

Supporting Information for the article entitled

“Synthesis, Photophysics, and Photovoltaic Properties of Low-band Gap
Conjugated Polymers Based on Thieno[3,4-*c*]-pyrrole-4,6-dione: A
Combined Experimental and Computational Study”

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Conformational Studies on Repeat Units. In the cases of coupling between TPD and thiophene or alkoxythiophene, the dihedral angle for the minima were observed at approximately 30° degrees from planarity, with heteroatoms in *cis*- conformation relative to each other. However, the potential energy surface between the DFT-optimized non-planar geometries and fully planar geometries has been found quite shallow. Thus, we have performed rigid geometry torsional potential calculations starting from fully planar structures. In all geometry optimizations and rotational barrier calculations that included the TPD unit, the lowest energy conformations occurred when heteroatoms of coupled units were *cis*- to each other along the backbone (Figure S2). In other words, the preference was to have the aromatic hydrogen rather than heteroatom facing the carbonyl group on TPD. Nonetheless, the hydrogen bonding interaction is not very strong as seen from the magnitude of relatively low rotational barriers between *trans*- and *cis*- conformers. The interatomic distances observed between oxygen and hydrogen (2.17 Å) are below the sum of van der Waals radii (2.72 Å), while those for oxygen and sulfur are close to the calculated interatomic distances based on van der Waals radii of each atom (3.25 Å), again suggesting the possible explanation for the lowest energy conformation as weak hydrogen bonding.

It is known that the B3LYP exchange-correlation functional underestimates long range dispersive binding energies, such as those observed for hydrogen bonding,¹ while the Perdew-Burke-Ernzerhof (PBE) generalized-gradient approximation overestimates these interaction energies with increasing error as the O...H-C angle decreases.² To further investigate the relative strength of hydrogen bonding and nonbonded S...O interactions, geometry optimizations on conformers were performed with extended 6-31+G(d,p) basis sets using B3LYP, PBE (for both exchange and correlation), MPW1B95, and MPW1BK functionals. The latter two functionals were parameterized by Zhau et al. from thermodynamic or kinetic databases, respectively and have been found to predict fairly accurate dispersive interaction energies and geometries, including hydrogen bonding interactions.³ The calculated energy difference for rotation between the two planar conformations of TCT repeat unit is given in Table S1. All of the theoretical methods predict hydrogen bonded conformers being the more stable structure for TPD containing repeat units. Yet, the energy difference is not very high between two conformers, hinting possible configurations where S...O interactions could also be observed in the solid state for non-equilibrium media. On the other hand, dialkoxybithiophene group adopts a trans-conformation unlike TPD-based structures.

References:

1. Del Bene, J. E.; Person, W. B.; Szczepaniak, K., Properties of Hydrogen-Bonded Complexes Obtained from the B3LYP Functional with 6-31G(d,p) and 6-31+G(d,p) Basis Sets: Comparison with MP2/6-31+G(d,p) Results and Experimental Data. *The Journal of Physical Chemistry* **1995**, 99, (27), 10705-10707.
2. Ireta, J.; Neugebauer, J.; Scheffler, M., On the Accuracy of DFT for Describing Hydrogen Bonds: Dependence on the Bond Directionality. *The Journal of Physical Chemistry A* **2004**, 108, (26), 5692-5698.
3. Zhao, Y.; Truhlar, D. G., Hybrid Meta Density Functional Theory Methods for Thermochemistry, Thermochemical Kinetics, and Noncovalent Interactions: The MPW1B95 and MPWB1K Models and Comparative Assessments for Hydrogen Bonding and van der Waals Interactions. *The Journal of Physical Chemistry A* **2004**, 108, (33), 6908-6918.

Table S1. Summary of differences in total energy for two TCT conformations and interatomic distances between the oxygen atom on TPD carbonyl and the nearest hydrogen and sulfur on CPDT unit computed with various functionals. Unless otherwise noted, the calculations were performed with 6-31+G(d,p) basis set.

