Supporting Information

Polymer library enables the rapid identification of a highly scalable and efficient donor material for organic solar cells

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Contents

Methods	3
Materials characterisation	3
Devices Fabrication	4
Synthetic procedures	6
Elemental Analysis	9
NMR spectroscopy	10
Solubility Limit Determination	27
Thermogravimetric Analysis (TGA)	31
Differential scanning calorimetry (DSC)	32
Optoelectronic characterisation	33

OTFTs	
Photovoltaic Properties	
Charge carrier mobility measurements	
GIWAXS	ments41
Contact Angle Measurements	
Synthetic Complexity (SC) Analysis	ysis53
Batch-to-batch reproducibility	
References	

Methods

Materials characterisation

All chemicals were used as received and purchased from major chemical suppliers. Synthetic reactions were carried out under nitrogen atmosphere using standard Schlenk techniques. Characterisation was carried out in air at room temperature unless stated otherwise.

¹H NMR, ¹⁹F NMR and ¹³C NMR were collected either on AV-400 (MHz) or AV-500 (500 MHz) Bruker Spectrometer using the *d*-chloroform as solvent. Polymers were purified prior to device fabrication on a Shimadzu GPC system running in chloroform at 40 °C with an Agilent PLgel 10 µm mixed-d column, DGU-20A3 Degasser, LC-20A Pump, CTO-20A Column Oven and SPD-20A UV Detector. UV-vis absorption spectra were recorded on an Agilent Cary 60 UV-vis spectrophotometer at room temperature. The measurements were carried out with 5 μ M solutions in CHCl₃ at a scan rate of 600 nm min-1 and a data interval of 1 nm. Films were prepared from 10 mg mL⁻¹ solutions and spun coated on glass slides and measured at same conditions. Photoluminescence (PL) spectra were acquired on an Agilent Cary Eclipse fluorescence spectrophotometer with 5 µM solutions in CHCl₃ at a scan rate of 120 nm min-1 and a data interval of 1 nm. The excitation and emission slits were set to 5 nm, the emission and excitation filters were set to 'auto' setting. Films were measured on a Fluorolog-3 spectrofluorometer (FL 3-22, Jobin Yvon, Horiba) and excited by a Xenon lamp source. The emitted photons were collected in the front face geometry with a photomultiplier tube (PMT) R928P detector with a slit width of 5 nm. Cyclovoltammetry experiments were performed with a Metrohm Autolab PGSTAT101 Electrochemical Analyser and spectra collected on NOVA software. The experiment was set up using a Ag/Ag⁺ reference electrode and a Pt wire counter electrode. The polymers were dropcasted on the glassy carbon working electrode and measurements taken at a scan rate of 0.1 V s⁻¹ with tetrabutylammonium hexafluorophosphate in acetonitrile (0.1 M) as the supporting electrolyte. Molecular weight analyses were carried out on an analytical GPC Agilent Technologies 1200 series GPC equipped with a RI and UV detector running in chlorobenzene at 80 °C. Two PL mixed-B columns were set up and narrow polydispersity standards were used to calibrate the system. Thermogravimetric analysis (TGA) was carried out using a Mettler Toledo TGA/DSC1, heating from 25 to 750 °C at 5 °C/min under N₂. Differential scanning calorimetry was carried out using a Mettler Toledo DSC1. Temperature dependent UV/vis spectroscopy was carried out using 5 µM solutions in chlorobenzene on a Cary UV/vis Multicell Peltier. Elemental Analysis was carried out by the London Metropolitan University Elemental Analysis Service.

GIWAXS measurements were performed at the SAXS/WAXS beamline at the Australian Synchrotron.¹ 2D scattering patterns were recorded using a Pilatus 2M detector, with the sample-to-detector distance calibrated using a silver behenate reference standard. The sample and detector were enclosed in a vacuum chamber to suppress air scatter. Scattering patterns were measured as a function of the angle of incidence, with data shown acquired with an angle of incidence near the critical angle that maximized scattering intensity from the sample.

Contact angle measurements: the surface tension was measured through pending drop technique on a drop shape analyser (Ossila) at room temperature.

Devices Fabrication

OTFTs: Bottom contact, top gate (BC-TG) thin film transistors were fabricated in a nitrogen-filled glovebox in order to evaluate the side chain and comonomer variation of the polymers. In particular we tested the charge transport of FO6-T, FO8-T. FO8-2T and F08-TT. Glass substrates were cleaned by sonication in a detergent solution (Decon 90), followed by sonication in acetone and isopropanol. Gold source drain electrodes of 40 nm were deposited via thermal evaporation through shadow masks (device channel length 30 nm and width 1000 nm) in high vacuum (5x10⁻⁶ mbar). A self-assembled monolayer PFBT was applied in 1:1000 solution in isopropanol for 10 minutes, followed by rinse with isopropanol. For the FO8-2T OTFTs no further treatment was applied to the Au source/drain electrodes. OSCs were spin coated from 5 mg/ml solutions in chlorobenzene at 2000 rpm for 30 seconds, followed by 10 minutes thermal annealing at 100 °C. As the dielectric layer, 900 nm of CYTOP were used, and 40 nm of aluminium were thermally evaporated as the gate electrodes. Electrical characterisation was conducted using a Keithley 4200 SCS.

