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Supporting Information for:

Screening semiconducting polymers to discover design principles for tuning charge carrier mobility

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S1. Boltzmann sampling for generating polymer conformations and tail slope calculation

We outline here the method for Boltzmann sampling using the torsional potential energies and tail slope at the density of states (DOS) band edge, discussed in section 2.3 of the main paper. A polymer chain conformation is defined by a sequence of N monomers and N-1 dihedral angles ϕ_3 between the pairs of adjacent monomers (dimers) in the chain; the Boltzmann sampling is used to select the N-1 values for ϕ_3 . The selection of dihedral angles ϕ_3 is done using a Boltzmann distribution, given in SE1 where the system temperature T is set at 300 K and k_B is the Boltzmann constant.

$$p_{s} = \frac{e^{\frac{\varepsilon_{s}}{k_{B}T}}}{\sum_{t=1}^{N} e^{\frac{\varepsilon_{t}}{k_{B}T}}}$$
(SE1)

From the torsional scan, we take the dimer conformations obtained over the range of dihedral angles ϕ_3 , indexed in SE1 by s, and use their torsional (single point) energies ε_s with the Boltzmann distribution in SE1 to calculate a probability p_s of selecting the dimer conformation s. These probabilities p_s are then used to calculate a set of cumulative probabilities for each dimer. A random number generator with output [0,1) is then used to select the dihedral angle ϕ_3 for each adjacent monomer pair along the N monomer sequence, where the value of ϕ_3 selected corresponds to the one with cumulative probability that is the upper bound of the cumulative probability range the randomly generated number falls in between. This selection of ϕ_3 is repeated N-1 times for each chain to generate the polymer conformation with sequences of N monomers and N-1 dihedrals ϕ_3 .

The tail slope in the density of states (DOS) is calculated using the method of finite differences for first derivatives and is defined as the inflection point on the DOS closest to the band gap. The finite differences derivative for the DOS point $f(E_n)$ at the nth energy E_n in the sampled energy range is calculated as a forward difference, given in SE2.

$$\frac{df(E_n)}{dE} \approx \frac{f(E_n) - f(E_{n-1})}{E_n - E_{n-1}}$$
(SE2)

The energy at which this inflection point occurs is defined as the band edge energy $E_n = E_{EDGE}$.

S2. Comparison of polymer chain contour length and localisation length for examining finite size effects

In consideration of finite size effects associated with our use of defined chain lengths in our calculations, we examined the relative sizes of the contour length for the polymer chains and the localisation length at the band edge. We defined a structural repeating unit (SRU) length in Figure 8 of the main manuscript which can be used to estimate the contour length of the polymer chains, defined here as the SRU length multiplied by the total number of monomers divided by the number of monomers in the SRU. The result of the comparison is shown in Figure S1, where the contour length is usually at least 4 times the localisation length for each polymer.



Figure S1: Plot comparing the contour length of the polymer chains and their localisation length at the band edge.

S3. Outlier polymers

This section of the supporting information will discuss the outliers and anomalies seen in the correlation plots of the main paper.

Section 3.1, Figure 4

We show the DOSs calculated for both polymers 4 (IDT-BT) and 22 (IIG-dSeV), which show outlier points in Figure 4, and that of polymer 36 (C5C6-BT), our "best" polymer for comparison in Figure S2. Both polymers 4 and 22 show a slightly broader tail in the DOS than our comparison example of polymer 36. Thus, the calculation of the tail slope, which is a finite differences first derivative, will be affected significantly by slight changes in the tail, even if the overall broadness is similar across the DOSs of the polymers that show higher localisation length.



Figure S2: Comparison of DOSs for anomalous points polymers 4 and 22 (bottom) in Figure 4 (top left, polymers 4 and 22 highlighted) from the main paper with that of polymer 36 (top right).

Section 3.2, Figure 6

The density of states (DOS) and localisation length (LL(E)) plots below are those obtained for the polymers discussed in section 3.2 of the main paper which show notable shifts in the localisation length on reducing the basis set of the LMOM calculation. Each DOS is calculated with broadening σ =0.016 eV. For polymer 22 (DOS in Figure S4) in particular, we attribute the larger shift in its localisation length due to having a higher density of Selenium compared to other polymers, with 2 Selenium atoms per SRU, thus making any basis set reductions have a bigger effect on the localisation length. The slightly smaller but significant shift in localisation length on reducing the basis set for polymer 18 (DOS in Figure S3) is attributed to the high lying states beyond 5 eV in the DOS that results from having the SeVT monomer which disappear when the basis set is reduced.



