Indan-1,3-dione electron-acceptor small molecules for solutionprocessable solar cells: a structure-property correlation

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Computational analysis

Quantum chemistry calculations have been carried using density functional theory (DFT) as implemented in the Gaussian 09 suite of programs.^[1] The B3LYP exchange-correlation functional^[2] was used in most computations. The geometry of the gas phase n-type acceptor model compound was optimized at the B3LYP/6-31+G(d) spin-restricted level of theory. Vibrational frequency calculations were performed to verify that all the optimized geometries correspond to minima on the potential energy surfaces. Single point energy calculations were then conducted employing the optimized geometries and a larger 6-311+G(d,p) basis set. The energies of the frontier molecular orbitals (MOs), highest occupied (HOMO) and lowest unoccupied (LUMO) are shown in the Table below.

Compound	
F8IDT	
HOMO 5.83 eV	
LUMO 3.15 eV	

Table S1 – Computational HOMO and LUMO orbital images for model n-type material.

Synthesis

All reactions using organolithium were performed under an inert atmosphere of nitrogen gas and with anhydrous solvents. Light petroleum refers to the fraction with a boiling point between 40 and 60°C. 9,9-Dioctyl-9H-fluorene-2,7-diboronic acid, bis(pinacol) ester was purchased from Boron Molecular Pty Ltd, Melbourne, Australia. 2,7-Dibromofluorene was purchased from Sigma-Aldrich. 9,9-Di-(2-ethylhexyl)-9H-fluorene-2,7-diboronic acid, bis(pinacol) ester was made by adapting literature procedures.^{[3] 1}H (400 MHz) and ¹³C NMR (100 MHz) spectra were recorded on a Bruker Av400 spectrometer or on a Bruker Av200 (75 MHz) spectrometer using CDCl₃ solutions, unless otherwise stated. Chemical shifts (δ) are reported in ppm. Melting points were recorded on a Thermo Scientific 9300 melting point apparatus and are uncorrected. Low resolution (LR) and high resolution (HR) mass spectra were measured on a ThermoQuest MAT95XL mass spectrometer using an ionization energy of 70eV or on a Thermo Scientific Q Exactive mass spectrometer fitted with an ASAP ion source (M&M Mass Spec consulting).^[4] The design and method of ionisation have been described previously.^[5,6] Positive and negative ions were recorded in an appropriate mass range at 70,000 mass resolution. The Atmospheric-pressure chemical ionization (APCI) probe was used without flow of solvent, although a solution of Reserpine was introduced through the APCI probe during the experiments to serve as a lock mass in both positive and negative ion modes. The nitrogen nebulizing/desolvation gas used for vaporization was heated to 450°C in these experiments. The sheath gas flow rate was set to 2, the auxiliary gas flow rate to 20 and the sweep gas flow rate to 5 (all arbitrary units). The discharge current was 4mA and the capillary temperature was 320°C. Elemental analysis was performed by the Campbell Microanalytical Laboratory at University of Otago, Dunedin, New Zealand.

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Scheme S1 – Synthesis of n-type acceptor derivatives.

F8IDT synthesis

5,5'-(9,9-dioctyl-9H-fluorene-2,7-diyl)bis(thiophene-2-carbaldehyde)



To a solution of freshly distilled 2-bromo-5-formylthiophene (5.29 g, 27.7 mmol) in DME (40 mL) and 1M Na₂CO₃ (30 mL), under nitrogen, was added 2,2'-(9,9-dioctyl-9H-fluorene-2,7diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (5.93)9.23 mmol) and g, tetrakis(triphenylphosphine)palladium (530 mg, 0.459 mmol). The reaction was refluxed under nitrogen for 4 hrs, cooled to room temperature and water (100 mL) was added. The product was extracted with DCM (2 x 75 mL). The organic layers were combined and washed with water (100 mL) and saturated brine (100 mL), then passed through a DryDiskTM. The solvent was evaporated and the resulting residue was recrystallised from DCM/light petroleum (30 mL/300 mL) to give the product as fine yellow crystals (4.60 g, 81.6%), m.p. 109-110°C. A sample for elemental analysis was recrystallised from DCM/diethyl ether/petroleum ether. ¹H NMR (CDCl₃, 400 MHz): δ 0.69 (m, 4H), 0.80 (t, 6H, J = 7.2 Hz), 1.14 (m, 20H), 2.06 (m, 4H), 7.51 (d, 2H, J = 4.0 Hz), 7.66 (d, 2H, J = 1.2 Hz), 7.72 (dd, 2H, J = 7.6 Hz, 1.2 Hz), 7.79 (d, 2H, J = 7.6 Hz), 7.80 (d, 2H, J = 4.0 Hz),

