Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information for

Why are S-F and S-O non-covalent interactions stabilising?

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Full FI-SAPT analysis of bithiophenes

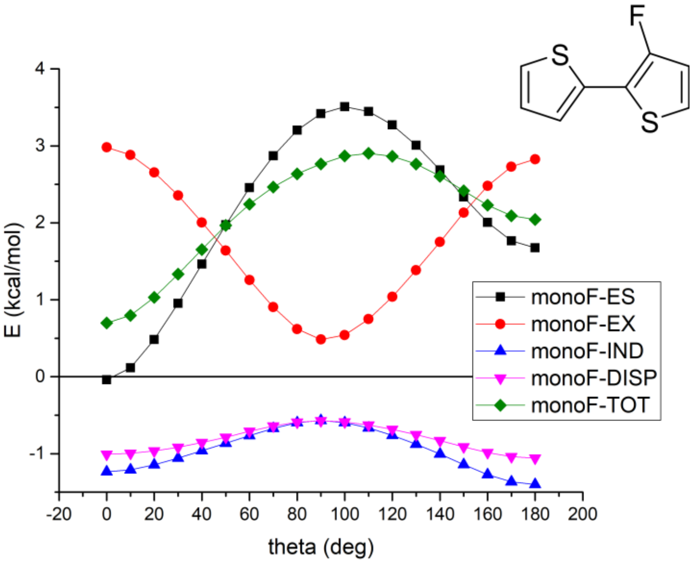


Figure S 1 FI-SAPT0/jun-cc-pVDZ analysis of monofluorobithiophene

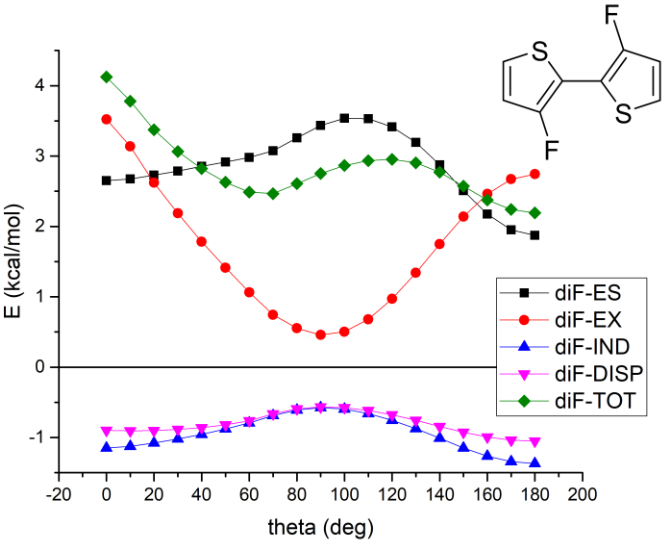


Figure S 2 FI-SAPT0/jun-cc-pVDZ analysis of difluorobithiophene

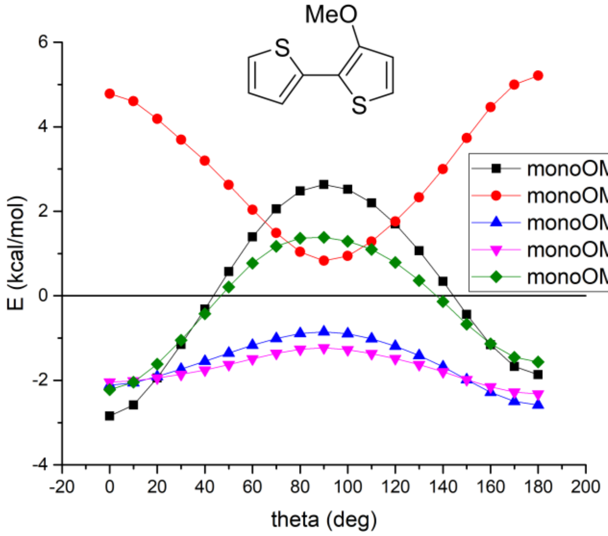


Figure S 3 FI-SAPT0/jun-cc-pVDZ analysis of monomethoxybithiophene

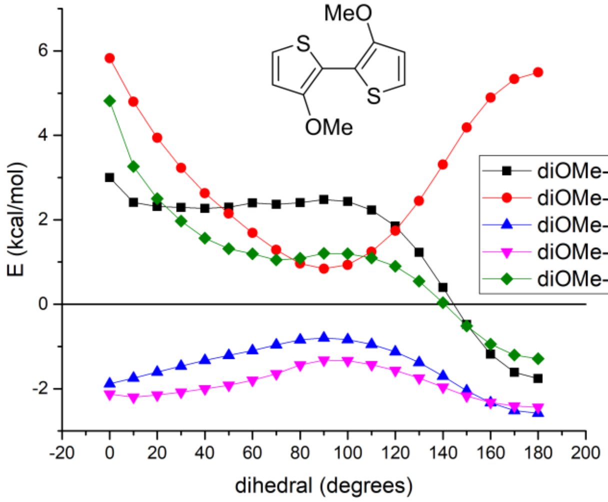


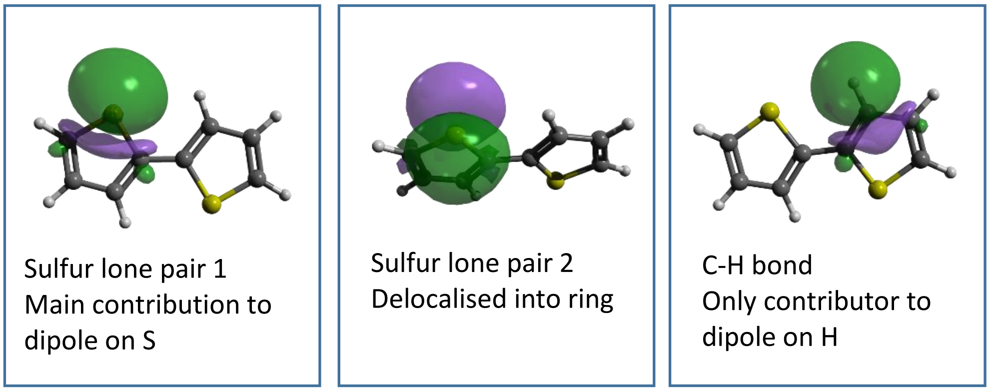
Figure S 4 FI-SAPT0/jun-cc-pVDZ analysis of dimethoxybithiophene

Natural bond orbital (NBO) analysis

NBO analysis was run using Gaussian 09 Rev D.01 interfaced to the NBO 6.0 program. Perturbation energy analysis was run with a cut-off of 0.1 kcal/mol in order to ensure intramolecular through-space interactions were reported. ‘Steric’, ‘dipole’, and ‘nce’ NBO keywords were used to obtain the relevant information.

Electronic structure of substituents

Natural bond orbitals of bithiophene structures which are of importance for this study are shown below. Atomic dipoles are largely dependent on one of these lone pairs, and augmented by polarities of adjacent bonds. Hyperconjugation stabilization by donation of lone pair electron density into σ* antibonding orbitals of the thiophene which the atom is directly bonded is observed for all lone pairs. Further, lone pair 1 of oxygen and lone pair 2 of fluorine donate electron density into the C-S σ* bond (pictured) of the other thiophene ring, to form a through space charge transfer stabilization. This is primarily due to overlap between the two orbitals, and so continues to rise with decreasing atomic distance. While this can be used to describe some of the stabilization, it needs to be taken into context with the simultaneously increasing steric exchange energy.

