Supporting Information

Side chain engineering in indacenodithiophene-*co*-benzothiadiazole and its impact on mixed ionic-electronic transport properties

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1 Experimental Details

Materials and measurements

All chemical used during this project were purchased from commercial suppliers or synthetised according to this document. ¹³C and ¹H NMR spectra were recorded at 101 MHz and 400 MHz respectively on a Bruker Avance III spectrometer. Chemical shifts (δ) are quoted to the nearest 0.01 ppm relative to tetramethylsilane, with the residual solvent peak CHCl₃ used as the internal standard (7.26 ppm) for ¹H NMR spectra. Coupling constants (J) are given to the nearest 0.1 Hz. Peak multiplicities for resonances are noted as: s, singlet; d, doublet; dd, doublet of doublets; t, triplet; m, unresolved multiplet. Chemical shifts (δ) are quoted to the nearest 0.1 ppm, with reference to the given solvent CDCl₃ (77.0 ppm) as the internal standard for ¹³C NMR spectra. Number-average (M_n) and weight-average (M_w) were determined by gel permeation chromatography (GPC) using a PhenogelTM 5 µm 10E4A, LC Column 300 x 7.8 mm running in chlorobenzene (CB) at 80°C and calibrated against narrow polydispersity polystyrene standards.

Column chromatography was carried out using VWR silica gel (40-60 μ m). Analytical thin layer chromatography was carried out on Merck Kieselgel 60 aluminium-backed silica plates, with visualization using short-wave ultraviolet light. Electrochemistry experiments were carried out using a PalmSens EmStat3+ potentiostat. UV-vis measurements were obtained from a Shimadzu UV-3600 Plus UV-Vis-NIR spectrophotometer; thin films were spin-cast from 10 mg/ml ODCB solutions at 80°C at 2000 rpm for 90 s then 8000 rpm for 30 s and subsequently dried in a vacuum oven at 40°C for 30 mins.

Monomer and polymer synthesis



Scheme S1: General synthetic procedure to obtain the IDTBT polymers.

Synthesis of 2,7-dibromo-4,9-dihydro-4,4,9,9-tetrahexadecyl-s-indaceno[1,2-b:5,6-b']-dithiophene (4) was carried out as reported in the literature without significant modifications.¹ The corresponding modifications to obtain the polar monomer and its corresponding polymerisation using different monomer ratios are described in the following section.

Synthesis of (2) 4,9-dihydro-(2,5,8,11-tetraoxahexadecan-16-yl)-indaceno[1,2-b:5,6-b']dithiophene

In a microwave vial 4,9-dihydro-s-indaceno[1,2-b:5,6-b']-dithiophene (0.92 g, 3.45 mmol) (1) was suspended in 20 mL of anhydrous DMSO with the addition of sodium tert-butoxide (1.99 g, 20.72 mmol, 6 equivalents). The mixture was stirred and heated at 80 °C under N₂ atmosphere by 30 min. 16-Bromo-2,5,8,11-tetraoxahexadecane (6.49 g, 20.72 mmol, 6 equivalents) was added dropwise to the reaction mixture. After the addition the reaction was heated to 90 °C overnight. The reaction mixture was then poured into ice-water and extracted with chloroform (3x50 mL), the combined organic phase washed with water, brine and dried over MgSO₄, the solvent was removed by rotary evaporation. The crude was purified by column chromatography on silica gel eluting with hexanes, to afford a beige solid (2.27 g, 55 %). ¹H NMR (CDCl₃, 400 MHz, ppm): 7.25-7.24 (m, 2H, Ar-H), 6.93-6.92 (d, 1H, Ar-H), 3.68-3.41 (m, 24H, CH₂), 3.38-3.34 (m, 6H, CH₃), 3.28 (t, 4H, CH₂-O), 2.02-1.74 (m, 4H, CH₂), 1.45-1.32 (m, 4H, CH₂), 1.20-1.06 (m, 4H, CH₂), 0.90-0.71 (m, 4H, CH₂). ¹³C NMR (CDCl₃, 101 MHz, δ (ppm)): 154.9, 153.1, 141.6, 135.6, 126.4, 121.6, 113.1, 72.0, 71.5, 70.7, 70.6, 70.6, 70.1, 59.2, 53.6, 39.1, 29.4, 26.5, 24.1.

Synthesis of (3) 2,7-Dibromo-4,9-dihydro-(2,5,8,11-tetraoxahexadecan-16-yl)-indaceno[1,2b:5,6-b']-dithiophene

In 100 mL round bottom flask (2) 4,9-dihydro-(2,5,8,11-tetraoxahexadecan-16-yl)-indaceno[1,2b:5,6-b']-dithiophene (2.27 g, 1.9 mmol) was solubilised with 50 mL of a mixture THF/DMF (2:1) under inert atmosphere (N₂). N-bromosuccinimide (0.743 mg, 4.18 mmol, 2.2 equivalents) was added to the solution. The reaction mixture was stirred at room temperature overnight and sheltered from the light. The mixture was poured into water and extracted with ethyl acetate (3x50 mL), the organic phases were combined, washed with water, brine and dried over MgSO4, and then the solvent was removed by rotary evaporation. The crude was purified by column chromatography on silica gel eluting with hexanes. The pure product was afforded as a dark oil which was dried under vacuum for 24 h (2.3 g, 89.5 %). ¹H NMR (CDCl₃, 400 MHz, δ (ppm)): 7.14 (s, 1H, Ar-H), 6.88 (s, 1H, Ar-H), 3.77-3.41 (m, 24H, CH₂), 3.39-3.33 (m, 6H, CH₃), 3.32-3.22 (t, 4H, CH₂-O), 1.99-1.71 (m, 4H, CH₂), 1.47-1.29 (m, 4H, CH₂), 1.22-1.06 (m, 4H, CH₂), 0.91-0.66 (m, 4H, CH₂). ¹³C NMR (CDCl₃, 101 MHz, δ (ppm)): 153.9, 152.1, 142.0, 135.6, 124.8, 113.1, 112.8, 72.0, 71.4, 70.7, 70.6, 70.6, 70.1, 59.1, 54.7, 39.0, 29.4, 26.5, 24.0.

General polymerisation procedure for IDTBT polymers

In a two neck round bottom flask the corresponding amount of the non-polar monomer 2,7-dibromo-4,4,9,9-tetrahexadecyl-4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithiophene was mixed with the corresponding proportion of the polar monomer 2,7-dibromo-4,9-dihydro-(2,5,8,11-tetraoxahexadecan-16-yl)-indaceno[1,2-b:5,6-b']dithiophene, 4,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)benzo[c][1,2,5]thiadiazole, Pd₂(dba)₃ (2 mol%), P(o-tol)₃ (4 mol%) and a drop of Aliquat 336. The monomers, catalyst and ligand were solubilised with degassed toluene and was further degassed with nitrogen for 30 min. Degassed Na₂CO₃ solution (1.0 M, 1 mL) was added to the mixture. The reaction mixture was degassed for 10 min then stirred and heated at 120 °C for 48 h. and then tributylstannylthiophene was added to the mixture solution and reacted for 6 h. Then, 0.3 ml of 2bromothiophene was added to the mixture and reacted another 6 h to complete the end-capping reaction. After the mixture was cooled to room temperature, it was precipitated into methanol. The solid was collected by filtration and further purified in a Soxhlet setup with methanol, acetone and hexane for 24 h each. Then the residue solid was redissolved in chloroform and precipitated into methanol. The polymer was filtrated and dried under vacuum overnight.