9.94 (s, 2H). ¹³C NMR (CDCl₃, 100 MHz): δ 14.19, 22.73, 23.91, 29.27, 29.30, 30.02, 31.89, 40.36, 55.70, 120.85, 120.93, 124.20, 125.88, 132.57, 137.59, 141.79, 142.39, 152.40, 154.94, 182.87. HRMS (APCI, +ve ion)) 610.2934 *m*/*z*, [M]⁺ requires 610.2934. Elemental analysis requires C 76.88%, H 7.31%. Found: C 76.73 %, H 7.67%.

2,2'-((5,5'-(9,9-Dioctyl-9*H*-fluorene-2,7-diyl)bis(thiophene-5,2-diyl))bis(methanylylidene))bis(1*H*-indene-1,3(2*H*)-dione) (F8IDT)



To a solution of 5,5'-(9,9-dioctyl-9*H*-fluorene-2,7-diyl)bis(thiophene-2-carbaldehyde) (2.80 g, 4.58 mmol) in *tert*-butanol (100 mL), under nitrogen, was added indandione (2.01 g, 13.8 mmol) followed by 3 drops of piperidine. The reaction was refluxed for 6 hrs, cooled to 50°C, then ethanol (50 mL) was added and the reaction allowed to cool to room temperature. The precipitate was filtered off, washed with ethanol and recrystallised twice from DCM/acetone (50 mL/200 mL) to give the product as red crystalline rods (2.94 g, 73.9%), m.p. 207-208°C. A sample for elemental analysis was recrystallised from toluene/petroleum ether. ¹H NMR (CDCl₃, 400 MHz): δ 0.64 (m, 4H), 0.75 (t, J = 6.8 Hz, 6H), 1.01-1.24 (m, 20H), 2.08 (m, 4H), 7.55 (d, J = 4.0 Hz, 2H), 7.73 (d, J = 1.2 Hz, 2H), 7.78-7.88 (m, 8H), 7.98-8.07 (m, 8H). ¹³C NMR (CDCl₃, 75 MHz): δ 14.02, 22.56, 23.80, 29.17, 29.19, 29.88, 31.74, 40.29, 55.79, 120.72, 120.80, 122.82, 123.05, 123.85, 124.87, 125.93, 132.72, 134.87, 135.06, 136.25, 136.62, 140.56, 141.92, 142.06, 143.76, 152.39, 157.91, 189.89, 190.38. HRMS (EI, 70eV) *m/z* 866.3467, [M] requires 866.3464. Elemental analysis requires C 78.95%, H 6.28%. Found: C 78.96 %, H 6.30%.

FEHIDT synthesis

2,7-Dibromo-9,9-bis(2-ethylhexyl)-9H-fluorene



To a solution of 2,7-dibromofluorene (2.25 g, 6.94 mmol) in dry THF (50 mL) under nitrogen at 0° C was added sodium tert-butoxide (1.70 g, 17.7 mmol). After stirring for 15 minutes 2-ethylhexyl bromide (4.94 mL, 27.8 mmol) was added dropwise, the reaction was warmed to room temperature and stirred for 16 hours. H₂O (100 mL) was then added and the reaction stirred for 15 minutes. The product was extracted into light petroleum (2 x 50 mL), washed with H₂O (100 mL), then sat. NaCl (50 mL) and dried over MgSO₄. The solvent and excess 2-ethylhexyl bromide was evaporated under reduced pressure to give an oil which was passed through a short silica plug with light petroleum to give the product as a clear oil (3.38 g, 88.8%). The ¹H and ¹³C NMR spectra of this product are in agreement with published spectra.^[7]

2,2'-(9,9-Bis(2-ethylhexyl)-9*H*-fluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)