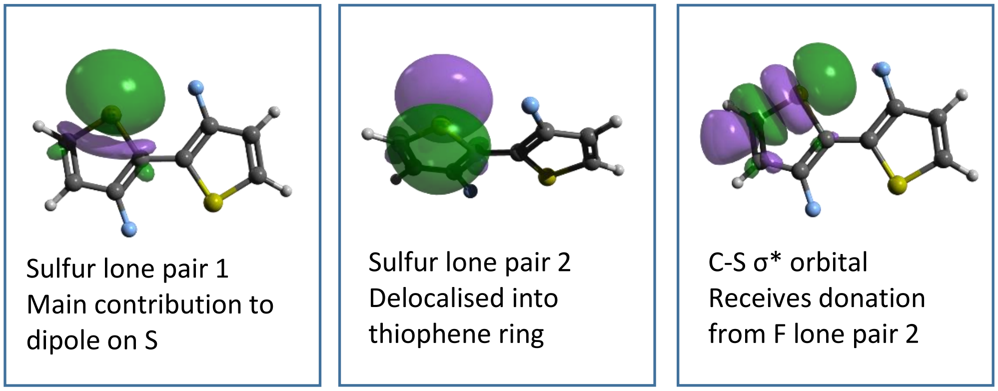


Sulfur lone pair 1
Main contribution to
dipole on S

Sulfur lone pair 2
Delocalised into ring

C-H bond
Only contributor to
dipole on H

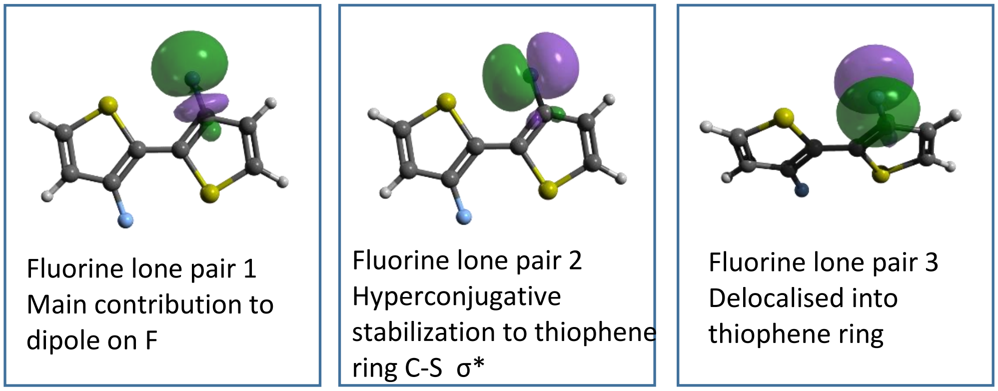
Figure S 5. Depiction of important NBO orbitals in bithiophene



Sulfur lone pair 1
Main contribution to dipole on S

Sulfur lone pair 2
Delocalised into thiophene ring

C-S σ* orbital
Receives donation from F lone pair 2

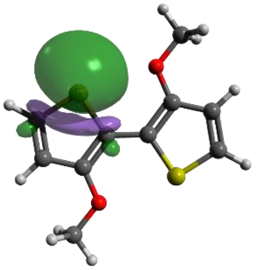


Fluorine lone pair 1
Main contribution to dipole on F

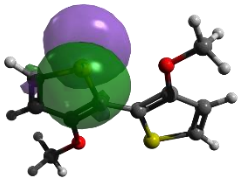
Fluorine lone pair 2
Hyperconjugative stabilization to thiophene ring C-S σ*

Fluorine lone pair 3
Delocalised into thiophene ring

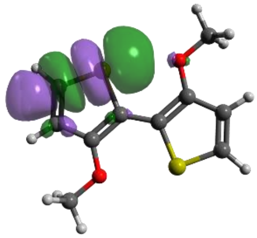
Figure S 6 Depiction of important NBO orbitals in difluorobithiophene



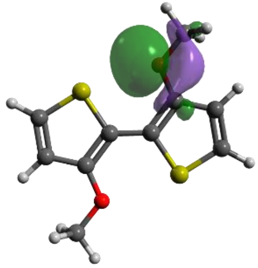
Sulfur lone pair 1
Main contribution to
dipole on S



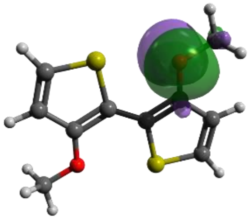
Sulfur lone pair 2
Delocalised into
thiophene ring



