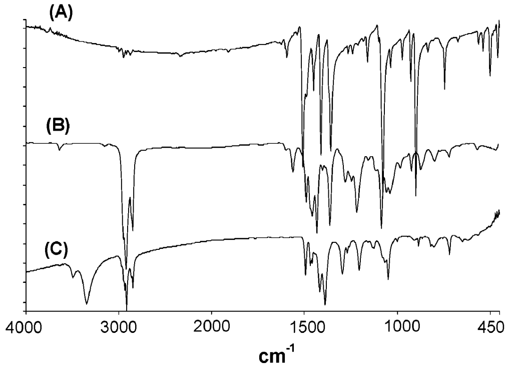


Figure 2. IR spectra of compound **7** (A), poly-**EP8** (B), and compound **6b** (C).

Structural Properties of the Copolymers. Raman scattering and infrared absorption spectroscopies are two complementary techniques to study the structure of the polymers and the doping process of CPs[31,32] since their structures change from benzenoid to quinoid forms during (electro)chemical doping/dedoping. Poly-**EP8**, poly-**EF8**, poly-**PyP8**, and poly-**PyF8** were investigated by FT-IR spectroscopy, in both their neutral and oxidized forms. FT-IR spectroscopy gives interesting information on the nature of the atoms and bonds present in a molecule or in a polymer. The IR spectrum of a copolymer resulting from the coupling between two different precursors A and B should contain the information on each precursor. The attribution of each vibration mode corresponding to the $C_{sp2}-C_{sp2}$, $C_{sp2}=C_{sp2}$, and $C_{sp3}-C_{sp3}$ bonds does not represent a valuable way to study the spectra of copolymers as well as the C−H ones. On the contrary, the vibration modes characteristic of the bromine and the boronic (acid or ester) substituents of the precursor **3**, **6a,b**, **7**, and **8** are of interest since their signature is expected to disappear on the spectra of the corresponding copolymers. The two bromine substituents of the EDOT and the pyridine units give a stretching vibration mode around 975 cm^{-1}. The diboronic acid gives three significant vibrations at 750, 1497, and 3338 cm^{-1}, corresponding to the O−B−O scissoring, B−O asymmetrical stretching, and O−H stretching vibration modes, respectively. The diboronic ester substituents are infrared-active at 630 cm^{-1} (O−B−O scis) and 1306 cm^{-1} ($O-C_{sp3}-C_{sp3}-O$ ring deformation). All these characteristic vibrations are not present in the case of corresponding copolymers as suggested by Figure 2. However, the characteristic vibration at 1081 cm^{-1} corresponding to ethylenedioxy ring deformation is still present in the copolymers poly-**EF8** at 1089 cm^{-1} and poly-**EP8** at 1082 cm^{-1}. Upon oxidation using $NOBF_4$ as chemical oxidizing agent, all copolymers become less transmissive in the IR region, as shown in Figure 3. Furthermore, the copolymers present a similar behavior in the 1000−1100 cm^{-1} region: two strong absorption bands appear, attributed to the ν_{B-F} stretching mode and characteristic of the incorporation of a counterion along the polymer chains during the oxidation process. Unfortunately, FTIR does

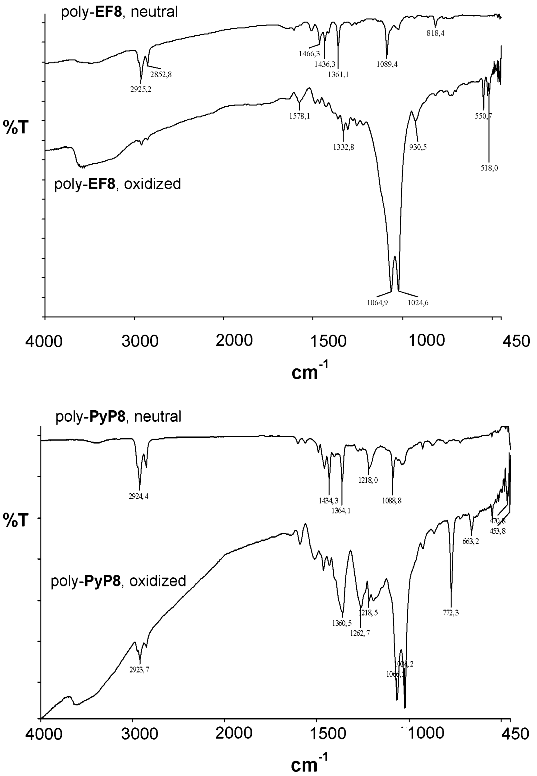


Figure 3. IR spectra of (A) neutral state (top) and oxidized (bottom) state of poly-**EF8** and (B) poly-**PyP8** coated on glass by spin-coating from a concentrated THF solution of polymers.

not give any information from the benzenic-to-quinoic variation of the benzene (or fluorene) rings resulting from the chemical oxidation.

