ChemComm

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

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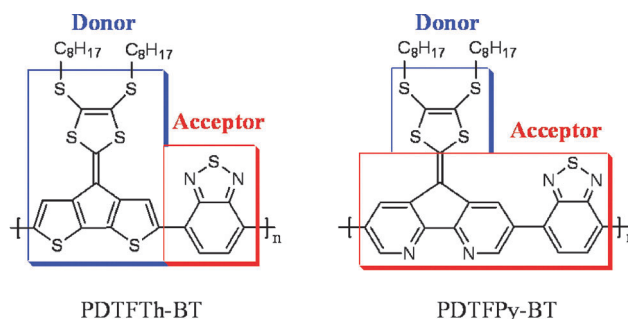
Two similar dithiafulvalene-fused conjugated polymers, with different donor–acceptor (D–A) structures, were synthesised. The polymers have different band gaps and stacking structures, as proven by the experimental results and computational studies.

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.
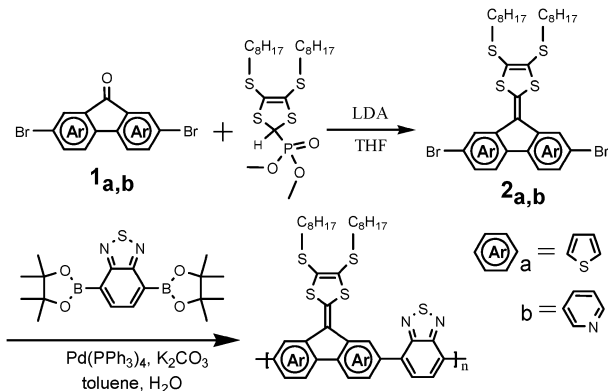
Dithiafulvalenes (DTFs), like tetrathiafulvalenes (TTFs), exhibit unique charge transport characteristics due to their coplanar molecular structures with strong π–π and S···S interactions.[6] Incorporation of DTF units into π-conjugated polymers may well utilise the strong self-assembling propensity 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

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Scheme 1 Molecular structures of two DTF-fused conjugated polymers with different D–A structures.

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.† 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

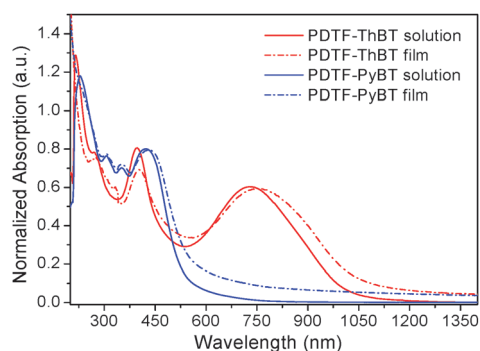**Scheme 2** The synthetic routes of PDTFTh-BT and PDTFPy-BT.

Fig. 1 UV-Vis-NIR absorption spectra of PDTFTh-BT and PDTFPy-BT solution in a CH$_2$Cl$_2$ solution and film on a quartz plate.

(M_n = 18 000, PDI = 2.15) and PDTFPy-BT (M_n = 23 000, PDI = 2.08), respectively. Both polymers could dissolve in common organic solvents, such as chloroform, tetrahydrofuran, and dichlorobenzene, but the dissolution of PDTFTh-BT requires the aid of ultrasonic vibration, indicating that strong intermolecular interactions exist in its solid state.

Thermogravimetric analysis (TGA) in an inert nitrogen atmosphere reveals that the onset temperatures of weight loss of the two polymers are about 230 °C (Fig. S1, ESI†). Differential scanning calorimetry (DSC) measurements of the two polymers were also conducted in an inert nitrogen atmosphere. No thermal transitions are observed below 230 °C, indicating that the two polymer chains are extremely rigid such that their glass transition temperatures may be higher than their decomposition temperatures.

The UV-Vis-NIR absorption spectra of the two polymers in a CH$_2$Cl$_2$ solution and thin film on a quartz substrate (Fig. 1) were recorded. PDTFTh-BT clearly exhibits a broad band covering the visible to near-infrared range. The broad band centered at 725 nm is characteristic for alternating donor–acceptor polymers.[7] The absorption bands at 400 and 220 nm
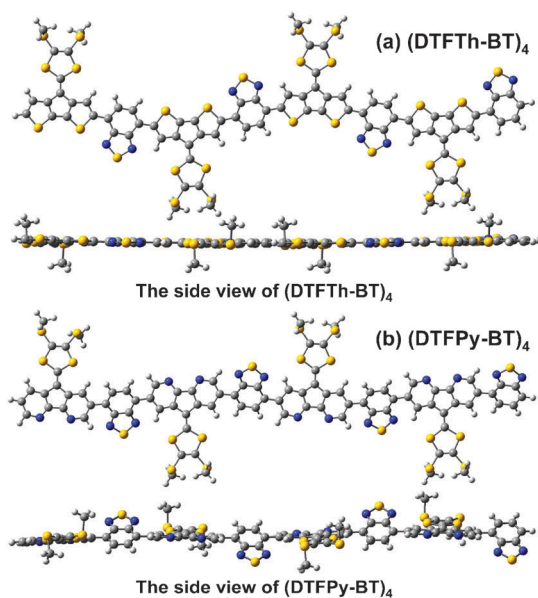

