

Supplementary Information

Impact of solution temperature-dependent aggregation on the solid-state packing and electronic properties of polymers for organic photovoltaics

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1. Initial models used for the MD simulations:

1.1. PBT4T-2OD

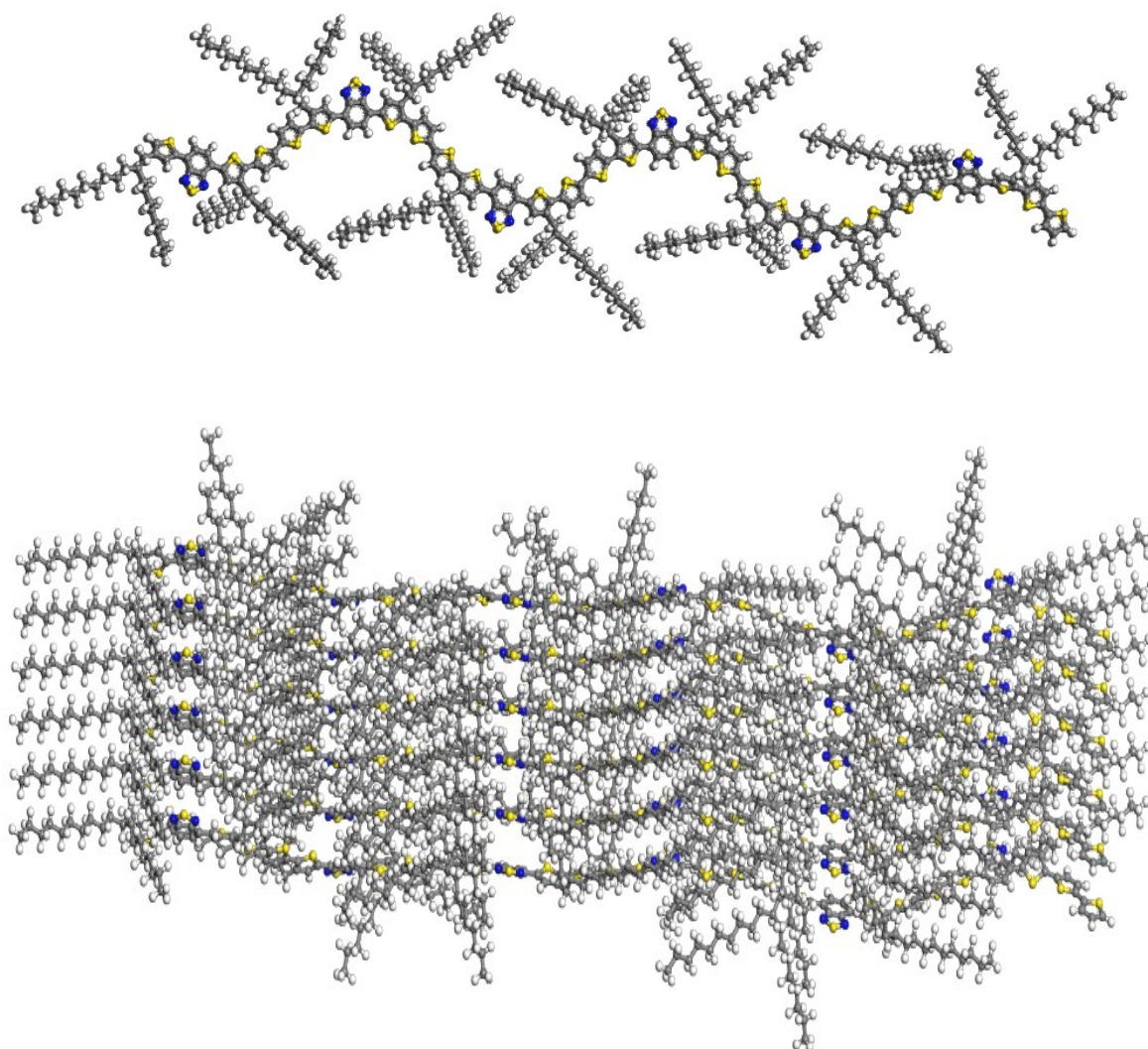


Figure S1. Illustration of the initial models used for the MD simulations: Top: A single polymer chain of PBT4T-2OD consisting of 6 repeat units. Bottom: A polymer stack made of 6 polymer chains perfectly packed on top of each other.

