

Supporting Information

Effects of lateral-chain thiophene fluorination on morphology and charge transport of BDT-T based small molecule donors: A study with multiscale simulations

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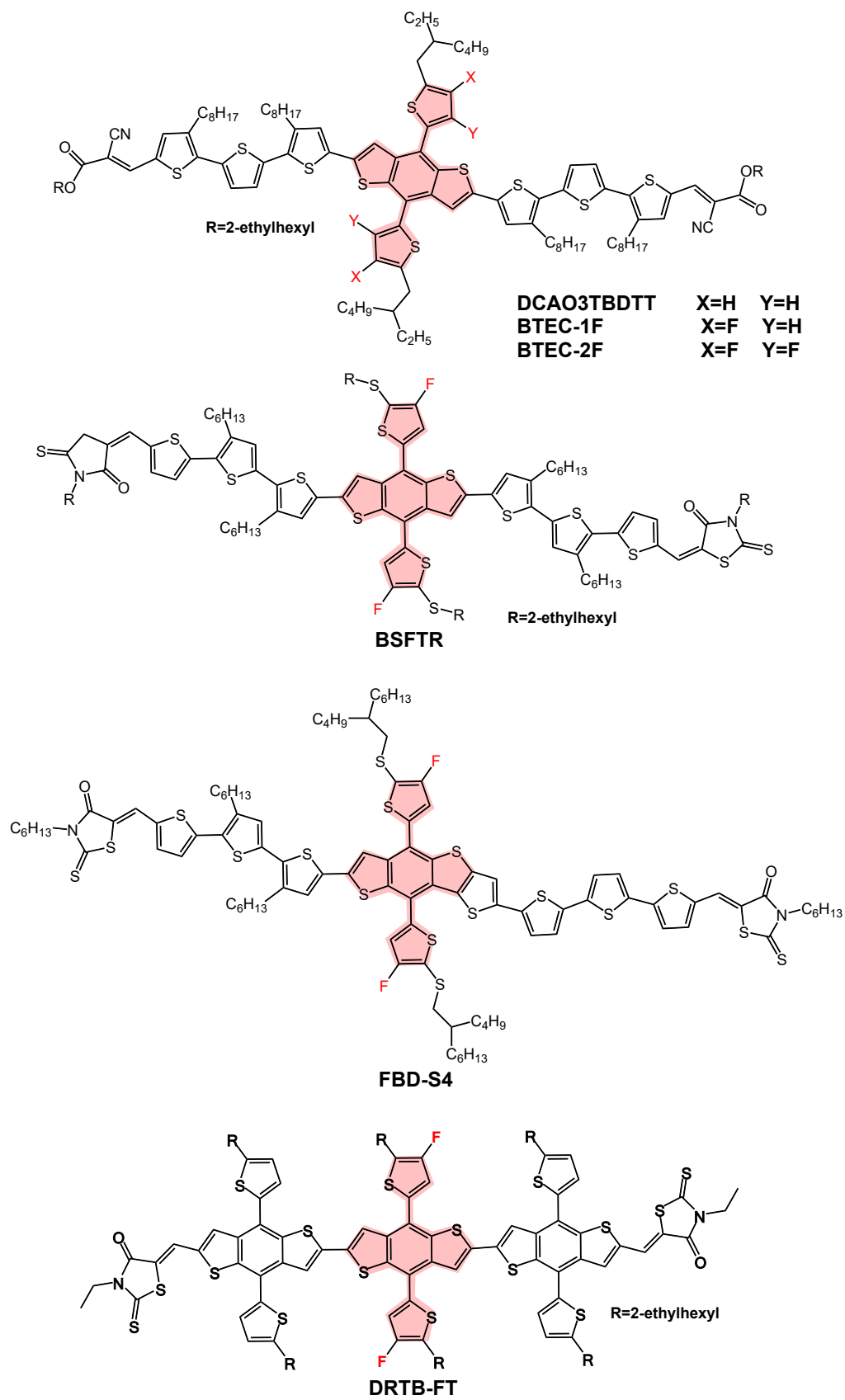


Fig. S1 Representative small-molecule donors using fluorinated BDT-Ts as building blocks.

