Novel Fluorene-Thiophene Copolymers: Synthesis, Photophysical and Electrochemical Properties

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Summary: Novel alternating fluorene - thiophene copolymers, **F3HT, FIPT**, and **FPyT**, consisting of 9,9-dihexylfluorene and 3-substituted (with hexyl, 3-methylbutyl and 2-(pyren-1-yl)vinyl, respectively) thiophene units were synthesized. Photoluminescence (PL) and electrochemical behavior of these polymers were studied. PL behavior of **FPyT** polymer differed from that of the other copolymers. Thin films of **F3HT** and **FIPT** showed an intense green PL emission whereas the PL emission of **FPyT** thin films was orange. The PL emission spectra in thin films differ from those measured in THF solutions. Aggregate formation played an important role in the solid state. The aggregation was more pronounced with **FPyT** than with **F3HT** and **FIPT** thin films. In all polymers reversible oxidation and reduction were observed. Similar values of ionization potentials and electron affinities were estimated for **F3HT** and **FIPT**, but a higher value of electron affinity for **FPyT**.

Keywords: conjugated polymers; electrochemical properties; fluorene-thiophene copolymers; photoluminescence; thin films

Introduction

π-Conjugated polymers are promising active materials for optoeletronic devices such as polymer light-emitting diodes (PLEDs), organic solar cells, and organic thin film transistors.[1–4] Polyfluorene and its derivatives have been preferred in such applications because of their good chemical and thermal stability, and high photoluminescence and electroluminescence quantum yields. Polyfluorenes emit in the blue region of the visible spectrum and a broad variation of emission colour can be achieved in copolymers with low-band-gap monomers. This copolymerisation approach is an effective tool to alter the band-gap and the energy position of the valence and conductive levels. The comonomers widely used in polyfluorene derivatives are thiophene, benzothiadiazole, and other heterocyclic rings. In this communication, we report on the syntheses, optical and electrochemical properties of three well defined alternating copolymers containing 9,9-dihexylfluorene and thiophene units substituted with alkyls or pyrene derivative (Figure 1).

Experimental Part

Materials and Monomer Syntheses

Bis(propane-1,3-diyl) 9,9-dihexylfluorene-2,7-diylbisboronate (**I**) and tetrakis(triphenylphosphine)palladium [Pd(PPh_3)$_4$] were commercial products (Aldrich, Fluka). Tetrahydrofuran (THF), methanol and sodium hydrogencarbonate were purchased from Lach-Ner, Ltd., Neratovice, Czech Republic. The aqueous $NaHCO_3$ solution and THF (distilled) were degassed with argon before polymerizations. The monomers 2,5-dibromo-3-hexylthiophene (**II**) and 2,5-dibromo-3-(3-methylbutyl)thiophene (**III**) were synthesized according to the published procedure.[5] The synthesis of 2,5-dibromo-3-[2-(pyren-1-yl)vinyl]thiophene (**IV**) is described elsewhere in this volume.[6]

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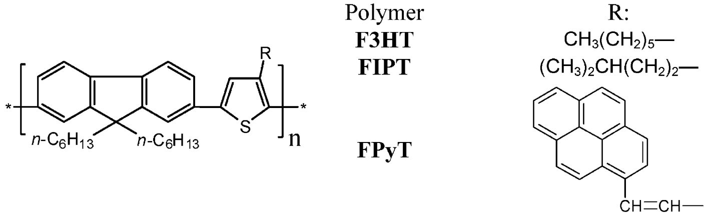


Figure 1.
Structures of synthesized alternating fluorene - thiophene copolymers.

