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p-Doping of polystyrene polymers with attached functional side-groups from solution

Supplementary Information

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1. Simulation of the ionization energy shift due to dopant and matrix molecule electrostatic interaction

As explained in the main manuscript, the simulations analyzed ionization energy E_I and electron affinity E_A of dopant and matrix molecules without consideration of charge transfer between dopant and matrix molecules. These calculations purely show the effect of electrostatic interaction between the matrix and the dopant molecules. The electronegative functional groups (fluorine atoms and cyano-groups) of the dopants lead to a -I effect which is responsible for the comparatively high E_I and E_A of the aromatic core of the dopant molecules. At the same time, they create high quadrupole moments as they are attached to the molecule in a symmetric way (δ- - δ+ - δ-). These quadrupole moments interact with the aromatic systems of neighboring molecules and further increase E_I and E_A. As a result, the E_I and E_A of pure F_4TCNQ and pure $HATCN_6$ systems are considerably lower than the E_I and E_A of the same molecules having only 20 mol% concentration in a matrix of MTDATA molecules. At the same time, they electrostatically interact with the MTDATA molecules and slightly increase their electron affinities. A MTDATA molecule surrounded only by other MTDATA molecules has a higher E_I than a MTDATA molecule surrounded by one or more dopant molecules. This is illustrated in Figure S1. Here, the HOMO energy distribution of MTDATA (as approximation of the E_I) is plotted as a function of the (center-of-mass) distance to the nearest dopant molecule (F_4TCNQ in the left panel and $HATCN_6$ in the right panel, respectively). At large MTDATA-dopant distances, a nearly Gaussian distribution of HOMO energies is visible, whereas at low distances this distribution is significantly shifted towards lower energies, therefore leading to higher ionization energies.

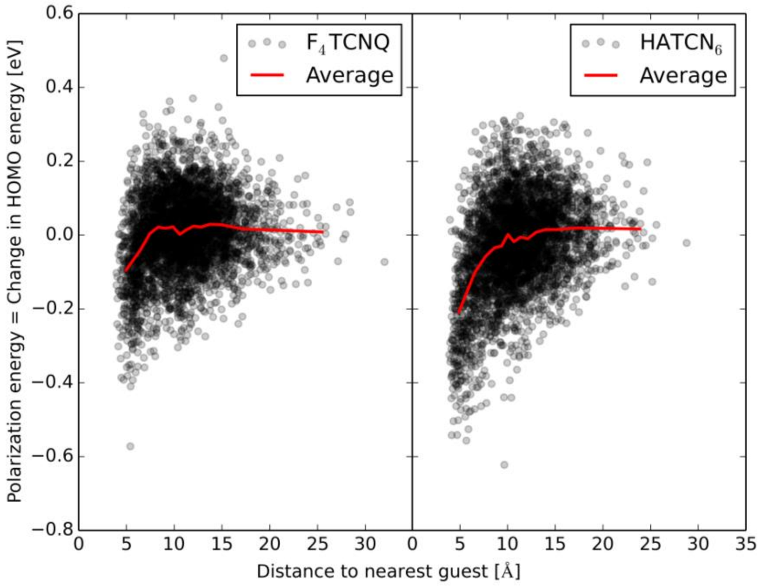

Figure S1: HOMO energy distribution of MTDATA plotted as a function of the (center-of-mass) distance to the nearest dopant molecule. At low MTDATA-dopant distances, the distribution is significantly shifted towards lower energies, therefore leading to higher ionization energies of MTDATA in the mixed system.

The data presented here only takes neutral molecules into account, whereas for the calculation of E_I and E_A in the manuscript explicit charges were added to the system and their polarization effect was evaluated. Different polarizabilities of dopant molecules and MTDATA molecules might play a role in the E_I/E_A calculation in our study, while in the distribution in Figure S1 only neutral molecules are taken into account and therefore only weak polarization and stabilization effects occur. This indicates that it is the electrostatic effect due to the quadrupole potential of the dopant molecules which is mainly responsible for the shift in ionization energy.

In all calculations in this study, the effect of depopulation of the HOMO density of states due to p-doping is not taken into account. This effect might even increase the overall shift in ionization energy. Nonetheless, due to the relatively low doping efficiency (< 1% of the MTDATA molecules are ionized), we assume the effect of depopulation of the highest occupied MTDATA orbitals in the disordered system as probably smaller compared to the electrostatic effects, which are shown to be strong enough to explain the experimentally observed shift of 0.07 ± 0.02 eV at a 20 mol% dopant concentration.

2. J-V curves of hole-only devices

Hole-only devices with an Ag / MoO_3 / HTL / MoO_3 / Ag architecture were employed to study the HTL conductivities. The respective J-V curves are depicted in Figure S2. The error bars mainly stem from small deviations in layer thicknesses which are summarized in Table S1.

