Supporting Information

N-type Doping of the Organic Non-Fullerene Acceptor O-IDTBR Leads to Transistors with Electron Mobility in Excess of 1 cm² V⁻¹s⁻¹

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Figure S1. Representative output curves for pristine and n-doped O-IDTBR thin-film transistors: (a) Pristine O-IDTBR, (b) O-IDTBR:TBAF (1 mol%), (c) O-IDTBR:TBAF (10 mol%), (d) O-IDTBR:DMBI-BDZC(1 mol%). (e) O-IDTBR:DMBI-BDZC (10 mol%). (f) O-IDTBR:N-DMBI (0.01 mol%) and (g) O-IDTBR:N-DMBI(10 mol%).



Figure S2. O-IDTBR organic thin-film transistors n-doped with (a) TBAF, (b) DMBI-BDZC and (c) N-DMBI. Transfer characteristics are shown at best-performing doping concentration, as well as highly doped to detect any increases in off-current, I_{OFF}. Saturation mobility statistics are also shown for OIDT-BR devices with best-performing and high (10 mol%) doping concentrations. All mobility values are compared to pristine OIDT-BR devices. Statistics are taken over at least 13 devices for each system.



Figure S3. Statistics for (a) linear and (b) effective mobility for OIDT-BR thin-film transistors with best-performing concentrations of TBAF (1 mol%), DMBI-BDZC (1 mol%) and N-DMBI (0.01 mol%), compared to pristine devices. The effective mobility shown in (b) is extracted from the linear regime to provide a mobility values that averages over both mobile and trapped charges^{1,2}:

$$\mu = \frac{L}{WC_i V_D (V_G - V_{on})}$$



Figure S4. Atomic force microscopy images for highly doped O-IDTBR thin-films: (a) TBAF (10 mol%), (b) DMBI-BDZC (10 mol%) (c) N-DMBI (10 mol%). (d) Summary and comparison of (RMS) values for all films: pristine, best-performing and highly doped.



Figure S5. Scattering patterns of the pristine, best-performing and highly-doped O-IDTBR films in q-space: (a) Pristine O-IDTBR, (b) O-IDTBR:TBAF(1 mol%), (c) O-IDTBR:TBAF(10 mol%), (d) O-IDTBR:DMBI-BDZC(1 mol%), (e) O-IDTBR:DMBI-BDZC(10 mol%), (f) O-IDTBR:N-DMBI(0.01 mol%) and (g) O-IDTBR:N-DMBI(10 mol%). Only the pristine O-IDTBR and 10 mol% TBAF films show neat [110] orientation. All other films show a mixture of the [110] and [020] orientations.



Figure S6. The integrated plots along q_z -direction for (a) all films and (b) 0.01% and 10% N-DMBI films, after normalization for the (020) peaks.



Figure S7. N-DMBI-doped O-IDTBR configurations. An O-IDTBR molecule with an H- anion attached (shown with a black arrow), where C: gray, S: yellow, N: blue, O: red, H: white spheres. The total energies, calculated with the B3LYP exchange-correlation functional and the 6-31g* orbital basis, are also shown. Overall, this shows that, when a

hydride is transferred to an O-IDTBR molecule, there are many possible configurations (with comparable energies). This leads to the possibility of various effects on crystal morphology and orientation.



Figure S8. DMBI-BDZC-doped O-IDTBR. A diazocine (DMBI-BDZC) complex with an O-IDTBR molecule, where: C: gray, S: yellow, N: blue, O: red, H: white spheres. The O-IDTBR molecule retains more or less a flat configuration – akin to those found for certain structures shown in Figure S7 and Figure S8 where O-IDTBR has H- or F- species attached. This shows that, although the doping mechanisms are different for DMBI-BDZC when compared to N-DMBI and TBAF, the ensuing structure for the O-ITDBR (or a number of possible such structures) can be similar in the different cases. This in turn leaves open the possibility that the presence DMBI-BDZC, N-DMBI or TBAF could have similar effects in terms of O-IDTBR crystal orientation.