To a solution of 2,7-dibromo-9,9-bis(2-ethylhexyl)-9*H*-fluorene (10.0g, 18.2 mmol) in dry THF (70 mL) under nitrogen at -78°C was added 1.6M BuLi in hexanes (35.0 mL, 55.0 mmol) dropwise. The solution was stirred at -78°C for 30 minutes then 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (22.3mL, 109 mmol) was added all at once. The reaction was slowly warmed to room temperature and stirred for 16 hours after which H₂O (100 mL) was added. The reaction was extracted into diethyl ether (2 x 100 mL), washed with H₂O (100 mL), then sat. brine (100 mL) and dried over MgSO₄. The solvent was evaporated under reduced pressure to give a clear oil which was taken up in isopropyl alcohol (200 mL) and chilled to -15°C overnight. The product formed as white crystals which were filtered off and washed with ice-cold isopropyl alcohol (8.54 g, 72.9%). The ¹H and ¹³C NMR spectra of this product are in agreement with published spectra.^[7]

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5,5'-(9,9-bis(2-ethylhexyl)-9H-fluorene-2,7-diyl)bis(thiophene-2-carbaldehyde)



The product was synthesised in the same manner as 5,5'-(9,9-dioctyl-9*H*-fluorene-2,7-diyl)bis(thiophene-2-carbaldehyde), using 2-bromo-5-formylthiophene (4.79 g, 25.1 mmol), 2,2'-(9,9-bis(2-ethylhexyl)-9*H*-fluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (5.37 g, 8.36 mmol), tetrakis(triphenylphosphine)palladium (483 mg, 0.418 mmol). The product crystallised as fine yellow crystals (2.70 g, 52.8%), m.p. 112-128°C. ¹H NMR (CDCl₃, 400 MHz): δ 0.51-0.59 (m, 8H), 0.59-0.66 (m, 6H), 0.68-0.96 (m, 16H), 2.03-2.15 (m, 4H), 7.46-7.50 (m, 2H), 7.69-7.74 (m, 4H), 7.77-7.82 (m, 4H), 9.94 (s, 2H). ¹³C NMR (CDCl₃, 100 MHz): δ 10.55, 14.06, 22.83, 27.33, 28.26, 34.01, 34.96, 44.43, 55.45, 120.86, 122.23, 124.06, 125.84, 130.45, 137.67, 141.95, 142.41, 152.14, 155.03, 182.90. HRMS (ACPI, +ve ion) 610.2924 *m/z*, [M]⁺ requires 610.2934. A satisfactory elemental analysis could not be achieved for this compound (HPLC 98.65%).

2,2'-((5,5'-(9,9-Bis(2-ethylhexyl)-9*H*-fluorene-2,7-diyl)bis(thiophene-5,2-diyl))bis(methanylylidene))bis(1*H*-indene-1,3(2*H*)-dione) (FEHIDT)



The product was synthesised in the same manner as 2,2'-((5,5'-(9,9-dioctyl-9H-fluorene-2,7-diyl))bis(thiophene-5,2-diyl))bis(methanylylidene))bis(1*H*-indene-1,3(2*H*)-dione) using 5,5'-(9,9-bis(2-ethylhexyl)-9*H*-fluorene-2,7-diyl)bis(thiophene-2-carbaldehyde) (2.70 g, 4.42 mmol), indandione (1.94 g, 13.3 mmol). The crude product was recrystallised (twice) from DCM/acetone to give the product as dark red rosettes (2.50 g, 65.2%), m.p. 235-252°C. ¹H NMR (CDCl₃, 400 MHz): δ 0.53-0.68 (m, 14H), 0.72-1.00 (m, 16H), 2.11 (m, 4H), 7.52 (d, 2H, J = 4.0 Hz), 7.79-7.88 (m, 10H), 7.97-8.10 (m, 8H). ¹³C NMR (CDCl₃, 75 MHz): δ 10.45, 13.92, 22.70, 27.19, 28.17, 33.81, 34.88, 44.38, 55.42, 120.77, 122.02, 122.84, 123.03, 123.91, 124.71, 125.97, 132.14, 134.83, 135.04, 136.19, 136.66, 140.54, 142.03, 142.09, 143.66, 152.16, 157.96, 189.76, 190.41. HRMS

(APCI, +ve ion) 866.3453 *m/z*, [M]⁺ requires 866.3458. Elemental analysis requires C 78.95%, H 6.28%, S 7.40%. Found: C 78.93%, H 6.32%, S 7.41%.





