Synthesis and Luminescent Properties of Novel Twisted Copolymers Containing Dithienophosphole Oxide/Dithienosilole and Spirobifluorene

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Two new series of twisted polymers, poly[fluorenedithieno[3,2-*b*:2′,3′-*d*]phosphole oxide-*alt*-2,2′-spirobifluorelene] (**PFDTPO-SBF**) and poly[fluorenedithieno[3,2-*b*:2′,3′-*d*]silole-*alt*-2,2′-spirobifluorelene (**PFDTS-SBF**), in which the backbone was sufficiently twisted and the effective conjugation length was controlled, were synthesized through Suzuki coupling reaction. The introduction of **DTPO** or **DTS** into π-conjugated main chains apparently turned the emission wavelength, and possessed the low-lying LUMO energy levels.

Bithiophene-based polymers are a burgeoning subject of considerable academic and commercial interest when used as the optoelectronic materials as photovoltaic cells,[1] organic/polymeric electroluminescent displays,[2] and field effect transistors.[3] Incorporating various fused rings with low HOMO–LUMO band gap into π-conjugated polymeric systems is a key for optoelectronic materials to possess extraordinary electrical and photophysical properties. Hereby, intensive investigations have been devoted to the multifarious bithiophene analogs intramolecular with heteroatom bridge comprising sulfur,[4] or nitrogen.[5] Bithiophene-incorporated silicon[6] (dithieno[3,2-*b*:2′,3′-*d*]silole, **DTS**) and phosphorus[7] (dithieno[3,2-*b*:2′,3′-*d*]phosphole oxide, **DTPO**), by contraries, has only recently been investigated as potential building blocks for the tailoring of π-conjugated systems. The incorporation of **DTS** into macromolecular chain, such as **PFDTS**[8] (Chart 1), enhanced the electron affinity, resulting in efficient charge recombination and energy transfer. On the other hand, the attempt of incorporating **DTPO** into macromolecular chain is confined due to the rigid configuration and its poor solubility.[7b]

In this paper, we describe the novel partially conjugated **PFDTPO-SBF** and **PFDTS-SBF**, containing low band gap **DTPO** (or **DTS**) for fine tuning the electric properties of copolymers, coped with spirobifluorene, an inimitable framework which can efficiently reduce close packing and restrain interchain excimers between chromophores in the solid state, exhibit significant augment in solubility, thermal stability, and more intense fluorescence, and provide a direct control of the conjugation length.[9]

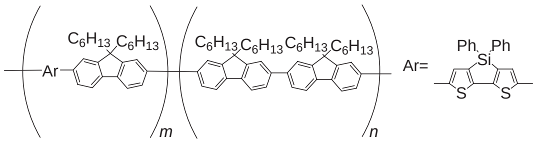
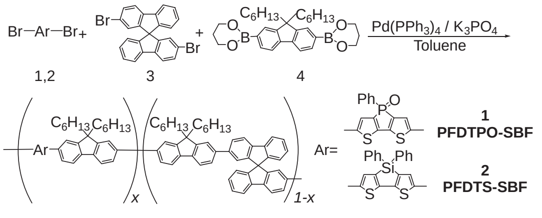


Chart 1. Structure of **PFDTS**.



Scheme 1. Synthesis of **PFDTPO-SBF** and **PFDTS-SBF**.

As shown in Scheme 1, Pd(0)-catalyzed coupling polymerization of **DTPO 1** (or **DTS 2**), **SBF** (**3**) and fluorene moiety (**4**), carried out in refluxing toluene/aq K_2CO_3 solution under an argon atmosphere, afforded **PFDTPO-SBF** or **PFDTS-SBF** as light-yellow or light-green fibriform solids, respectively. The feeding molar ratios of **DTPO** (**1**) or **DTS** (**2**), **SBF** (**3**), and fluorene (**4**) were 1:4:5 (**PFDTPO-SBF-10** or **PFDTS-SBF-10**), 2:3:5 (**PFDTPO-SBF-20** or **PFDTS-SBF- 20**) respectively for the polymer synthesis to give alternating copolymers containing all the components. ^{31}P NMR spectroscopy of **PFDTPO-SBF** displayed a single peak at 20.1 ppm, same as the chemical shift of authentic monomer **1** (+20 ppm). Accordingly GPC analyses of the $CHCl_3$-soluble fractions of **PFDTPO-SBF** showed M_n from 48,000 (PDI 1.23) to 53,000 (PDI 1.30), with the average number of the repeat units in the polymer as 37 and 41, while that of **PFDTS-SBF** did from 12,000 (PDI 1.77) to 15,000 (PDI 1.53), with the average number of the repeat units, 16 and 12, respectively. The isolated polymeric materials, yielding from 57 to 76%, were readily soluble in THF, $CHCl_3$, and other common solvents, which profited from the partially conjugated polymers, mainly resulting from the non-planar **SBF** moieties. Thermogravimetric analysis revealed that the copolymers were thermally stable up to 410 °C in N_2 only with 5% weight loss.