IDTBT-P0

The non-polar IDTBT polymer was prepared according to the general polymerisation procedure, using (**4**) 2,7-dibromo-4,4,9,9-tetrahexadecyl-4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithiophene (560 mg, 0.424 mmol) and (**5**) 4,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[c][1,2,5]thia-diazole (164 mg, 0.424 mmol). Yield: 0.46 g (84 %). ¹H NMR (CDCl₃, 400 MHz, δ (ppm)): 8.11 (s, 2H), 7.95 (s, 2H), 7.41 (s, 2H), 2.41-1.77 (m, 8H), 1.38-1.94 (m, 112H), 0.86 (t, 12H). GPC in CB at 80°C; *M_n*: 58 KDa, PDI: 1.2

IDTBT-P10

The 10% polar IDTBT polymer was prepared according to the general polymerisation procedure. Using (**4**) 2,7-dibromo-4,4,9,9-tetrahexadecyl-4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithiophene (617 mg, 0.467 mmol), (**3**) 2,7-dibromo-4,9-dihydro-(2,5,8,11-tetraoxahexadecan-16-yl)-indaceno[1,2-b:5,6-b']dithiophene (70 mg, 0.052 mmol), and (**5**) 4,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[c][1,2,5]thiadiazole (201 mg, 0.519 mmol). Yield: 0.28 g (42 %). GPC in CB at 80°C; M_n : 48 KDa, PDI: 1.2. ¹H NMR (CDCl₃, 400 MHz, δ (ppm)): see spectrum on page 8. * Polar content calculated at 10.7 % from integration of CH₂-O protons (~3.5 ppm, 8.63H) relative to corresponding value for IDTBT-P100 (80.6H).

IDTBT-P50

The 50% polar IDTBT polymer was prepared according to the general polymerisation procedure. Using (**4**) 2,7-dibromo-4,4,9,9-tetrahexadecyl-4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithiophene (547 mg, 0.414 mmol), (**3**) 2,7-dibromo-4,9-dihydro-(2,5,8,11-tetraoxahexadecan-16-yl)-indaceno[1,2-b:5,6-b']dithiophene (560 mg, 0.414 mmol), and (**5**) 4,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[c][1,2,5]thiadiazole (321 mg, 0.828 mmol). Yield: 0.40 g (37 %). GPC in CB at 80°C; M_n : 48 KDa, PDI: 1.3. ¹H NMR (CDCl₃, 400 MHz, δ (ppm)): see spectrum on page 9. * Polar content calculated at 50.9 % from integration of CH₂-O protons (~3.5 ppm, 41.0H) relative to corresponding value for IDTBT-P100 (80.6H).

IDTBT-P100

The 100% polar IDTBT polymer was prepared according to the general polymerisation procedure. Using (**3**) 2,7-dibromo-4,9-dihydro-(2,5,8,11-tetraoxahexadecan-16-yl)-indaceno[1,2-b:5,6-b']dithiophene (560 mg, 0.414 mmol) and (**5**) 4,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo-[c][1,2,5]thiadiazole (161 mg, 0.414 mmol). Yield: 0.50 g (93 %). GPC in CB at 80°C; M_n : 18 KDa, PDI: 1.8. ¹H NMR (CDCl₃, 400 MHz, δ (ppm)): see spectrum on page 9. * Integration ratio between aromatic IDT proton (7.4 ppm, 2H) and CH₂-O protons (~3.5 ppm, 80.6H) used to calculate polar content in IDTBT-P10 and IDTBT-P50; deviation from theoretical integration ratio (2H:68H) ascribed to different relaxation times.

¹H and ¹³C NMR spectra

¹H NMR (CDCl₃ 400 MHz), (2)



¹³C NMR (CDCl₃ 100 MHz), (2)



¹H NMR (CDCl₃ 400 MHz), (3)



¹³C NMR (CDCl₃ 100 MHz), (3)



¹H NMR (CDCl₃ 400 MHz), IDTBT-P0



¹H NMR (CDCl₃ 400 MHz), IDTBT-P10



¹H NMR (CDCl₃ 400 MHz), IDTBT-P50



¹H NMR (CDCl₃ 400 MHz), IDTBT-P100



2 Contact Angle Measurements

The IDTBT polymers were drop-cast onto silicon substrates from 10 mg ml⁻¹ ODCB solutions and dried overnight at room temperature. Images were captured using a Huawei P-smart POT-LX1 with a 13-megapixel camera (right). Contact angle measurements calculated using the sphere approximation, $\theta = 2 \arctan (2h/l)$ where h and l are the height and length of the droplet respectively (left). The images were processed using ImageJ and a contact angle plugin (https://imagej.nih.gov/ij/plugins/contact-angle.html).

| POLYMER | CONTACT ANGLE Ø (°) | PO | P10 |
|--------------|------------------------|-----|------|
| IDTBT-C16 P0 | 85 ± 0.3 | | |
| IDTBT P10 | 74 ± 0.2 | P50 | P100 |
| IDTBT P50 | 61 ± 0.6 | | |
| IDTBT P100 | 63 ± 0.3 | | |

Figure S1: Contact angles (left) and photographs (right) of IDTBT polymer films with a 20 μ L water droplet on the surface after 5 minutes of depositing.

3 Kelvin Probe Measurements

Kelvin Probe measurements were performed under ambient conditions using 2 mm diameter gold tip amplifier (Ambient Kelvin Probe Package from KP Technology Ltd.). Ten independent measurements were performed for each IDTBT polymeric film. The achieved work function standard error is about 20 meV. Calibration of the probe was performed against a freshly cleaved High Oriented Pyrolytic Graphite (HOPG) surface.



Figure S2: Surface work function of polymer films spin-cast onto p-doped silicon substrates at 2000 rpm for 90 seconds from 50 μ L of 10 mg ml⁻¹ ODCB solutions at 80 °C.

4 Cyclic Voltammetry



Figure S3: Thin film cyclic voltammograms of IDTBT polymers at scan rates of 50 (left) and 5 mV s⁻¹ (right); films were drop-cast onto glassy carbon electrode from 1 mg ml⁻¹ CHCl₃ solutions. Glassy carbon, platinum wire and Ag/Ag⁺ was used as working, counter, and reference electrodes and 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile was used as the supporting electrolyte.

