Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information for:

Comprehensive Modelling Study of Singlet Exciton Diffusion in Donor-Acceptor Dyads: When Small Changes in Chemical Structure Matter

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For the Dreiding(1) Force Field (FF) paramterization, the torsion terms were expressed as:

$$E_T = \sum_{n=1}^{6} \frac{1}{2} B_n \left(1 - d_n \cos(n\phi)\right) \tag{1}$$

Using eq. (1), a fitting procedure was set up, where B_n, d_n, and n were adjustable parameters, in order to reproduce as close as possible the minima and the barriers of the energy profiles. MP2/cc-pVDZ calculations highlitgth that **1** and **2** tend to be almost in the same conformation regarding the torsion angle between the triphenylamine (TPA) phenyl ring and the thiophene unit and the thiophene itself and the dicyanovynil (DCV) group. Then, for **2** the two thiophene units should adopt the usual anti conformation, while for **1** two twisted almost isoenergetic conformers are found with respect to the torsion between the DCV and the terminal phenyl group and no planarization in the solid state should be expected for this torsion due to the large energetic barrier (about 6 kcal mol^{-1}) at 0° and 180°.

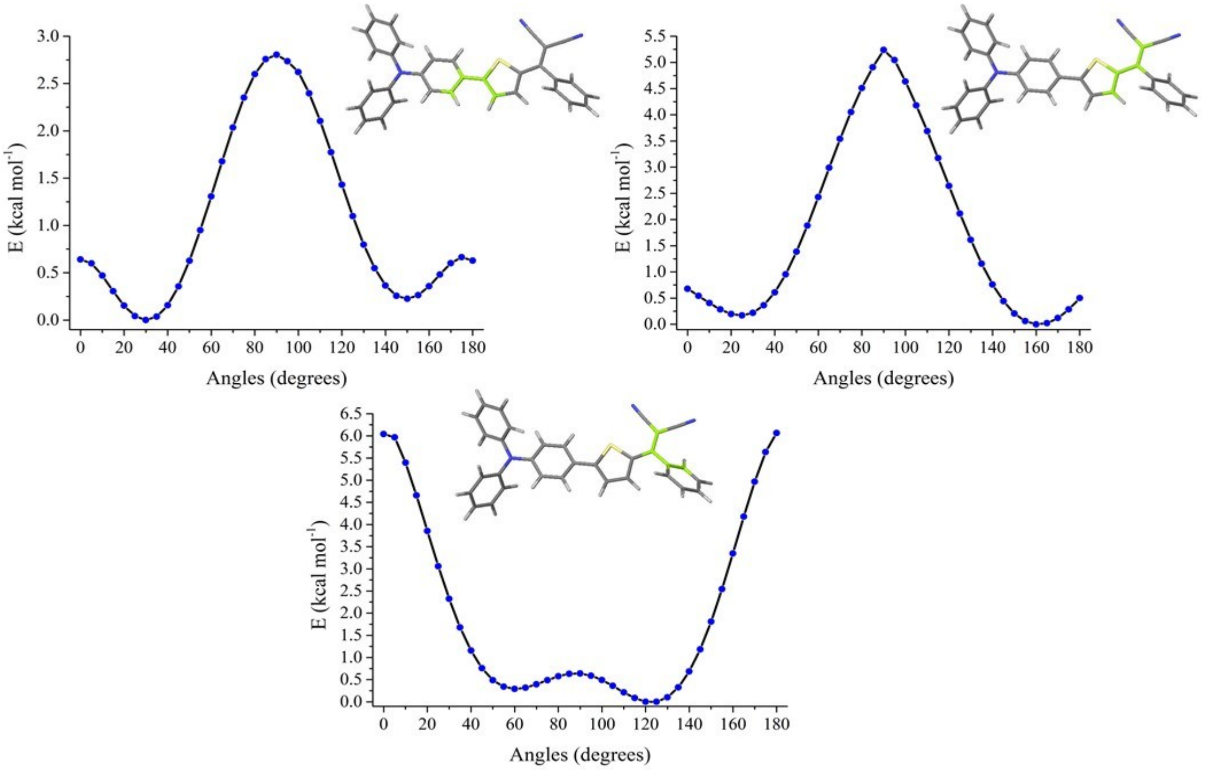

Figure S1: MP2/cc-pVDZ calculated characteristic torsion potentials of **1**. In each of the three graphs, the atoms in light green are those involved in the definition of the 0° dihedral angle.

