Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

SUPPORTING INFORMATION

Ab initio modelling of local interfaces in doped organic semiconductors

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Supplementary tables and figures

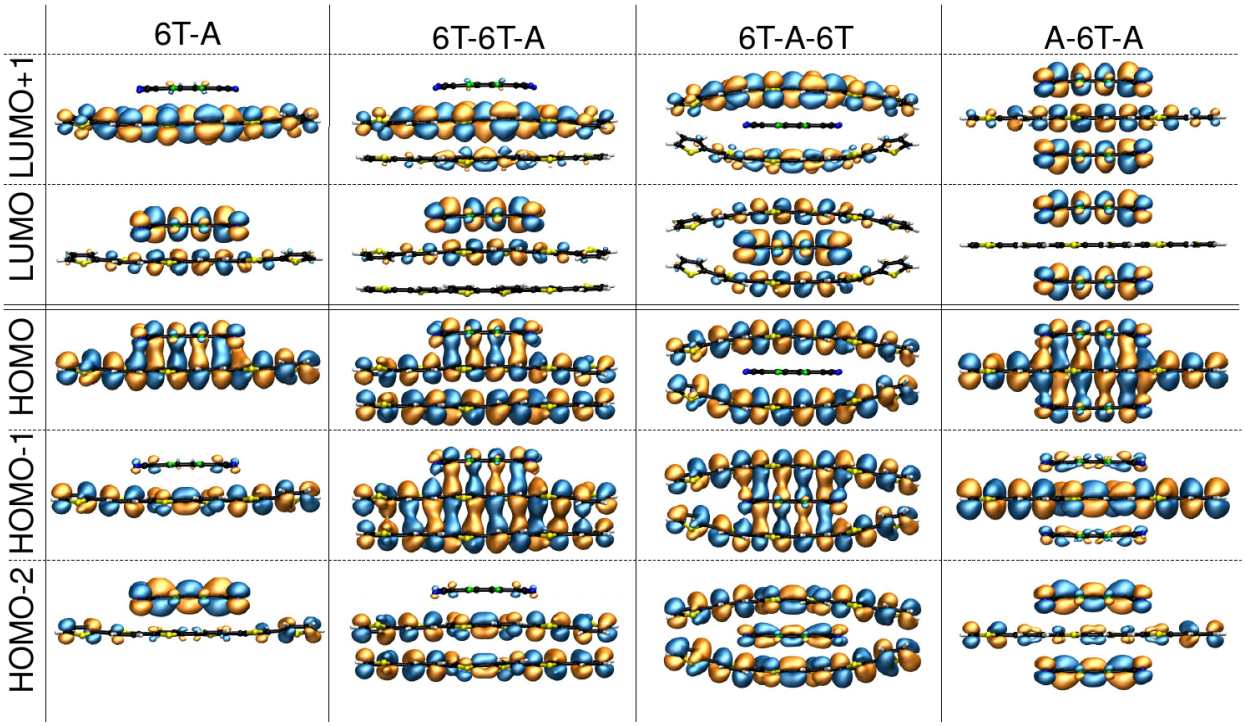


Figure S1: Molecular orbitals of 6T-F4TCNQ, 6T-6T-F4TCNQ, 6T-F4TCNQ-6T, and F4TCNQ-6T-F4TCNQ complexes, calculated with DFT using the CAM-B3LYP exchange-correlation functional.

Table S1: Energy levels in eV of the dimer and trimers computed from CAM-B3LYP (in parenthesis) and G_0W_0 on top of CAM-B3LYP.