5 Grazing-Incidence Wide-Angle X-ray Scattering

Grazing-Incidence Wide-Angle X-ray Scattering measurements were performed at the Advanced Photon Source Beamline 8-ID-E with 10.91 keV photons in a beam 200 μ m x 10 μ m (horiz, x vert.) incident on the sample in a vacuum environment at an incident angle of 0.14°.² A Pilatus 1M detector (Dectris) positioned 217 mm from the sample captured the scattered x-rays with exposure times of 5 s. Corrections for detector uniformity and efficiency, polarization, and geometry, and integrations were performed with the Matlab-based package GIXSGUI.³



Figure S4: In-plane (left) and out-of-plane (right) linecuts of GIWAXS scattering patterns for the IDTBT polymer series.

6 Organic Electrochemical Transistor Characterisation

Thin IDTBT polymer films were cast and patterned to define the OECT channel area ($W/L = 1000 \mu$ m/30 μ m or 100 μ m/10 μ m). An aqueous solution of 0.1 M NaCl and non-aqueous solutions of 0.1 M LiOTf and 0.1 M NaClO₄ in acetonitrile were used as the electrolytes. An Ag/AgCl pellet was used as the gate electrode. To obtain output curves in 0.1 M NaCl solution, the drain voltage was scanned between 0 and -0.7 V, while the gate voltage was fixed at different biases between 0 and -0.7 V. To obtain transfer curves, the gate voltage was scanned between 0 and -0.7 V, while the drain current was fixed at -0.7 V. The transfer curves of IDTBT-P10, IDTBT-P50, IDTBT-P100-based OECTs in 0.1 M LiOTf and 0.1 M NaClO₄ acetonitrile solutions were obtained at source-drain voltage $V_{DS} = -0.6$ V while the gate voltage (V_G) was scanned between 0.05 V and -1.5 V (-2.0 V). We also tested the device performance using the ionic liquid [EMIM] [TFSI] as the electrolyte and Au or PEDOT:PSS as the gate electrode materials.



Figure S5: Electrical performance of IDTBT-P0, IDTBT-P10, IDTBT-P50, and IDTBT-P100-based OECTs in 0.1 M NaCl aqueous electrolyte. The scan rate is 100 mV/s.



Figure S6: Electrical performance of IDTBT-P10, IDTBT-P50, and IDTBT-P100-based OECTs in 0.1 M LiOTf and 0.1 M NaClO4 acetonitrile electrolytes. The scan rate is 100 mV/s.



Figure S7: *Transfer curves of IDTBT-P0, IDTBT-P10, IDTBT-P50, and IDTBT-P100-based transistors with ionic liquid [EMIM] [TFSI] as the electrolyte and Au as the gate electrode.*



Figure S8: Transfer curves of OECTs based on IDTBT-P0 (a), IDTBT-P10 (b), IDTBT-P50 (c), IDTBT-P100 (d) and output curves of OECTs based on IDTBT-P10 (e) and IDTBT-P50 (f) in ionic liquid electrolyte with PEDOT:PSS as the gate. The scan rate is 100 mV/s.



Figure S9: *Output (a,b) and transfer (c,d) curves of OECTs based on IDTBT-P0 in 0.1 M TBAPF*⁶ *in acetonitrile as electrolyte. The devices consisted of gold electrodes on a quartz coated glass*

substrate, which were used as drain and source, the channel had a length of 2 mm and a width of 3 mm. The IDTBT-PO film had a thickness of 129 nm. The overlap of the channel with the gold electrodes was 1 mm. The measurements were carried out using an Ag/AgCl gate electrode. The output curve was measured for V_{GS} -0.9 to -1.2 V ($\Delta V = 0.1$ V) and V_{DS} from 0.2 to -0.4 V with a scan rate of 50 mV/s, the transfer curve was measured from V_{GS} -0.9 to -1.2 V with a constant V_{DS} of -0.2 V with a scan rate of 50 mV/s.

7 Electrochemical Quartz Crystal Microbalance Measurements

Table S1: Static swelling of the IDTBT polymer series in 0.1 M aqueous NaCl solution calculated as described in reference 2.⁴

| IDTRT | fr | ferman | ٨fa | Δm/Δ | f | f.c | Af | ۸m/۸ | Swelling |
|-------|-----------|----------|------|---------------------|-----------|----------|-------|---------------------|--|
| | ∎bare,ury | 111m,ury | | | •Dare,wet | *mm,wet | ⊥iwet | | $(\Delta m_{wet}-\Delta m_{dry})/\Delta m_{dry}$ |
| | Hz | Hz | Hz | ng cm ⁻² | Hz | Hz | Hz | ng cm ⁻² | |
| P100 | 14834592 | 14833800 | -792 | 4725.6 | 14834187 | 14833298 | -889 | 5304.4 | 12.25% |
| P50 | 14834592 | 14833974 | -618 | 3687.4 | 14834187 | 14833514 | -673 | 4015.6 | 8.90% |
| P10 | 14837426 | 14836807 | -619 | 3693.4 | 14837026 | 14836396 | -630 | 3759.0 | 1.78% |
| PO | 14833956 | 14833296 | -660 | 3938.0 | 14833545 | 14832886 | -659 | 3932.0 | -0.15% |





Figure S10: *Raw data for the EQCM measurements performed on the IDTBT polymer series in 0.1 M aqueous NaCl solution.*

8 Computational Modelling

- 1. Development and validation of a force field / Structural characterization
 - 1.1 Methodology

A first step in the use of classical molecular mechanics (MM) and molecular dynamic (MD) simulations involves the choice of a force field that accurately describes both intra- and intermolecular interactions for the systems at hands. Here, the Dreiding force field, as implemented in the Materials Studio 2018 package, and one of its modified versions,⁵ have been selected and subjected to slight modifications. Namely, the torsion potentials between adjacent polymer subunits, between the conjugated cores and the alkyl chains and along the side chains have been reparameterised and benchmarked against Density Functional Theory (DFT) calculations (performed using the B3LYP functional and the cc-pVTZ basis set). The atomic charges of the conjugated cores have been assigned by fitting the electrostatic potential (ESP charges) calculated at the B3LYP/cc-pVTZ level on an isolated dimer. The atomic charges of the polar side chains of P100 have been estimated at the same level of theory from a tetramer of polyethylene glycol while the atomic charges of the apolar alkyl side chains of P0 have been set to zero. The electrostatic term follows here Coulomb's law (r⁻¹) instead of the potential in r⁻² defined by default in Materials Studio and is calculated using the Ewald summation method. The van der Waals parameter associated to the hydrogen atom has been set to 2.50 Å instead of the 3.195 Å default value, in line with earlier studies.⁶⁻⁸

To validate our force field, a conformational search has been performed to extract the most stable supramolecular organizations of P0 and P100 films and to compare their characteristic distances to experimental X-Ray diffraction results reported here and available in the literature.^{9,10} The conformational search procedure involves four steps: (i) all starting structures (differing by the cell parameters, the number of molecules in the unit cell, the relative orientation and position of the conjugated cores and side chains, the interdigitation of the side chains, ...) are optimized at the MM level using 3D periodic boundary conditions; (ii) 100ps-quenched MD runs (NPT, T = 300 K, quench frequency = 1 ps) are then performed on each optimized structure until the energy between two successive quenched systems no longer decreases; (iii) on the most stable structures obtained at step (ii), 100 ps-quenched MD runs are performed at higher temperature, namely at 600 K first and then at 1000 K; and (iv) longer quenched simulations (t = 500 ps), using as starting points the most stable structure of the last quenched systems in step (iii), are performed at increasing temperature (300 K, 600 K, and 1000 K) following the procedure developed in steps (ii) and (iii) to finally extract the most stable structures.