C-S σ* orbital
Receives donation
from O lone pair 1



Oxygen lone pair 1
Main contribution to
dipole on O +
hyperconjugative effects



Oxygen lone pair 2
Delocalised into
thiophene ring

Figure S 7. Depiction of important NBO orbitals in dimethoxybithiophene

Electrostatic interactions

Atomic charges were taken from the NBO natural coulomb electrostatics (NCE) analysis. Charge-charge potential energies were calculated using **Equation 1**:

$$V_{qq} = -\frac{1}{4\pi\varepsilon_0}\frac{q_1 q_2}{R}$$

Where q_i is the charge on atom *i*, and *R* is the distance between atoms. Coulomb constant, $1/4\pi\varepsilon_0$, is given as 332.0637 kcal Å / e mol. This gives the potential energy directly in kcal/mol using Angstrom and electronic charge units for *R* and q_i. All dipoles acting on a particular atom of interest were extracted from the NBO dipole analysis, using the natural localised molecular orbital (NLMO) derived vectors. This takes into account the delocalization effects of NBOs into one another. The vector sum of all dipoles acting on the atom was used as an overall atomic dipole, with the centre point assumed to be the atomic co-ordinate. For calculation, all dipole vectors are defined in a physical rather than chemical manner, i.e. the vector points in the direction from the negative pole to the positive pole, as reported by the NBO program.

Charge-dipole interactions were calculated using **equation 2**:

$$V_{qd} = -\frac{1}{4\pi\varepsilon_0}\frac{q_1 \mu_2}{R^2}cos\theta$$

Where q_i is the charge on atom *i*, μ_i is the strength of the dipole acting on atom *i*, θ is the angle between the vector connecting atomic centres and the summed atomic dipole vector. Dipole strength is converted from Debye to eÅ (1D = 0.20819434 eÅ) to give potentials in kcal/mol. Charge-dipole interactions were calculated in both directions (i.e. q_1-d_2 and q_2-d_1) taking care to reverse the atomic position vector to ensure the correct angle, and therefore correct sign, is obtained.

Finally, the dipole-dipole interaction is given by **equation 3**:

$$V_{dd} = \frac{1}{4\pi\varepsilon_0}\frac{1}{|r|^3}[\mu_1 \cdot \mu_2 - \frac{3\,(\mu_1 \cdot r)(\mu_2 \cdot r)}{|r|^2}]$$

Where μ_i and *r* are the dipole and position vectors, which are processed by their dot product, and |*r*| is the distance between atoms. Equation 3 can be re-written with scalar only terms as **equation 4:**

$$V_{dd} = \frac{1}{4\pi\varepsilon_0}\frac{\mu_1 \mu_2}{R^3}(cos\theta_{12} - 3\,cos\theta_1 cos\theta_2)$$

Where the terms are defined as in equation 2. The additional θ_{12} term is defined as the angle between the two dipoles. All cosine terms were derived from the dot product of the two vectors:

$$cos\theta = \frac{a \cdot b}{|a||b|}$$

Intermolecular model

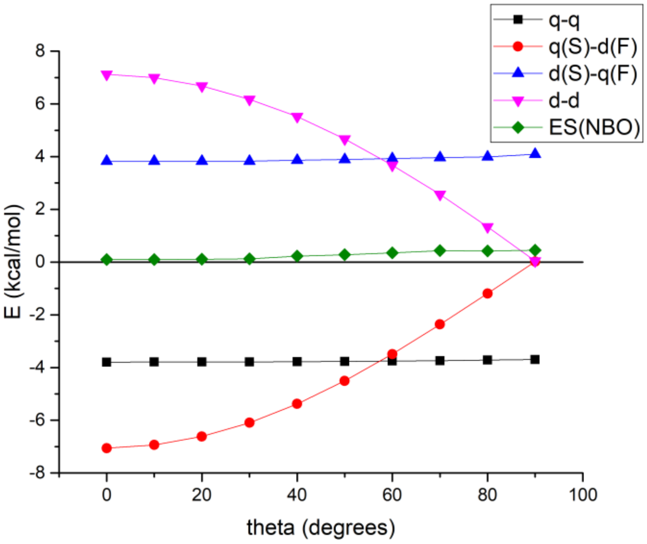


Figure S 8. NBO electrostatic analysis of intermolecular thiophene-fluoromethane interaction as a function of rotation of fluoromethane about its y-axis, where the fluorine atom is at the origin and S-F separation is 4 Å.

