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## Doping of semicrystalline conjugated polymers: dopants within alkyl chains do it better Electronic supporting information

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Figure S1: Convergence of the electronic properties with the size of a PBTTT polymer segment (measured by the number of repeating units n) for an isolated oligomer (right) and its complex with F4TCNQ (right). Left: Kohn-Sham (KS) and evGW gap for the isolated oligometry, along with the evGW gap extrapolated for an infinite chain (dashed horizontal line). Right: Kohn-Sham, evGW gap and lowest-energy optical excitation (S<sub>1</sub>) from BSE for the complex formed by F4TCNQ with oligomers of variable length. The insets shows a trimer (n = 3, 3-BTTT) and its complex with F4TCNQ, which corresponds to the system size chosen for the calculations in the main paper, in virtue of the almost converged electronic properties. Kohn-Sham calculations have been performed at the  $PBE0/6-311G^*$  level of theory. GW and BSE employed the Weigend universal Coulomb fitting basis[1] in the RI-V scheme.[2] All results have been obtained in the gas phase. These calculations have been performed on geometries obtained form an infinite PBTTT chain, obtained upon energy minimization in 1D-periodic DFT calculation at the PBE0/6-31G\* level (geometry optimization performed with the CRYSTAL17 code [3]). The inter-ring torsional angles of the polymer have been constrained in the structural relaxation, in order to impose the planarity of solid-state structures. The F4TCNQ position has been optimized (PBE0-D3/6-31G\* level) on top of a clamped PBTTT monomer extracted from the periodic calculation. The same dopant geometry has been retained for complexes formed with longer oligomers.



Figure S2: Tuning of the PBEh<sup>\*</sup>=PBEh( $a^*$ ) DFT functional against an embedded GW calculation for 3-BTTT-F4TCNQ complex. The Kohn-Sham gap equals the embedded GW value for a fraction of Hartree-Fock exchange  $a_x = a^* = 0.47$ . The rounded value  $a^* = 0.45$  has been used throughout the paper. The embedding in GW considered a polarizable medium with dielectric constant  $\varepsilon_r = 3.5$ , realized with a face-centered-cubic mesh of polarizable points, with lattice constant of 1.4 Å.

	PEN		PFP	
method	$\Delta_h$	$\Delta_e$	$\Delta_h$	$\Delta_e$
DFT/MM	1.22	-0.72	0.53	-1.21
GW/MM	1.34	-0.78	0.43	-1.45
CR	1.33	-0.61	0.43	-1.31

Table S1: Comparison of bulk hole (h, in the HOMO for GW) and electron (e, in the LUMO for GW) environmental energies (eV units) for pentancene (PEN) and perfluoropentacene (PFP) computed as total energy differences in DFT/MM, with the charge response model (CR)[4, 5] and with GW/MM. In DFT/MM and GW/MM the MM environment has been described with the CR model. DFT/MM energies have been computed as  $\Delta_{h/e} = U_{h/e} - U_0$ ), where  $U_{h/e}$  is the extensive energy of the QM/MM system with one h/e localized on a molecule (QM region), and  $U_0$  is the extensive energy of the neutral system. QM/MM energies have been computed through Eq. 1 in the paper. These results prove the good agreement among the different techniques, validating our approach to the calculation of total (extensive) energies in a QM/MM framework.



Figure S3: Rendering of the electron-averaged hole density (red) and holeaveraged electron density (blue) for the two lowest-energy optical excitations from embedded BSE-TDA calculations for the  $\pi$  (top) and  $\alpha$  (bottom) complexes. The corresponding energies are annotated in eV units. These excitations feature a charge-transfer character, with an electron being transferred from the dopant to the polymer donor to the dopant acceptor, starting from a weakly hybridized ground state ( $Q_{dop} \sim 0.2$  in both cases).

## References

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