Figure S3: DOS and LL(E) plots for polymer 18 calculated using the full and reduced basis sets.



Figure S4: DOS and LL(E) plots for polymer 22 calculated using the full and reduced basis sets.

Using the HOMO per monomer only basis set is especially detrimental for polymer 7 (DOS in Figure S5) due to the mismatch between the HOMO energies and symmetry of the CDT and mdFP monomers, shown in Figure S6, which results in weak coupling between these two MOs. The existence of the topmost band in the DOS thus depends on the coupling between the HOMO on CDT and HOMO-1 on mdFP, which ceases when the HOMO-1 per monomer is removed from the basis set.



Figure S5: DOS and LL(E) plots for polymer 7 calculated using the full and reduced basis sets.



Figure S6: The CDT HOMO (left), mdFP HOMO (top right) and mdFP HOMO-1 (bottom right) juxtaposed, with isolated monomer HOMO energies and raw coupling values for each possible coupling pair with the shown MOs.

Polymer 32 (DOS in Figure S5) exhibits a unique shift in localisation length which increases when the basis set is HOMO and HOMO-1 per monomer but decreases further back reducing the basis set to HOMO only per monomer. The main cause of these shifts in localisation length is the HOMO of the oPy monomer, which has been calculated by DFT as a σ -symmetry MO, shown in Figure S7, whereas all other MOs included in the full basis set for this monomer are π -symmetry. This problem is unique to polymer 32 and thus does not affect the interpretation of the results for the other polymers.



Figure S7: TOP: The HOMO and HOMO-1 of the oPy monomer. The HOMO is σ -symmetry as there is density along the plane of the monomer (bottom left), whereas the HOMO-1 is π -symmetry as there is no density along the plane of the monomer (bottom right). BOTTOM: DOS and LL(E) plots for polymer 32 calculated using the full and reduced basis sets.

Section 3.5, Figure 12

In Figure 12 of the main paper there is a single notable outlier point for the torsional entropy $^{S_{\phi}}$ and relative coupling fluctuation $\sigma_{i,i+1}^{rel}$ correlation plot corresponding to the DPP-oPy[A] dimer, highlighted in Figure S8. Figure S7 shows the oPy monomer has a sigma symmetry HOMO orbital calculated at B3LYP/3-21G* level of theory, which causes dimers with this monomer to display a non-cosine (sine-like) dependence of the HOMO-HOMO coupling on the dihedral angle, shown in Figure S8 for the DPP-oPy[A] dimer. While the torsional potential of the DPP-oPy[A] dimer has deep minima around $\phi=0^{\circ}$, the coupling profile in this region of the torsional potential has a varied slope leading to very high coupling fluctuation. Thus, the combination of features in the torsional potential and coupling profile results in a very strong outlier point.



Figure S8: Highlight of outlier point in Figure 12 of the main paper (left), and the torsional potential and coupling profile for the DPP-oPy[A] dimer (right).

S4. Full plot for curvature vs relative coupling fluctuation

The full plot for relative coupling fluctuation $\sigma_{i,i+1}^{rel}$ with each the curvature in the relative coupling profile measured at the global minima $d^2 J_{i,i+1}^{rel}(\phi)/d\phi^2$ in the torsional potential for each dimer is shown in Figure S9. The points which deviate significantly from the cluster below $\sigma_{i,i+1}^{rel}<0.5$ can be attributed to a non-cosine dependence of the coupling on the dihedral angle. The most significant deviations are from dimers with the oPy monomer, described previously in Supporting Information S3 and Figure S8. Another example for one of these dimers, CDT-mdFP[A], is shown in Figure S10.



Figure S9: Full plot for $d^2 J_{i,i+1}^{rel}(\phi)/d\phi^2$ vs $\sigma_{i,i+1}^{rel}$ including all dimers.



Figure S10: The relative torsion energy and relative coupling $J_{i, i+1}^{rel}$ plot for a dimer, CDT-mdFP[A] which displays non cosine dependence of the coupling on the dihedral angle ϕ .

S5. Lowest and highest relative coupling dimers

In Figures S10 and S11 are shown the 10 lowest and highest relative coupling fluctuation dimers from those in our sample. Dimers involving the oPy monomer, which is only relevant for polymer 2, were excluded from the sample when determining the 10 lowest and highest relative coupling fluctuation dimers due to the issue with oPy having a σ -symmetry HOMO, as described in section S2 Figure S7 of this Supporting Information.



Figure S11: Dimers with highest 10 relative coupling fluctuation