Supporting information for "Narrower Bands with Better Charge Transport: the Counterintuitive Behaviour of Semiconducting Co-Polymers"

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1. *Mobility averaging and activation energy*

To further justify the geometric averaging of the computed mobility performed in the main manuscript we report in Figure S1 the distribution of the mobility computed for different realizations of disorder to illustrate that the log of this mobility is normally distributed.

In the main manuscript we have attributed the increased mobility when increasing the parameter Δ to a decrease in the activation energy E_b, assuming that the relation $\mu \approx \mu_0 \exp(-E_b/k_B T)$ is valid. In Figure S2 we show that indeed the relation between $\log \mu$ and $1/k_B T$ is approximately linear. Additional analysis is discussed in the manuscript.

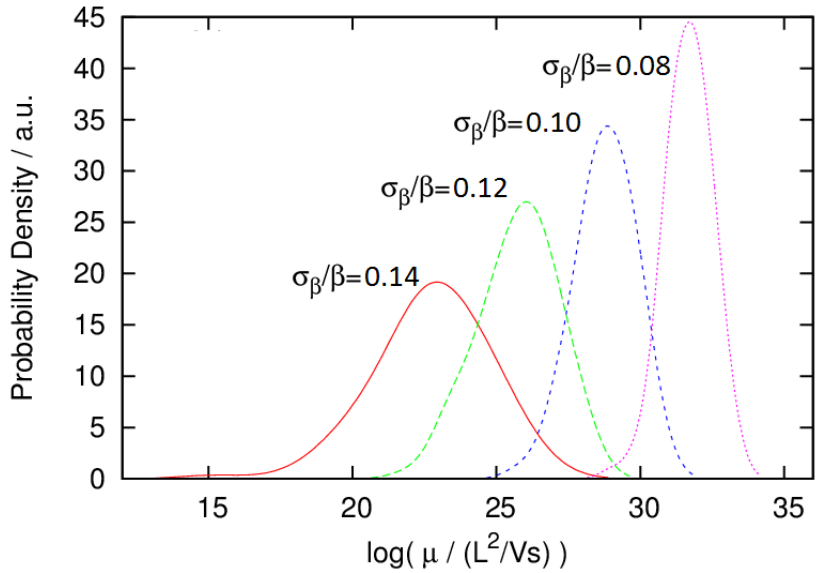

Figure S1. Distribution of computed mobilities for 100 realization of disorder with $\Delta = 0$ and different values of the parameter σ_β / β.

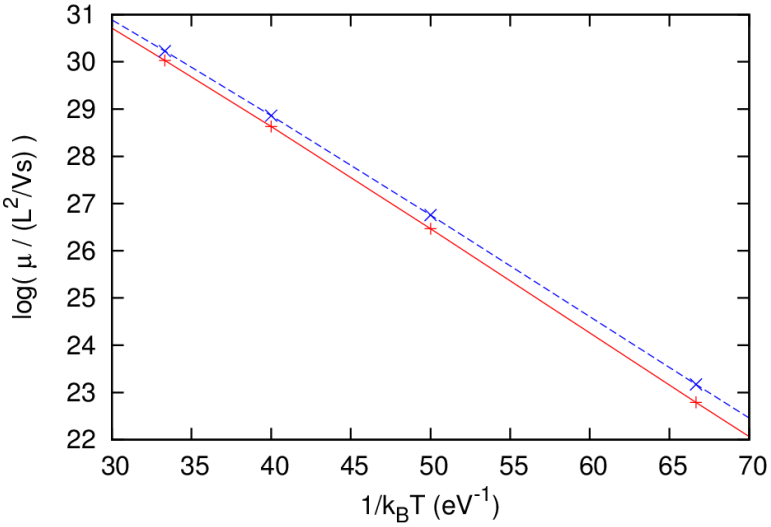

Figure S2. Arrhenius plot of the log of the average mobility plotted against the inverse temperature for $\sigma_\beta / \beta = 0.10$ and $\Delta / \beta = 0$ (solid line) and 1 (dashed line).

2. *Effect of on-site disorder*

To evaluate the effect of on-site disorder we considered the same Hamiltonian of the main manuscript

$$H_0^{el} = \sum_i \alpha_i |i\rangle\langle i| + \sum_i \beta_i |i\rangle\langle i+1| + h.c. \qquad \text{(S1)}$$

where β_i is, as before, a random variable distributed normally around an average value β with standard deviation σ_β. The on site energy was set to $\alpha_i = \Delta/2 + F_i$ for odd values of i and $\alpha_i = -\Delta/2 + F_i$ for even values of i with R_i a random variable distributed normally around an average value 0 with standard deviation $f\sigma_\beta$. f is therefore the strength of the on-site disorder relative to the off-diagonal disorder. Selected results of the main manuscript are recomputed with f varying between 0 (no on-site disorder) to $f = 1.5$ (on-site disorder 50% larger than off-diagonal disorder).

It was shown in ref. [1] that the DOS of an atomistic model of PPV can be reproduced rather well by considering only the off-diagonal disorder and a similar model was adopted in ref. [2]. The charge-dipole interaction $\mu_1 e / \varepsilon_r R^2$ between a large dipole of $\mu_1 = 1$ Debye at separation R =6 Å (monomers are often larger) and relative dielectric constant ε_r =2.5 is only about 0.03 eV confirming the indication of the detailed computation. Many polymers are formed by monomers possessing symmetry centers of inversion (e.g. PBTTT or DPP-based polymers), i.e. the net dipole of each monomer is negligible, which further reduces the ability to modulate the on-site energy of the neighboring chain via electrostatic interactions.