	4T-A	**4T-4T-A**	**4T-A-4T**	**A-4T-A**
LUMO+1	-1.04 (-1.76)	-1.00 (-1.65)	-0.71 (-1.41)	-3.29 (-4.01)
LUMO	-3.02 (-3.84)	-2.96 (-3.72)	-2.79 (-3.50)	-3.58 (-4.40)
HOMO	-6.58 (-6.72)	-6.15 (-6.28)	-6.17 (-6.32)	-6.74 (-6.96)
HOMO-1	-7.55 (-7.62)	-6.61 (-6.76)	-6.38 (-6.58)	-7.69 (-7.83)
HOMO-2	-8.12 (-8.26)	-7.21 (-7.34)	-7.14 (-7.26)	-8.38 (-8.43)
	6T-A	**6T-6T-A**	**6T-A-6T**	**A-6T-A**
LUMO+1	-1.26 (-1.92)	-1.23 (-1.83)	-0.95 (-1.58)	-3.30 (-3.90)
LUMO	-3.04 (-3.77)	-2.97 (-3.64)	-2.82 (-3.45)	-3.60 (-4.33)
HOMO	-6.18 (-6.36)	-5.78 (-5.98)	-5.84 (-6.04)	-6.24 (-6.49)
HOMO-1	-6.84 (-6.98)	-6.23 (-6.43)	-5.98 (-6.21)	-6.88 (-7.09)
HOMO-2	-7.75 (-7.89)	-6.46 (-6.64)	-6.52 (-6.68)	-8.04 (-8.20)

Table S2: Charge transfer in the ground state quantified through the Bader analysis as the charge transferred from the donor(s) to the acceptor(s) in all the CTCs. The error associated to each value results from the numerical integration of the total charge density, enforced to be equal to the total number of electrons in the systems, which is performed on a finite spatial mesh.

	$\delta[e^-]$
4T-A	0.34 $\pm$0.03
6T-A	0.40 $\pm$0.06
4T-4T-A	0.37 $\pm$0.01
6T-6T-A	0.40 $\pm$0.03
4T-A-4T	0.46 $\pm$0.01
6T-A-6T	0.47 $\pm$0.04
A-4T-A	0.48 $\pm$0.03
A-6T-A	0.57 $\pm$0.08

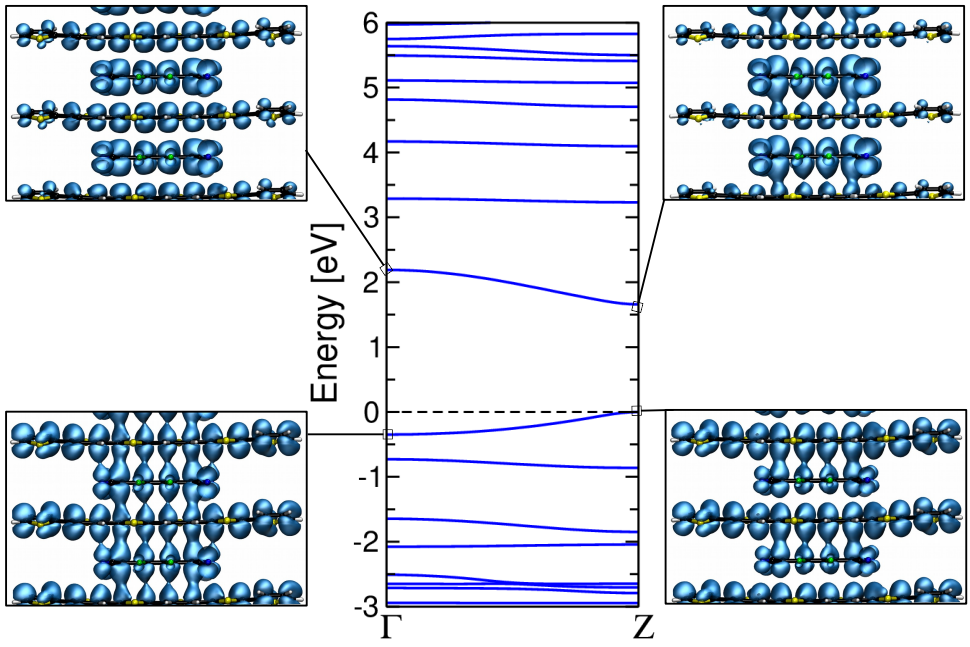


Figure S2: Quasi-particle band structure of the periodic 6T-F4TCNQ stack. The square modulus of the Kohn-Sham states at Γ (left) and at Z (right) are shown.

