Different donor–acceptor structures of dithiafulvalene-fused semiconducting polymers with different band gaps†

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Received 14th June 2011, Accepted 28th July 2011
DOI: 10.1039/c1cc13511b

Two similar dithiafulvalene-fused conjugated polymers, with different donor–acceptor (D–A) structures, were synthesised. The polymers have different band gaps and stacking structures, as proven by the experimental results and computational studies.

As potential low-cost alternatives to inorganic semiconductors, π-conjugated oligomers and polymers have become the focus of intense research.1 In recent years, considerable research efforts were made to synthesize low band gap polymers for applications in organic photovoltaic devices (OPVs)2 and field-effect transistors (OFETs).3 By incorporating well-matched donor (D) and acceptor (A) units in polymer backbones, it is easy to obtain the low band gap conjugated polymers with absorption edges > 800 nm in their neutral state (with $E_g < 1.5$ eV).4 However, compared with wide absorption, high charge carrier mobility in the polymer is more important for organic optoelectronic devices.5 Thus, exploring new polymers with high mobilities is a central challenge in the field of organic electronics.

Dithiafulvalenes (DTFs), like tetrathiafulvalenes (TTFs), exhibit unique charge transport characteristics due to their coplanar molecular structures with strong π–π and S–C1/C1/C1/C1 interactions.6 Incorporation of DTF units into π-conjugated polymers may well utilise the strong self-assembling propensity of DTFs to indirectly control the long-range order of the conjugated chains, thereby improving the charge-carrier mobilities of the polymers. Thus, two new DTF conjugated polymers, PDTFTh-BT and PDTFPy-BT, were designed (Scheme 1). From the perspective of their molecular structures, the difference between the two polymers lies in the bithiophenes and bipyridines in the DTF monomers. However, the compositional difference also results in the different D–A structures due to the different electronic effects of thiophene and pyridine. PDTFTh-BT has an alternating D–A main chain structure, whilst PDTFPy-BT is composed of an acceptor conjugated main chain and the donor DTF side chains. Herein, we present the synthesis of two new DTF polymers and initially explore the influence of the different D–A structures on their properties.

The synthesis of the DTF monomers and polymers is shown in Scheme 2. The detailed procedure is provided in the ESI.w Briefly, the heterocyclic fluorenone dibromides 1a,b were reacted with a carbanion, which was generated from the phosphonate ester and LDA at 78 °C, to afford 1,3-dithiol-2-ylidene derivatives 2a,b. 2a and 2b were subsequently copolymerized with 4,7-diboronic ester-2,1,3-benzothiadiazole by Suzuki coupling reactions to produce polymers PDTFTh-BT and PDTFPy-BT.

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w Electronic supplementary information (ESI) available: Experimental sections, physical properties and computation methodology. See DOI: 10.1039/c1cc13511b
The optimized geometries of (a) (DTFTh-BT)_4 and (b) (DTFPy-BT)_4 model systems calculated at the B3LYP/6-31G(d) level of theory.

Fig. 2

The optimized geometries of (a) (DTFTh-BT)_4 and (b) (DTFPy-BT)_4 model systems calculated at the B3LYP/6-31G(d) level of theory.

Fig. 3

The HOMO/LUMO energy levels and the energy gap as a function of 1/N, where N is the number of repeating units in the polymer chains of PDTFTTh-BT and PDTFPy-BT.
values for (DTFPy-BT)_n changed very little as the chain length increased.

The difference in the band gaps of the two polymers could be explained by their different effective π-electron conjugation lengths. The coplanar main chain of PDTFTh-BT brings about a larger effective π-conjugation length, and results in a low band gap. However, for PDTFPy-BT, the conjugation in the main backbone is broken by the torsion between the DTFPy and BT monomers. The coplanar structure of PDTFTh-BT also makes it easy to form strong π−π interactions in the solid state. Therefore, it is reasonable to see that the long-wavelength absorption of PDTFPy-BT shows a 30 nm red shift from solution to solid state.

To clarify the molecular stacking of PDTFTh-BT and PDTFPy-BT, X-ray diffraction (XRD) patterns were collected from powder samples of the two polymers (Fig. S4, ES†). Obviously, the two polymers show different diffraction patterns, especially at wide angles. PDTFPy-BT gives a single broad peak centred at about 2θ = 21.4°, corresponding to a d-spacing of 4.2 Å, whilst the XRD pattern for PDTFTh-BT shows a broad peak at 2θ = 21.4° and a peak at 2θ = 25.2°, corresponding to a d-spacing of 3.5 Å. The latter peak can be attributed to the π−π stacking distance between the coplanar π-conjugated main chains. For the former peak, it is reasonable to assign it to the distance between disordered alkyl chains, because the effective cross section of alkyl chains is about S = 20 Å^2 and their hexagonal-like aggregation gives about d = 4.2 Å.\(^1\)

Considering the low band gap and close π−π stacking property of PDTFTh-BT, its field effect mobility was preliminarily investigated by applying it to an OFET with a bottom-gate, bottom-contact configuration. The output and transfer curves show that PDTFTh-BT is a typical p-semiconductor (Fig. S5, ES†). The field-effect mobility (μ_{\text{FET}}) evaluated from the saturation regime is 0.14 cm^2 V^{-1} s^{-1}, with an on/off ratio of 3 × 10^4 and a threshold voltage of −6.9 V.

In summary, two new DTF-fused conjugated polymers with different D-A structures were synthesized and characterized. Although their chemical structures were very similar, the different D-A structures of the polymers resulted in obviously different band gaps. Only PDTFTh-BT had a coplanar main chain structure, which produced a larger effective π-conjugation length and resulted in a low band gap. The coplanar structure also ensured the formation of close π−π stacking. A preliminarily investigation on the field effect mobility of PDTFTh-BT showed its promising semiconducting property. Further structural functionalization and device optimization based on the DTF-fused polymers are in progress.

The present research was financially supported by the NSFC (#21004043, 50933003, 50903044) and the MOST (#2009AA032304).

Notes and references