Garreau et al.[33] and Lapkowski et al.[34] recently published an interesting study on Raman properties of PEDOT using two excitation lines at $\lambda_{ex} = 514$ nm (green) and 1064 nm (NIR). By studying the shift and the intensity of the peaks for the neutral and oxidized states, the authors claimed that the bipolaronic form of the oxidized PEDOT could be benzenoid while the polaronic form could be quinoid and the neutral PEDOT form being intermediate (certainly due to the mixture of neutral and polaronic species in free-standing PEDOT). Between 1300 and 1600 cm^{-1}, both C=C and C−C stretching vibrations are active. An intense peak attributed to the C_α=C_β symmetric stretching occurs at 1420 cm^{-1} followed by two weaker peaks around 1500 cm^{-1} attributed to asymmetric C_α=C_β modes. A weak peak at 1370 cm^{-1} is assigned to the C_β−C_β stretching vibration. The region between 1000 and 1300 cm^{-1} corresponds to the C−C intercycle vibration modes, and the C−O−C_β deformation gives a weak peak at 1100 cm^{-1}. PPV and PPP polymers were also investigated by Raman spectroscopy.[35,36] The phenylene ring shows an intense peak around 1600 cm^{-1} and a weaker peak at 1280 cm^{-1}, corresponding to the C=C ring stretching and C−C ring stretching vibration modes, respectively. The polyfluorenes were studied by Ariu et al.[37] The C=C ring stretching is shown at 1609 cm^{-1} and the C−C stretching between 1100 and 1400 cm^{-1} (eight weak peaks); 1300 cm^{-1} corresponds to the monomeric intercycle C−C vibration mode. On the basis of the previous literature data, we have studied by Raman spectroscopy our four copolymers in both the neutral and oxidation states. The spectra are shown in Figure 4 for poly-**EP8** and poly-**PyP8** as examples. The Raman data of all the four copolymers are given in Table 2. In this study, we focus on the intense peak corresponding to the C=C stretching mode in the different rings. As stated in the previous paragraph, these peaks are located in the 1300−1600 cm^{-1} region of the Raman spectra. In the case of poly-**EP8**, these peaks are measured at 1605 cm^{-1} (phenylene) and 1430 cm^{-1} (EDOT) (Figure 4). The other peaks were assigned according to refs 33 and 35. Upon oxidation, the peak at 1605 cm^{-1} is red-shifted to 1599 cm^{-1}, and 1430 cm^{-1} is shifted to 1425 cm^{-1} with a decrease of their intensities. At the same time, the peak attributed to the C_β−C_β stretching vibration mode is blue-shifted from 1368 to 1375 cm^{-1} with an increase of its intensity. The changes observed in the region 1300−1500 cm^{-1} are very similar to that reported by

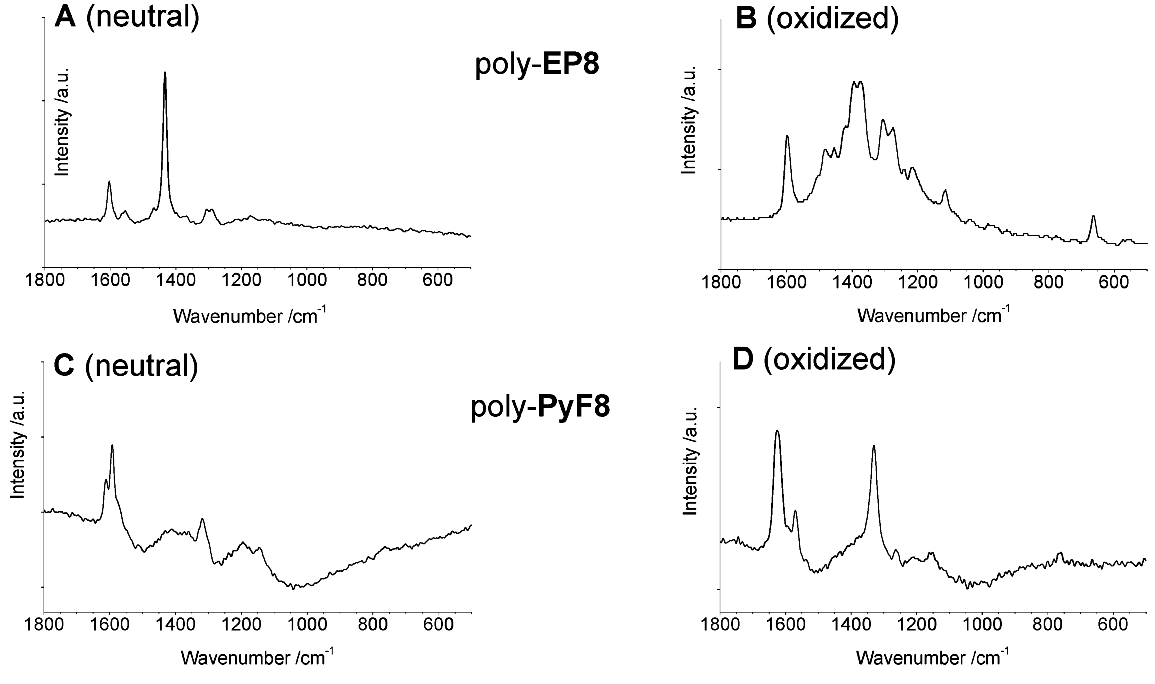
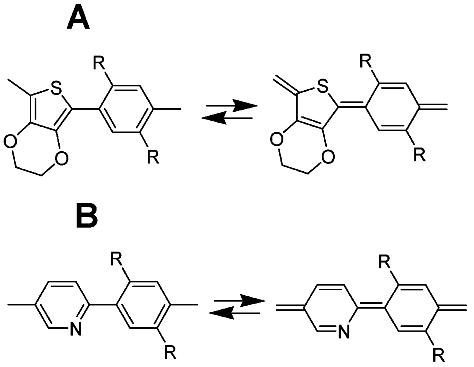