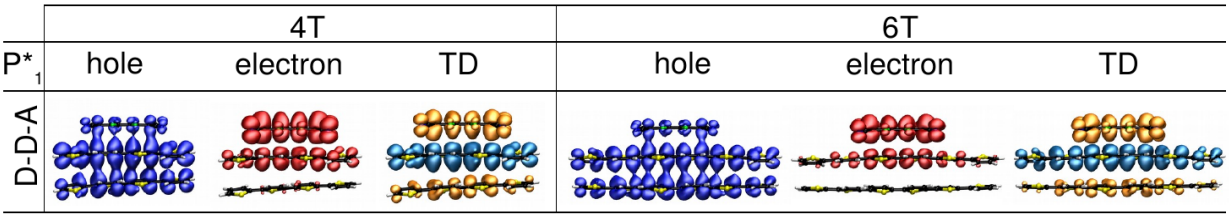
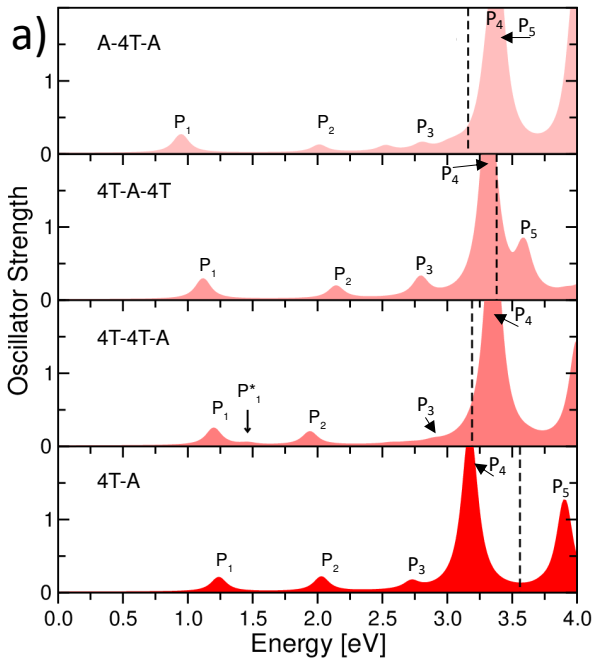


Figure S3: Hole, electron, and transition densities associated to excited state P_1^* of the D-D-A trimers.



	Excitation	Energy	OS	Composition	Weight
A-4T-A	P_3	2.80 eV	0.09	H-3 → L+1	75 %
	P_4	3.31 eV	0.48	H-8 → L+1	79 %
	P_5	3.38 eV	2.59	H → L+5	24 %
				H-2 → L	21 %
				H-8 → L+1	17 %
4T-A-4T	P_3	2.79 eV	0.26	H-4 → L	63 %
	P_4	3.32 eV	2.85	H → L+1	49 %
				H-4 → L	19 %
	P_5	3.59 eV	0.62	H-1 → L+1	76 %
4T-4T-A	P_{1*}	1.46 eV	0.03	H-1 → L	91 %
	P_3	2.89 eV	0.02	H-4 → L	35 %
				H-3 → L	18 %
				H → L+1	13 %
	P_4	2.97 eV	3.51	H → L+2	33 %
				H-1 → L+1	31 %
4T-A	P_3	2.72 eV	0.10	H-2 → L	49 %
				H → L+1	45 %
	P_4	3.17 eV	2.03	H → L+1	38 %
				H-2 → L	22 %
	P_5	3.90 eV	1.24	H → L+3	77 %