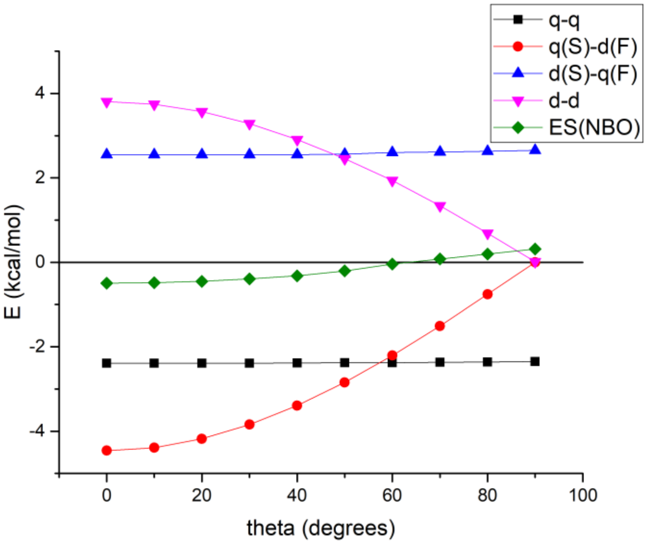


Figure S 9. NBO electrostatic analysis of intermolecular thiophene-fluoromethane interaction as a function of rotation of fluoromethane about its y-axis, where the fluorine atom is at the origin and S-F separation is 5 Å.

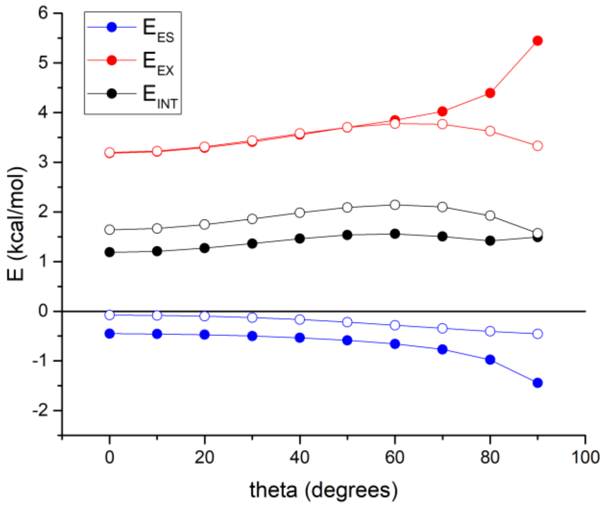


Figure S 10. SAPT0 (filled circles) and FI-SAPT (open circles) analysis of intermolecular thiophene-fluoromethane interaction as a function of rotation of fluoromethane about its z-axis, where the fluorine atom is at the origin.

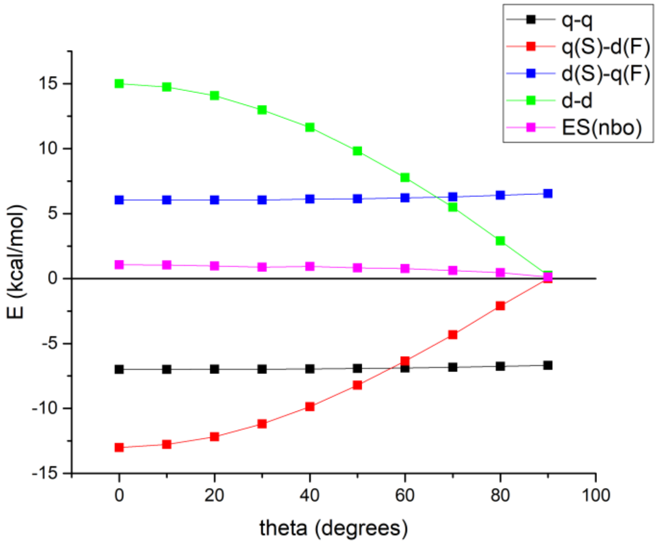
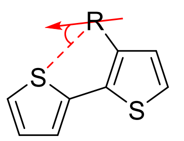
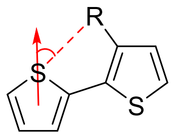