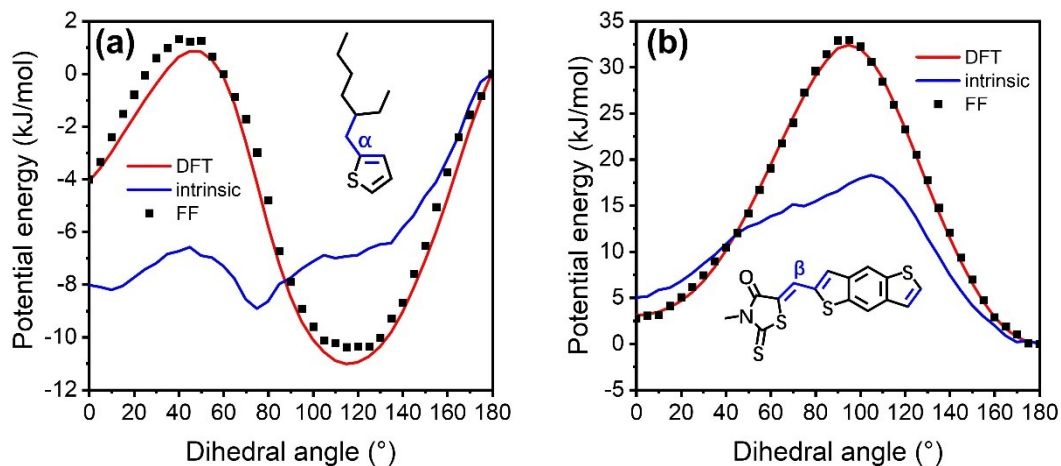


Fig. S2 Potential energies of dihedral angles between alkyl side-chain and backbone (a) and dihedral angles between terminal group and BDT unit (b) calculated by DFT B3LYP/6-31G** and GAFF with the fitted intrinsic potentials.