Figure S1 – ¹H NMR of F8IDT.



Figure S2 - ¹H NMR of FEHIDT, multiple triplets between 0.50 and 0.70 ppm indicate the presence of diastereomers.



Figure S3 – ¹³C NMR of F8IDT.



Figure S4 – ¹³C NMR of FEHIDT.

Crystallographic information

Detailed crystallographic data for the structure of F8IDT and FEHIDT have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 931067 and CCDC 931066, respectively.

Crystals of F8IDT were grown by recrystallisation from DCM/acetone

F8IDT
Red Rods
$C_{57}H_{54}O_4S_4$
<i>M_r</i> 867.17
Triclinic, P-1
<i>a</i> = 12.0144(9) Å
<i>b</i> = 12.2700(8) Å
c = 16.4130(14) Å
$\alpha = 85.003(6)^{\circ}$
$\beta = 75.213(7)^{\circ}$
γ=74.553(6)°
V = 2254.4 (3) Å ³
Z = 2
$D_c = 1.277 \text{ mg/m}^3$
$R_{I} = 0.0568$
wR2 = 0.1265

Table S2 – Crystallographic data for F8IDT.



Figure S5 – Molecular diagram of F8IDT with non-hydrogen atoms represented by 50% thermal ellipsoids and hydrogen atoms as spheres of arbitrary size.



Figure S6 – View of 2D brickwork type packing in which the interplanar separation is approximately 3.4 Å (a) side view (b) top view. F8IDT has 2 interplanar overlap distances of 3.36 and 3.81 Å.

Only one stereoisomer of FEHIDT was isolated (RS form). Crystals of FEHIDT were grown by recrystallisation from $Et_2O/CHCl_3$.

Table	S3 –	Crystallog	raphic	data	for	FEHIDT	
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FEHIDT
Red Rods
$C_{57}H_{54}O_4S_4$
<i>M_r</i> 867.17
Triclinic, P-1
<i>a</i> = 9.4579(9) Å
<i>b</i> = 14.041(2) Å
c = 18.191(3) Å
$\alpha = 103.997(14)^{\circ}$
$\beta = 100.110(11)^{\circ}$
$\gamma = 98.796(11)^{\circ}$
$V = 2258.9(6) \text{ Å}^3$
Z = 2
$D_c = 1.275 \text{ mg/m}^3$
$R_1 = 0.0650$
wR2 = 0.1740



Figure S7 - Molecular diagram of FEHIDT with non-hydrogen atoms represented by 50% thermal ellipsoids and hydrogen atoms as spheres of arbitrary size.



Figure S8 – Stacking of neighbouring molecules into pairs through near parallel overlap of two planar thiophene-indane-1,3-dione moieties. The mean planes of the terminal groups are twisted relative to the central fluorene moiety by $24.3(2)^{\circ}$ and $17.3(2)^{\circ}$. The two end groups are also not coplanar by $7.1(2)^{\circ}$.



Figure S9 – Propagation of the two component stacks into a 2D sheet through further overlap of the terminal benzo rings and the thiophene rings of neighbouring pairs of molecules (a) side view (b) top view. FEHIDT has 3 overlaps, 3.05, 3.34 and 3.50 Å depending on which sections of the molecules are overlapping

UV-visible absorption spectroscopy

All UV-visible absorption spectra were recorded on a Hewlett Packard HP 8453 Diode array UVvisible spectrophotometer. Thin films were spin-coated from either chlorobenzene (CB) or *o*-chlorobenzene (*o*-DCB) at a spin speed of 3000 rpm for 60 s onto cleaned glass slides. FxIDT derivatives were spin-coated from solutions at a concentration of 30 mg/mL. P3HT:FxIDT blend solutions were prepared in the same manner as for devices, i.e. P3HT (18 mg) and FxIDT (15 mg) in a total volume of 1 mL. Where specified, films were annealed at 120°C for 10 min.



