Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A

Supporting information for

Synthesis and photovoltaic properties from inverted geometry cells and roll-to-roll coated large area cells from dithienopyrrole-based donor-acceptor polymers

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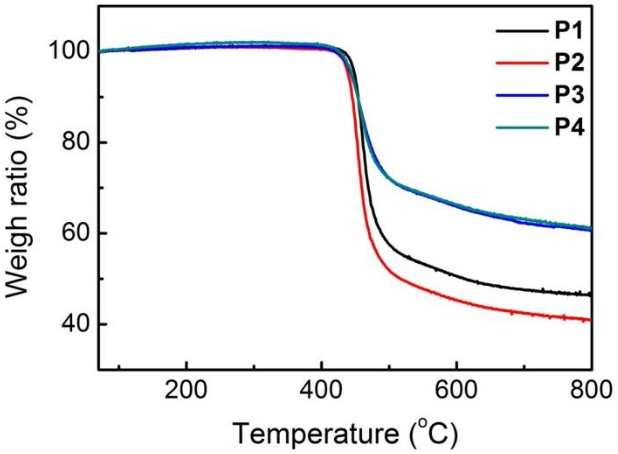

Figure S1. TGA plots of **P1-P4**.

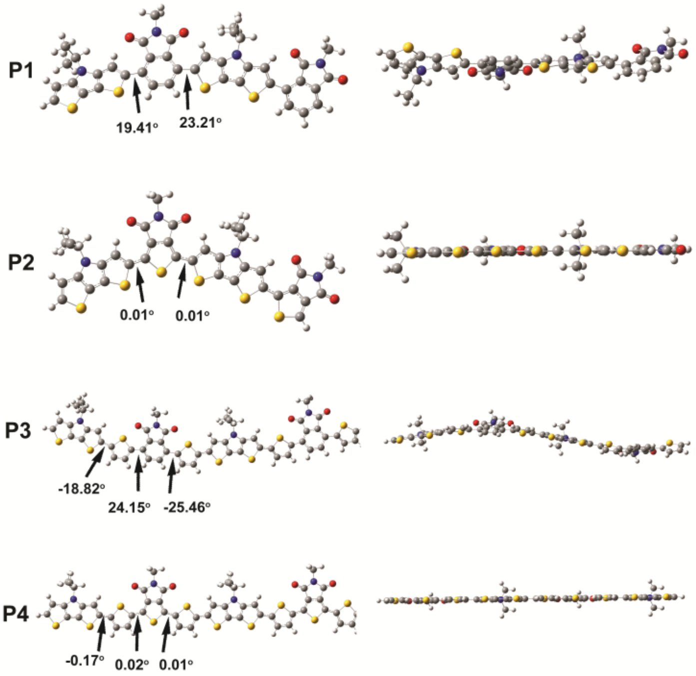

Figure S2 Top view (left) and side view (right) of optimized geometries of **P1**-**P4** with a chain length $n = 2$ obtained from DFT calculations.

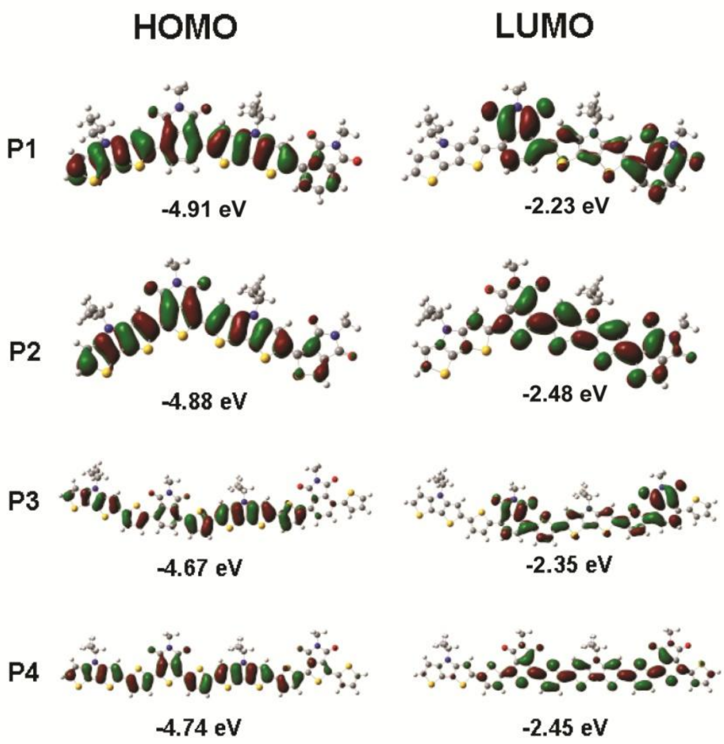

Figure S3 The frontier molecular orbital (HOMO, LUMO) obtained from DFT calculations.

For better understanding of the electronic properties of these four polymers, computational studies using density functional theory (DFT) approaches were carried out at the B3LYP/6-31G* level on model compounds using Gaussian 09 program suite. The alkyl chains were replaced by methyl groups to simplify the calculations. The optimized structures are shown in Figure S2, the backbones of **P2** and **P4** are in good coplanarity, all units are nearly in the same plane with small dihedral angles. In the contrary, the backbones of **P1** and **P3** have very big twist.

The wave functions of the frontier molecular orbital are depicted in Figure S3. The HOMOs of all the compounds are delocalized along the conjugated backbones, while the LUMOs are mainly localized on the acceptor groups. It implies that the HOMO energy levels are independent of the identity of the acceptor. **P1** and **P2** have similar HOMO energy levels of -4.91 and -4.88 eV, while **P3** and **P4** have similar HOMO levels of -4.67 and -4.74 eV. These results are consistent with the experimentally determined results (Table 1). Note that due to the small number of aromatic cycles being taken into account by the calculation, and the possible twist of the polymer backbones caused by the long alkyl chains , the absolute energy values are not reliable.