Fig. 2 The optimized geometries of (a) (DTFTh-BT)$_4$ and (b) (DTFPy-BT)$_4$ model systems calculated at the B3LYP/6-31G(d) level of theory.

could be assigned to π–π* and n–π* transitions, respectively.[8] Comparing the solution absorption spectra, a red-shift of ~30 nm is observed for long-wavelength absorption of the thin film, indicating that there exists a π–π stacking alignment of polymer chains in the solid state.[9] PDTFPy-BT shows absorption bands only at 220 and 430 nm. In addition, only a small red-shift (<10 nm) is found between its solution and solid state spectra, suggesting that PDTFPy-BT may have similar conformations in both solution and solid states.[10] Optical band gaps (E_g^{opt}) of the two polymers could be deduced from their absorption edges in the solid state. Evidently, the different absorptions of the two polymers also result in significant differences in their optical band gaps (1.18 eV for PDTFTh-BT and 2.07 eV for PDTFPy-BT).

The band gaps of the polymers were further investigated by cyclic voltammetry (CV, Fig. S2, ESI†). The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels could be calculated on the basis of onset oxidation (E_{ox}) and onset reduction (E_{red}) potentials. The HOMO level of PDTFTh-BT (−4.8 eV) is higher than that of PDTFPy-BT (−5.2 eV), but the LUMO level of PDTFTh-BT (−3.6 eV) is lower than that of PDTFPy-BT (−3.2 eV). These results further confirm that the alternating D–A polymer PDTFTh-BT has a lower band gap.

In order to shed light on the difference in band gaps between the two DTF polymers, computational studies using density functional theory approaches were carried out. Oligomers (DTFTh-BT)$_n$ and (DTFPy-BT)$_n$ with n = 1, 2, 3, and 4 were subjected to the calculations, with the alkyl chains replaced by CH$_3$ groups for simplicity. The optimised geometries and electron density distributions of the polymers were calculated at the B3LYP/6-31G(d) level (Fig. 2 and Fig. S3, ESI†). The electron densities of the HOMO and LUMO of (DTFTh-BT)$_4$ are all localized along the conjugated backbone, and the electron densities of DTF units are limited. As well, good coplanarity exists between the comonomers. The electron density of the HOMO of (DTFPy-BT)$_4$ is localized on the main chain and DTF units. However, that of its LUMO is mainly localised on BT monomers. In addition, an approximately 36° dihedral angle exists between the DTFPy and BT monomers. Fig. 3 exhibits the dependence of the HOMO, LUMO, and band gap of (DTFTh-BT)$_n$ and (DTFPy-BT)$_n$ on the reciprocal of the number of calculated repeating units. For (DTFTh-BT)$_n$, the LUMO energy level decreases and the HOMO level significantly increases with increasing number of repeating units included in the calculations, leading to a rapidly decreasing energy gap. However, the corresponding
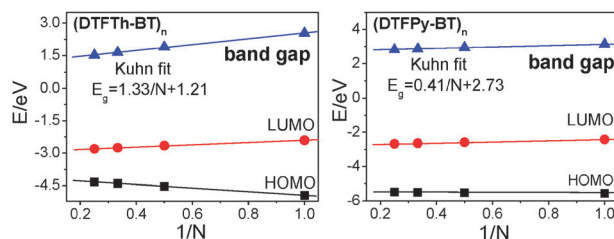

Fig. 3 The HOMO/LUMO energy levels and the energy gap as a function of 1/N, where N is the number of repeating units in the polymer chains of PDTFTh-BT and PDTFPy-BT.

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 PDTFTh-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, ESI†). Obviously, the two polymers show different diffraction patterns, especially at wide angles. PDTFPy-BT gives a single broad peak centred at about $2\theta = 21.4°$, corresponding to a d-spacing of 4.2 Å, whilst the XRD pattern for PDTFTh-BT shows a broad peak at $2\theta = 21.4°$ and a peak at $2\theta = 25.2°$, 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.[11] 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.[12]

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, ESI†). The field-effect mobility (μ_{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.

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