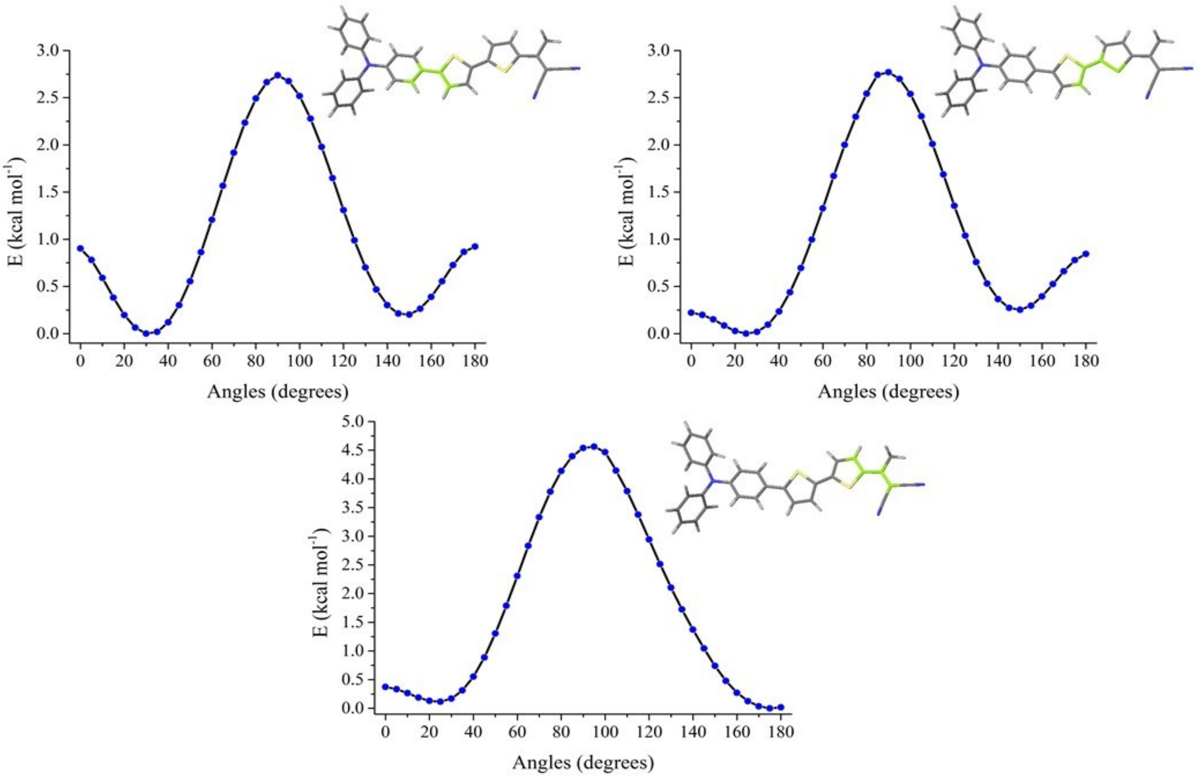

Figure S2: MP2/cc-pVDZ calculated characteristic torsion potentials of **2**. In each of the three graphs, the atoms in light green are those involved in the definition of the 0° dihedral angle.

The parametrized FF was validated by performing Molecular Dynamics (MD) simulations on a **1x** triclinic supercell. In order to reach comparable dimensions of the supercell in terms of size and number of molecules, the crystallographic **1** unit cell(3) was replicated 8 times along *a,* 6 times along *b* and 5 times along *c*, conserving the triclinic simmetry. Then, the standard condition NPT-MD run described in the main text was applied. The resulting cell parameters from the equilibrated MD simulations for the three samples are reported in Table S1, along with the obtained density.

	a (Å)	*b* (Å)	*c* (Å)	*α* (°)	*β* (°)	*γ* (°)	*d* (g cm^{-3})	# *molecules*
1x	86.120	83.070	88.539	89.91	100.29	89.96	1.23	960
***1** unit cell*	10.753 (x8)	13.951 (x6)	17.404 (x5)	90.00	99.37	90.00	1.24	4

1a	92.063	92.063	92.063	90.00	90.00	90.00	1.02	1000
2a	94.958	94.958	94.958	90.00	90.00	90.00	0.97	1000

Table T1: Cell parameters for the three built samples.

Time-Dependent DFT (TD-DFT) calculations at the Optimally Tuned Range Separated Hybrid (OT-RSH) functional ωB97X-D/6-31G(d,p) level were performed on all the molecules extracted from the MD last frame of the three investigated samples. Figure S3 shows the lowest excited state S_1 hole and electron density overlap, Φ_s, dependency on the torsional degree of freedom regarding the dihedral angles previously parametrized in the FF. For **1a**, the rotation along the TPA and the thiophene bond (black squres) and the rotation along the thiophene and the DCV bond (blue triangles) affects mostly the Φ_s character of S_1, leading to improved CT states and thus to red-shift excitations. Apparently, the rotation along the DCV and the terminal phenyl ring bond (orange stars) does not have a such large impact on Φ_s, since the phenyl ring is not involved in the densities overlap (see Figure 2 in the main text). Moreover, as expected, the molecules in **1x** probe a smaller region of configurations in the conformational space, due to the long-range order induced by the crystal packing. The Φ_s character remains quite costant, around 0.70, despite the rotation freedom of the terminal phenyl ring. At last, for **2a** again the rotation along the thiophene and the DCV bond (blue triangles) and the rotation along the two thiophenes bond (red dots) seems to play a key role in the Φ_s character determination, while the rotation along the TPA and the thiophene bond (black squares) does not change the nature of S_1, probably in virtue of a longer conjugation length.