Figure 4. Raman spectra of (A) neutral poly-**EP8**, (B) oxidized poly-**EP8**, **(**C) neutral poly-**PyF8**, and (D) oxidized poly-**PyF8**.

Table 2. Raman Data of the Copolymers in Neutral and Oxidized State

entry	reduced films ν(cm^{-1})	oxidized films ν (cm^{-1})	assignment	unit
poly-**PyP8**	1610	1626	sym C=C ring stretch	phen
	1592	1570	sym C=N ring stretch or asym C=C stretch	pyr, fluo
			C−C stretch	fluo
	1318	1331		phen
	1197		C−O−C deform	
	1142			phen
poly-**PyF8**	1611	1610	sym C=C ring stretch	fluo
	1589	1584	sym C=N ring stretch or asym C=C stretch	pyr, fluo
			C−C stretch	fluo
	1417		C−C stretch intercycle	
	1324	1365		fluo
	1296		n.a.	fluo
	1140	1155		
poly-**EP8**	1605	1599	sym C=C ring stretch	phen
	1554		asym C_α=C_β ring stretch	EDOT
	1464		−CH_2− scissoring	
	1430	1425	sym C_α=C_β ring stretch	EDOT
	1368	1375	C_β−C_β stretch	EDOT
	1306		−CH_2− twisting	
	1289		C−C stretch intercycle	
	1165		C−O−C deform	EDOT
poly-**EF8**	1606	1601	sym C=C ring stretch	fluo
	1511		asym C=C ring stretch	fluo
	1479		asym C=C ring stretch	EDOT
	1451		−CH_2− scissoring	EDOT
	1441		C−C stretch intercycle	
	1339	1348	−CH_2− twisting	fluo
	1310			EDOT
	1271		C−C stretch	fluo
	1140		C−O−C deform	EDOT
		663	C−S−C ring deform	EDOT

Scheme 2. Structural Change of the Copolymer Containing EDOT (A) and Pyridine (B) in the Backbones upon Oxidation, from Neutral (Left) to Oxidized (Right) Configurations



Lapkowski et al. in the case of PEDOT during the polymer oxidation. This region contains significantly the fingerprints of the EDOT units. The backbone of the poly-**EP8** is subject to changes during oxidation; C=C bonds get more single bond character and vice versa, as suggested by Scheme 2.[38] The polymeric structure switches from benzenic (neutral state) to quinoid (oxidized state) form. We point out that the oxidized state is assumed to be the polaronic state, as will be demonstrated by UV−vis−NIR. The C−S−C bond deformation characteristic of the thiophene ring is observed at 663 nm. This peak is active only in the case of the oxidized poly-**EP8**, in contrast with results reported in the literature.[33,34] Poly-**EF8** is similar to poly-**EP8**. The C=C stretching is pointed to 1606 cm^{-1} in the case of the fluorene rings and shifts to 1601 cm^{-1}; the C−C intercycle stretching observed at 1339 cm^{-1} is shifted to 1348 cm^{-1} as a consequence of the quinoid transformation of the fluorene ring. The cases of poly-**PyP8** and poly-**PyF8** are more complicated. The Raman spectra of the neutral and oxidized form of poly-**PyP8** are given in Figure 4. The peak at 1592 cm^{-1} is red-shifted to 1570 cm^{-1}. This peak may be attributed to the asymmetric C=C stretching of the phenylene rings, given that the C−C stretching mode is blue-shifted from 1318 to 1331 cm^{-1} or to the C=N stretching vibration mode by comparison with pyridine-containing complexes spectra.[39] The shift of the peak at 1610 cm^{-1} is somewhat surprising since it is blue-shifted to 1626 cm^{-1} and contains several shouldering peaks.