1.2 Results

Stable crystal arrangements for both polymers (see Figure S11) correspond to a cofacial arrangement of two inequivalent polymer chains. In both cases, the side chains are interdigitated between the successive layers of π -stacked chains. For P0, the cofacial arrangement of the chains leads to an interlamellar distance d₁₀₀ of 26.1 Å and a π -stacking distance of 3.93 Å, while for P100, the interlamellar distance is 25.3 Å and the π -stacking distance is 3.98 Å. These results are in good agreement with our measured X-Ray characteristic distances for both polymers and also with already reported structural characteristic distances of P0 (d₁₀₀ = 26.0 Å and π - π distance = 3.8 Å in Ref ⁹). Thus, we are confident our modified-Dreiding force field can be applied to model IDTBT copolymers of various chemical compositions and morphologies.



Figure S11: *Representation of the two stable structures for IDTBT-P0 (left) and IDTBT-P100 (right) with their structural characteristic distances.*

- 2. Modelling of water dispersion in IDTBT-P0 and P100 and modelling of interchain contacts
 - 2.1 Methodology

Given the reported near-amorphous nature of IDTBT copolymer films,^{11,12} we have applied the following modelling protocol: (i) a large box containing 20 hexamers of P0 or P100 has been prepared with random orientations of the polymer backbones, in absence or presence of additional water molecules (~300 Å x ~300 Å x ~300 Å; target density of 0.01 g/cm³); (ii) the systems were then subjected to a 500 ps long MD run at high temperature (NVT, T= 1000 K) while keeping the density low (0.01 g/cm³) to favour a random spatial distribution of the chains; (iii) 5 successive 500 ps-long MD runs (NPT, P = 1 atm) were performed at decreasing temperature (1000 K, 500 K, 400 K, 350 K, 298 K); (iv) a long (tens of ns) MD simulation (NPT, P = 1 atm, T = 298 K) was performed until convergence of the cell parameters and total energy is reached; and (v) a 2 ns-long MD simulation

was carried out and snapshots are saved every 200 ps for further analysis. Note that the last two steps were performed using the NAMD package.

Charge transport in amorphous polymers proceeds by percolation, hence the number and 'quality' of interchain contacts is expected to play a major role. We have assessed the number of contact pairs taking as criterion a cut-off value for the distance between any two conjugated atoms belonging to any of the monomers of two distinct polymer chains. As a proxy for the quality of the electronic contact between the chains, we have calculated the electronic couplings or transfer integrals for holes between the close-contact pairs at the DFT level (B3LYP/DZ) using a fragment-based approach implemented in the ADF package.¹³

2.2 Results



Figure S12: Distribution of the number of contacts between P0 (blue) and P100 (orange) chains as a function of the distance (left). Cumulative number of contacts for P0 (blue) and P100 (orange) (right).

Table S2: Coordination numbers between the chlorine anions and different parts of the IDTBT units at 4 Å and 5 Å; as calculated from the analysis of the 10 snapshots of the MD trajectory for the system containing 20 charged hexamers of IDTBT, 25 wt% of water and 60 chlorine anions.

| Label | 4Å | 5Å |
|-------|------|------|
| C1 | 0.00 | 0.09 |
| C2 | 0.02 | 0.05 |
| C3 | 0.01 | 0.07 |
| C5 | 0.03 | 0.05 |
| S1 | 0.03 | 0.14 |
| C8 | 0.00 | 0.02 |
| C9 | 0.00 | 0.14 |
| C10 | 0.15 | 0.25 |
| N_R | 0.00 | 0.07 |
| S_3 | 0.03 | 0.06 |
| C4 | 0.02 | 0.11 |
| C6 | 0.13 | 0.28 |
| C7 | 0.02 | 0.21 |



3. Increasing energetic disorder

3.1 Methodology

Based on the modelling of the structural characterization presented previously, we would expect P100 to perform well as a charge transport material. This is, unfortunately and surprisingly, not the case, see main manuscript. We know this is neither because of poor water and ion insertion into the films nor resulting from degraded interchain percolating pathways. We then hypothesized that the polar side chains could contribute an additional energetic disorder to charge migration along and between the polymer chains. To test this hypothesis, we ran calculations of the electrostatic energetic disorder in P100 (both dry and wet) versus P0 films. For comparison, similar calculations were performed for the crystalline P0 and P100, used as benchmarks for the force field. Super-cells were generated that are made of two layers of ten π -stacked hexamers. For all systems, 1ns-long MD runs (NPT, p = 1 atm, T = RT) were performed, starting from the equilibrated structures, during which ten snapshots were recorded. For each snapshot, we calculated the variation in the total energy (mostly sourced from electrostatics) as an excess positive charge (mimicking hole carrier) is successively moved from one monomer to another (considering, to first approximation, that the positive charge is uniformly distributed over all conjugated atoms of each monomer). A uniform charged (-1) background was added to the systems to ensure electroneutrality. Also, to account for fast electronic polarization (not

included in the force field), a dielectric constant of 2.25 has been enforced in the Ewald electrostatic energy calculations. In view of the roughness of the model, we are mostly interested in a qualitative or semi-quantitative assessment of the relative energy disorder in the samples investigated.

9 Spectroelectrochemistry

Vis-NIR spectroelectrochemistry



Figure S13: Absorption spectra upon application of doping voltage ranging from -0.1 V to -1.3 V $(\Delta V = -0.1 \text{ V})$ versus Ag/AgCl for a) IDTBT-P0 (21 nm), b) IDTBT-P0 (204 nm), c) IDTBT-P10 (27 nm), d) IDTBT-P10 (222 nm), e) IDTBT-P50 (28 nm), f) IDTBT-P50 (203 nm), g) IDTBT-P100 (26 nm) and h) IDTBT-P100 (192 m), the MCR fits are depicted as black, dashed lines.

Multivariate Curve Resolution

Multivariate curve resolution (MCR) is a chemometric method to analyse data from mixtures, by extracting the relative abundances and signature of pure analytes. The most common uses of MCR are for spectroscopy, here it was utilized to extract spectra and concentration of different species (neutral segments, polarons, bipolarons) from a series of spectra, therefore it is applied to the Vis-NIR spectra obtained during the operation of the devices. The core of the analysis is the following formula.

$$D = CS^T + \varepsilon$$

Here D is a matrix corresponding to the series of spectra. MCR finds the solution through an iterative alternating regression (AR), where C is the concentration and S the spectral signatures and ε represents the error, noise or other feature not considered by the model.