Functional	d(H [⋯] O) (Å)	d(S [⋯] O) (Å)	ΔE_{rot} (kcal/mol)
B3LYP/6-31G(d)	2.17	3.00	1.30
B3LYP	2.19	3.03	1.58
PBEPBE	2.17	3.01	1.54
MPW1B95	2.20	3.04	1.53
MPWB1K	2.19	3.03	1.60

Table S2: Summary of TD-DFT calculations on two repeat units of polymers with B3LYP/6-31G(d) method.

ID	Excited State	E and f	Transitions	CI Coeff.
TC1 Dimer	S ₁	2.17 eV 570.1 nm f=1.18	H-2 -> L+2 H-1 -> L H-1 -> L+1 H -> L H -> L+1	0.10431 0.20314 0.20693 0.55958 -0.15379
	S ₂	2.31 eV 536.4 nm f=1.18	H-1 -> L H-1 -> L+2 H -> L+1 H -> L+2	0.42860 0.12828 0.44969 -0.12248
TC2 Dimer	S ₁	1.92 eV 644.0 nm f=2.35	H-2 -> L+1 H-1 -> L H-1 -> L+2 H -> L+1	-0.10001 -0.38968 0.12937 0.49670
	S ₂	2.07 eV 596.5 nm f=3.11	H-2 -> L+2 H-1 -> L+1 H -> L H -> L+1	0.12179 -0.24163 0.59251 -0.11563
TCT Dimer	S ₁	1.68 eV 734.7 nm f=2.16	H-1 -> L+1 H -> L	0.11072 0.64552
TBT Dimer	S ₁	1.53 eV 808.9 nm f=0.76	H -> L H -> L+1 H-1 -> L	0.67584 -0.11517 0.10752
	S ₂	1.74 eV 708.6 nm f=1.97	H-1 -> L H-1 -> L+1 H -> L H -> L+1 H -> L+2	-0.33069 0.10824 0.18650 0.52996 0.12292

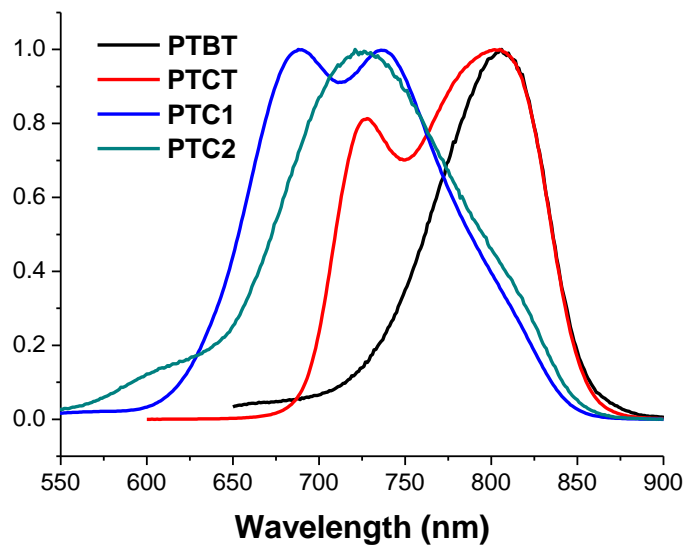
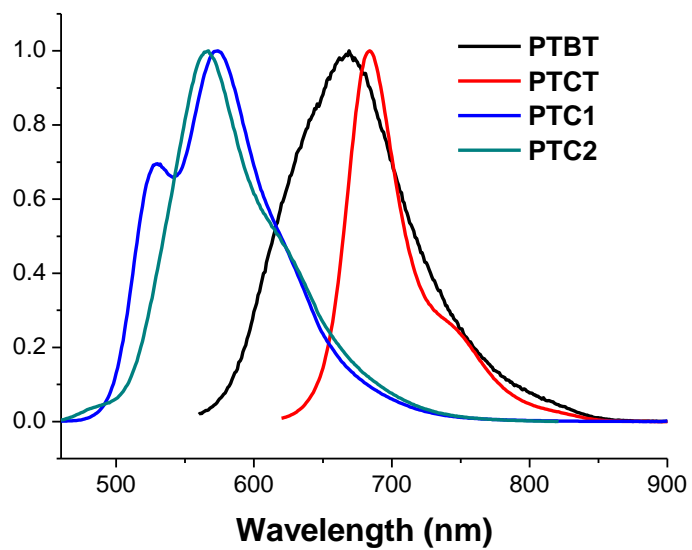