Electrochemical Properties and Band-Gap Evaluation. As an electropolymerizable unit, EDOT monomer can be easily attached to a wide variety of conjugated rings. This work was mainly achieved by the Reynolds group[40−43] and by others[44,45] with the electrochemical synthesis of poly(bisEDOT-arylenes) with the main goal to develop transmitting and reflecting electrochromic devices.[46] The resulting $(A_2B)_n$ regular sequence of the poly(bisEDOT-arylenes) allows to decrease the oxidative potential of the copolymers and to control its optical properties through the whole visible window (1.2−3.0 eV).[47] Despite this, little is know about the electrical and optical properties of the $(AB)_n$ sequence containing EDOT monomers. The reason is most probably the complexity in the synthesis such $(AB)_n$ sequence compared to the $(A_2B)_n$ ones, the latter being easily and efficiently obtained via electrochemical route. The electrochemical behavior of the four copolymers was investigated by cyclic voltammetry (CV). CVs were performed in a solution of Bu_4NClO_4 (0.10 M) in acetonitrile at 50 mV/s under nitrogen. The setup was a three-electrode configuration with a Ag/Ag$^+$ reference electrode, a platinum button electrode (0.08 cm^2) coated with a thin copolymer film as working electrode, and a platinum grid as counter electrode. The corresponding data are summarized in Table 3. The electrochemical band gap is evaluated between the onset potential of oxidative and reductive waves. We found E_g = 2.38 and 2.12 eV for

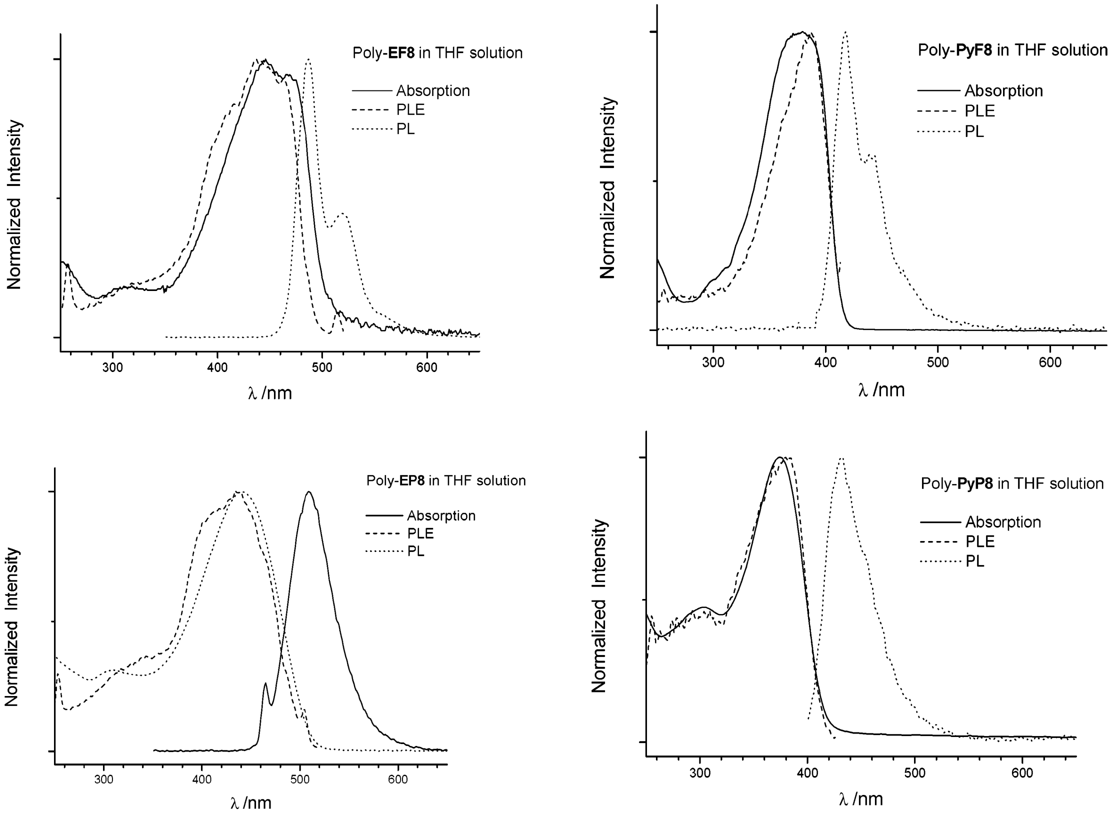


Figure 5. Absorption and emission spectra of the copolymers: solid line, in THF solution; dashed line, solid-state films (films spin-coated on quartz glass); scattered line, emission of the films in THF solution.