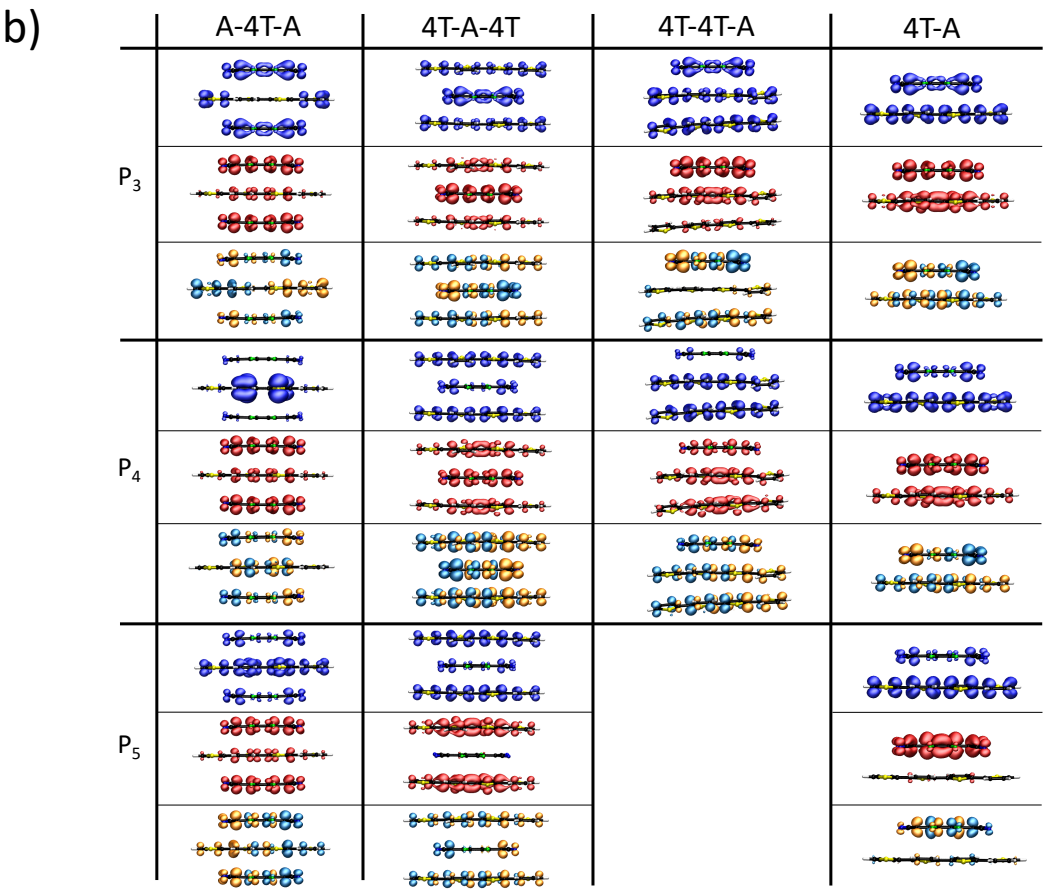
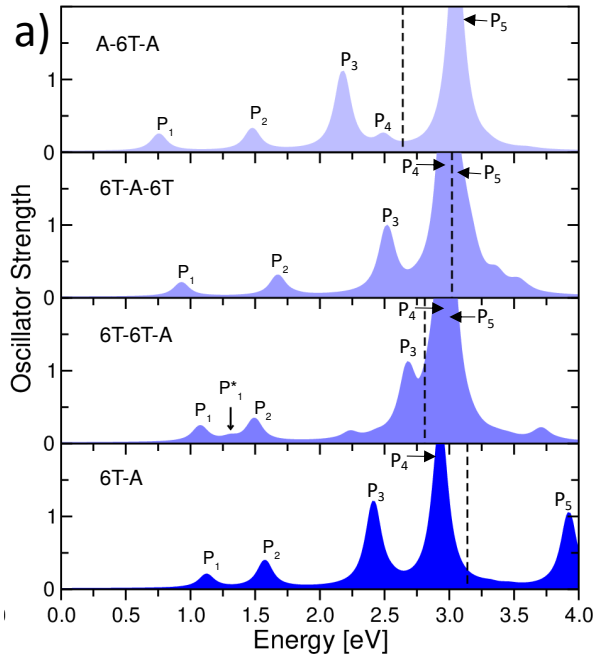


Figure S4: (a) Analysis of higher energy excited states beyond $P1$ and $P2$ for dimer and trimer CTCs composed by 4T donor species. In the spectra, the QP gap is marked by a vertical dashed line. (b) Hole densities (blue); electron densities (red); transition densities (light-blue for positive and orange for negative values) associated to the excited states reported in (a).