Figure S10 – Thin film UV-visible absorption spectra of pristine F8IDT and P3HT:F8IDT blends from *o*-DCB.



Figure S11 – Thin film UV-visible absorption spectra of pristine FEHIDT and P3HT:FEHIDT blends from *o*-DCB.



Figure S12 – Thin film UV-visible absorption spectra of P3HT:F8IDT and P3HT:FEHIDT blends from CB.

Photo-electron spectroscopy in air (PESA)

PESA measurements were recorded with a Riken Keiki AC-2 PESA spectrometer with a power setting of 5 nW and a power number of 0.5. Samples for PESA were prepared on cleaned glass substrates. Thin films were spin-coated (3000 rpm, 60s) from solutions prepared in a N_2 glovebox (FxIDT (16 mg) dissolved in CB or *o*-DCB (0.5 mL), heated to 80°C for 10 min then cooled to room temperature. Thin films were annealed at 120°C for 10 min in the glovebox and then the PESA measurements were repeated.



Figure S13 – PESA spectra of thin films of F8IDT from *o*-DCB (left) and CB (right) before and after annealing. The dashed lines show the fits to extract ionisation potentials.

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Figure S14 – PESA spectra of thin films of FEHIDT from *o*-DCB (left) and CB (right) before and after annealing. The dashed lines show the fits to extract ionisation potentials before (small dash) and after (large dash) annealing.

Table S4 – Estimates of HOMO and LUMO energy levels from PESA and UV-visible	e
absorption spectra for pristine and annealed films from <i>o</i> -DCB.	

Compound	НОМО	НОМО	UV-Vis onset	UV-Vis onset	LUMO	LUMO
	(pristine)	(annealed)	(pristine)	(annealed)	(pristine)	(annealed)
	(eV)	(eV)	(eV)	(eV)	(eV)	(eV)
F8IDT	-5.85	-5.85	2.10	2.10	-3.75	-3.75
FEHIDT	-5.95	-5.95	2.10	2.00	-3.85	-3.95

Differential scanning calorimetry (DSC)

Differential scanning calorimetry was preformed on a Mettler Toledo DSC821 instrument with a heating rate of 10 °C per minute from 40 °C to 600 °C.



Figure S15 – DSC curve for F8IDT.



Figure S16 – DSC curve for FEHIDT.

Thermogravimetric analysis (TGA)



Figure S17 – TGA of F8IDT.



Figure S18 – TGA of FEHIDT.

Photoluminescence studies (PL)

Photoluminescence (PL) spectra were recorded with a Perkin Elmer Luminescence Spectrometer LS 50. Spectra were recorded of thin films spin-coated (3000 rpm/s, 60 s) onto cleaned glass slides from *o*-DCB. FxIDT derivatives were spin-coated from solutions at a concentration of 30 mg/mL. P3HT:FxIDT blend solutions were prepared in the same manner as for devices, i.e. P3HT (18 mg) and FxIDT (15 mg) in a total volume of 1 mL. Films were annealed at 120°C for 10 min.



Figure S19 – PL spectra of pristine films of F8IDT and FEHIDT, together with PL spectra of their blends with P3HT, spin-coated from *o*-DCB ($\lambda_{exc} = 355$ nm).

Atomic force microscopy (AFM)

AFM topographic maps were performed directly on the active layer of the P3HT:FxIDT blends using an Asylum Research MFP-3D-SA instrument. The AFM was run in intermittent contact mode (tapping mode) using MicroMasch NSC18 tips (typical resonant frequency ~100 kHz, typical probe radius ~10 nm and typical aspect ratio 3:1).



Figure S20 – AFM image for thin film P3HT annealed at 120°C for 10 min (from 30 mg/mL in *o*-DCB, 3000 rpm/s for 60 s).



Figure S21 – AFM image for thin film P3HT:F8IDT blend unannealed (left) and annealed at 120°C for 10 min (right) (18 mg P3HT, 15 mg F8IDT in 1 mL o-DCB, 3000 rpm/s for 60 s).



Figure S22 – AFM image for thin film P3HT:FEHIDT blend unannealed (left) and annealed at 120°C for 10 min (right) (18 mg P3HT, 15 mg FEHIDT in 1 mL o-DCB, 3000 rpm/s for 60 s).