During the AR the C is fixed while performing multivariate multiple regression for S and *vice versa*, this continues until the best possible estimation is accomplished.¹⁴



Figure S14: Normalised spectral signatures for the different IDTBT polymers and their thicknesses.

Evolution of the concentrations in IDTBT



Figure S15: Normalised species concentrations as a function of voltage for a) IDTBT-P0 (21 nm), b) IDTBT-P0 (204 nm), c) IDTBT-P10 (27 nm), d) IDTBT-P10 (222 nm), e) IDTBT-P50 (28 nm), f) IDTBT-P50 (203 nm), g) IDTBT-P100 (26 nm) and h) IDTBT-P100 (192 m).



Figure S16: Normalised concentrations as function of voltage for a, d) the neutral species; b, e) the polarons and c, f) bipolarons, the upper row depicts the films of ~25 nm and the lower row the films of ~200 nm.

Charge carrier density

During the spectroelectrochemical measurements, the device current is also measured by chronoamperometry. This is related to the ionic current and charge injected/extracted from the polymer at the electrode during the doping/dedoping processes. In contrast to the OECTs, the charges flow through the much smaller vertical film thickness, explaining why the current could be detected here. In Figure S17 a) and b) the time-resolved current for the doping respectively dedoping is shown. The current dynamics were integrated to determine the injected/extracted charge carrier density, which is normalised to the thickness of the films.¹⁵ To remove the effect of leak current at long times, the cumulative integral was linearly fitted, with the intercept corresponding to the total transferred charge.



Figure S17: Current of a) the doping process and b) dedoping process of IDTBT-P0 (21 nm) upon application of doping voltages ranging from -0.1 V to -1.3 V ($\Delta V = -0.1$ V) versus Ag/AgCl. Integrated current of c) the doping process and d) the dedoping process and the linear fit (black).

The charge carrier densities as a function of voltage are depicted in Figure S18. IDTBT-P0 and P10 follow a very similar trend, P50 shows an onset at higher doping voltage and P100 is the polymer starting to change at the lowest potential. From this data, two voltages were chosen, where the polymers have a similar overpotential with respect to the oxidation onset. The voltages picked are - 1.0 and -1.3 V for P0 and P10 V, -0.9 and -1.2 V for P50 and -0.8 and -1.1 for P100. They were further used for the investigation of the dynamics.



Figure S18: Injected/extracted charge carrier density for IDTBT-P0 to P100 a) for the doping and b) dedoping process.

Single-wavelength dynamics (film thickness and voltage dependence)

Single wavelength-dynamics were used to show the relation of the oxidation reaction rate on the applied voltage and thickness. In Figure S20-21 we show that the doping rate of the thicker films slows down, becoming less exponential, while the time to reach 1/e of decay/rise of concentration increases sub-linearly with the thickness. For thicker films the doping process is ion-transport limited whereas for the thinner films the ion-transport is not the limiting factor anymore and the kinetics mainly depend on the redox reaction taking place at the electrodes.^{16,17}



Figure S19: Single-wavelength dynamics at the neutral band for IDTBT-P50 (28 nm) for the doping voltages from -0.7 to -1.3 V versus Ag/AgCl.



Figure S20: Single-wavelength dynamics for the doping process at the neutral band for different thicknesses for a) IDTBT-P0 (-1.0 V), b) IDTBT-P0 (-1.3 V), c) IDTBT-P10 (-1.0 V), d) IDTBT-P10 (-1.3 V), e) IDTBT-P50 (-0.9 V), f) IDTBT-P50 (-1.2 V), g) IDTBT-P100 (-0.8 V) and h) IDTBT-P100 (-1.1 V).



Figure S21: Time to reach 1/e of decay/increase in concentration for a), b) neutral species; c), d) polarons and e), f) bipolarons as a function of polymer film thickness (single wavelength dynamics). In the left column, the times at low doping level (-0.8 to -1.0 V) are depicted, in the right column the times at high doping level (-1.1 to -1.3 V) are depicted. Additionally, the time found for the MCR dynamics to reach 1/e is indicated for selected samples.

| Polymer | Thickness | N (s) | | | P (s) | | | B (s) | | | | | |
|----------|-----------|-------------------|---|-----------------|--------------|-----------------|---|-----------------|---|-----------------|---|-----------------|----|
| | | -0.8 to -1.0 V | 7 | -1.1 to -1.3 | V | -0.8 to -1.0 | V | -1.1 to -1.3 | V | -0.8 to -1.0 | V | -1.1 to -1.3 | V |
| | 8 nm | 0.148 0.018 | ± | 0.020 0.013 | Ŧ | 0.065 0.010 | ± | 0.01 0.016 | ± | 0.230 0.004 | ± | 0.031 0.001 | ± |
| | 21 nm | 0.753 0.016 | ± | 0.070 0.002 | ± | 0.54 0.008 | ± | 0.04 0.007 | ± | 0.771 0.004 | ± | 0.112 0.000 | ± |
| 04-T | 44 nm | 0.867 0.008 | ± | 0.144 0.003 | ± | 0.755 0.004 | ± | 0.170 0.005 | ± | 1.181 0.001 | ± | 0.249 0.000 | ± |
| IDTB | 68 nm | 0.825 0.007 | ± | 0.099 0.001 | ± | 0.473 0.004 | ± | 0.045 0.005 | ± | 1.002 0.002 | ± | 0.171 0.000 | + |
| | 103 nm | 1.044 0.005 | ± | 0.131 0.002 | Ŧ | 0.727 0.003 | Ŧ | 0.102 0.003 | Ŧ | 1.363 0.001 | Ŧ | 0.211 0.000 | ± |
| | 204 nm | 0.971 0.007 | ± | 0.201 0.001 | ± | 0.952 0.003 | ± | 0.158 0.001 | ± | 1.502 0.001 | ± | 0.275 0.000 | + |
| | 8 nm | 0.117 0.015 | ± | 0.025 0.019 | ŧ | 0.070 0.007 | ± | 0.013 0.028 | ŧ | 0.177 0.004 | Ŧ | 0.043 0.003 | I+ |
| | 27 nm | 0.389 0.007 | ± | 0.036 0.005 | ± | 0.127 0.005 | ± | 0.021 0.009 | Ŧ | 0.293 0.002 | Ŧ | 0.064 0.001 | ± |
| DTBT-P10 | 62 nm | 0.58 0.002 | ± | 0.069 0.003 | ± | 0.321 0.003 | ± | 0.086 0.003 | ± | 0.532 0.001 | ± | 0.118 0.001 | ± |
| I | 98 nm | 0.601 0.007 | ± | 0.094 0.002 | ± | 0.442 0.002 | ± | 0.081 0.001 | ± | 0.881 0.001 | ± | 0.203 0.000 | ± |
| | 222 nm | 0.674 0.003 | ± | 0.167 0.001 | ± | 0.501 0.003 | ± | 0.131 0.001 | ± | 1.084 0.001 | ± | 0.27 0.001 | + |

Table S3: Time to reach 1/e of the formation respectively decay of the species at the different doping levels for the doping processes as a function of polymer film thickness.