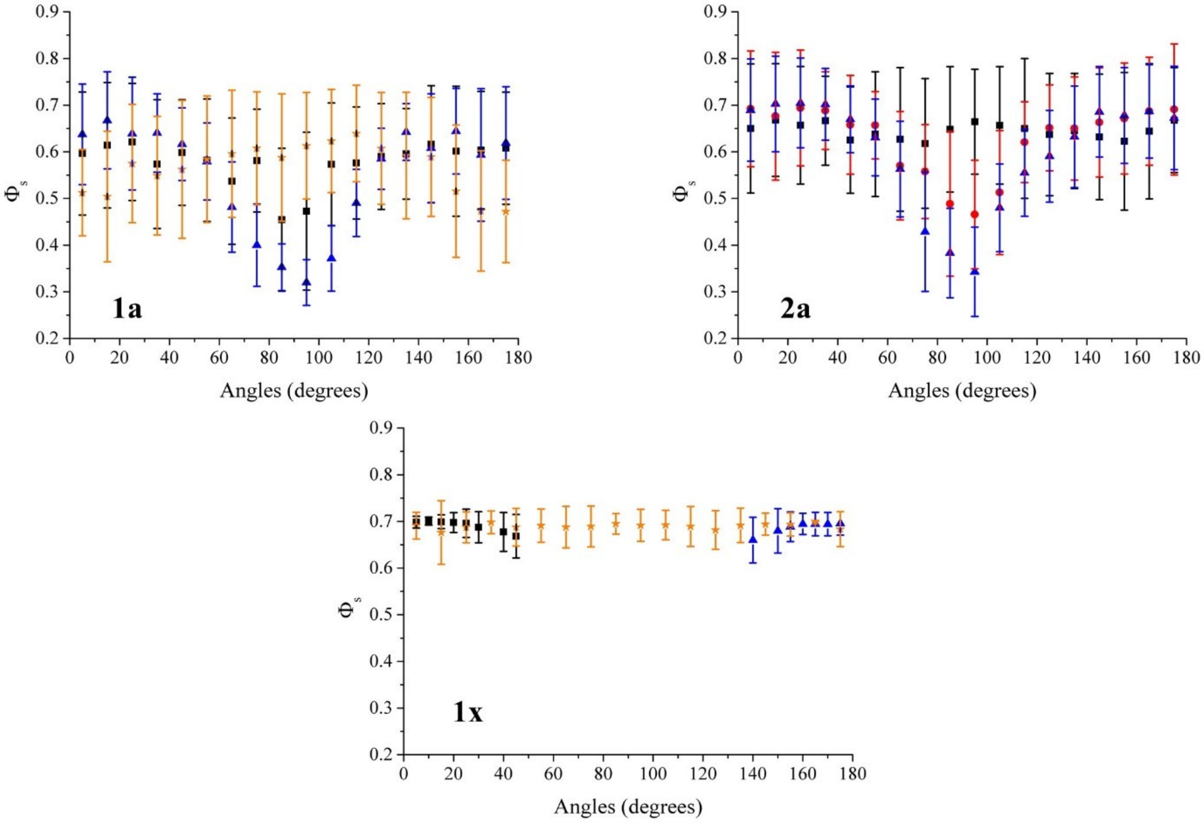

Figure S3: Calculated Φ_s dependency on the parametrized torsion angles for **1a**, **1x** **2a**. Black squares indicate the dihedral angle between the TPA phenyl ring and the thiophene unit, both for **1** and **2**; blue triangles the dihedral angle between the thiophene and the DCV group, both for **1** and **2**; orange stars the dihedral angle between the DCV and the terminal phenyl ring in **1**; red circles the dihedral angle between the two thiophenes in **2**. Data set standard deviation is represented by vertical bars.

References

1. Mayo SL, Olafson BD, Goddard WA. DREIDING: a generic force field for molecular simulations. J Phys Chem. 1990 Dec 1;94(26):8897–909.
2. Courtesy of Enikolopov Institute of Synthetic Polymeric Materials of the Russian Academy of Sciences.