1.2. PffBT4T-2OD

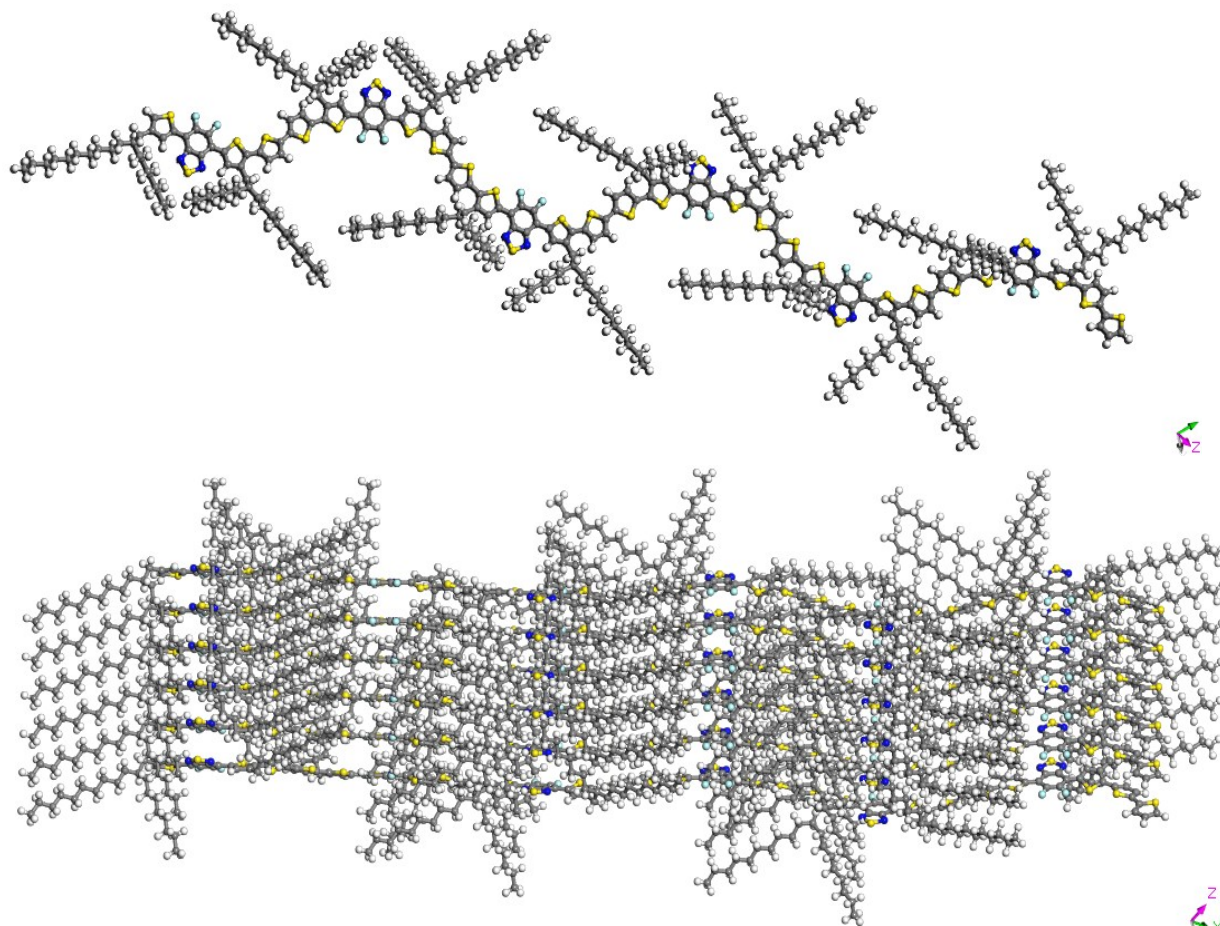


Figure S2. Illustration of the initial models used for the MD simulations: Top: A single polymer chain of PffBT4T-2OD consisting of 6 repeat units. Bottom: A polymer stack made of 6 polymer chains perfectly packed on top of each other.