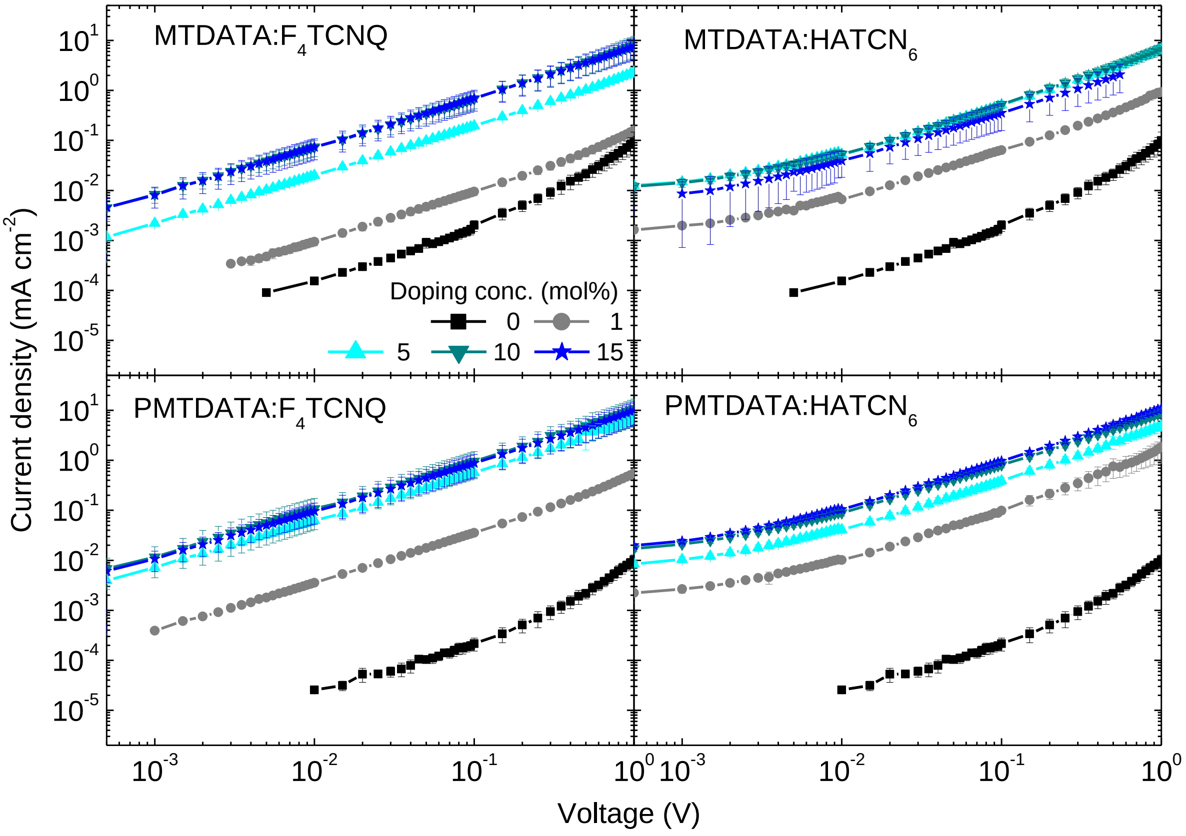

Figure S2: *J-V* curves of the hole-only devices comprising undoped or doped MTDATA and PMTDATA. The data was used for the conductivity analysis in Figure 5.

Table S1: Average and standard deviation of the layer thicknesses of the undoped and doped MTDATA and PMTDATA layers used in hole-only devices.

	Layer thickness (nm)
MTDATA:	
F_4TCNQ (0 mol%)	324 ± 4
F_4TCNQ (1 mol%)	232 ± 18
F_4TCNQ (5 mol%)	218 ± 11
F_4TCNQ (10 mol%)	208 ± 13
F_4TCNQ (15 mol%)	203 ± 5
$HATCN_6$ (0 mol%)	324 ± 4
$HATCN_6$ (1 mol%)	191 ± 11
$HATCN_6$ (5 mol%)	182 ± 17
$HATCN_6$ (10 mol%)	228 ± 60
$HATCN_6$ (15 mol%)	273 ± 29
PMTDATA:	
F_4TCNQ (0 mol%)	323 ± 12
F_4TCNQ (1 mol%)	174 ± 0
F_4TCNQ (5 mol%)	218 ± 5
F_4TCNQ (10 mol%)	214 ± 6
F_4TCNQ (15 mol%)	223 ± 6
$HATCN_6$ (0 mol%)	323 ± 12
$HATCN_6$ (1 mol%)	335 ± 48
$HATCN_6$ (5 mol%)	318 ± 25
$HATCN_6$ (10 mol%)	295 ± 4
$HATCN_6$ (15 mol%)	303 ± 12