Methods and Procedures

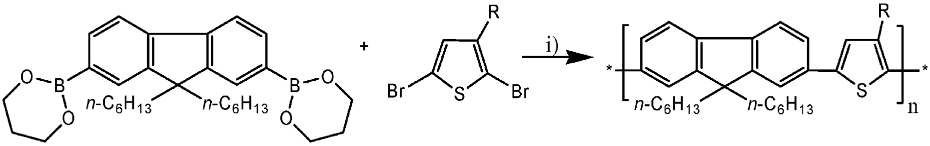
^{1}H NMR spectra were taken on a Bruker ACF-300 spectrometer at 300.1 MHz in deuterated tetrahydrofuran using hexamethyldisiloxane as an internal standard. Number-average (M_n) and weight-average (M_w) molecular weights were estimated by gel permeation chromatography (GPC), using monodisperse polystyrene standards. UV-vis spectra were taken on a Perkin-Elmer Lambda 35 spectrometer. Steady state fluorescence spectra were measured using a Perkin-Elmer LS 55 spectrometer. Both UV-vis and fluorescence spectra were measured in thin films or in tetrahydrofuran solution at room temperature. PL quantum yield was determined using quinine sulfate in 0.10 M H_2SO_4. Cyclic voltammetry (CV) was performed with a PA4 polarographic analyzer (Laboratory Instruments, Prague, CZ) with a three-electrode cell. Platinum wire electrodes were used as both working and counter electrodes, and Ag/Ag$^+$ electrode (Ag in 0.1 M $AgNO_3$ solution) was used as the reference electrode. CV measurements were made in solution of 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF6) in acetonitrile in nitrogen atmosphere. Typical scan rate was 50 mV s^{-1}. The ionization potential (HOMO level), E_{IP}, and electron affinity (LUMO level), E_A, were estimated from the onsets (E_{onset}) of the oxidation and reduction potential on the basis of the reference energy level of ferrocene (4.8 eV below the vacuum level) using the equation[7] E_{IP} (E_A) $= -(E_{onset} - E_{ferr}) - 4.8$ eV, where E_{ferr} is the measured value for ferrocene vs. the Ag/Ag$^+$ electrode.

Sample Preparation

Thin polymer films were prepared by spin coating from THF solutions. All solutions were filtered with 0.45 μm Millex-FH13 Millipore syringe filters prior to spin-coating. Thin films for optical studies were made by spin coating on fused silica substrates and for CV measurements coated on a Pt wire by dipping into the polymer solution. All polymer films were dried in vacuum (10^{-3} Pa) at 353 K for 1 h. Film thicknesses were measured using a KLA-Tencor P-10 profilometer.

Results and Discussion

Syntheses of copolymers were performed using the palladium–catalyzed Suzuki coupling reaction (Scheme 1). The polymerizations were carried out in a refluxing THF/15 wt. % aqueous $NaHCO_3$ solution (80 ml, 1:1 by vol.) containing equimolar amounts



Scheme 1.
Synthetic route for the polymers: i) aqueous (15 wt. %) $NaHCO_3$/THF (1:1 by vol), [$Pd(PPh_3)_4$] (1 mol.% per monomers), reflux in the dark for 72 h in argon.

(2.5 mmol) of comonomers (**I** and **II**, **III**, or **IV**) and the catalytic amount of [Pd(PPh$_3$)$_4$] (1 mol % per monomers). The reaction mixture was refluxed in a glass reactor with vigorous stirring for 72 h in the dark and under argon. After cooling to room temperature the reaction mixture was precipitated into methanol. The crude copolymer was filtered off, dissolved in THF, filtered and reprecipitated into methanol. The copolymer was collected and dried in vacuum to constant weight. The chemical structures of the polymers were confirmed by ^{1}H NMR, FT-IR, and elemental analyses. The M_n and M_w were determined by GPC.

F3HT: ^{1}H NMR (300 MHz, THF-d_4, δ, ppm): 8.25–6.9 (m, 7H, Ar), 2.77 (s, 2H, CH$_2$), 1.99 (s, 4H, CH$_2$), 1.60–0.8 (m, 3H, 24H, CH$_2$), 0.76 (s, 9H, CH$_3$); $M_w = 10\ 700$, $M_n = 6\ 700$.