	Excitation	Energy	OS	Composition	Weight
A-6T-A	P_3	2.18 eV	0.99	H → L+2	85 %
	P_4	2.49 eV	0.16	H-2 → L+1	55 %
				H-4 → L	43 %
	P_5	3.05 eV	2.83	H-4 → L	27 %
				H-2 → L+1	27 %
				H → L+5	24 %
6T-A-6T	P_3	2.52 eV	0.88	H-4 → L	41 %
				H → L+1	27 %
	P_4	2.99 eV	3.95	H-4 → L	40 %
				H → L+1	37 %
	P_5	3.10 eV	0.49	H-1 → L+1	50 %
				H → L+1	20 %
6T-6T-A	P_{1*}	1.31 eV	0.05	H-1 → L	98 %
	P_3	2.68 eV	0.83	H-5 → L	39 %
				H-1 → L+1	31 %
	P_4	2.97 eV	3.51	H-5 → L	32 %
				H-1 → L+1	23 %
	P_5	2.98 eV	0.93	H-20 → L	30 %
				H-10 → L	22 %
6T-A	P_3	2.41 eV	1.15	H → L+1	78 %
	P_4	2.93 eV	2.24	H-2 → L	64 %
	P_5	3.92 eV	1.01	H → L+3	60 %

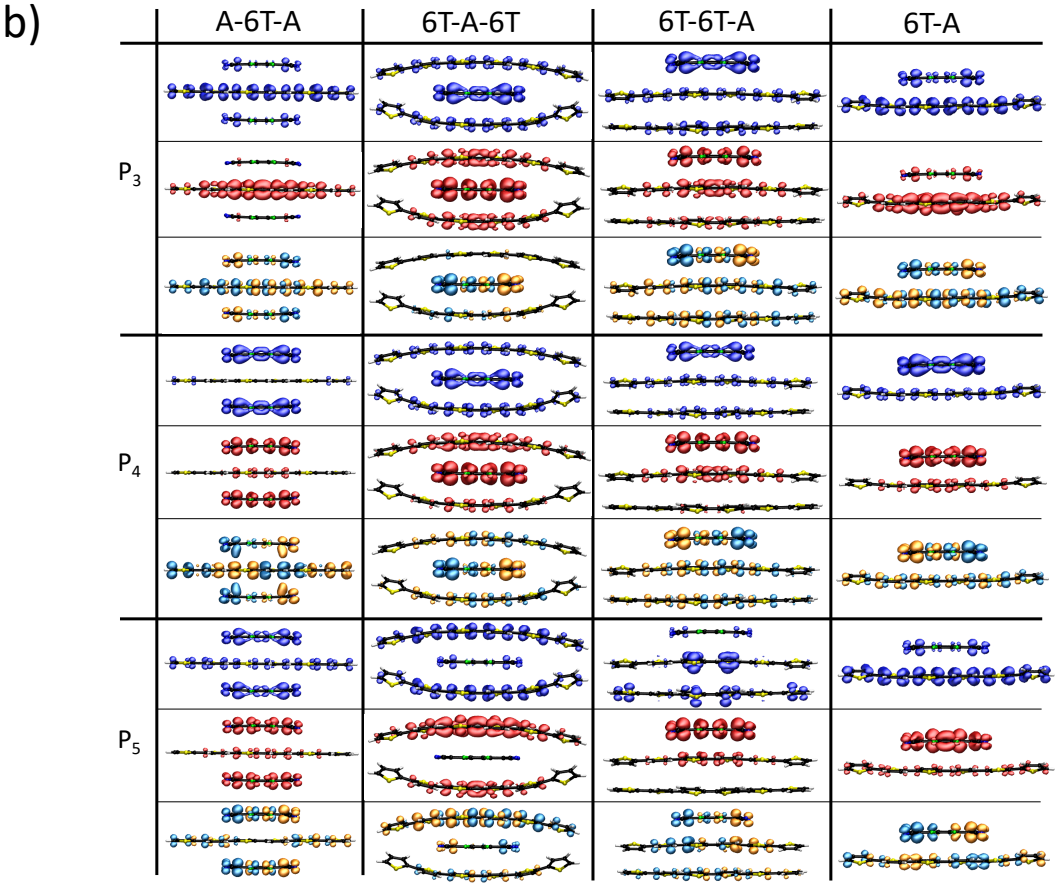


Figure S5: (a) Analysis of higher energy excited states beyond $P1$ and $P2$ for dimer and trimer CTCs composed by 6T donor species. In the spectra, the QP gap is marked by a vertical dashed line. (b) Hole densities (blue); electron densities (red); transition densities (light-blue for positive and orange for negative values) associated to the excited states reported in (a).