Thin film X-ray diffraction (XRD)

The structure of the thin films was studied with a Bruker D8 Advance X-ray Diffractometer using CuKa radiation (40kV, 40mA) equipped with a LynxEye silicon strip detector to obtain the XRD patterns. Each sample was scanned over the 2 θ range 5° to 60° with a step size of 0.02° 2 θ and a count time of 1.2 seconds per step. Data was collected both before and after thermal annealing (120°C for 10 min in glovebox).



Figure S23 – XRD patterns from pristine F8IDT films from *o*-DCB, before and after annealing at 120°C for 10 min.



Figure S24 – XRD patterns from pristine FEHIDT films from *o*-DCB, before and after annealing at 120°C for 10 min.



Figure S25 – XRD patterns from pristine P3HT films from *o*-DCB, before and after annealing at 120°C for 10 min.



Figure S26 – XRD patterns from pristine P3HT films and P3HT:F8IDT blend films from *o*-DCB.



Figure S27 – XRD patterns from pristine P3HT films and P3HT:FEHIDT blend films from *o*-DCB.

Devices

Device preparation

ITO-coated glass substrates (Lumtec, 5 Ω sq⁻¹) were cleaned by standing in a stirred solution of 5% (v/v) Deconex 12PA detergent at 90°C for 20 min. The substrates were then successively sonicated for 10 min each in distilled water, acetone and *iso*-propanol, and then exposed to a UV-ozone clean (Novascan PDS-UVT) for 10 min. PEDOT:PSS (HC Starck, Baytron P AI 4083) was filtered (0.2 μ m RC filter) and deposited onto these substrates by spin-coating at 5000 rpm for 20 s. The PEDOT:PSS layer was then annealed on a hotplate in a N₂ glovebox at 150°C for 5 min.

P3HT (18 mg, Merck) and F8IDT (15 mg) or FEHIDT (15 mg) were dissolved in individual vials in chlorobenzene or *o*-dichlorobenzene (0.5 mL, Aldrich, anhydrous) in a N₂ glovebox. The solutions were stirred at 90°C for 1 hr, then allowed to cool to room temperature (with stirring) for >30 min. Immediately prior to spin-coating, the P3HT and either F8IDT or FEHIDT solutions were mixed and stirred for 30 s. The blended solution was filtered (0.2 μ m RC filter) and deposited by spin-coating at 3000 rpm for 1 min. Unless otherwise specified, the resulting films were then annealed on a hotplate at 120°C for 10 min.

The coated substrates were then transferred (without exposure to air) to a vacuum evaporator (Angstrom Engineering Inc.) operating at a base pressure below 2×10^{-6} mbar. A layer of Ca (Sigma-Aldrich, 20 nm, 0.5 Å s⁻¹) and Al (Kurt J. Lesker, 100 nm, 1 Å s⁻¹) were deposited through a shadow mask to make the cathode. The area defined by the shadow mask gave device areas of 0.1 cm².

P3HT:PCBM reference devices were prepared in a similar manner. P3HT (15 mg) and PCBM (12 mg, Nano-C) were dissolved in 0.5 mL chlorobenzene in a N_2 glovebox, stirred at 90°C for 1 hr then cooled to room temperature prior to mixing. The blended solution was filtered (0.2 μ m RC filter) and deposited by spin-coating at 2000 rpm for 30 s. The resulting films were then annealed on a hotplate at 120°C for 10 min.

Device characterisation

The devices were tested (without exposure to air) with an Oriel solar simulator fitted with a 1000W Xe lamp filtered to give an output of 100 mW cm⁻² at AM1.5. The lamp was calibrated using a standard, filtered Si cell from Peccell Limited which was subsequently cross-calibrated with a standard reference cell traceable to the National Renewable Energy Laboratory. The devices were tested using a Keithley 2400 Sourcemeter controlled by Labview software. The J-V characteristics of the solar cells were measured and device performance extracted from the J-V data.