2. Dihedral-angle distributions at various temperatures.

2.1. 40°C

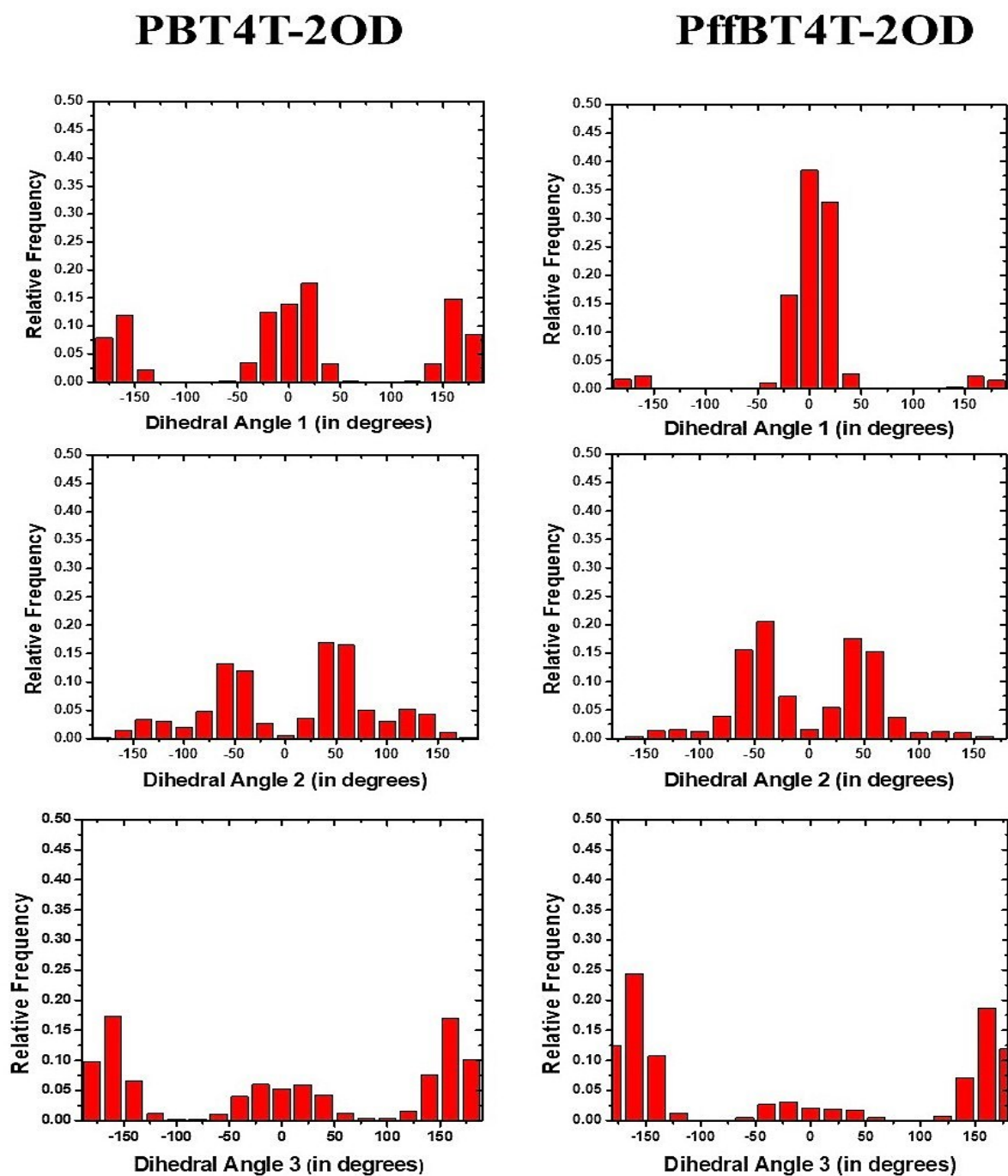


Figure S3. Distribution of the dihedral angles along the PBT4T-2OD (left) and PffBT4T-2OD (right) chains after MD simulations of the respective polymer stacks in solution at 40°C.

