Synthesis and Luminescent Properties of Two Copolymers Containing Dithienothiophene and Fluorene

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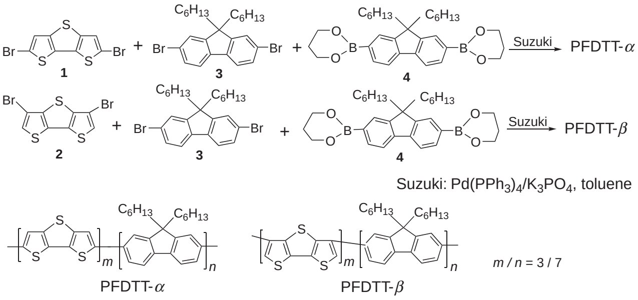
Two new copolymers, poly[fluorene-co-α-dithieno[3,2-*b*:2′,3′-*d*]thiophene] (PFDTT-α) and poly[fluorene-co-β-dithieno[3,2-*b*:2′,3′-*d*]thiophene] (PFDTT-β) were synthesized through the Suzuki coupling reaction, where dithieno[3,2-*b*:2′,3′-*d*]thiophene (DTT) was introduced into the backbones of polyfluorenes by two different linkage styles, which distinctively tuned HOMO/LUMO levels of the copolymers and the effective conjugation length.

Intensive investigations have been recently devoted to the multifarious bithiophene analogs with intramolecular heteroatom bridges comprising boron, sulfur, nitrogen, silicon, or phosphorus due to their great potential for application in optoelectronic devices such as photovoltaic cells, organic polymeric electroluminescent displays, field effect transistors, electrochromic or smart windows, nonlinear optical (NLO) devices, or polymeric sensors.[1] Amongst, dithienothiophene (DTT) has been subjected to an impressive amount of work since the late of 1960's.[2] Thus, bisdithienothiophene has been used as a high-mobility material in a field effect transistor,[3] and DTT derivatives have been used in photonic and electroluminescent devices,[4] two-photon absorption[5] and excited fluorescence,[6] non-linear optical chromophores,[7] and photochromic materials.[8] However, it is quite strange that DTT-based polymers and/or copolymers have been scarcely reported, except the preparation of polydithienothiophene by electrochemical[9] and photochemical oxidation,[10] probably owing to the poor solubility of the resulting materials. Recently, we have designed and synthesized two novel copolymers containing DTT and fluorene segments, where DTT affords smaller HOMO–LUMO gaps for the materials due to its rigidified and planar structure, and will act as effective energy traps for excitons formed at the fluorene segments with higher-energy.[11] In conjugated polymers, Forster energy transfer is known to be fast and efficient between two chromophore segments of different energy and will shift the emission to longer wavelengths.[12] Employing this approach will effectively tune the light-emitting color, even for full-color displays.

In this paper, we describe the synthesis of two novel conjugated copolymers PFDTT-α and PFDTT-β, containing low band gap DTT in different linkage, and investigate how the different linkage positions (α-link or β-link) of DTT affect the electric properties and tune the fluorescent wavelength of copolymers.



Scheme 1. Synthesis of PFDTT-α and PFDTT-β.

As shown in Scheme 1, The copolymers are prepared through Pd^0-catalyzed Suzuki coupling polymerization carried out in refluxing toluene/aq K_3PO_4 solution under an argon atmosphere, respectively. The feeding molar ratios of α-DTT or β-DTT,[13] and fluorene moieties **3** and **4** were controlled as 3:2:5 to give products soluble in organic solvents. The actual ratio of DTT to fluorene segments in the copolymers calculated from elemental analysis is close to the feed ratio. GPC analyses of the $CHCl_3$-soluble fractions of PFDTT-α showed M_n 10,600 with a polydispersity (M_w/M_n) 1.86, while that of PFDTT-β did M_n 6700 with a polydispersity 2.85, respectively. The higher molecular weight of PFDTT-α relative to PFDTT-β was possibly ascribed to the stronger reactivity of the α-position than β-position of DTT. The isolated polymeric materials, yielding from 54 to 72%, were readily soluble in THF, $CHCl_3$, and other common solvents. Thermo-gravimetric analysis revealed their good thermal stability, the decomposition temperatures (5% weight loss in N_2) of both copolymers were 418–419 °C.

The normalized UV–vis absorption and PL emission spectra of PFDTT-α and PFDTT-β in dilute chloroform solutions are shown in Figure 1. PFDTT-α exhibits an absorption maximum at about 436 nm, a red-shift of 50 nm relative to that of polyfluorenes (ca. 386 nm). In contrast, PFDTT-β exhibits an absorption maximum at higher energy wavelength (ca. 357 nm), about 30 nm blue-shift relative to that of polyfluorenes. The red shift is consistent with the extension in π-conjugation induced by the introduction of DTT moieties with α-linkage into polyfluorenes. However, β-linkage of DTT renders the reduction in the

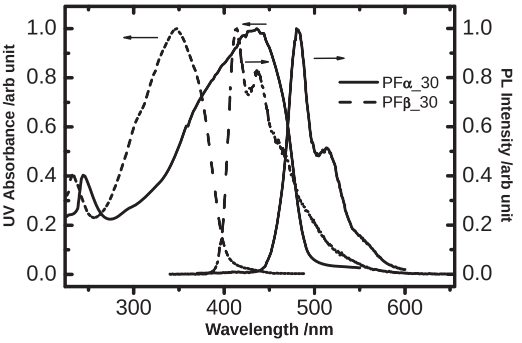


Figure 1. Solution UV–vis absorption and PL emission spectra of PFDTT-α and PFDTT-β.