Table 3. Electrochemical Properties of Polymers

	cyclic voltammetry									UV−vis
polymer	$E_{\text{onset,Ox}}$ vs Ag	$E_{1/2}$	$E_{\text{onset,Ox}}$ vs Fe	HOMO I_p	$E_{\text{onset,Red}}$ vs Ag	$E_{1/2}$ vs Fe	$E_{\text{onset,Red}}$ vs Fe	LUMO E_a	band gap (eV)	band gap (eV)
poly-**PyP8**	0.960	1.06	0.53	−5.33	−1.730	−1.83	−2.16	−2.64	2.69	2.84
poly-**PyF8**	0.916	1.02	0.49	−5.29	−1.777	−1.88	−2.20	−2.60	2.69	2.87
poly-**EP8**	0.304	0.31	−0.12	−4.68	−1.819	−1.93	−2.25	−2.55	2.12	2.18
poly-**EF8**	0.820	0.95	0.39	−5.19	−1.559	−1.67	−1.99	−2.81	2.38	2.44

poly-**EF8** and poly-**EP8**, respectively, and 2.69 eV was obtained for poly-**PyF8** and for poly-**PyP8**. As expected, it is found that the oxidative potentials of the EDOT-based copolymers are lower than their pyridine-based analogues, while the reduction is easiest for the pyridine-type copolymers. In addition, the values of the oxidative potential of poly-**EF8** and poly-**EP8** are higher than that recorded in the case of poly(bisEDOT-fluorene) and poly(bisEDOT-phenylene).[27,42a]

The optical band gap E_g was calculated also at λ_{onset} of the π−π^* absorption from the UV−vis spectra recorded for solid-state films. Polypyridines and polyfluorenes, as blue-light-emitting polymers, have E_g values around 3.0 eV, while the E_g of the PEDOT derivatives is around 1.6−1.7 eV. The E_g's measured for poly-**EF8** and poly-**EP8** are respectively 2.44 and 2.18 eV. These values are consistent with a well-defined copolymer; in all cases, the UV−vis spectra do not show any characteristic absorption of blend of homopolymers. As expected, poly-**PyP8** and poly-**PyF8**, containing an equimolar mixing of pyridine and phenylene or fluorene have a higher E_g respectively of 2.87 and 2.84 eV. These results are in accordance with the band gap obtained from the cyclic voltammetry study.

Optical Properties of the Copolymers in Solution. *(a) UV−vis Properties in THF Solution.* UV−vis spectra of the copolymers were recorded in diluted THF solutions (12 μg/L). The pyridine-containing copolymers show a maximum absorption wavelength $\lambda_{\max}$ around 380 nm while the EDOT-containing copolymers absorb at a $\lambda_{\max}$ around 440−450 nm. Only poly-**EF8** exhibits two melt absorption bands in THF solution as shown in Figure 5, consistent with previously reported measurements.[48] The absorption is assigned to the π−π^* transition between the valence and the conducting bands. Data are summarized in Table 4. Chevrot et al. recently reported the UV−vis properties of copolymers of a random copolymer of EDOT and dihexylfluorene.[49] For a 1:1 random material, two $\lambda_{\max}$ were measured as a result of a blend of oligomers of EDOT (λ_{abs} around 500−600 nm) and polydihexylfluorene (λ_{abs} around 380 nm). Here, the regular sequence of 1:1 EDOT and fluorene units produce a unique π-conjugated delocalized system, which absorption is measured between the one of the homopolymers. This observation is also valid for poly-**EP8**.

(b) Electrochromic Properties. The UV−vis−NIR of each copolymer was monitored during a chemical oxidation process by adding successively 10 μL of $NOBF_4$/THF (10^{-3} M) as the chemical oxidizing agent. The polymers were previously diluted in THF solution (12 μg/L). The UV−vis−NIR spectra shown in Figure 5

