

Supplementary Information for

Decoupling Planarizing and Steric Energetics to Accurately Model the Rigidity of π -Conjugated Polymers

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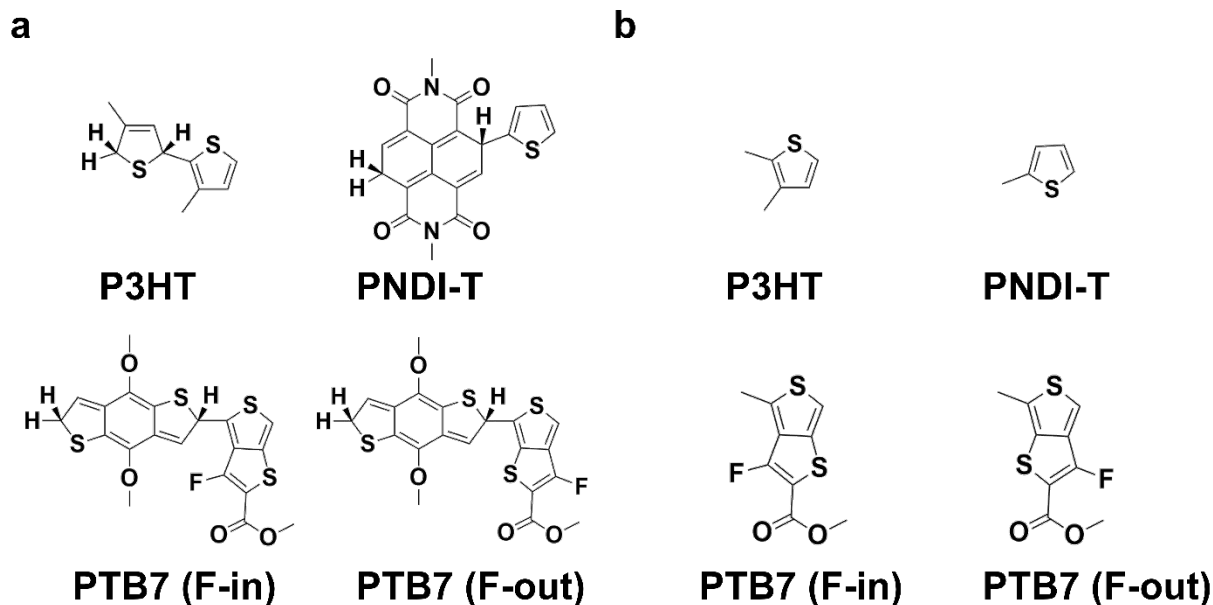


Figure S1. The (a) hydrogenated dimers and (b) methylated monomers used to decouple the nonbonded forces and delocalization energy.