Table 1. Electrochemical properties[a] of copolymers PFDTT-α and PFDTT-β

Copolymer	$E_{\text{onset}}^{\text{red}}$ /eV	LUMO /eV	$E_{\text{onset}}^{\text{ox}}$ /eV	HOMO /eV	E_g /eV
PFDTT-α	−2.35	−2.45	0.77	−5.57	3.12
PFDTT-β	−2.57	−2.23	1.08	−5.88	3.65

[a] All the potentials vs. the ferrocene reference (Fc/Fc^+).

effective conjugate length of the copolymer. These distinct differences in the absorption spectra of two copolymers in the solution indicate that linkage position (α-link or β-link) of DTT segments imposes significant effect to the π-conjugation extent of the backbone of the copolymers even DTT is well known as a low band gap rigid planar aromatic ring. The same tendency also presents in the PL spectra, PFDTT-α emits strong green fluorescence with an emission maximum at 481 nm and a small shoulder occurring at 520 nm upon photoexcitation, while PFDTT-β exhibits strong blue fluorescence emission with a main peak at 413 nm and a shoulder at 436 nm, in comparison with the emission maximum at 422 nm of polyfluorenes. In general, the presence of well-defined vibronic structures in the emission spectra indicates that the polymer has a rigid and well defined backbone structure.[14]

The redox behavior of the copolymers was investigated by cyclic voltammetry with a ferrocene/ferrocenium internal standard (Table 1). The copolymers exhibited quasireversibility in both n-doping and p-doping processes. HOMO and LUMO levels are calculated according to an empirical formula, $\text{HOMO} = -([E_{\text{onset}}]^{\text{ox}} + 4.8)\,\text{eV}$ and $\text{LUMO} = -([E_{\text{onset}}]^{\text{red}} + 4.8)\,\text{eV}$, and from the onset potentials of the oxidation and reduction processes, it can be estimated that the electrochemical band gaps, $E_g = (E_{\text{onset}}{}^{\text{ox}} - E_{\text{onset}}{}^{\text{red}})$. In comparison with the data ($\text{HOMO} = -5.8\,\text{eV}$, $\text{LUMO} = -2.12\,\text{eV}$) of polyfluorenes,[15] PFDTT-α exhibits a higher HOMO level by 0.23 eV and a lower LUMO level by −0.23 eV, so that the bandgap is reduced to 3.12 eV, indicating that the effective conjugation length of the copolymer is increased apparently by the introduction of DTT segments with α-linkage into the polyfluorenes main chain. On the other hand, in the case of PFDTT-β, β-linkage of DTT gives rise to a distinct reverse effect on the conjugation extent of the copolymer. The HOMO level of PFDTT-β is even 0.08 eV lower than that of polyfluorenes owing to the negative disturbance in the effective conjugation length of the polymer backbone caused by the β-linkage of DTT units in the backbone chain.

We measured the electroluminescent behavior based on a device: ITO/PEDOT/PVK/PFDTT-α/Ba/Al, where PEDOT, PVK are used as the anode buffer and Ba as the cathode (Figure 2). The device emits yellow-green light with a maximum peak at 538 nm and a small shoulder at 507 nm, obvious red shift in comparison to PL spectrum in the solution, indicating that the aggregate state in the solid film improves the Forster energy transfer from the fluorene segments of higher energy to the DTT segments of lower energy. The turn-on voltage is 6.6 V, and the brightness reaches 248 cd/m^2 at a bias voltage of 10.6 V. The maximum external quantum efficiency was measured to be 0.091% at 8.6 V with a current density of 13.2 mA/cm^2. The low efficiency was possibly aroused by the rigid planar structure of DTT moieties, which is prone to intermolecular stacking in the solid sate. This dense intermolecular stack will be favor of charge transporting not trapping, which implies PFDTT-α might be a potential candidate for organic transistor material.

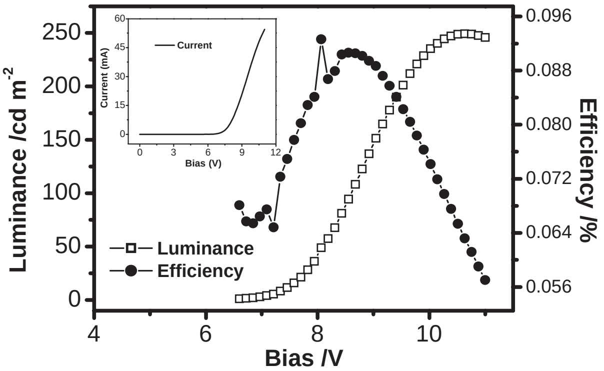


Figure 2. Luminance, efficiency, and current density (inset) versus voltage characteristics of the device: ITO/PEDOT/PFDTT-α/Ba/Al.

In conclusion, two soluble copolymers PFDTT-α and PFDTT-β containing DTT and fluorene moieties were successfully synthesized through the Suzuki coupling polymerization, in which the effective conjugation lengths of the polymeric backbone were adjusted distinctively by the different linkage style of DTT moieties. α-linkage of DTT apparently increases the HOMO level and reduces the band gap of the copolymer, in contrast, β-linkage gives arise to a reverse effect on the electric properties of the copolymer.

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