OPVs: Devices from all polymers FOX-T, FOX-2T and FOX-TT were prepared based on an inverted device architecture consisting of ITO/ZnO/Active layer/MoO₃/Ag. The indium tin oxide (ITO, 15 Ω sq⁻¹) was pre-patterned on the glass substrates (12 mm*12 mm). The substrates were firstly cleaned by sonication in acetone for 10 min, followed by detergent and deionized water. After another 10 min sonication in acetone, the substrates were cleaned by isopropanol and then immediately transferred into a vacuum environment for 8 min oxygen plasma treatment. A 40nm thickness ZnO layer was deposited on the ITO by 4000 rpm, 40 s spin-coating using a zinc acetate dihydrate precursor solution (219 mg zinc acetate dihydrate precursor dissolved in 60.4 µl 1-ethanolamine and 2 ml 2-methoxyethanol) followed by annealing at 180 °C for 10 min. The ZnO coated substrates were transferred into a dry nitrogen glove box (< 0.1 ppm H₂O, < 0.1 ppm O₂). The ratio of polymer to Y6 was kept constant at 1:1.5 by weight (D:A). Spun coat (2000 rpm) from solutions (20 mg/mL) in chloroform with 0.5 v% 1,8-diiodooctane and annealed at 100 °C for 10 min. For the thermal evaporation, a 10 nm MoO₃ and

a 100 nm Ag layer was sequentially deposited. The MoO₃ layer was deposited at a 0.15 Å s⁻¹ rate and in terms of Ag layer, deposition speed ranged from 0.5 Å s⁻¹ to 1 Å s⁻¹.

Devices with *o*-xylene were prepared using the same device architecture. A D:A ratio of 1:1.5 was used, spun coat from solutions (30 mg/ml) in *o*-xylene and annealed at 100 C for 10 min.

The structure for FO6-T: L8BO devices is the following: ITO/PEDOT:PSS/Active later/PDINO/Ag. The PEDOT:PSS was deposited on ITO by spin-coating to form a 40 nm layer and then put on a 150 °C for 10 min. The blend was dissolved in Chloroform at 15.4 mg/ml concentration using a 1:1.2 D:A ratio with 0.5 v% 1,8-diiodooctane as the additive. The active layer was spun coat (3000 rpm) and annealed at 100 °C for 10 min. PDINO (1 mg/ml) was then deposited by spin-coating for 30 s at 3000 rpm speed followed by 100 nm Ag via thermal evaporation. Through a shadow mask, the area for each pixel is 0.045 cm². J-V characteristics were measured using a Keithley 4200 Source-Measure unit (scan rate 25 mV s⁻¹). An Oriel Instruments Solar Simulator with a Xenon lamp and calibrated to a silicon reference cell was used to provide AM1.5G irradiance.

SCLC Mobility:

The structure for hole only devices is the following: ITO/PEDOT:PSS(40nm)/Active layer/Au The structure for electron only devices is the following: ITO/ZnO/Active Layer/DPO/Ag *Active layer processing condition*: All polymers are processed with a concentration of 10mg/mL in Chloroform. For the blends a 20 mg/mL total concentration is used, with a D:A ratio of 1:1.5. All active layer films are spin coated at 2000 rpm. All thicknesses are measured with a Dektak profilometer. SCLC results – Calculated mobilities:

To fit the J-V curves of the hole only devices I used the Mott-Gurney equation.

$$J = \frac{9}{8}\varepsilon_0\varepsilon_\mathrm{r}\mu\frac{V^2}{d^3}$$

Where ε is the relative dielectric constant of the material (3 was assumed), ε_0 the vacuum permittivity, μ the mobility, *d* the film thickness, γ is the field activation factor of mobility, and *V* is the applied voltage.

Synthetic procedures

General procedure for the fluorobenzo[c][1,2,5]thiadiazole

preparation

of





NaH (60% dispersion in mineral oil) was washed with hexane prior to use. The grey solid was dispersed in hexane and stirred for 10 minutes, after which the solid was filtered off and washed with another portion of hexane on the filter. The obtained powder was weighed for the reaction.