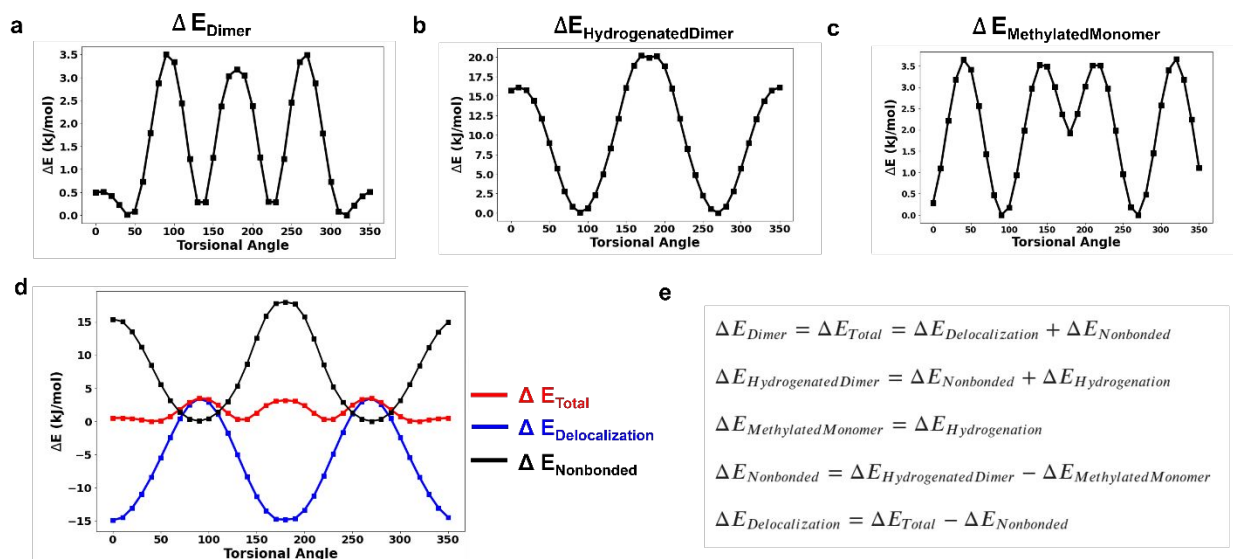


Figure S2. Torsional scans of the P3HT (a) dimer, (b) dimer with a hydrogenated monomer, and (c) methylated monomer as shown in the **Figure 1** schematic. From these torsional scans, the (d) energy of delocalization and nonbonded energy are isolated using the (e) system of equations relating the torsional scans of the modified chemical structures.

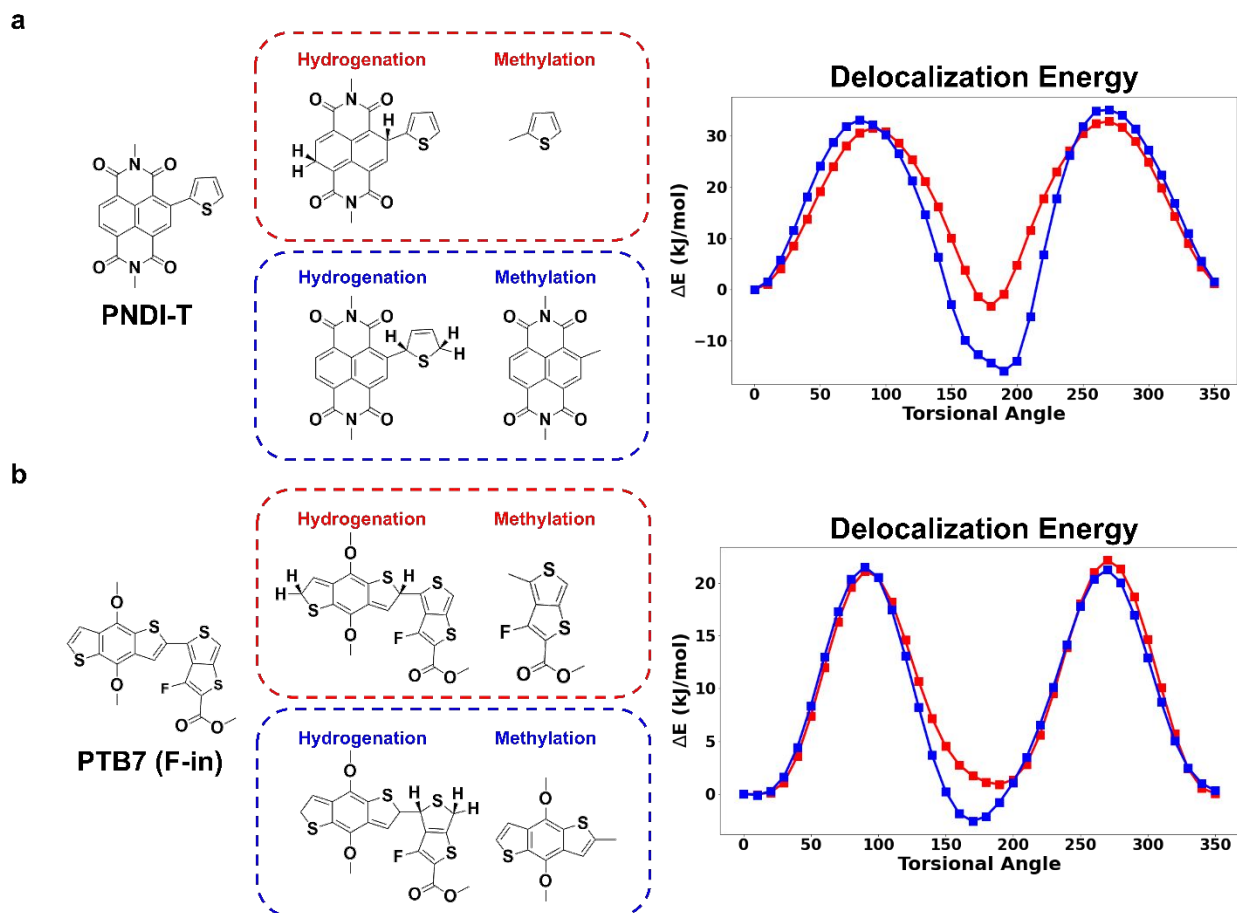


Figure S3. Comparison of the calculated delocalization energy when performing the structural modifications on the larger monomer (as done in this study, red) and the smaller monomer (blue) for (a) PNDI-T and (b) PTB7 (F-in). Hydrogenation of the smaller monomer results in a similar torsional profile to the hydrogenation of the larger monomer, but replacing the smaller monomer with a methyl group results in larger energetic penalties, particularly at high torsional angles. As a result, the calculated delocalization energy has deeper potential wells around 180°.