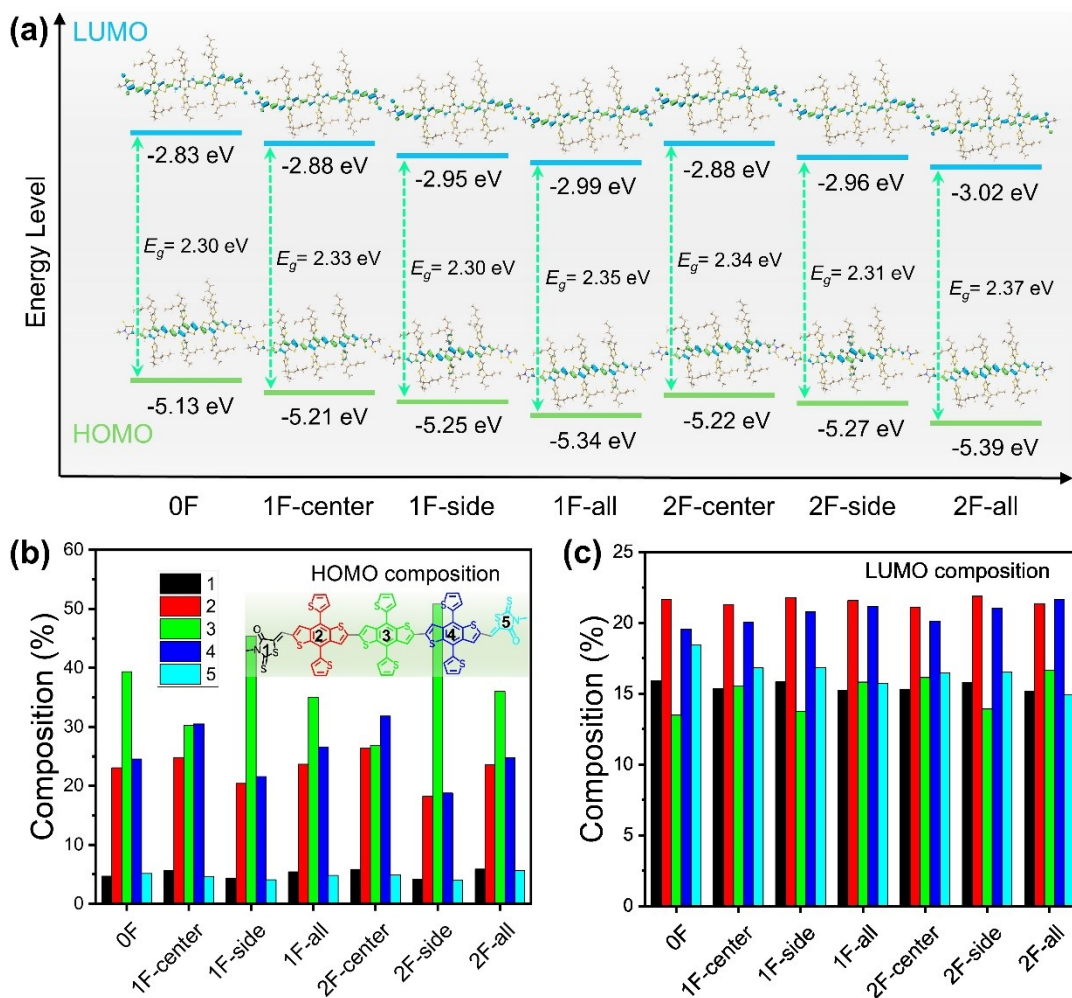


Fig. S3 (a) FMOs and (b), (c) the compositions of FMOs calculated by DFT B3LYP/6-

31G** level.

As expected, both the HOMO and LUMO energies are downshifted after fluorinations, and the energy gaps (E_{gs}) are slightly widened. The decrease of HOMO can improve the V_{OC} of OSC device, but lessen the driving force for hole transfer at donor-acceptor interface. Therefore, it is hard to make a judgement for the change of performance of the OSCs based on these fluorinated donors. When fluorine-substitutions occur on side TBDT units (1F-side and 2F-side), the decreases of HOMO and LUMO energies are close, so the E_{gs} are almost unchanged compared to prototype DRTB-T (0F). Furthermore, the electron density distribution of FMOs determines the electronic coupling between neighboring molecules. As shown in Fig. S2b and Fig. S2c, the HOMO density of 0F is mainly distributed on the donor part, i.e., with a composition of 39.4% electronic density locating on the central TBDT unit and 9.8% locating on two terminal groups. After fluorination on the side-chain thiophenes of TBDT unit, the HOMO composition on this TBDT unit decreased, and this effect raises with the increasing number of fluorine atoms on single thiophene. Besides, the HOMO composition on two terminal groups increased in 1F-center, 1F-all, 2F-center and 2F-all, while decreased in 1F-side and 2F-side. In addition, the effect of fluorination on the LUMO composition is on the contrary to that of HOMO, i.e. the HOMO density on the fluorinated TBDT unit decrease while the LUMO density increases. But the changes of LUMO density are not as obvious as HOMO density.