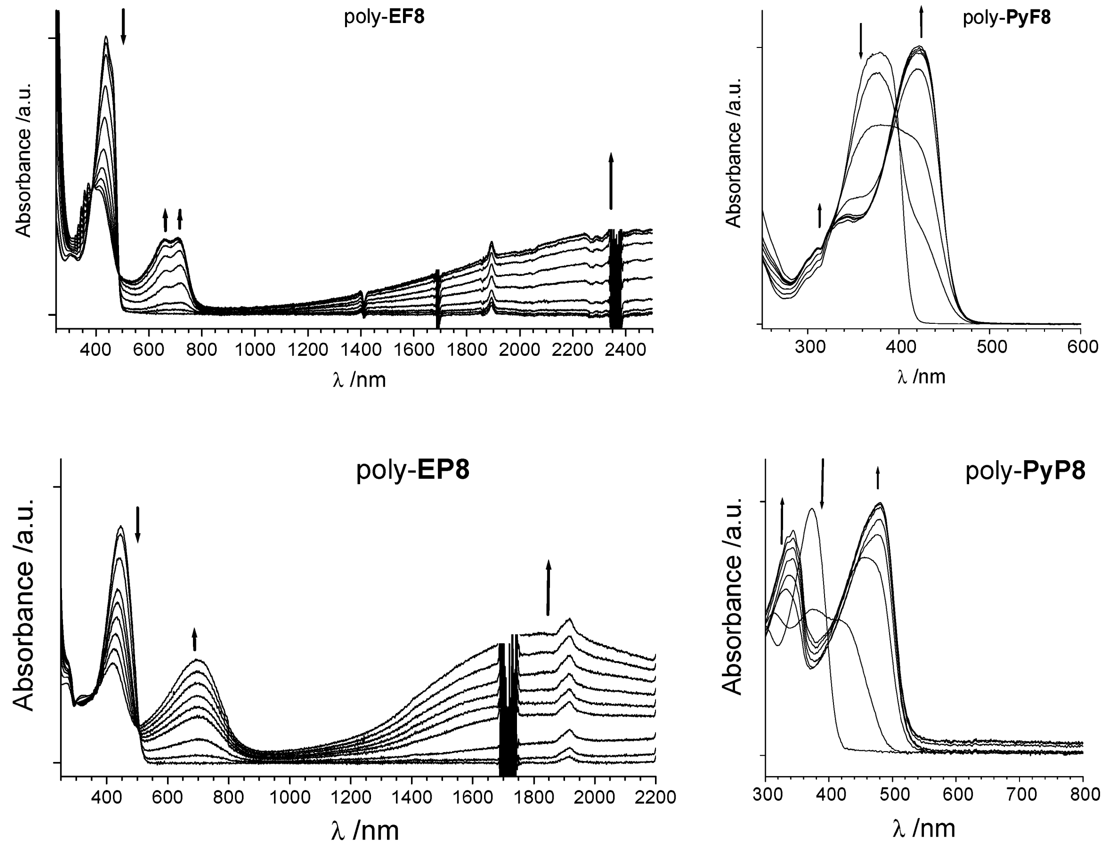


Figure 6. Spectroelectrochemistry of poly-**EF8** (top left), poly-**PyF8** (top right), poly-**EF8** (bottom left), and poly-**PyP8** (bottom right). Films were diluted ($c° = 12\ \mu$g/L) in THF.

Table 4. Optical Properties of the Copolymers in THF Solution and on Solid State (T_1 and T_2 Are the Polaronic Levels Calculated from Figure 6)

	copolymers in THF solution			solid-state copolymers			T_1		T_2			
entry	$\lambda_{abs,max}$ (nm)	$\lambda_{abs,onset}$ (nm)	optical band gap (eV)	$\lambda_{abs,max}$ (nm)	$\lambda_{abs,onset}$ (nm)	optical band gap (eV)	nm	eV	nm	eV	$\lambda_{excitation}$, nm	$\lambda_{emission}$, nm
poly-**PyP8**	374	420	2.94	380	435	2.84	344	3.59	481	2.57	374	428/449
poly-**PyF8**	380	420	2.94	388	432	2.87	307	4.03	423	2.93	378	416/438
poly-**EP8**	447	525	2.36	460/495/530	575	2.18	691	1.79	1730	0.715	452	512
poly-**EF8**	445/465	500	2.47	415/445/470	528	2.44	655/712	1.89/1.73	2720	0.45	439	485/518

indicate clearly the electronic transition resulting in the conjugated chain during this process. The $\pi-\pi^*$ absorption attributed to the neutral form of the polymers backbone decreases progressively when simultaneously new energetic interbands increase corresponding to the polaronic levels. This transition is followed by a color change from orange to deep blue for poly-**EP8**, from yellow to deep blue for poly-**EF8**, and from yellowish to brown for both poly-**PyP8** and poly-**PyF8**. Only poly-**EP8** and poly-**EF8** exhibit two electronic transitions, one in the visible range and the second in the NIR region.[50−52] These bands are characteristic of the formation of polaronic charge carriers at 691 and 1730 nm for poly-**EP8** and 655, 712, and 2700 nm for poly-**EF8**. The origin of the two fused bands at 655 and 712 nm may be due to colloidal aggregates in solution resulting from the π-stacking of the oxidized poly-**EF8**. This hypothesis is supported by the fact that poly-**EP8** forms aggregates during the oxidation turning finally into polymer precipitation after several minutes. In all cases, these two bands correspond to the same polaronic species since they increase simultaneously with the NIR band. The intense absorption in the NIR is especially of interest in the field of reflecting materials such as gold surface. The behaviors of poly-**PyP8** and poly-**PyF8** are strongly different. Only one peak appears centered on 481 and 424 nm respectively for poly-**PyP8** and poly-**PyF8**, suggesting that only bipolaronic species with short conjugation length are produced. This idea is supported by the trapping of the motion of the charge carriers in a finite conjugated length between two nitrogen heteroatoms. Moreover, during the chemical oxidation, the absorbances at 344 nm for poly-**PyP8** and at 307 nm for poly-**PyF8** slightly increases. The energy levels corresponding to these absorbance peaks are higher than the gap energy E_g, supporting again that the conjugated length is reduced during the oxidation process. The origin of this high energetic absorption may be attributed to distortion of the inter-ring bonds, increasing the steric repulsions.[53]