2.2. 60°C

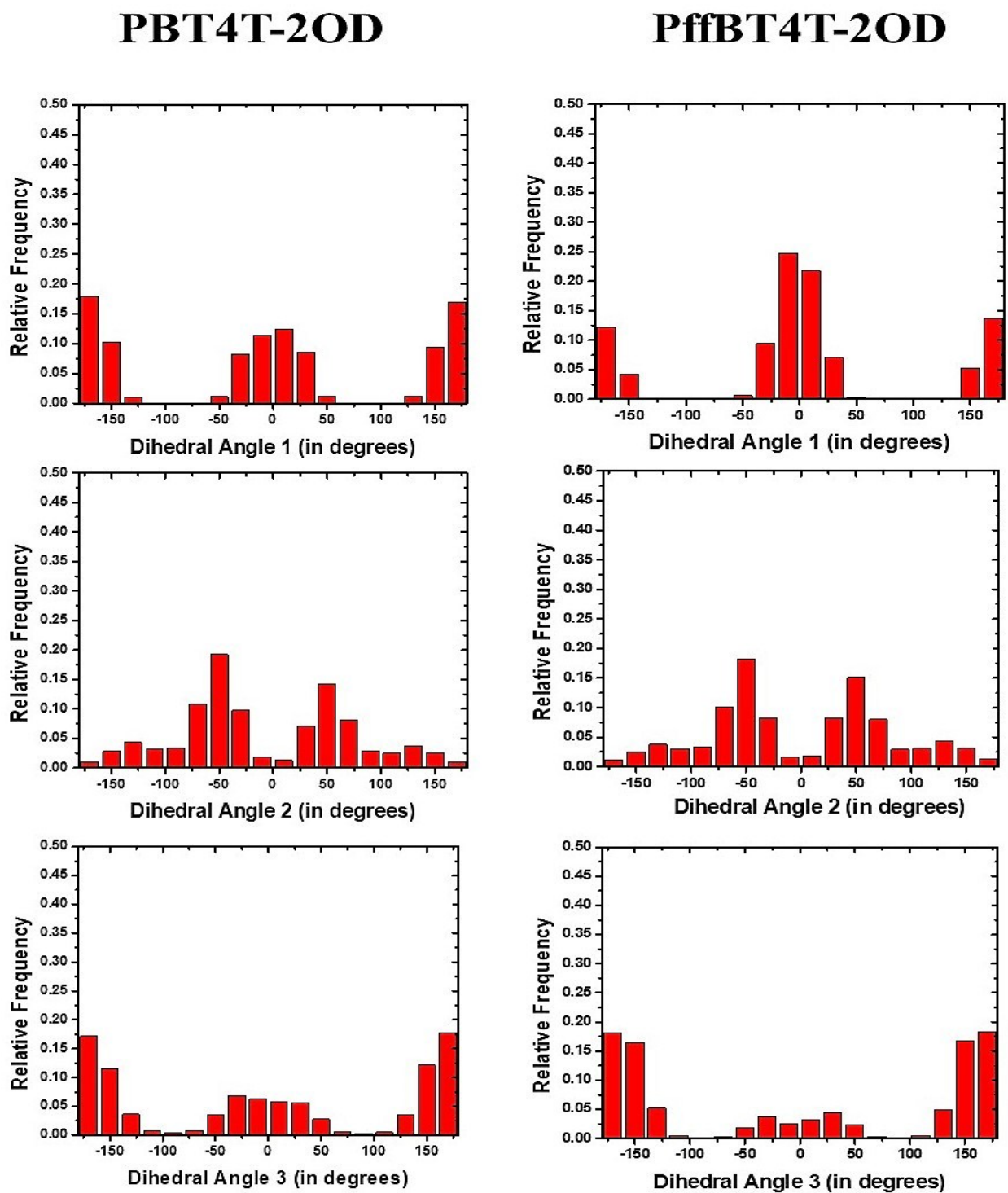
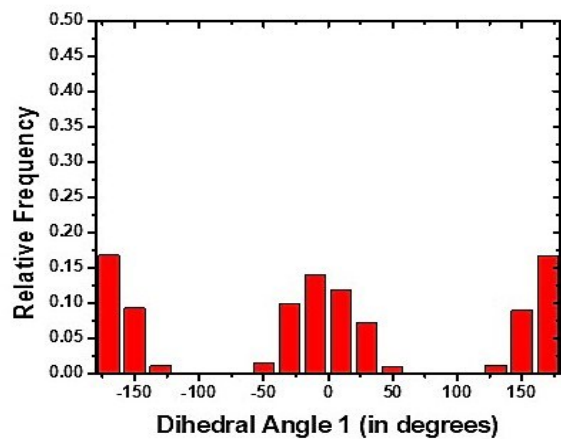


Figure S4. Distribution of the dihedral angles along the PBT4T-2OD (left) and PffBT4T-2OD (right) chains after MD simulations of the respective polymer stacks in solution at 60°C.