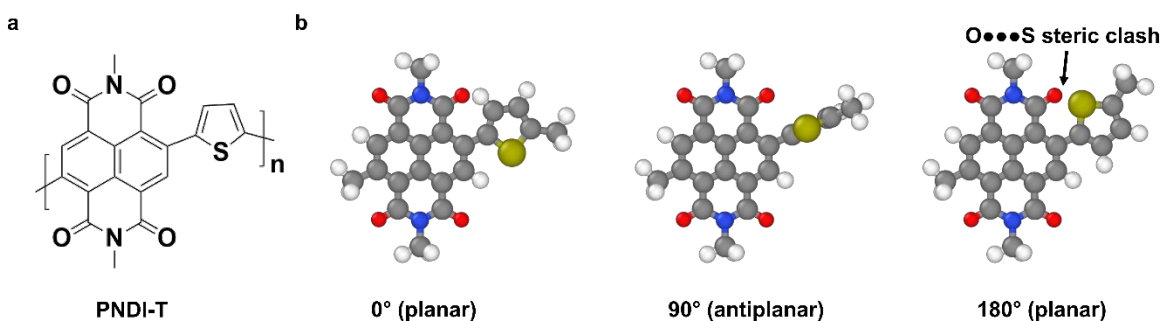


Figure S4. (a) Chemical structure of PNDI-T and the (b) resulting steric clash between the oxygen and sulfur at planarity. As a result, the calculated energies from the torsional scan differ greatly at 0° and at 180°.

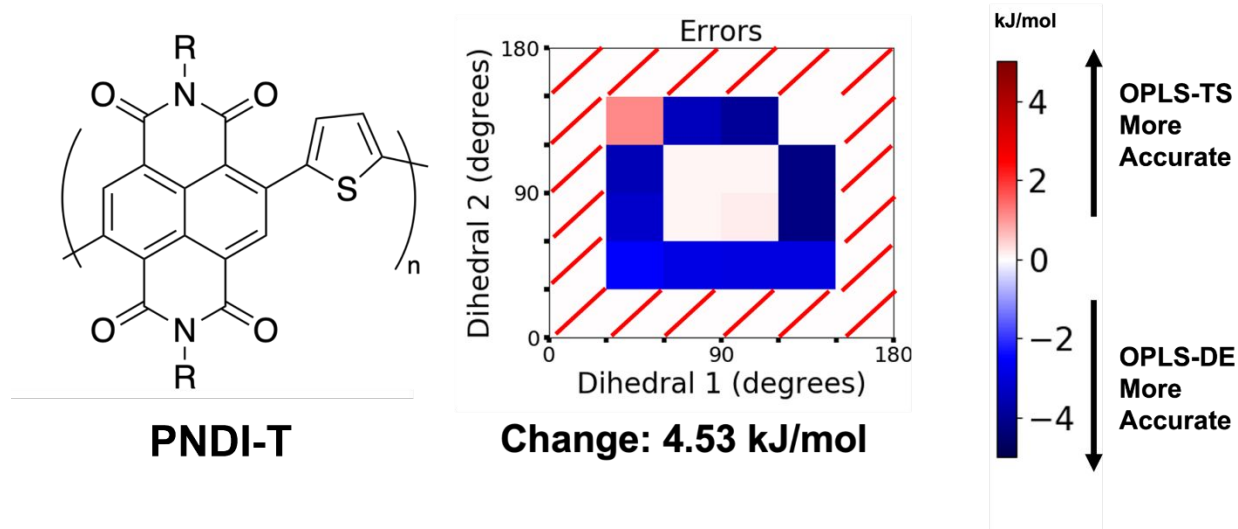


Figure S5. Comparison of the calculated energy of torsion of PNDI-T using OPLS-TS (with no corrections made for nonbonded interactions) and OPLS-DE methods. The relative accuracy of each method is determined by comparison to energies derived from quantum mechanical calculations. Red indicates that the OPLS-TS force field performs better, while blue indicates the OPLS-DE force field performs better. A red slash through a box indicates that no configuration of dimers with those dihedral angles were sampled. For the case of PNDI-T, a highly sterically hindered polymer, the OPLS-TS method that did not consider nonbonded interactions was more accurate than the OPLS-TS method that did.