(c) PLE and PL Properties in THF Solution. The PL excitation (PLE) spectra of the copolymers in THF displayed maximum ($\lambda_{ex,max}$) at 380 nm for poly-**PyP8**, 390 nm for poly-**PyF8**, 440 nm for poly-**EP8**, and 437 nm for poly-**EF8** (as shown in Figure 5). The PLE maxima are very slightly red-shifted in comparison with the absorption maximum of only 0−10 nm. All polymers exhibit a strong photoluminescence (PL) in THF. Using

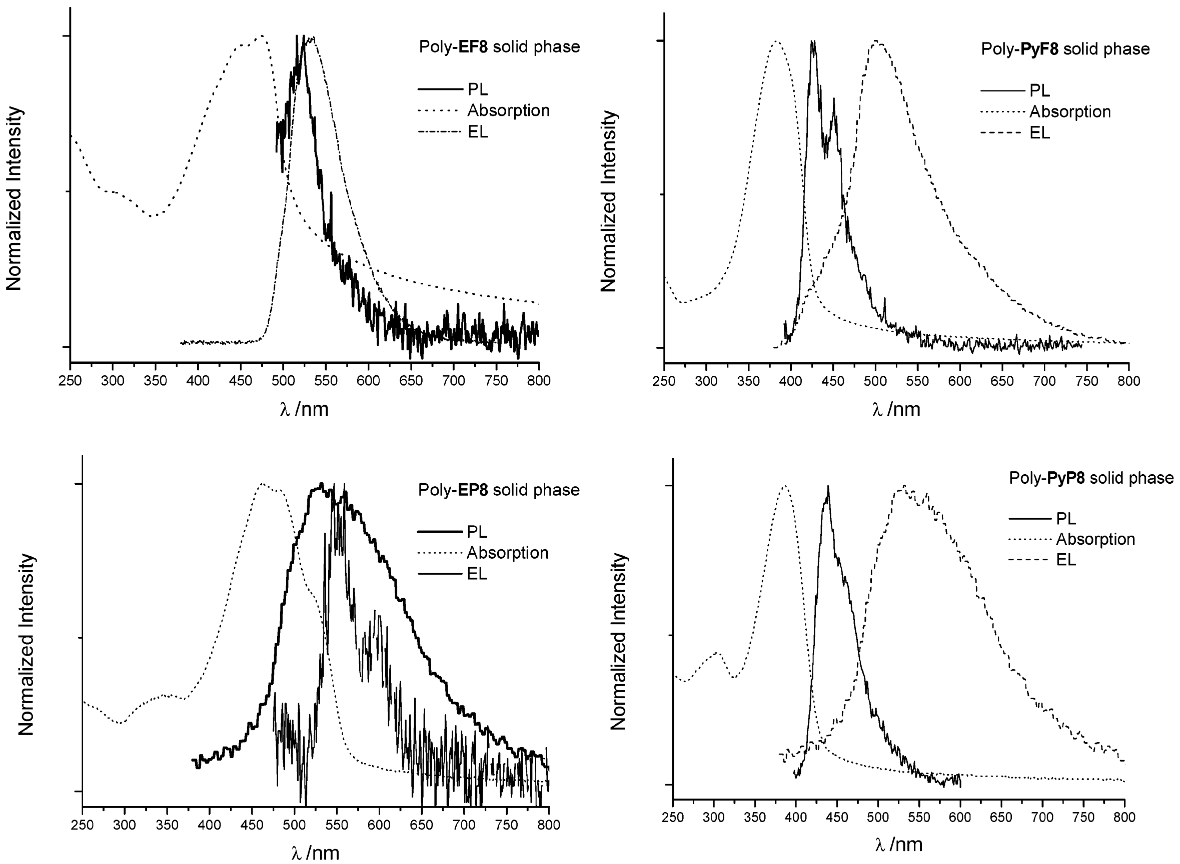


Figure 7. UV−vis and PL spectra of poly-**EP8**, poly-**EF8**, poly-**PyP8**, and poly-**PyF8** in solid state.

$\lambda_{\mathrm{ex,max}}$ as the exciting wavelength, the PL spectra show main emission maxima at $\lambda_{\mathrm{em,max}} = 510$ nm (poly-**EP8**), 485 nm (poly-**EF8**), 435 nm (poly-**PyP8**), and 420 nm (poly-**PyF8**). Thus, PL spectra are attributed to fluorescence as the values are similar to that of the optical band gap. A second and weaker peak is measured at 520 nm (poly-**EF8**) and 440 nm (poly-**PyF8**) attributed to some structural relaxation such as isolated polarons.[54]

Table 5. UV−vis Absorption, Photoluminescence Excitation, and Photoluminescence Data of the Copolymers in THF Solution

$\lambda_{\max}$ (nm)	UV−vis	PLE	PL
poly-**PyP8**	375	380	435
poly-**PyF8**	380	390	420/sh 440
poly-**EP8**	440	440	510
poly-**EF8**	445/sh 465	437/sh 460	485/sh 520