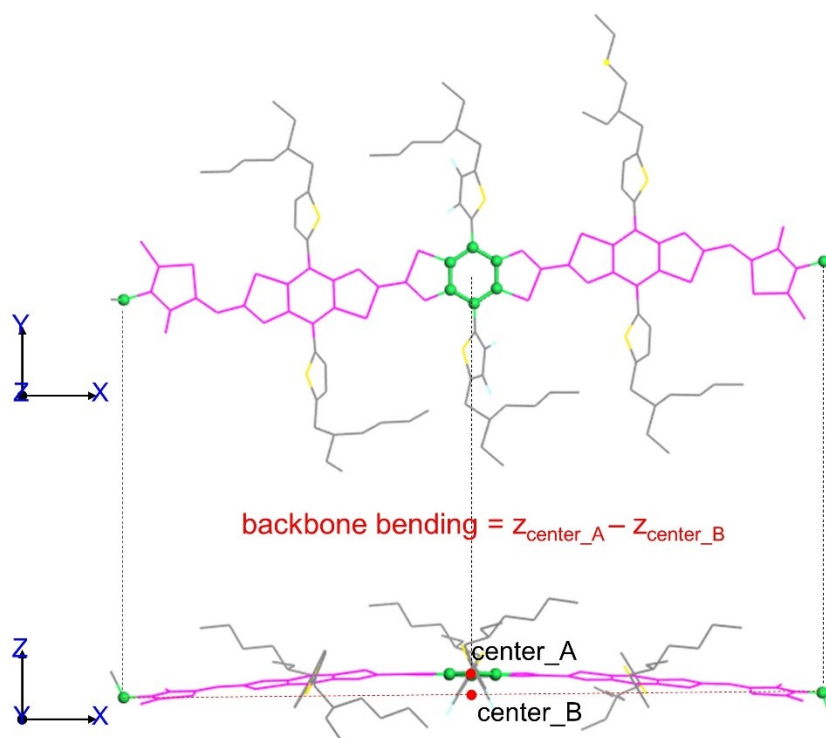


Fig. S4 Estimation method of backbone bending, in which the backbone bending is estimated by the z axis coordinate difference between the geometry center of terminal carbon atoms and center benzene ring, when the molecule backbone is put in xy plane. The backbone atoms are highlighted in pink, and the key atoms for backbone bending estimation are in green. Note the hydrogen atoms are omitted for clarity.

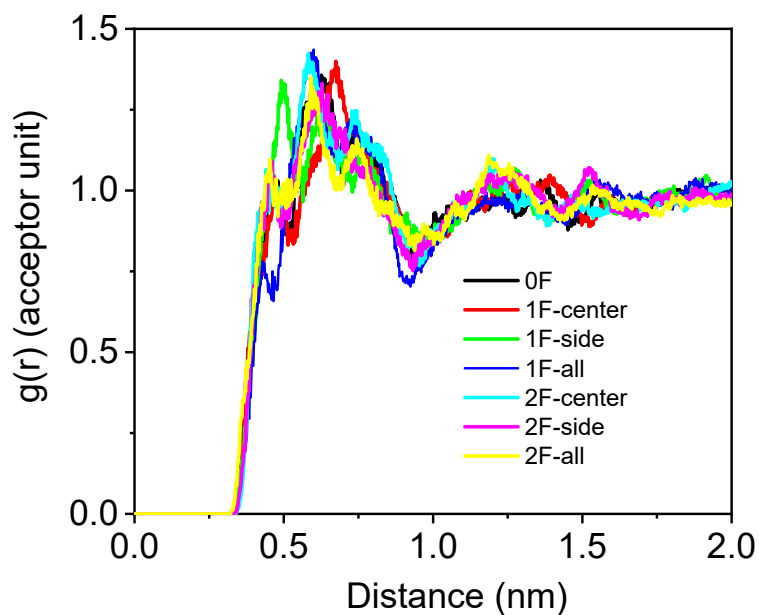


Fig. S5 The RDF of acceptor part extracted from MD simulations.