2.3. 80°C

PBT4T-2OD



PffBT4T-2OD

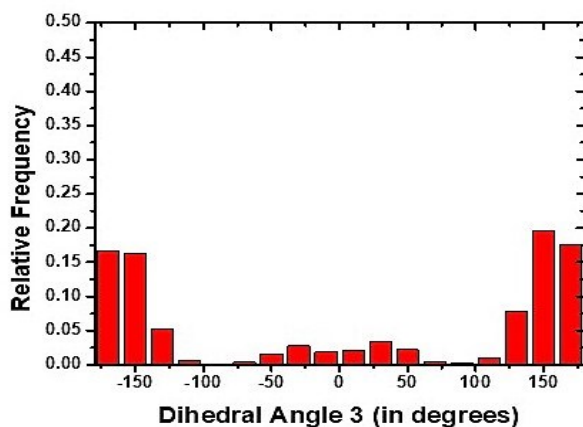
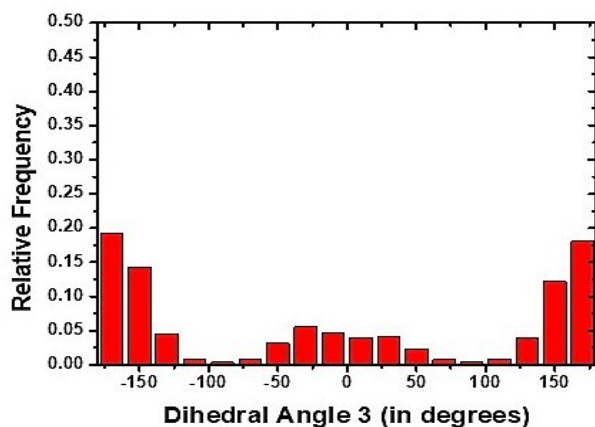
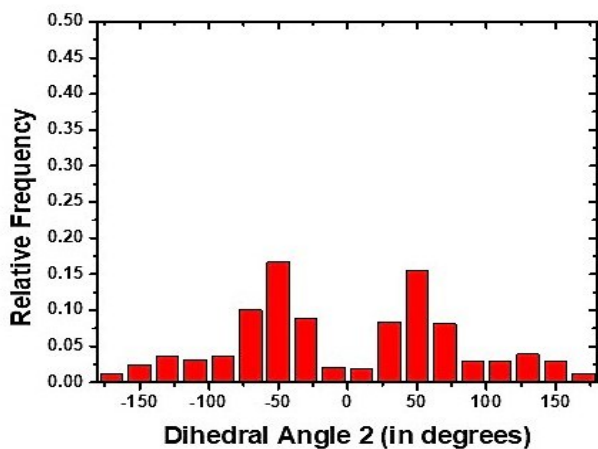
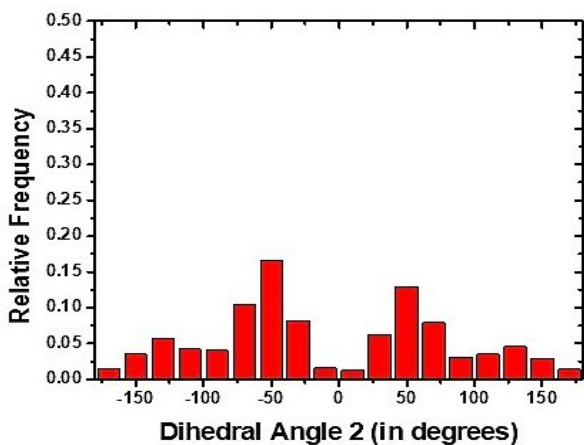
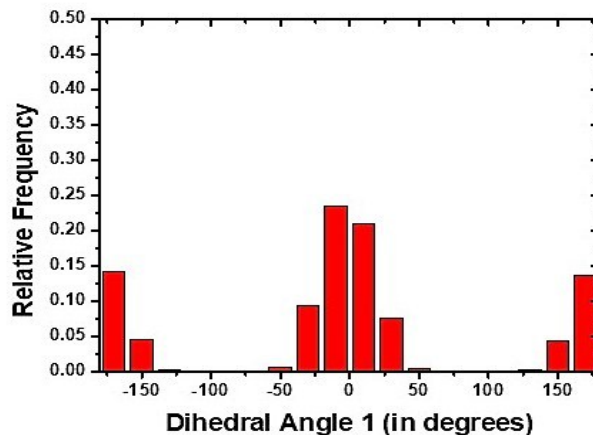
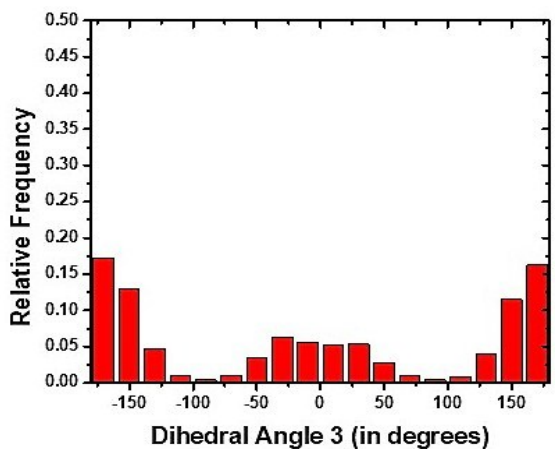
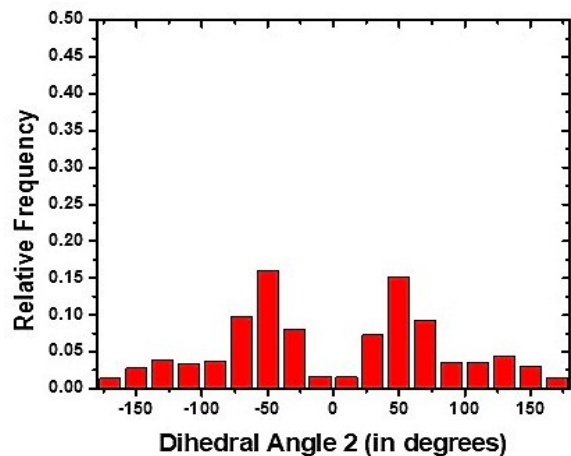
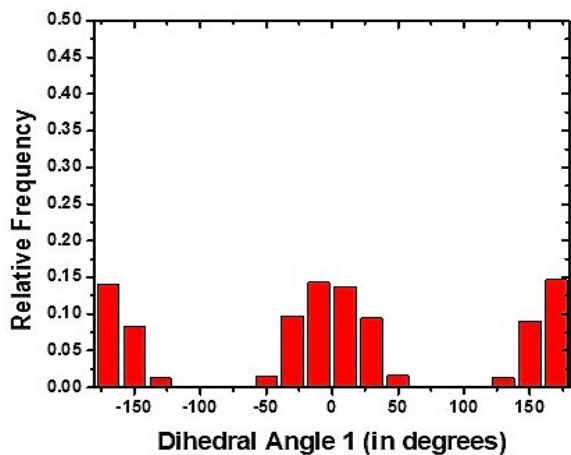