The photophysical properties of **PFDTPO-SBF** and **PFDTS-SBF** were investigated in both solution and solid state (Figure 1). Absorption spectra in dilute solution and solid state are quite similar in both series respectively, showing the absence of aggregation effects in their ground electronic states, suggesting the reduce of close packing and intermolecular interaction between chromophores in the solid state which is contributed to the spiro linkage. In dilute chloroform solution, the lower proportion of **SBF** in the main chain, the more red shift of $\lambda_{\mathrm{max(abs)}}$ of the polymers, suggested that the **SBF** could finely tune the effective conjugated length. The $\lambda_{\mathrm{max(abs)}}$ of **PFDTS-SBF-10** revealed a blue shift of 27 nm compared with **PFDTS-10**[8] which bore the same feed ratio of **DTS**, also indicating that the **SBF** could distinctly tune the effective conjugated length. PL emission spectrum in chloroform showed both the **DTPO** (ca. 540 nm) or **DTS** (ca. 520 nm) and fluorene emission (ca. 410, 430 nm) in quite high quantum yields (Φ_{fl}) ranging from 0.72 to 0.85. **PFDTPO-SBF-10** emitted strong blue fluorescence while **PFDTPO-SBF-20**, yellow. In addition, **PFDTS-SBF** series emitted green light. The emission intensity from **DTPO** or **DTS** enhanced remarkably with the amount of **DTPO** increasing in the polymer, illuminating the intermolecular and/

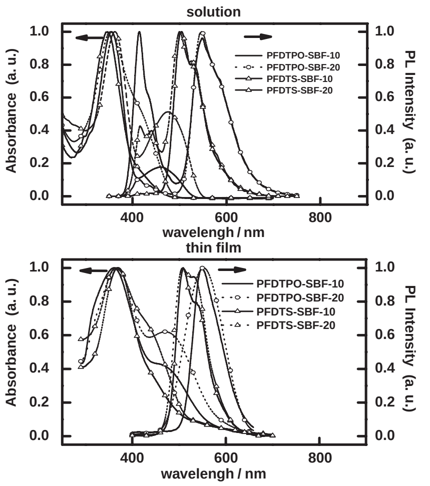


Figure 1. The optical absorption and PL spectra of copolymers in chloroform solution and thin film.

or intramolecular energy-transfer efficiently from the fluorene segments to **DTPO** (or **DTS**). The $\lambda_{\text{max(em)}}$ of **PFPTPO-SBF** bear a red shift of 40–50 nm than that of **PFDTS-SBF** in both solution and thin film.

The electrochemical properties of the synthesized polymers, dip-coated on a Pt disc with a solution of 0.10 M Bu_4NBF_4 in acetonitrile under argon, were characterized using cyclic voltammetry (CV) versus Ag wire, with a ferrocene/ferrocenium internal standard, which is assumed that the energy level is 4.8 eV below vacuum.[10] Ionization potential (IP, HOMO levels) $= -([E_{\text{onset}}]^{\text{ox}} + 4.8)$ eV and electron affinities (EA, LUMO levels) $= -([E_{\text{onset}}]^{\text{red}} + 4.8)$ eV, where $[E_{\text{onset}}]^{\text{ox}}$ and $[E_{\text{onset}}]^{\text{red}}$ are the onset potentials for the oxidation and reduction of the polymer vs the ferrocene reference, are estimated. From the onset potentials of the oxidation and reduction processes, it can be estimated that the electrochemical band gaps, $E_g = (E_{\text{onset,ox}} - E_{\text{onset,red}})$. **PFDTPO-SBF-20**, as a typical example, underwent an irreversible electrochemical reduction with the onset potential at minus 1.61 V vs Ag wire, rooting in the electron-deficient nature of **DTPO**, while an reversible oxidation occurred at 1.43 V could be observed (Figure 2). With the increasing ratio of **DTPO** (or **DTS**), the polymers showed consecutive lower LUMO energy levels, which is important for the materials to match their conduction band energy levels with work functions of the electrodes. The HOMO energy levels of all the polymers were higher than that of polyfluorene films.[11] On the other hand, the LUMO energy levels of those are remarkably lower than that of polyfluorene films,[11] continuously decreasing with the increasing ratio of **DTPO** (or **DTS**). Even compared with **PFDTS-10**,[8] the two series copolymers possessed ca. 0.18 eV lower LUMO energy levels. The higher electron affinity of **PFDTPO-SBF** and **PFDTS-SBF** copolymers will play an important role in electron-transporting materials because of their obviously decreased energy barrier for electron injection. It can be estimated that the electrochemical band gaps of the copolymers ranged from 2.98 to 3.05 eV, much narrower than that of polyfluorene,[11] indicative of green and yellow light emission. Compared with the bandgap of **PFDTS-10**, **PFDTPO-SBF**, and **PFDTS-SBF** bore distinctly lower HOMO–LUMO energy gaps, implying the more efficient π-conjugation extent obtained in **PFDTPO-SBF** and **PFDTS-SBF** owing to the intramolecular or intermolecular charge-transfer interaction between the electron-deficient **DTPO** and **DTS** rings and electron-rich bithiophene system as we expected initially.

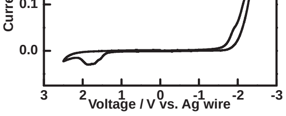


Figure 2. Cyclic voltammogram of **PFDTPO-SBF-20**.

In conclusion, two series luminescent copolymers containing **DTPO** or **DTS** linked with spirobifluorene was synthesized, in which the backbone was sufficiently twisted and the effective conjugation length was controlled. The introduction of **DTPO** or **DTS** into π-conjugated main chains apparently turned the emission wavelength and reduced the energy levels, which can be readily fabricated in the OLED or OFET.

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