| | 6 nm | 0.082 0.025 | ± | 0.027 0.010 | Ŧ | 0.054 0.016 | ± | 0.015 0.013 | ± | 0.162 0.005 | ± | 0.067 0.004 | ± |
|-------|--------|----------------|---|----------------|---|-----------------|---|----------------|---|----------------|---|----------------|---|
| | 18 nm | 0.087 0.017 | ± | 0.044 0.006 | ± | 0.058 0.013 | ± | 0.019 0.011 | Ŧ | 0.197 0.009 | ± | 0.106 0.002 | ± |
| -P50 | 28 nm | 0.226 0.009 | Ŧ | 0.045 0.002 | Ŧ | 0.174 0.007 | Ŧ | 0.024 0.004 | ± | 0.315 0.003 | Ŧ | 0.094 0.001 | ± |
| IDTBT | 42 nm | 0.353 0.007 | ± | 0.079 0.001 | ± | 0.275 0.007 | ± | 0.045 0.006 | ± | 0.512 0.001 | ± | 0.172 0.000 | ± |
| | 105 nm | 0.323 0.008 | ± | 0.095 0.003 | ± | 0.235 0.004 | ± | 0.035 0.004 | ± | 0.533 0.001 | ± | 0.167 0.000 | ± |
| | 203 nm | 0.504 0.008 | ± | 0.133 0.001 | Ŧ | 0.366 0.003 | Ŧ | 0.055 0.005 | ± | 0.816 0.001 | ± | 0.252 0.000 | ± |
| | 8 nm | 0.076 0.040 | ± | 0.020 0.008 | Ŧ | 0.032 0.016 | ± | 0.013 0.010 | ± | 0.145 0.015 | ± | 0.044 0.004 | ± |
| | 22 nm | 0.113 0.015 | ± | 0.026 0.005 | ± | 0.074 0.1002 | ± | 0.02 0.014 | ± | 0.272 0.011 | ± | 0.094 0.001 | ± |
| -P100 | 26 nm | 0.243 0.002 | ± | 0.044 0.003 | ± | 0.163 0.006 | ± | 0.031 0.019 | ± | 0.341 0.004 | ± | 0.121 0.000 | ± |
| IDTB1 | 39 nm | 0.266 0.009 | ± | 0.052 0.003 | ± | 0.169 0.009 | ± | 0.021 0.006 | ± | 0.389 0.002 | ± | 0.147 0.000 | ± |
| | 84 nm | 0.284 0.004 | Ŧ | 0.088 0.006 | Ŧ | 0.178 0.008 | Ŧ | 0.04 0.007 | ± | 0.553 0.003 | Ŧ | 0.224 0.001 | ± |
| | 192 nm | 0.285 0.003 | ± | 0.065 0.002 | Ŧ | 0.217 0.009 | ± | 0.026 0.007 | ± | 0.495 0.002 | ± | 0.231 0.000 | ± |

MCR dynamic curves

The time to reach 1/e of the formation respectively the depletion of the different species and the corresponding curves for each of the polymers and the used voltages can be found in the table below.



Figure S22: Time-resolved normalised species concentration for the different polymers at lower (-0.8 to -1.0 V) doping level, a) neutral species, doping, b) neutral species dedoping c) polarons, doping d) polarons, dedoping, e) bipolarons, doping, f) bipolarons, dedoping.



Figure S23: Time-resolved normalised species concentration (from MCR) for the different polymers at higher (-1.1 to -1.3 V) doping level, a) neutral species, doping, b) neutral species dedoping c) polarons, doping d) polarons, dedoping, e) bipolarons, doping, f) bipolarons, dedoping.

| | Polymer | N (s) | | Р | (s) | B (s) | | |
|-------------------------|------------|------------------|---|---|-------------------|---|---|--|
| | | thin | thick | thin | thick | thin | thick | |
| | IDTBT-P0 | 0.682 ± 0.015 | 0.958 ± 0.000 | 0.624 ± 0.025 | 0.839 ± 0.012 | 0.759 ± 0.006 | 1.374 ± 0.003 | |
| Low doj (-0.8 te | IDTBT-P10 | 0.336 ± 0.007 | $\begin{array}{l} 0.650 \ \pm \\ 0.016 \end{array}$ | 0.212 ± 0.014 | 0.413 ± 0.031 | 0.512 ± 0.002 | 1.067 ± 0.008 | |
| ping level o -1.0 V) | IDTBT-P50 | 0.138 ± 0.009 | 0.328 ± 0.013 | 0.083 ± 0.020 | 0.155 ± 0.026 | 0.264 ± 0.002 | 0.690 ± 0.12 | |
| | IDTBT-P100 | 0.187 ± 0.010 | 0.235 ± 0.012 | 0.145 ± 0.007 | 0.154 ± 0.020 | 0.309 ± 0.003 | 0.319 ± 0.005 | |
| | IDTBT-P0 | 0.087 ± 0.003 | 0.208 ± 0.000 | 0.065 ± 0.008 | 0.162 ±0.007 | 0.135 ± 0.000 | 0.287 ± 0.001 | |
| High doj (-1.1 tc | IDTBT-P10 | 0.062 ± 0.003 | 0.201 + 0.000 | 0.053 ± 0.007 | 0.177 ± 0.039 | 0.125 ± 0.001 | 0.310 ± 0.002 | |
| ping level) -1.3 V) | IDTBT-P50 | 0.048 ± 0.007 | 0.113 ± 0.008 | 0.024 ± 0.005 | 0.041 ± 0.026 | 0.106 ± 0.001 | $\begin{array}{ccc} 0.253 & \pm \\ 0.002 \end{array}$ | |
| | IDTBT-P100 | 0.072 ± 0.001 | 0.101 ± 0.009 | 0.046 ± 0.007 | 0.054 ± 0.025 | 0.164 ± 0.001 | 0.244 ± 0.001 | |
| | IDTBT-P0 | 0.157 ± 0.017 | 0.586 ± 0.005 | 0.129 ± 0.000 | 0.649 ± 0.007 | 0.085 ± 0.007 | 0.522 ± 0.005 | |
| Low ded (-0.8 t | IDTBT-P10 | 0.028 ± 0.006 | 0.068 ± 0.013 | 0.030 ± 0.005 | 0.089 ± 0.017 | $\begin{array}{c} 0.020 \ \pm \\ 0.000 \end{array}$ | $\begin{array}{ccc} 0.051 & \pm \\ 0.001 & \end{array}$ | |
| pping level 1.0 V) | IDTBT-P50 | 0.011 ± 0.006 | 0.035 ± 0.015 | $\begin{array}{c} 0.011 \ \pm \\ 0.000 \end{array}$ | 0.036 ± 0.12 | 0.006 ± 0.004 | $\begin{array}{ccc} 0.025 & \pm \\ 0.003 & \end{array}$ | |
| | IDTBT-P100 | 0.028 ± 0.009 | 0.021 ± 0.006 | 0.028 ± 0.000 | 0.020 ± 0.014 | 0.022 ± 0.000 | 0.016 ± 0.004 | |