For incident-photon-to-converted electron (IPCE) measurements, the devices were encapsulated with glass and a UV-cured epoxy (Summers Optical, Lens Bond type J-91) by exposing to 365 nm UV light inside a N_2 glovebox for 10 min. The encapsulated devices were then removed from the glovebox and tested in air. IPCE ratio data was collected using and Oriel 150W lamp coupled to a monochromator and an optical fibre. The output of the optical fibre was focused to give a beam that was contained within the area of the device. IPCE data was calibrated with a standard, unfiltered Si cell.



Figure S28 – IPCE spectra from unannealed devices.



Figure 29 – IPCE spectra from annealed devices.

Table S5 – Comparison of key device parameters before and after thermal annealing of the
active layer (i.e. annealing applied to blended films prior to deposition of Ca/Al electrode).

n-type	solvent	annealed	V _{oc} (V)	J_{sc} (mA/cm ²)	FF	PCE (%)
F8IDT	СВ	_	0.68	-2.12	37.84	0.55
		120°C 10 min	0.68	-3.55	0.35	0.85
F8IDT	ODCB	_	0.71	-3.78	40.50	1.09
		120°C 10 min	0.72	-4.82	0.48	1.67
FEHIDT	СВ	_	0.66	-2.73	34.55	0.62
		120°C 10 min	0.96	-3.72	0.50	1.77
FEHIDT	ODCB	_	0.74	-4.86	41.23	1.48
		120°C 10 min	0.95	-3.82	0.67	2.43

Dark current analysis

Dark currents from the devices were measured and analysed in the manner described by Thompson *et al.*.^[8] J-V characteristics were collected as detailed above, but without illumination. The dark current J-V characteristics were then fitted to a simplified Shockley equation (see equation (2) in

[8]) to extract values for the diode ideality factor (*n*) and the saturation current density (J_S). The preexponential saturation dark current term (J_{S0}) was then calculated according to:^[8]

$$J_S = J_{S0} \exp\left(-\frac{\Delta E_{DA}}{2nkT}\right) \tag{1}$$

where ΔE_{DA} is the interfacial energy gap corresponding to the difference in energy between the HOMO of the donor and the LUMO of the acceptor. Here, the position of the HOMO for P3HT (-4.7 eV) was obtained from the literature^[9] and the LUMOs for FxIDT were obtained from the results of PESA and UV-visible spectroscopy measurements. V_{oc} was then calculated using J_{SO} , ΔE_{DA} and the measured value for J_{sc} as previously described^[8] using the following equation:

$$V_{oc} = \frac{nkT}{q} ln \left(\frac{J_{sc}}{J_{s0}}\right) + \frac{\Delta E_{DA}}{2q}$$
(2)

where q is the fundamental charge and the temperature T = 298 K.

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	F8IDT	F8IDT	FEHIDT	FEHIDT
	(ODCB)	(CB)	(ODCB)	(CB)
$\Delta E_{DA} (eV)$	0.93	0.93	0.75	0.75
J_{S0} – calc (A/cm ²)	2×10^{-5}	6×10^{-5}	6×10^{-9}	6×10^{-8}
V_{oc} – calc (V)	0.74	0.68	1.03	1.08
V_{oc} – meas (V)	0.63	0.54	0.95	0.96

Table S6 – Comparison of measured and calculated parameters based on dark and light performance measurements.

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Figure S30 – Dark current density versus voltage characteristics used for J_{S0} calculations.

Photo-charge extraction by linear increasing voltage (CELIV)

The charge extraction properties of P3HT, FxIDT and P3HT:FxIDT blends were studied by the photo-CELIV technique as described elsewhere.^[10] Photo-CELIV measurements were performed on sealed OPV devices using a nitrogen pulsed laser (3 ns at 337 nm) as the excitation source with low peak power of 300 μ J/pulse. An Agilent function generator 33250A was used to supply the voltage pulse. The extraction currents were recorded using a 500 MHz Tektronix oscilloscope and a set of resistors. The delay time between the laser pulse and the voltage pulse was set using a digital delay generator, Stanford Research System DG535. Charge carriers were excited by a short light pulse and within the given delay duration (t_{delay}) the linearly increasing voltage pulse (increase rate A=dU/dt) of reverse direction was applied onto the sample electrodes. The pulse of current transient consisting of inter-electrode capacity current ($j(0) = \varepsilon \epsilon_0 \cdot A/d$, where *d* is layer thickness) was analysed. The possible influence of the intrinsic potential of the OPV to the amount of extracted charge was eliminated using a compensating offset voltage (U_{offset}). From the time when extraction current reaches maximum (at t_{max}) the charge carrier mobility, μ can be estimated according to the expression:

$$\mu = \frac{2d^2}{3At_{\text{max}}^2} \tag{3}$$

Figure S31 shows the photo-CELIV transient of a pure film of F8IDT and a binary blend film of P3HT:F8IDT (1.2:1 w/v). Due to the very low mobility of F8IDT, the photo-CELIV transient in Figure S31(a) demonstrates no extraction of charge carrier under dark or under light. The photo-CELIV transient of the blend film demonstrates a typical dark CELIV transient with increasing extraction current due to an increase of the applied voltage, U_{max} and carrier drift velocity. When the charge carrier current starts to decrease, due to the carrier arrival at the electrode, it forms an extraction maximum, t_{max} . The position of the peak markers indicate that t_{max} is shorter with $U_{max}.$ The estimated μ mobility using equation (3) remains as $1.3\text{--}2.1\times10^{\text{--}4}$ cm²/Vs. Figure S32 shows the photo-CELIV transients of a pure film of FEHIDT and a blend film of P3HT:FEHIDT (1.2:1 w/v). Analogous to the measurements on the pristine film of F8IDT, FEHIDT films show no photo-CELIV transient and demonstrate no extraction of charge carrier in the dark or under light. The photo-CELIV transient of the P3HT:FEHIDT blend film demonstrates a typical CELIV transient. From the position of t_{max} , μ was estimated as $1.6\times 10^{\text{-4}}\ \text{cm}^2/\text{Vs}.$ As a reference, we have measured the pure film of P3HT with $\mu=4\ x\ 10^{\text{-3}}$ cm^2/Vs as shown in Figure S33. Given the very low mobilities of the pure films of F8IDT and

FEHIDT, mobilities of the respective blend films with P3HT are substantially higher suggesting that crystallinity of the P3HT is not affected by blending with F8IDT or FEHIDT. This also explains the relatively high fill factor and short circuit current in the BHJ solar cells.



Figure S31 – Photo-CELIV transients for devices based on (a) a pure film of F8IDT and (b) a P3HT:F8IDT (1.2:1 w/v) blend film at different applied U_{max} at $t_{\text{delay}} = 1 \ \mu s$.



Figure S32 – Photo-CELIV transients for devices based on (a) a pure film of FEHIDT and (b) a P3HT:FEHIDT (1.2:1 w/v) blend film at $t_{delay} = 1 \mu s$.



Figure S33 – Photo-CELIV transients for devices based on a pure film of P3HT.

References

- M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. Montgomery, J. A., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT., **2010**.
- [2] A.D. Becke, J. Chem. Phys. **1993**, 98, 5648.
- [3] Irene I. Perepichka, Igor F. Perepichka, Martin R. Bryce and Lars-Olof Pålsson, *Chem. Comm.*, 2005, 31, 3397-3399
- [4] http://www.asap-ms.com/
- [5] C. Petucci and J. Diffenda, J. Mass Spectrom., 2008, 43, 1565.
- [6] A. D. Ray, J. Hammond and H. Major, *Euro. J. Mass Spectrom.*, **2010**, *16*, 169.
- [7] Jungho Jo, Chunyan Chi, Sigurd Höger, Gerhard Wegner and Do Y. Yoon, *Chem. Eur. J.***2004**, *10*, 2681 2688.
- [8] M. D. Perez, C. Borek, S. R. Forrest and M. E. Thompson, J. Am. Chem. Soc. 2009, 131, 9281.
- [9] Y. Zhou, L. Ding, K. Shi, Y. -Z. Dai, N. Ai, J. Wang and J. Pei, Adv. Mater., 2012, 24, 957-961.
- [10] Th. B. Singh, X. Chen, W.W.H. Wong, T. Ehlig, P. Kemppinen, M. Chen, S.E. Watkins, K.N. Winzenberg, S. Holdscroft, D.J. Jones and A.B. Holmes, *Appl. Phys. A*, **2012**, *108*, 515-520.