Figure S5. Distribution of the dihedral angles along the PBT4T-2OD (left) and PffBT4T-2OD (right) chains after MD simulations of the respective polymer stacks in solution at 80°C.

2.4. 100°C

PBT4T-2OD



PffBT4T-2OD

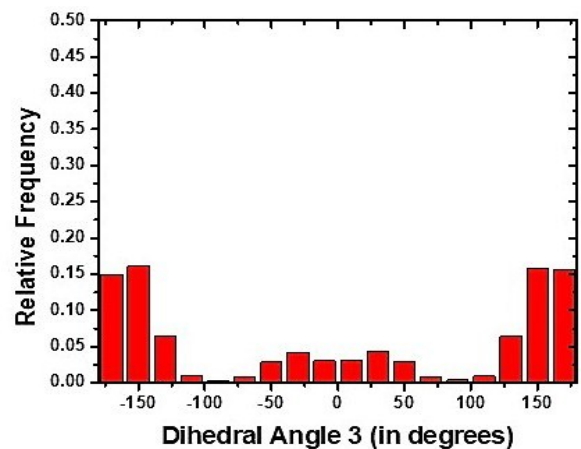
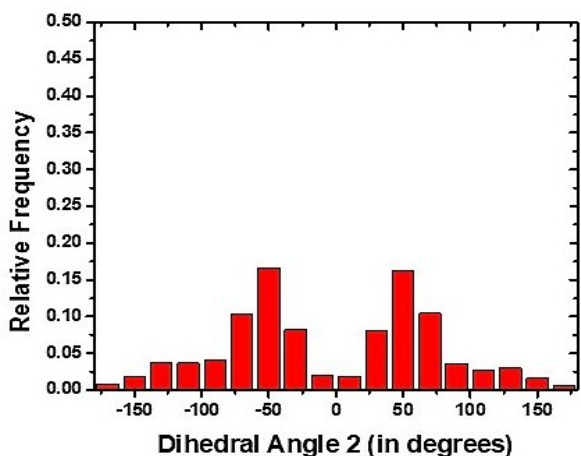
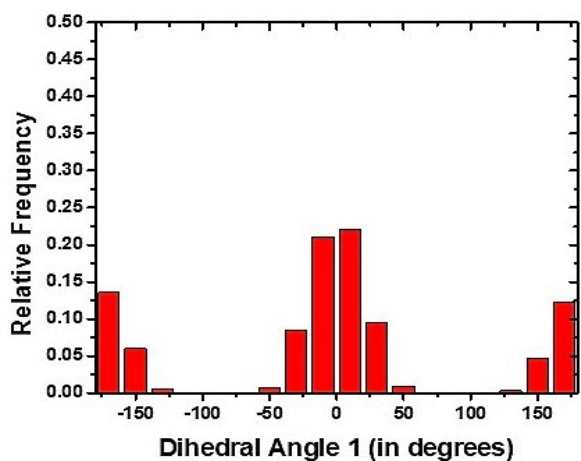