Table S4: Time to reach 1/e of the formation respectively decay of the species at the different dopinglevels for the doping and dedoping processes (from MCR dynamics).

| | IDTBT-P0 | 0.103 ± 0.003 | 0.275 ± 0.003 | 0.150 ± 0.005 | 0.533 ± 0.004 | 0.054 ± 0.000 | $\begin{array}{c} 0.056 \pm \\ 0.000 \end{array}$ |
|--------------------------|------------|-------------------|-------------------|-------------------|-----------------|-------------------|---|
| High ded (-1.1 t | IDTBT-P10 | 0.045 ± 0.003 | 0.095 ± 0.003 | 0.051 ± 0.007 | 0.125 ± 0.013 | 0.034 ± 0.001 | $\begin{array}{cc} 0.065 & \pm \\ 0.011 \end{array}$ |
| oping level o -1.3 V) | IDTBT-P50 | 0.032 ± 0.003 | 0.082 ± 0.004 | 0.036 ± 0.000 | 0.092 ± 0.021 | 0.021 ± 0.001 | $\begin{array}{c} 0.055 & \pm \\ 0.002 & \end{array}$ |
| | IDTBT-P100 | 0.043 ±0.004 | 0.100 ± 0.002 | 0.047 ± 0.002 | 0.109 ±0.014 | 0.027 ± 0.001 | 0.064 ± 0.001 |

Data reproducibility



Figure S24: Time-resolved normalised species concentration for a) IDTBT-P0 thick films, dedoping step at -1.3 V, b) IDTBT-P0 thick films, doping step at -1.0 V, c) IDTBT-P100 thin films, dedoping step at -1.1 V and d) IDTBT-P100 thin films, doping step at -0.8 V. The measurements were taken on different samples several months apart to show the reproducibility of our results.

Table S5: Time to reach 1/e of decay/increase in concentration at two distinct doping scenarios forIDTBT-P0 thick films and IDTBT-P100 thin films measured at different occasions.

| Polymer | Doping | Thickness | N (s) | P (s) | B (s) |
|---------|--------------|-----------|-------------------|-------------------|-------------------|
| | ping V | 103 nm | 0.122 ± 0.001 | 0.282 ± 0.000 | 0.056 ± 0.000 |
| T-P0 | Dedo -1.3 | 106 nm | 0.112 ± 0.001 | 0.245 ± 0.000 | 0.059 ± 0.000 |
| IDTB | ing V | 103 nm | 0.966 ± 0.004 | 0.720 ± 0.007 | 1.295 ± 0.003 |
| | Dop -1.0 | 106 nm | 0.732 ± 0.005 | 0.499 ± 0.004 | 1.001 ± 0.002 |
| | ping V | 26 nm | 0.029 ± 0.021 | 0.033 ± 0.032 | 0.016 ± 0.000 |
| -P100 | Dedo -1.1 | 22 nm | 0.043 ± 0.004 | 0.047 ± 0.033 | 0.027 ± 0.000 |
| DTBT | ing V | 26 nm | 0.096 ± 0.006 | 0.054 ± 0.016 | 0.367 ± 0.003 |
| | Dop -0.8 | 22 nm | 0.187 ± 0.013 | 0.145 ± 0.019 | 0.309 ± 0.002 |

10 Organic Field-Effect Transistor Characterisation

OFET fabrication and analysis

Top-gate, bottom-contact field effect transistors were fabricated on glass substrates with photolithographically defined electrodes of Cr/Au (5 nm/ 25 nm, L = 20 μ m and W = 1 mm). Polymers (IDTBT and its derivates with different polar side chain) were then deposited by spin coating from 5 mg mL⁻¹ 1,2-dichlorobenzene solution at 1500 rpm for 30 s, followed by an annealing step at 100 °C for 60 minutes to drive out residual solvent from the film. To leave residual solvent in the film intentionally, annealing was done for 10 seconds only. For devices comprising a solid additive (F4TCNQ), the material was added to the polymer solution in 5%. For a dielectric layer, a 500 nm layer of CYTOP (Asahi Glass) was spin coated (CYTOP was annealed at 80 °C for 15 minutes) and devices were finished off by evaporating a 30 nm thick aluminium top gate through a shadow mask. Transistor transfer characteristics were measured with an Agilent 4155B Semiconductor Parameter Analyser. To guarantee reproducibility, all fabrication steps as well as all electrical measurements were performed in a N₂ glove box.

The reported OFET transistor characteristics are extracted as follows:

$$\mu_{\text{sat}} = \left(\frac{\partial \sqrt{I_{D,sat}}}{\partial V_G}\right)^2 \frac{2L}{WC_i}$$

 V_{th}^{sat} (V): transfer characteristics in the saturation regime ($V_{ds} > V_g - V_{Th}$), indicating the threshold voltage V_{Th} , where the linear fit to the square root of the drain current intersects with the x-axis.

 I_{on}/I_{off} : The on-off ratio that comprises the ratio between the drain current when the transistor is "on" and the current when the transistor is "off." Off current happens due to an absence of an accumulation layer when $V_G < V_{Th}$. The onset voltage V_{on} at which point the drain current rises sharply exceeding the off-current level.



Figure S25: OFET transfer curves (left) collected with $V_{DS} = -60$ V and extracted saturation mobility as a function of gate voltage (middle, linear plot; right, semi-log plot) for the IDTBT polymer series.



Figure S26: OFET output curves for IDTBT-P0 (left), IDTBT-P10 (middle) and IDTBT-P50 (right).



Figure S27: OFET characteristics including transfer curves (left), extracted saturation mobility as a function of gate voltage (middle), and output curves (right) for IDTBT-P10 (top) and IDTBT-P50 (bottom) with and without F4TCNQ added at 5 wt%.

| Polymer | μ_{sat} (cm ² /Vs) | $V_{th}^{sat}\left(V ight)$ (reverse/forward) | I_{on}/I_{off} |
|------------|-----------------------------------|---|---------------------------------------|
| IDTBT-P0 | 1.02 ± 0.08 | -27.8±0.79/-27.2±0.63 | $4.08 \cdot 10^5 \pm 1.66 \cdot 10^5$ |
| IDTBT-P10 | 0.35 ± 0.07 | $-18.7 \pm 0.84/-18.5 \pm 0.89$ | $6.47 \cdot 10^4 \pm 2.03 \cdot 10^4$ |
| IDTBT-P50 | 0.013±0.001 | -4.14±2.04/-8.79±1.22 | $65.7 \pm 2.22 \cdot 10^{1}$ |
| IDTBT-P100 | / | / | / |

Table S6: OFET characteristics with standard deviations extracted from 6-10 devices for eachIDTBT polymer.

11 Chemical Doping

For the chemical doping, tris(4-bromophenyl)ammoniumyl hexachloroantimonate (Magic Blue) was used. Polymer films were sequentially doped from acetonitrile solution using two different concentrations. 0.5 mg/ml Magic Blue resulted in a higher doping level and 0.25 mg/ml in a lower doping level. The amount of doping can be seen in Figure S28.