Figure S 11. NBO electrostatic analysis of intermolecular thiophene-fluoromethane interaction as a function of rotation of fluoromethane about its z-axis, where the fluorine atom is at the origin.

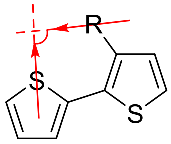
Commercially available polymers



θ_1 qS-dR angle



θ_2 dS-qR angle



θ_{12} dS-dR angle

Table S1. Interatomic distances, charges (a.u.) and dipole angles (degrees) of planar fragments of commercially available polymers

Structure	S…R distance (Å)	Charge S	Charge R	θ_1	θ_2	θ_{12}
diOMe bithiophene	2.86	0.44	-0.65	14	93	73
diF bithiophene	2.94	0.44	-0.40	86	33	61
PEDOT	2.94	0.44	-0.64	27	99	58
PCE10	2.84	0.41	-0.37	70	69	41
PCE11	2.72	0.45	-0.39	80	36	64
PCE12	2.76	0.53	-0.66	63	69	48
PDPP4T	2.94	0.49	-0.73	83	58	39

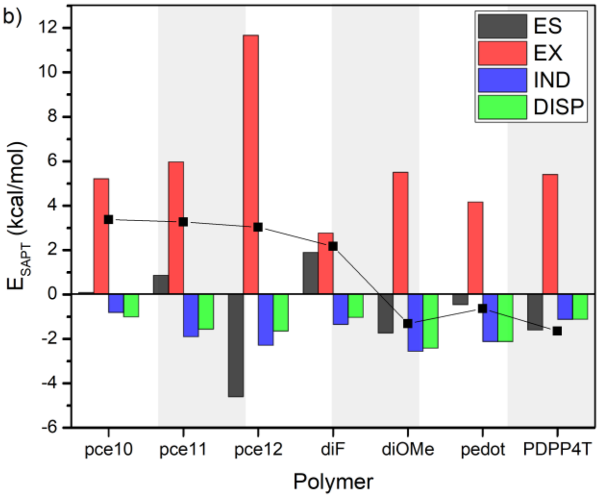


Figure S 12. FI-SAPT analysis of substructures of commercial polymers. Electrostatic energies may differ due to interacting fragmentation dipoles.

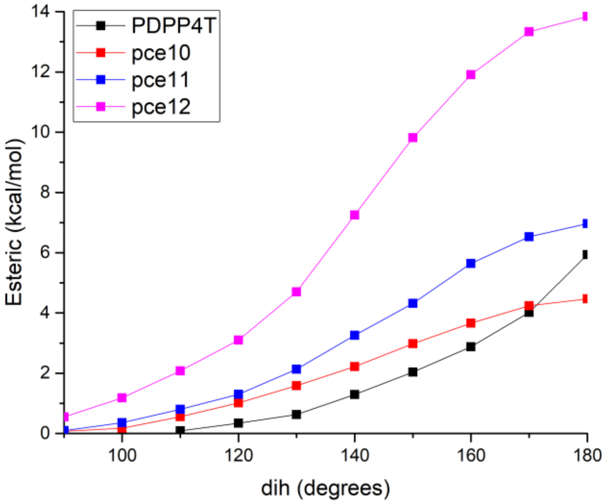


Figure S 13. NBO pairwise steric energies between S and O/F in commercial polymer fragments as function of dihedral angle.