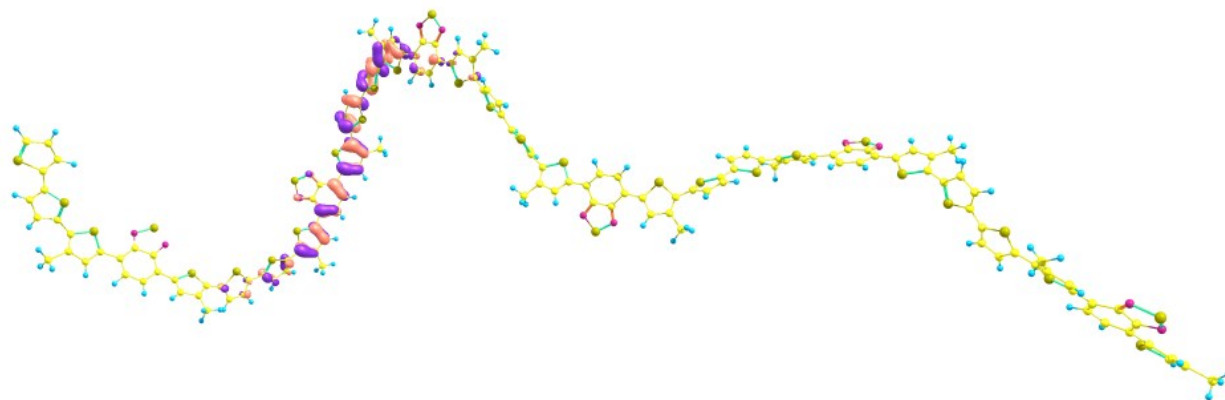
Figure S6. Distribution of the dihedral angles along the PBT4T-2OD (left) and PffBT4T-2OD (right) chains after MD simulations of the respective polymer stacks in solution at 100°C.

3. Binding energy

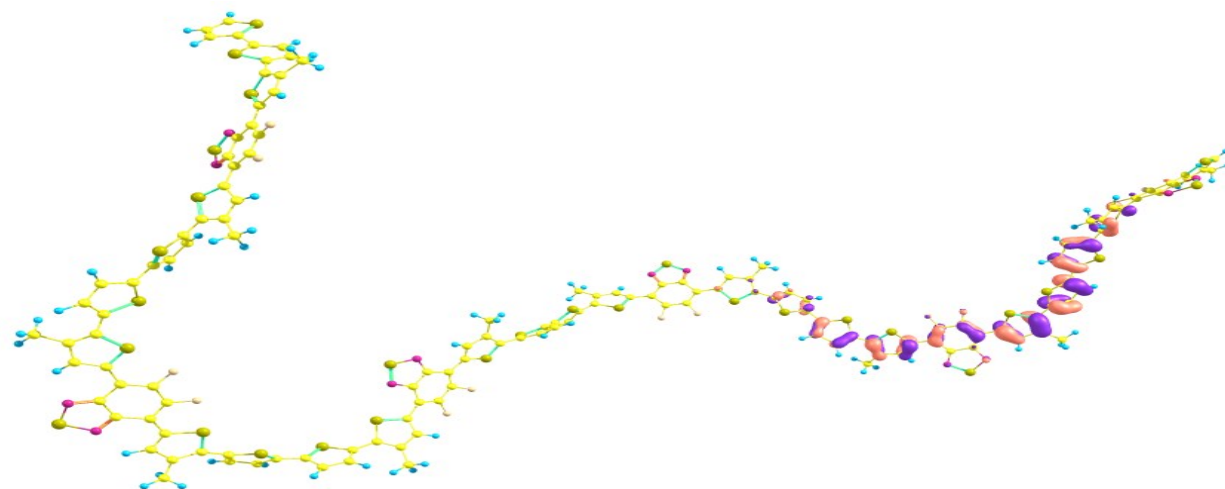
Table S1. Binding energies between two perfectly stacked dimer units, as calculated at the ω B97XD/6-31G** level of theory. A negative value indicates an attractive interaction.

Polymer	Binding Energy (in kcal/mol)
PBT4T-2OD	-56.7
PffBT4T-2OD	-58.6

4. Molecular orbital distributions



PBT4T-2OD



PffBT4T-2OD

Figure S7. HOMOs of PBT4T-2OD and PffBT4T-2OD, as calculated at the ω B97XD/6-31G** level of theory.