Figure S28: Comparison of doping level for a) IDTBT-P0, b) IDTBT-P10, c) IDTBT-P50 and d) IDTBT-P100.

12 Photothermal Deflection Spectroscopy

The entire setup is custom-built out of many components from different companies or even "homebuilt" (completely custom design by the local mechanical/electronic workshop). Photothermal deflection spectroscopy (PDS), an ultrasensitive absorption research method, is insensitive to reflection and scattering but detects heating of the material as a result of the nonradiative relaxation of absorbed light. With PDS, it is possible to detect absorbance signals that are 5-6 orders of magnitude weaker than band edge absorption.¹⁸ To perform the measurements, a monochromatic pump beam was employed to illuminate the sample (film on quartz substrate). Light absorption causes a thermal gradient to form near the surface of the sample through non-radiative relaxation induced heating. In turn, this creates a refractive index gradient in the zone around the sample surface. The sample can be immersed in an inert liquid called FC-72 Fluorinert (3M Company) to further enhance this refractive index gradient, as it has a high refractive index change per unit change in temperature. Passing a fixed wavelength cw laser probe beam through this refractive index gradient created a deflection that was proportional to the absorbed light at the specific wavelength, the latter of which can be detected using a photodiode and lock-in amplifier combination. The whole absorption spectra are obtained by scanning over various wavelengths. This method involves the use of nonradiative relaxation processes and thus it is not affected by optical effects such as interference and scattering.19



Figure S29: PDS spectra for (a) IDTBT-P0, (b) IDTBT-P10, (c) IDTBT-P50, and (d) IDTBT-P100. *The peak around 1.12 eV is an artifact associated with the spectrometer.*

13 References

- W. Zhang, J. Smith, S. E. Watkins, R. Gysel, M. McGehee, A. Salleo, J. Kirkpatrick, R. S. Ashraf, T.
 D. Anthopoulos, M. Heeney and I. McCulloch, *J. Am. Chem. Soc.*, 2010, **132**, 11437–11439.
- 2 Z. Jiang, X. Li, J. Strzalka, M. Sprung, T. Sun, A. R. Sandy, S. Narayanan, D. R. Lee and J. Wang, *J. Synchrotron Radiat.*, 2012, **19**, 627–636.
- 3 Z. Jiang, J. Appl. Crystallogr., 2015, 48, 917–926.
- J. Surgailis, A. Savva, V. Druet, B. D. Paulsen, R. Wu, A. Hamidi-Sakr, D. Ohayon, G. Nikiforidis, X.
 Chen, I. McCulloch, J. Rivnay and S. Inal, *Adv. Funct. Mater.*, 2021, **31**, 2010165.
- V. Lemaur, J. Cornil, R. Lazzaroni, H. Sirringhaus, D. Beljonne and Y. Olivier, *Chem. Mater.*, 2019, 31, 6889–6899.
- 6 A. R. Kulkarni and D. S. Sholl, *Langmuir*, 2015, **31**, 8453–8468.
- 7 S. Saiev, L. Bonnaud, P. Dubois, D. Beljonne and R. Lazzaroni, *Polym. Chem.*, 2017, **8**, 5988–5999.
- 8 S. Hoyas, V. Lemaur, Q. Duez, F. Saintmont, E. Halin, J. De Winter, P. Gerbaux and J. Cornil, *Adv. Theory Simulations*, 2018, **1**, 1–14.
- 9 D. Venkateshvaran, M. Nikolka, A. Sadhanala, V. Lemaur, M. Zelazny, M. Kepa, M. Hurhangee, A. J. Kronemeijer, V. Pecunia, I. Nasrallah, I. Romanov, K. Broch, I. McCulloch, D. Emin, Y. Olivier, J. Cornil, D. Beljonne and H. Sirringhaus, *Nature*, 2014, **515**, 384–388.
- I. E. Jacobs, G. D'avino, V. Lemaur, Y. Lin, Y. Huang, C. Chen, T. F. Harrelson, W. Wood, L. J. Spalek, T. Mustafa, C. A. O'keefe, X. Ren, D. Simatos, D. Tjhe, M. Statz, J. W. Strzalka, J. K. Lee, I. Mcculloch, S. Fratini, D. Beljonne and H. Sirringhaus, *J. Am. Chem. Soc.*, 2022, 144, 3005–3019.
- 11 X. Zhang, H. Bronstein, A. J. Kronemeijer, J. Smith, Y. Kim, R. J. Kline, L. J. Richter, T. D. Anthopoulos, H. Sirringhaus, K. Song, M. Heeney, W. Zhang, I. McCulloch and D. M. Delongchamp, *Nat. Commun.*, 2013, 4, 2238.
- I. Dobryden, V. V. Korolkov, V. Lemaur, M. Waldrip, H.-I. Un, D. Simatos, L. J. Spalek, O. D. Jurchescu, Y. Olivier, P. M. Claesson and D. Venkateshvaran, *Nat. Commun.*, 2022, 13, 3076.
- 13 L. Viani, Y. Olivier, S. Athanasopoulos, D. A. da Silva Filho, J. Hulliger, J. L. Brédas, J. Gierschner and J. Cornil, *ChemPhysChem*, 2010, **11**, 1062–1068.
- 14 C. H. Camp, J. Res. Natl. Inst. Stand. Technol., 2019, 124, 124018.
- 15 D. Tsokkou, P. Cavassin, G. Rebetez and N. Banerji, *Mater. Horizons*, 2022, 9, 482–491.
- 16 P. Shiri, E. J. S. Dacanay, B. Hagen and L. G. Kaake, J. Mater. Chem. C, 2019, 7, 12935–12941.
- 17 G. Rebetez, O. Bardagot, J. Affolter, J. Réhault and N. Banerji, Adv. Funct. Mater., 2022, 32, 2105821.
- 18 T. A. S. Doherty, A. J. Winchester, S. Macpherson, D. N. Johnstone, V. Pareek, E. M. Tennyson, S.

Kosar, F. U. Kosasih, M. Anaya, M. Abdi-Jalebi, Z. Andaji-Garmaroudi, E. L. Wong, J. Madéo, Y. H. Chiang, J. S. Park, Y. K. Jung, C. E. Petoukhoff, G. Divitini, M. K. L. Man, C. Ducati, A. Walsh, P. A. Midgley, K. M. Dani and S. D. Stranks, *Nature*, 2020, **580**, 360–366.

J. Ye, Z. Li, D. J. Kubicki, Y. Zhang, L. Dai, C. Otero-mart, M. A. Reus, R. Arul, K. R. Dudipala, Z. Andaji-garmaroudi, Y. Huang, Z. Li, Z. Chen, P. Mu, H. Yip, S. D. Stranks, C. P. Grey, J. J. Baumberg, N. C. Greenham, L. Polavarapu, A. Rao and R. L. Z. Hoye, J. Am. Chem. Soc., 2022, 144, 12102–12115.