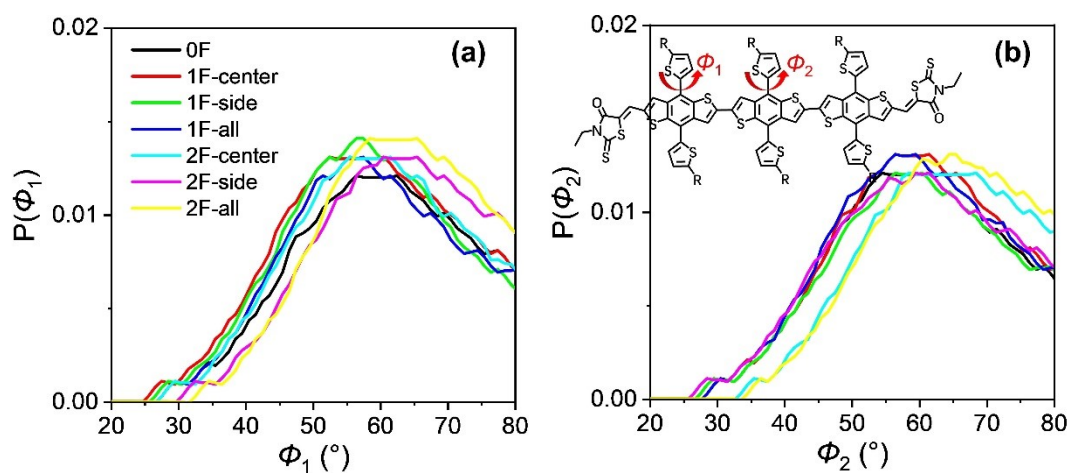


Fig. S6 The distribution of dihedral angle between lateral-chain thiophene and center BDT.

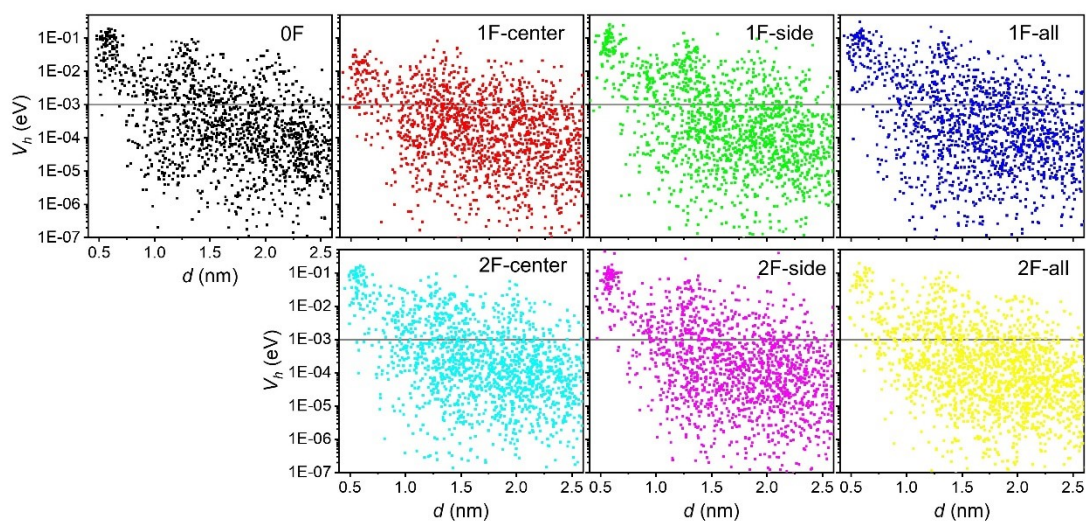


Fig. S7 Charge transfer integral as a function of backbone-backbone COM distance of molecular pairs inside the final boxes of MD simulations.

Tbl. S1 Comparisons between experimental and theoretical μ_{hs} in the present work.

Experimental μ_{h} ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)		Theoretical μ_{h} ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	
0F:F-2Cl ¹	2.50×10^{-4}	0F	1.89×10^{-3}
1F-center:F-2Cl ²	8.56×10^{-5}	1F-center	1.15×10^{-3}
DCAO3TBDTT:Y6 ³	4.60×10^{-4}	0F	1.89×10^{-3}
BTEC-1F:Y6 ³	4.17×10^{-4}	1F-center	1.15×10^{-3}
BTEC-2F:Y6 ³	5.43×10^{-4}	2F-center	2.23×10^{-3}

References:

- 1 Y. Wang, Y. Wang, B. Kan, X. Ke, X. Wan, C. Li and Y. Chen, *Adv. Energy Mater.*, 2018, **8**, 1802021.
- 2 C. Liu, N. Qiu, Y. Sun, X. Ke, H. Zhang, C. Li, X. Wan and Y. Chen, *Front. Chem.*, 2020, **8**, 329.
- 3 J. Ge, L. Xie, R. Peng, B. Fanady, J. Huang, W. Song, T. Yan, W. Zhang and Z. Ge, *Angew. Chem. Int. Ed.*, 2020, **59**, 2808-2815.