5. Sample selection for electronic coupling calculations

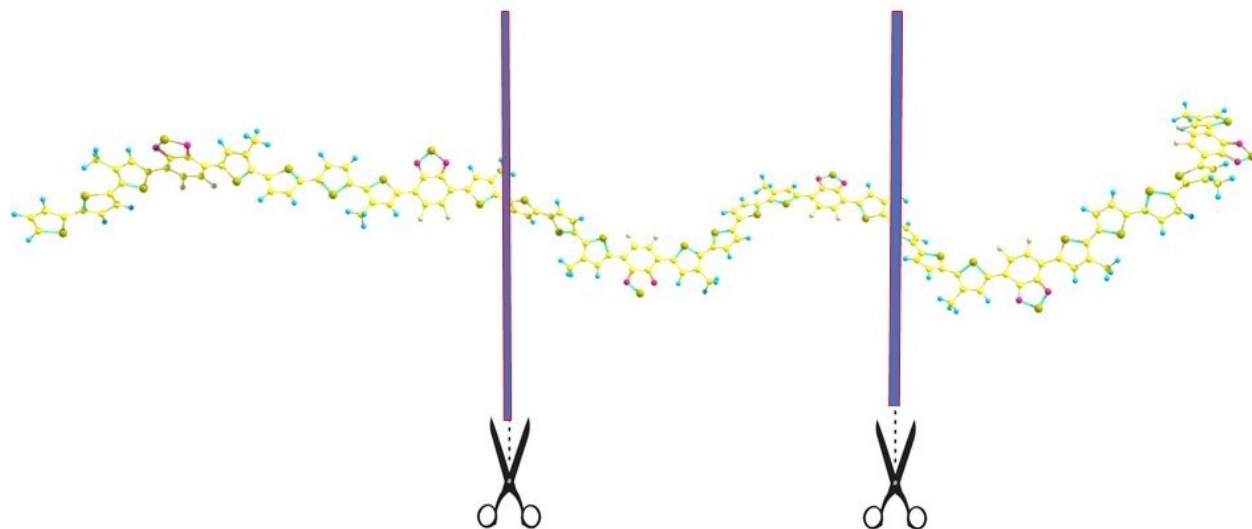


Figure S8. Illustration of the cut of a polymer chain with six repeat units into segments of two repeat units each.

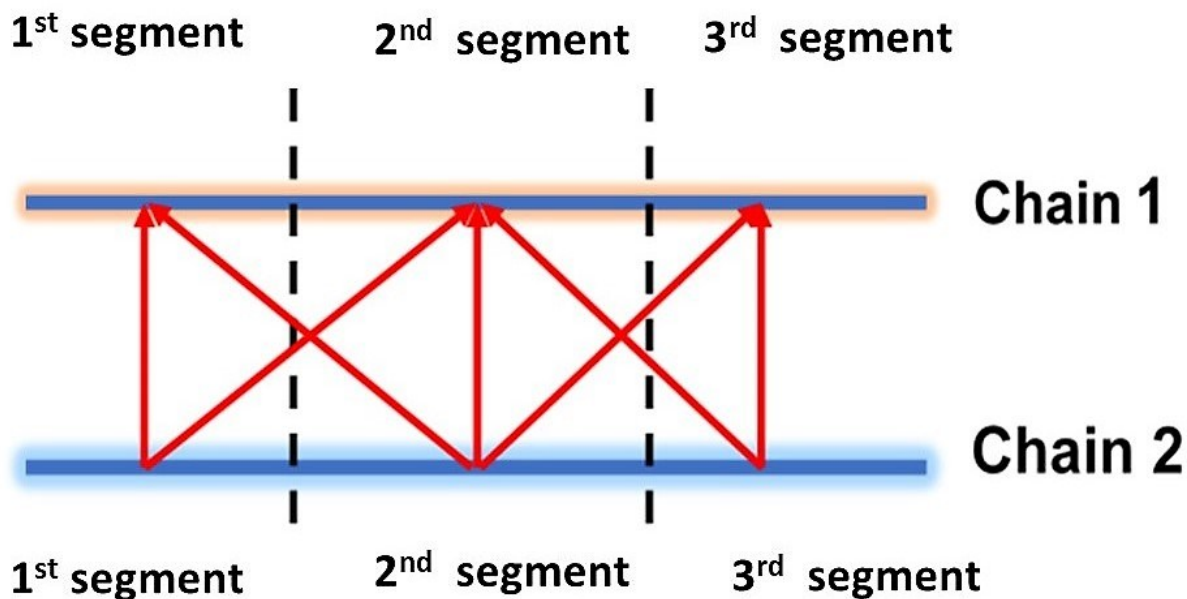


Figure S9. Illustration of the protocol for the calculation of the electronic couplings between adjacent chains.

For the electronic-coupling calculations, the polymer chains extracted from the stacks given by the MD simulations are cut into three segments of two repeat units each (see **Figure S8**). As shown above, every pair of adjacent chains in the polymer stacks are cut and the HOMO-HOMO couplings between the corresponding segments are calculated. We have considered the electronic couplings between the segments connected by arrows in **Figure S9**.