Figure S9. TBAF-doped O-IDTBR configurations. An O-IDTBR molecule with an F- anion attached (shown with an arrow), where C: gray, S: yellow, N: blue, O: red, H: white, F: green spheres. The total energies, calculated with the B3LYP exchange-correlation functional and the 6-31g* orbital basis, are also shown. Overall, this shows that, when a fluoride is transferred to an O-IDTBR molecule, there are many possible configurations (with comparable energies). This leads to the possibility of various effects on crystal morphology and orientation.



Figure S10. Three projections of the O-IDTBR crystal structure.



Figure S11. Electron affinities EA (on the left) and ionization energies IE (on the right) Gaussian DOS. The top insert shows table with calculated O-IDTBR gas-phase (EA_0 , IE_0) and solid state (EA_1 , IE) ionization energies and electron affinities, energetic disorder.



Figure S12. At the top, crystal surfaces and two directions with high mobility and diffusion tensor components (m^2) for electrons (blue) and holes (red). Atoms of hydrogen are omitted for better representation. At the bottom, displacements after $10^{-2}s$ for electrons and holes under applied electrical field in x and z directions.



Figure S13. Distribution of transfer integrals J for holes (on the left) and electrons (on the right).



Figure S14. Schematic representation of monocrystal of the IDTBR (on the left) and polycrystal with rotation about y axis (on the right).

 Table S1. Calculated charge mobility tensors and diffusion tensors for holes and electrons.

Electron	Hole	
μ (cm²/Vs)	μ (cm²/Vs)	

$\left(\begin{matrix} -\ 0.048 \\ 0.007 \\ 0.110 \end{matrix} \right)$	0.007 - 0.037 0.001	$ \begin{pmatrix} 0.110 \\ 0.001 \\ - 0.442 \end{pmatrix} $	$\begin{pmatrix} 0.004 \\ -0.001 \\ -0.017 \end{pmatrix}$	- 0.001 0.000 0.001	$\left. \begin{array}{c} -\ 0.017 \\ 0.001 \\ 0.123 \end{array} \right)$	
D (cm²)				D (cm²)		
(20.112 (2.592 – 79.117	2.594 0.033 – 9.191	– 79.113 – 9.196 306.381	$\begin{pmatrix} 0.522 \\ -0.044 \\ -3.621 \end{pmatrix}$	- 0.043 0.001 0.262	- 3.622 0.261 25.381)	

Table S2. The integrated intensity and integrated plots along q_z direction of Figure S6 (a) all films and (b) 0.01% and 10% N-DMBI films after normalization for (020) peaks.

	Form Factor	O-IDTBR:N-DMBI(0.01 mol%)	O-IDTBR:N-DMBI(10 mol%)
(020) Intensity	194.331	5.3	5.3
(110) Intensity	115.254	12.3	16.7
[020] %	N/A	20.4	15.8

The fraction of the [020] orientations is calculated by the intensity of corresponding scattering peak in q_z direction for both orientations. The grazing incident x-ray geometry allows to present statistical structural ratio in the large scale of films. The calculation also needs to consider the structure factors of corresponding indexes calculated by the single crystal structure. The fraction of [020] orientation can be calculated as:

$$[020]\% = \frac{I_{(020)}/F_{(020)}}{I_{(020)}/F_{(020)} + I_{(110)}/F_{(110)}}$$

Computer simulations of charge transport in crystalline O-IDTBR

1. Force-field parameterization and molecular dynamics simulations

Morphology simulations were performed using the GROMACS simulation package, with initial cell parameters and atomic positions taken from the analysis of the X-Ray scattering pattern. **Figure S10** shows three projections of the X-Ray-based supercell.