Figure S1: Normalized PL spectra of PTCT, PTBT, PTC1, and PTC2 in chloroform solution (top) and as a film (bottom).

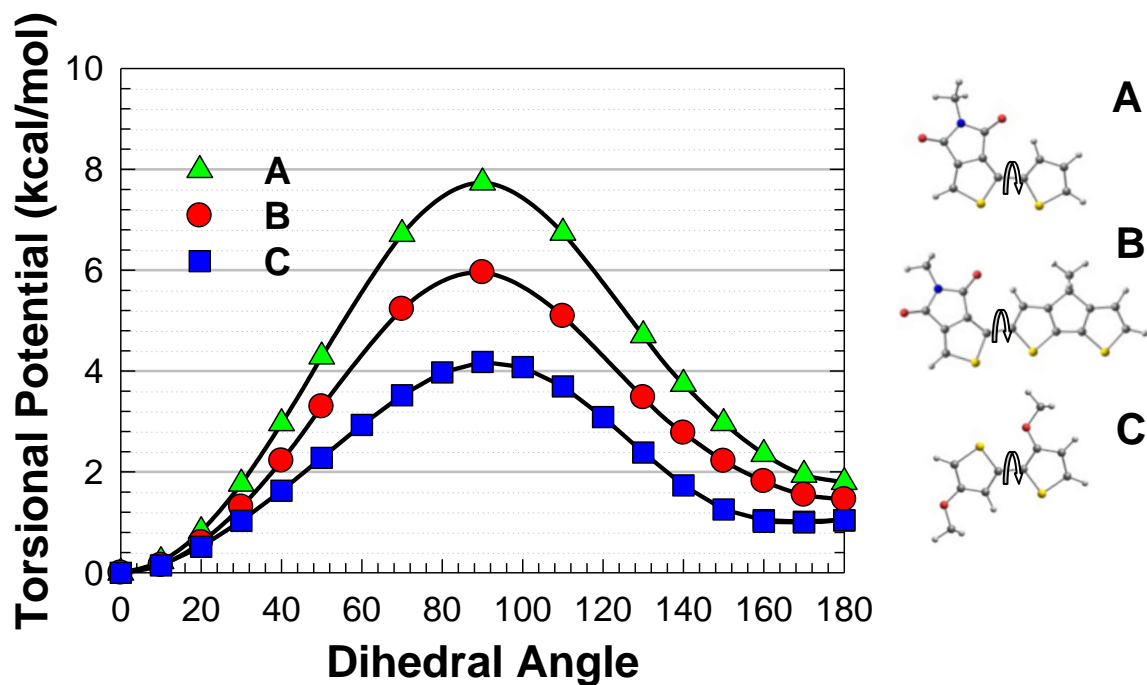


Figure S2. Variation of relative energies of repeat unit conformations with the twisting angle between the comonomers calculated with B3LYP/6-31G(d) method. The most stable conformation is given in the graph. Dialkoxybithiophene shows the lowest energy geometry with alkoxy groups trans- to each other, while those for thiophene or CPDT show the lowest energy structure in planar conformation with aromatic hydrogen facing the oxygen on TPD.