As illustrated by figure S3, the general shape of the DOS hardly changes with the addition of the off-diagonal disorder (because the disorder terms are always smaller than the parameters Δ and β dictating the shape of the DOS). The DOS tail becomes slightly broader with the addition of the on-site disorder.

Figure S4 reports the mobility computed as in Figure 2 (top) of the main manuscript but with the addition of a variable amount of on-site disorder. The computed mobility decreases only very slightly with the addition of a reasonable amount of on-site disorder (f<0.5) and the general trend of mobility increasing with increasing Δ is maintained until very high (probably unreasonable) values of the relative on-site disorder (f~1.0).

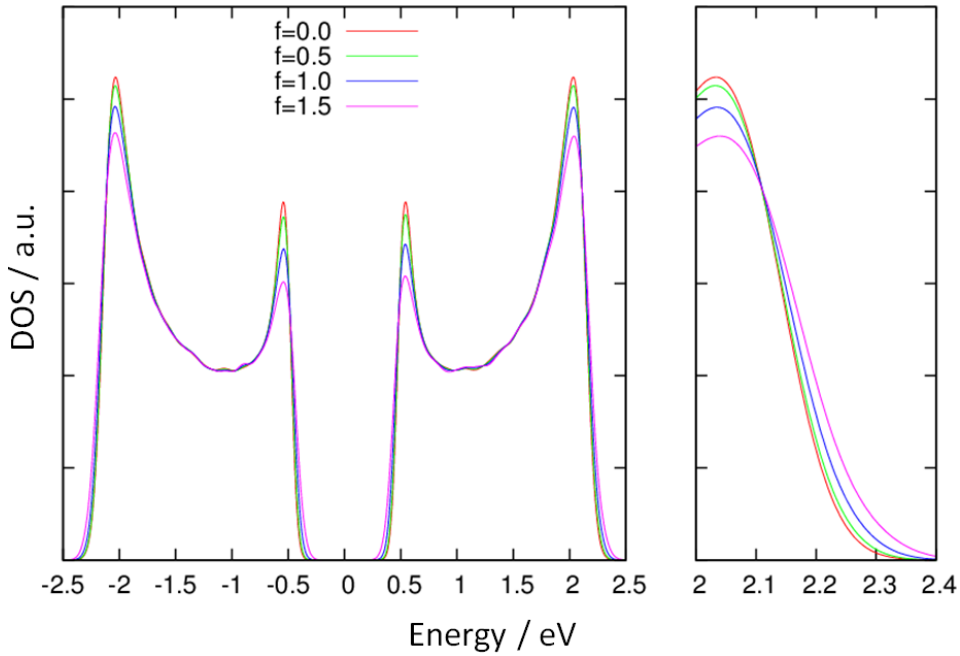

Figure S3. DOS computed with the model in eq. (S1) for different values of relative on-site disorder f on top of the off-diagonal disorder. In this plot Δ=1 eV, β=1 eV, σ_β=0.1 eV. The general shape of the DOS is not changed except for an additional broadening caused by the on-site disorder, more evident from the right panel.

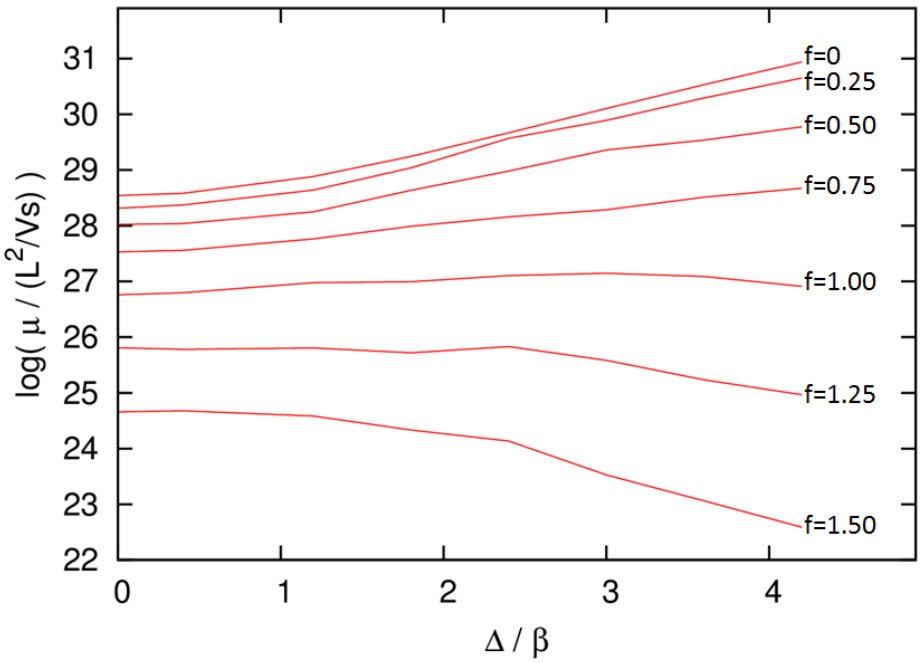

Figure S4. Effect of the inclusion of on-site disorder on the computed mobility as a function of the parameter Δ . In this plot β=1 eV, σ_β=0.1 eV and *f* is the strength of the on-site disorder relative to the off-diagonal disorder σ_β.

References

[1] T. Qin, A. Troisi, *J. Am. Chem. Soc.* **2013**, *135*, 11247-11256.

[2] R. Noriega, J. Rivnay, K. Vandewal, F. P. V. Koch, N. Stingelin, P. Smith, M. F. Toney, A. Salleo, *Nat. Mater.* **2013**, *12*, 1038–1044