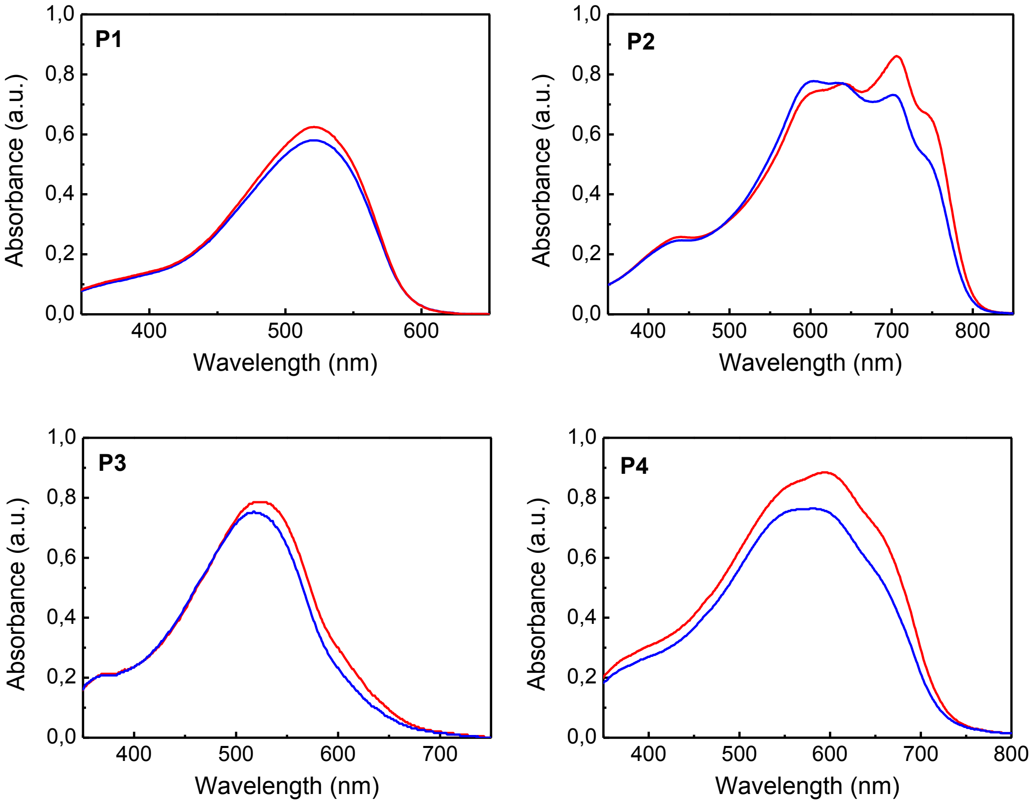

Figure S4 UV-vis spectra of **P1-P4** in chlorobenzene (CB) solution at room temperature (red line) and at 70 ^{o}C (blue line).

We suppose that the polymer chains form aggregation in solutions.[1,2] As shown in Figure S4, the absorption maximum of **P2**, **P3** and **P4** in chlorobenzene solution at 70 ^{o}C exhibit blue shifts of 5, 6 and 13 nm, respectively, while **P1** also exhibits a minor blue shift of 1 nm. The blue shift can be attributed to breakup of interchain aggregates in CB solution. For **P2** and **P4**, the decrease of the intensity of the absorption in the long wavelength region at 70 °C further proves that there has strong aggregation at room temperature.

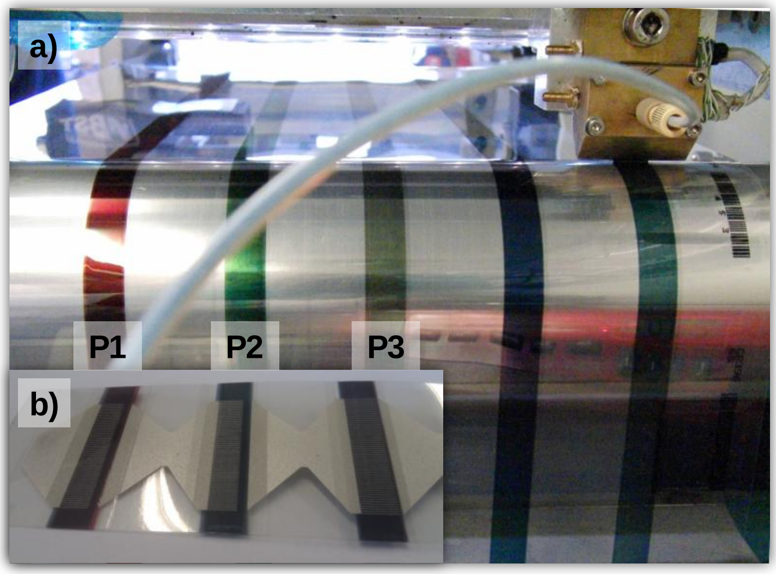

Figure S5 (a) Slot-die coating of the active layers, and (b) the final device. In both cases the polymer type is indicated.

References

1. M. M. Wienk, M. Turbiez, J. Gilot, R. A. J. Janssen, *Adv. Mater.* 2008, **20**, 2556.
2. E. Wang, L. Hou, Z. Wang, S. Hellström, F. Zhang, O. Inganäs, M. R. Andersson, *Adv. Mater.* 2010, **22**, 5240.