Optical Properties of the Copolymers in the Solid State. *(a) UV−vis Properties.* The optical behaviors on solid state are rather different from those of the polymers in solution (Figure 7). (i) The $\lambda_{\mathrm{em,max}}$ of the copolymers are 5−10 nm red-shifted except for poly-**EP8**, which is more red-shifted of about 30 nm. The onset wavelength λ_{onset} is also more red-shifted for poly-**EP8** and poly-**EF8** (50 and 30 nm, respectively) compared to that of poly-**PyP8** and poly-**PyF8** (15 and 12 nm, respectively). (ii) The absorption spectra of poly-**EP8** and poly-**EF8** exhibits a splitting in three well-defined peaks at 460, 495, and 530 nm and at 415, 445, and 470 nm, respectively, corresponding to vibronic fine structures. The pyridine-based copolymers show a unique absorption in the solid state around 380−390 nm. Such red-shift behaviors are the consequence of a noticeable conformation change during the solvent evaporation: the π-stacking of the polymer backbones occurs simultaneously with the interlacement of the alkyl (or alkoxy) chains. The difference of the observed red shifts may be explained by the following points: (i) The octyloxy chains are grafted on two opposite carbon atoms of the phenylene ring giving better interchain interaction. The phenylene-based copolymer exhibits therefore the highest solvatochromic effect. (ii) The random set of asymmetric pyridine rings along the polymer chains affords more disorder, hence reducing the solvatochromic effect.

(b) PL Properties in the Solid State. The copolymers were drop-casted from chloroform solution on quartz plate. The photoluminescence (PL) maxima (upon irradiative excitation at $\lambda_{\mathrm{abs,max}}$) occur at 430 and 450 nm for poly-**PyF8**, 440 nm for poly-**PyP8**, 525 nm for poly-**EF8**, and 550 and 600 nm for poly-**EP8**. Emission colors were determined by CIE coordinates calculated from the PL spectra. Data are summarized in Table 5. All the four copolymers exhibit a more or less deep blue PL emission.

(c) EL Properties in Solid State. Devices were fabricated using the four copolymers as active layers. The electroluminescence (EL) characteristics of the four copolymers are very different from the photoluminescence (PL) properties. Especially, we observed that the shapes of the EL spectra were broadened at long wavelengths compare with the EL spectra. This shift is may be attributed to radiative decay from longer conjugated segments (smaller E_g) or, as it was cited in the literature by Burrows et al.,[55] a cavity effect due to an excess of injected electrons. Copolymers containing EDOT units exhibit greenish EL or closed to it, and copolymers containing pyridine units give rise to a yellow light. Here, we clearly see that the applied

Table 6. Photoluminescence Data of the Copolymers Films Drop-Casted on Quartz Pellets and Electroluminescence Data of the Copolymers Used as Active Layer in ITO/PEDOT/PSSA/Polymer/Ba/Al Structures

		λ_{PLmax} (nm)	CIE$_x$	CIE$_y$	color
poly-**EP8**	(a)	550, 600	0.187	0.252	blue (PL)
	(b)	550, 600	0.496	0.499	deep yellow (EL)
poly-**EF8**	(a)	525/sh 580	0.187	0.096	deep blue (PL)
	(b)	530	0.330	0.605	yellow-greenish (EL)
poly-**PyP8**	(a)	440/sh 460	0.154	0.065	deep blue (PL)
	(b)	530	0.375	0.467	yellow (EL)
poly-**PyF8**	(a)	430, 450	0.163	0.062	deep blue (PL)
	(b)	500	0.277	0.421	greenish (EL)

[a] PL data: polymer drop-casted on quartz from chloroform solution. [b] EL data: polymer used as active layer ITO/PEDOT/PSSA/polymer/Ba/Al.

voltage shifts the EL relative to the PL. The formation of exiplex at the interface regions which light intensity is voltage dependent may be suggested.[48] Another reason is a possible modification of the polymer structure under high electrical fields. The CIE coordinates were calculated from the obtained EL spectra and are presented in Table 5. For comparison, NTSC requirement for RGB displays are for red: CIE$_x$ = 0.67, CIE$_y$ = 0.33; for green: CIE$_x$ = 0.21, CIE$_y$ = 0.71; and for blue: CIE$_x$ = 0.14, CIE$_y$ = 0.08.[56]

Conclusion

In summary, four copolymers of 3,4-ethylenedioxythiophene and of pyridine containing regularly inserted fluorene or phenylene units were synthesized by the Suzuki cross-coupling reaction and characterized. The four copolymers showed good solubility in common organic solvents and are thermally stable up to 375 °C. They also exhibit strong blue photoluminescence emission. Devices prepared using these polymers ITO/PEDOT/PSSA/polymer/Ba/Al gave yellow or greenish electroluminescence.

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