Molecular dynamics force filed is based on the OPLS-AA [^{3 4 5} S1–S3], with partial reparametrization of the missing improper and torsional potentials. Reparatmetrizations are performed by scanning the cross-sections of the potential energy surfaces using density functional theory (at B3LYP/6-311g(d,p) level).⁶ Quantum mechanical calculations are performed using the GAUSSIAN package. Since all Lennard–Jones parameters are taken from the OPLS-AA force field, the combination rules and the fudge-factor of 0.5 are used for 1–4 interactions. Atomic partial charges are computed via the CHELPG scheme.⁷ The long-range electrostatic interactions are treated by using a smooth particle mesh Ewald

technique. All calculations were performed in the NPT ensemble using the canonical velocity-rescaling thermostat ⁸ and the Berendsen barostat, ⁹ as implemented in the GROMACS simulation package.¹⁰ ¹¹ Supercells of 300 molecules were equilibrated for 10 ns at 400 K using a timestep of 1 fs.

2. Calculation of electrostatic contribution in the energy profile of the gas phase

With the molecular dynamics trajectories at hand, the solid state ionization energies and electron affinities of all molecules were evaluated in a perturbative way, starting from the gas-phase quantum chemical calculations and then taking into account environmental effects as a perturbation[13, STONE_BOOK], by adding the electrostatic and induction energies to the gas phase ionization potential of a molecule. Gas phase vertical ionization potential was calculated at the B3LYP/6-311g(d,p) level. The electrostatic and induction contributions to site energies were calculated self-consistently using the Thole model ¹² on the basis of the atomic polarizabilities and distributed multipoles obtained by the GDMA program ¹³ for cation, anion, and neutral molecules. This approach, in combination with an aperiodic inclusion of charges to a neutral periodic morphology, is available in the VOTCA-CTP.¹⁴ Results on energy calculations are summarized in **Figure S11**.

3. Calculation of charge transport properties

Charge mobilities were calculated by solving the master equation, with rates based on semi-classical Marcus rate equation. Kinetic Monte Carlo algorithm was used to provide the solution of the master equation for one charge (cation, anion) in an applied external field. Resulting mobility and diffusion tensors were averaged over ten molecular dynamics snapshots (see Table S1).

The difference in mobilities of holes and electrons can be seen in **Figure S13** from the displacements of carriers under fields applied in x and z directions. The most preferable direction for hole and electron transport is along the z-axis. This case corresponds to the carriers transport along the molecule and hopping through π - π -staking. We also observe high motilities along x-axis, which corresponds to π - π -stacks hopping.

Electronic coupling elements were evaluated for all molecule pairs in the neighbor list using the dimer projection method ^{15 16} by approximating the diabatic states of the molecular dimer with the highest molecular orbitals (HOMOs) of monomers. The neighbor list was constructed using a cutoff of 0.7 nm between the closest atoms in molecules. All calculations are performed at B3LYP/6-311g(d,p) level of theory using the Gaussian 09 ¹⁷ and VOTCA-CTP packages. To clarify the differences in carriers dynamics we plot a distribution of transfer integrals J for holes and electrons (see **Figure S13**). Distribution for holes is narrow and centered around zero, while for electrons distribution is broader. This indicates higher electron transport in the system.

3.1 Averaging of mobility tensor over different orientation of O-IDTBR crystals.

In order to get into account different orientations of crystal regions in polycrystal (see **Figure S14**) we do average along y-axis. At the first step we do elemental rotations in order to orient tensor in (110) and

(020) planes. For (110) we rotate $\mu_{e}^{[110]}$ about x-axis by 90° and for (020) – first about y by 90° and then about z by 45° , using rotation matrixes R, $\mu_{e}^{r} = R\mu_{e}R^{T}$. We then convert μ_{e}^{r} to the spherical coordinate system (r, θ, φ) and average it over angle φ using:

$$\left\langle \mu_{e}^{r,xz}\right\rangle = \int_{0}^{2\pi} R_{\varphi} \mu_{e}^{r} R_{\varphi}^{T} d\varphi, \ R_{\varphi} = \begin{pmatrix} \cos\varphi & -\sin\varphi & 0\\ \sin\varphi & \cos\varphi & 0\\ 0 & 0 & 1 \end{pmatrix},$$

giving:

$$\left\langle \mu_{e}^{r,xz}\right\rangle = (\mu_{e}^{r,x} + \mu_{e}^{r,z})/2.$$

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