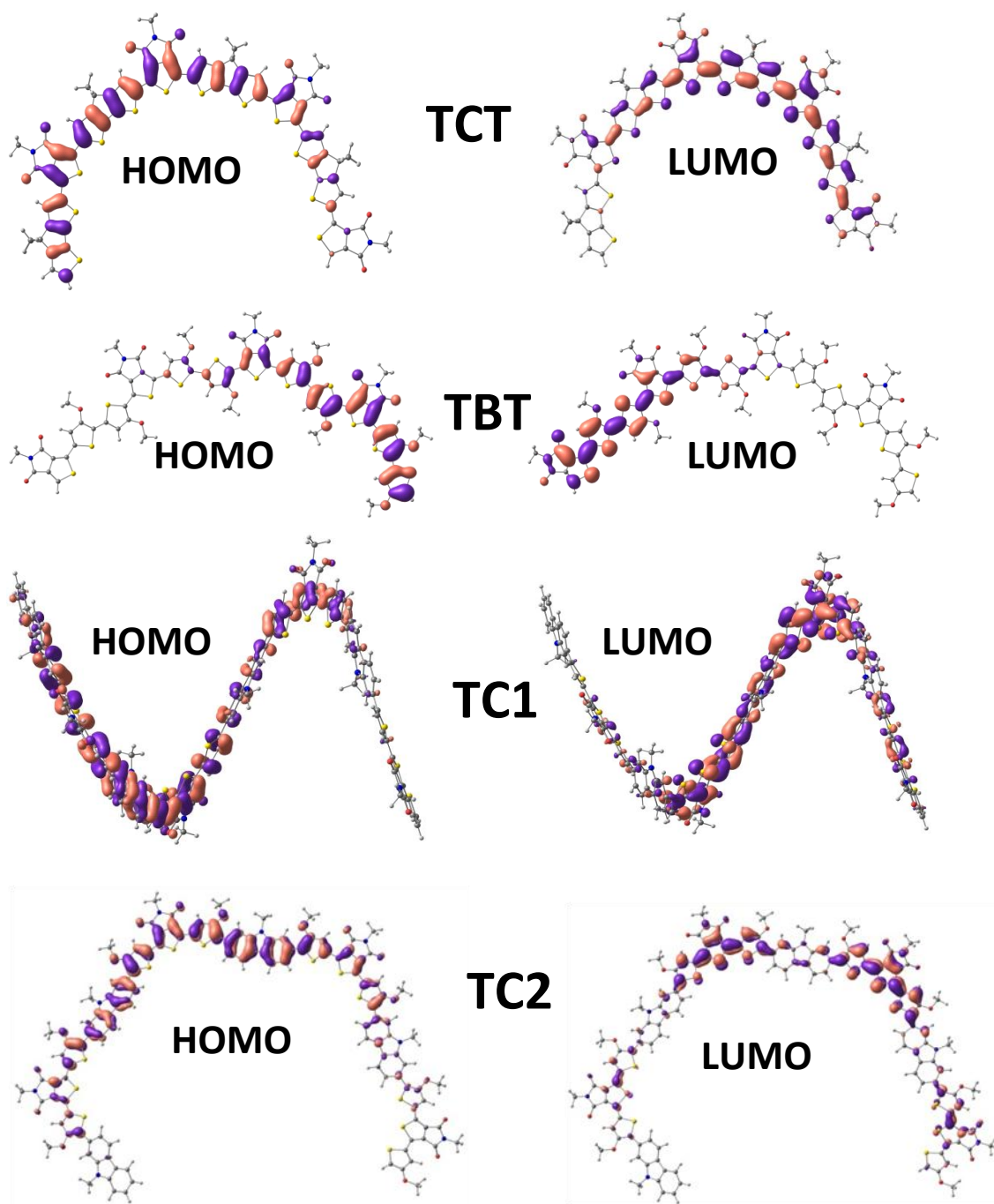


Figure S3: HOMO and LUMO plots of oligomers with four repeat units.