FIPT: ^{1}H NMR (300 MHz, THF-d_4, δ, ppm): 8.40–6.85 (m, 7H, Ar), 2.79 (s, 2H, CH$_2$), 2.11 (s, 4H, CH$_2$), 1.62 (s, 3H, CH, CH$_2$), 1.10, 0.77 (m, 16H, CH$_2$), 0.92 (s, 6H, CH$_3$), 0.77 (s, 6H, CH$_3$); $M_w = 26\ 250$, $M_n = 7\ 800$.

FPyT: ^{1}H NMR (300 MHz, THF-d_4, δ, ppm): 8.85–7.10 (m, 16H, Ar), 8.85–7.10 (m, 2H, CH), 2.18 (s, 4H, CH$_2$), 1.11, 0.78 (m, 16H, CH$_2$), 0.78 (s, 6H, CH$_3$); $M_w = 26\ 460$, $M_n = 11\ 110$.

The optical properties of polymers were investigated in both dilute THF solutions (conc. 4×10^{-6} mol/dm^3) and thin films. The UV-vis absorption spectra of polymers in thin films are displayed in Figure 2. The lowest-energy absorption maxima, corresponding to the absorption of the conjugated backbone, were located at 400, 401 and 391 nm for **F3HT, FIPT** and **FPyT**, respectively, at about the same wavelengths as in THF solutions. The absorption coefficients of the maxima are slightly higher for **FIPT** and **FPyT** than for **F3HT**, which is in accord with their higher molecular weights. The onset of the absorption in **F3HT** and **FIPT** thin films was nearly the same at about 470 nm, whereas in **FPyT** at ca. 500 nm. The optical

previous papers.[8,9]

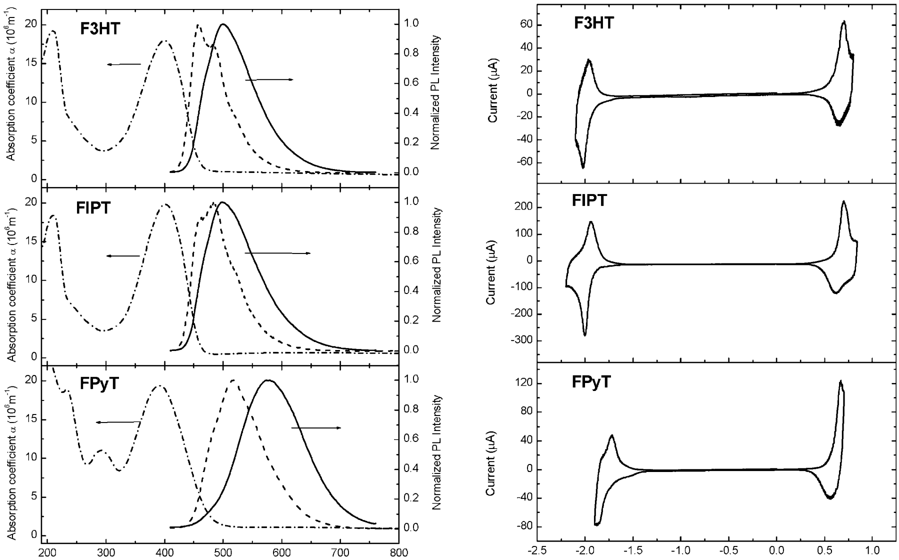


Figure 2.

Left: UV-vis absorption spectra (dash and dot) in thin films and PL emission spectra in thin films (solid) and in THF solution (dash) for the **F3HP**, **FIPT**, **FPyT**. Excitation was at absorption maximum. Right: The cyclic voltammograms of the polymers.

Table 1.
UV–vis and PL characteristics of the polymers in solution and thin films.

