Electronic Supplementary Information (ESI)

## Computational modelling of donor-acceptor conjugated polymers through engineered backbone manipulations based on a thiophene-quinoxaline alternating copolymer

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Materials and characterization. All reagents, unless otherwise specified, were purchased from Sigma-Aldrich, TCI, Alfa Aesar, or Acros and used as received. The synthesized polymers in this study were reported elsewhere.<sup>1</sup> All manipulations involving air-sensitive reagents were carried out in an atmosphere of high purity nitrogen. All electrochemical measurements (cyclic voltammetry or square wave voltammetry) were performed on a CH Instruments Model 650A Potentiostat/Galvanostat Electrochemical Workstation. In the voltammetry experiments, a three electrode setup was used, with two platinum electrodes as the working and counter electrodes, respectively, together with a  $Ag/Ag^+$  quasi-reference electrode. A nitrogen-saturated solution of 0.1 M tetrabutylammonium hexafluorophosphate ( $Bu_4NPF_6$ ) in anhydrous acetonitrile was used as a supporting electrolyte. Thin polymer films were cast from chloroform solution onto the working electrode. In order to remove oxygen, the electrolyte was purged with nitrogen gas prior to each experiment. During the scans the nitrogen inlet was moved above the electrolyte surface. The third scan of the anodic and cathodic electrochemical waves was recorded and calibrated against the ferrocene/ferrocenyl ( $Fc/Fc^+$ ) redox couple. HOMO and LUMO levels were deduced from their respective ionization potentials and electron affinities, estimated from the first oxidation and reduction onset potentials according to the formulae HOMO =  $-(E^{ox} + 5.13)$  eV and LUMO =  $-(E^{red} + 5.13)$  eV, by setting the oxidative peak potential of  $Fc/Fc^+$  vs. the normal hydrogen electrode (NHE) to 0.63 V,<sup>2</sup> and the NHE vs. the vacuum level to  $4.50 \text{ V}^{3}$ 

**Variety of conformations**. Alongside different conformations influenced by structural asymmetry due to such as single fluorination and use of pyridopyrazine as an acceptor unit (Figure S6), there are also a variety of conformations arising from *cis-trans* isomerism along the backbone, as well as from different configurations of side chains attached to the backbone. The presence of aromatic rings in the side chains may not only allow for different substitution sites, but also present us different arrangements of the adjacent aromatic rings. The latter has rarely been discussed in a system like the TQ or TF<sub>2</sub>Q polymer. Actually there are two possible arrangements for these two phenyl rings in the quinoxaline acceptor unit of a single backbone due to the biphenyl twisting. This enantiomerism can be well-understood as occurs for *o*-terphenyl due to the biphenyl twisting. Consequently, the prepared quinoxaline unit for the TQ polymer should be a racemate without any further resolution, that is, there are equal probabilities

of the two arrangements to be present. Therefore, when such two different arrangements are adopted in the adjacent repeating units, the closest two phenyl rings from different repeating units may interact very differently. In a previous modelling work based on the TQ polymer,<sup>4</sup> one particular phenyl ring pattern has been employed, where in the same acceptor unit of a single backbone, the relative disposition of the two phenyl rings in the side chains are fixed to be enantiopure. Meanwhile, we also find for the *meta*-alkoxy substitutions on the phenyl side chains, the lower energy comes from the conformation where oxygen atoms are more close to the backbone. The energetic effects of side chain patterns have been evidenced in the DAD segments (Figure S1). By taking into account of the *meta*-alkoxy substitution patterns as well as *cis-trans* isomerism, we find that the *trans*-conformation is slightly more favored. When enantiomerism in the two aromatic side chains is also considered, the more energetically stable conformation corresponds to the trans conformation as well. Therefore, while staying with the same enantiomer in terms of the biphenyl twisting, it is reasonable to use *trans* conformations as the basis of comparison, which generally lessen the side chain steric hindrance effect, present more coplanar conjugated backbones, and are expected to favor stronger interchain interactions. We have to mention that it is really unique for a system like TQ or TF<sub>2</sub>Q to show such a large variety of conformations for the aforementioned reasons even when some have been skipped due to symmetry considerations, and that the polymer backbone is unnecessarily just helical if a nonenantiopure or racemic monomer has been used without any further resolution. It is still not clear to us at this point whether such a variety of conformations are accountable for the reported processing sensitivity of active layer morphology control and photovoltaic performance optimization.<sup>5</sup>



Figure S1 Different configurations of alkoxyphenyl side groups and different conformers of  $TF_2Q$  calculated by DFT.



**Figure S2** Energy level diagrams of different acceptor units (with isodensity plots, isovalue surface 0.02 au) and their combination with tellurophene in the calculation dimer models.



**Figure S3** Frontier orbitals of TQ monomer arising from the respective separated units (with isodensity plots, isovalue surface 0.02 au).



**Figure S4** Molecular orbitals of the separated units that constitute the frontier molecular orbitals of donor–acceptor polymers (isovalue surface 0.02 au).



**Figure S5** Energy level diagram of DTP-based polymers from DFT and their absorption spectra simulated by TD-DFT (the full width at half-maximum of the Gaussian curves used to convolute the spectrum =  $1500 \text{ cm}^{-1}$ ) with singlet excitations.



Figure S6 Energy level diagram of different configurations in the calculation dimer models and their chemical structures.



**Figure S7** Energy level diagrams of different chalcogenophene units (with isodensity plots, isovalue surface 0.02 au).



**Figure S8** Heteroatom effect of chalcogen substitution to the donor moiety (combined with FPP as the acceptor moiety) on energy levels calculated by DFT and absorption spectra simulated by TD-DFT (the full width at half-maximum of the Gaussian curves used to convolute the spectrum  $= 1500 \text{ cm}^{-1}$ ) with singlet excitations.



**Figure S9** Comparison of absorption spectra of BDT-, DT- and DT-based polymers simulated by TD-DFT (the full width at half-maximum of the Gaussian curves used to convolute the spectrum  $= 1500 \text{ cm}^{-1}$ ) with singlet excitations.

## References

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