Polymer	solution			thin film			
	λ_{absmax} (nm)	λ_{PLmax} (nm)	Φ_{PL} (%)	λ_{absmax} (nm)	λ_{PLmax} (nm)	E_g^{opt} (eV)	Φ_{rel}
F3HT	395	459	45	400	499	2.76	25
FIPT	398	483	39	401	499	2.76	7.6
FPyT	395	490	11	392	575	2.65	1

energy band gap (E_g) of polymers was evaluated from the thin film absorption edge and it was estimated as 2.76 and 2.65 eV for **F3HT, FIPT** and **FPyT**, respectively. Photoluminescence (PL) emission spectra in THF solution (conc. 4×10^{-6} mol/dm^3) and in thin film are also displayed in Figure 2. PL emission spectra of **F3HT** and **FIPT** in dilute THF solutions exhibit vibronic structure with main maxima at 457 and 483 nm, respectively. Their contributions to the overall PL emission slightly differ. In **F3HT** the band with a maximum at 457 nm has a slightly higher intensity, whereas in **FIPT** the 483 nm band is higher. In thin layers, PL spectra of **F3HT** and **FIPT** are similar - broad-band with a maximum at 499 nm with similar values of PL efficiency. PL maxima in **FPyT** both in thin layers and solutions were red-shifted compared with **F3HT** and **FIPT** and a lower PL efficiency was observed. A bluish-green PL emission was observed in THF solution for the excitation in maximum whereas thin films exhibited an orange emission with a maximum at 580 nm. In solution the maximum position of broad-band emission depended on the excitation wavelength. In dilute solution some contribution of UV emission at about 380–400 nm corresponding to the pyrene monomer fluorescence was also observed. The red shifts of the PL maxima and large Stokes shifts in thin films indicate aggregation in the solid state. A very large Stokes shift up to 186 nm was observed, indicating a most pronounced excimer or aggregate formation in this polymer. The strong tendency to form excimers or aggregates was observed in several PPV-based polymers and also in poly(fluorenediylvinylene)s as shown, e.g., in our previous papers.[8,9]

Cyclic voltammetry was used to study redox properties of the polymers. Cyclic voltammograms (CV) of the polymers are displayed in Figure 2 (right). The CV curves show clear p- and n-doping peaks followed by corresponding undoping peaks. All polymers show also reversible electrochromism upon reduction and oxidation. The yellow color of the polymers changes to a dark green after p- or n-doping and reveals back again after p- or n-undoping. Electrochemical data for p- and n-doping are summarized in Table 2. It is evident that the presence of pyrene moiety affects mainly the reduction process (n-doping). Figure 2 (right) shows cyclic voltammograms (CV) of the polymers. The onset of oxidation potential was nearly the same for all polymers. Using this value, HOMO levels E_{IP} in the range 5.2–5.3 eV were estimated. From the onset of the reduction similar electron affinity (LUMO levels), 2.7–2.8 eV, were obtained for **F3HT** and **FIPT**. A higher electron affinity of 3 eV was determined for **FPyT**. The values of band-gap from the electrochemical measurements are slightly lower in comparison with those evaluated from the absorption edge of thin films. Electroluminescence and photoelectric properties of the polymers are studied and the results will be published elsewhere.

Table 2.
Electrochemical properties of the polymers.

Polymer	p-doping			n-doping		
	E_{pa} (V)	E_{pc} (V)	$E_{1/2}$ (V)	E_{pc} (V)	E_{pa} (V)	$E_{1/2}$ (V)
F3HT	0.70	0.65	0.63	−2.02	−1.95	−1.97
FIPT	0.70	0.62	0.66	−2.00	−1.94	−1.97
FPyT	0.67	0.57	0.62	−1.88	−1.72	−1.79

E_{pa} = anodic, E_{pc} = cathodic peak potential vs. Ag/Ag$^+$ reference electrode.

These polymers are tested as an active layer, particularly in polymer blend (donor-acceptor) for photovoltaic, light-emitting or electrochromic devices.

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