4,7-dibromo-5,6-difluorobenzo[c][1,2,5]thiadiazole (1 g, 3.03 mmols, 1 eq.) and NaH (146 mg, 6.06 mmol, 2 eq.) was added to a 100 mL two-necked round bottom flask and flushed with nitrogen three times before dry THF (30 mL) was added via syringe. The respective alcohol (3.03 mmol, 1 eq.) was added via syringe and the mixture was heated to reflux while stirring for 2 days. Over the course of the reaction, the mixture turned brown. The reaction was allowed to cool to room temperature and transferred to a separating funnel with dichloromethane and brine and extracted with dichloromethane (3 x 50 mL). The combined organic layers (brown solution) were dried over Na₂SO₄, filtered and the solvent was removed under reduced pressure. The crude brown residue was purified using column chromatography with petroleum ether and ethyl acetate (20:1 v:v) to obtain the product as a light-yellow oil.

Name	Alcohol	Yield
FO2	2-ethyl-1-hexanol (0.48 mL)	0.608 g, 46 %
FO4	2-butyl-1-octanol (0.67 mL)	1.13 g, 75 %
FO6	2-hexyl-1-decanol (0.88 mL)	1.05 g, 63 %
FO8	2-octyl-1-dodecanol (1.08 mL)	1.47 g, 80 %
FO10	2-decyl-1-tetradecanol (1.28 mL)	1.50 g, 75 %

FO2: ¹H NMR (400 MHz, CDCl₃) δ 4.13 (d, *J* = 5.4 Hz, 2H), 1.80 (p, *J* = 5.9 Hz, 1H), 1.71 – 1.43 (m, 4H), 1.42 -1.30 (m, 4H), 1.00 (t, J = 7.5 Hz, 3H), 0.95 - 0.88 (m, 3H). ¹⁹F NMR (377 MHz, CDCl₃) δ -111.36. ¹³C NMR (101 MHz, CDCl₃) δ 158.09, 155.51, 150.12, 149.72, 149.53, 149.20 (d), 106.09 (d), 98.82, 98.58, 77.85 (d), 14.25, (APCI): 40.68, 30.30, 29.19, 23.72, 23.16, 11.29. HRMS m/z calcd. for C14H18FN2OS[79]Br[81]Br+ = 440.9465 [M+H]+; found: 440.9476

FO4: ¹H NMR (400 MHz, CDCl₃) δ 4.12 (d, J = 5.2 Hz, 2H), 1.91 – 1.77 (m, 1H), 1.66 – 1.53 (m, 2H), 1.51 – 1.24 (m, 15H), 0.91 (m, 6H). ¹⁹F NMR (377 MHz, CDCl₃) δ -111.29. ¹³C NMR (101 MHz, CDCl₃) δ 158.78, 155.51, 150.12, 149.73, 149.54, 149.18 (d), 106.05 (d), 98.81, 98.57, 78.25 (d), 39.22, 31.99, 31.13, 30.81, 29.79, 29.18, 26.94, 23.17, 22.81, 14.25. HRMS (APCI): m/z calcd. for C18H26FN2OS[79]Br[81]Br+ = 497.0091 [M+H]+; found: 497.0082

FO6: ¹H NMR (400 MHz, CDCl₃) δ 4.12 (d, J = 4.1 Hz, 2H), 1.85 (p, J = 6.0 Hz, 1H), 1.68 – 1.52 (m, 2H), 1.50 – 1.19 (m, 23H), 0.89 (m, 6H). ¹⁹F NMR (377 MHz, CDCl₃) δ -111.27. ¹³C NMR (101 MHz, CDCl₃) δ 158.10, 155.52, 150.13, 149.74, 149.56, 149.20 (d), 106.06 (d), 98.81, 98.58, 78.26 (d), 39.24, 32.04, 32.00, 31.13, 30.12, 29.79, 29.73, 29.47, 26.95, 22.83, 14.26. HRMS (APCI): m/z calcd. for C22H34FN2OS[79]Br[81]Br+ = 553.0717 [M+H]+; found: 553.0721

FO8: ¹H NMR (400 MHz, CDCl₃) δ 4.12 (d, J = 5.2 Hz, 2H), 1.89 – 1.78 (m, 1H), 1.71 – 1.51 (m, 4H), 1.51 – 1.17 (m, 33H), 0.88 (t, J = 6.6 Hz, 6H). ¹⁹F NMR (377 MHz, CDCl₃) δ -111.25. ¹³C NMR (101 MHz, CDCl₃) δ 158.09, 155.51, 150.12, 149.73, 149.54, 149.18 (d), 106.05 (d), 98.81, 98.57, 78.24 (d), 39.23, 32.07, 32.04, 31.12, 30.11, 29.81, 29.78, 29.74, 29.50, 29.47, 26.97, 22.83, 14.27. HRMS (APCI): m/z calcd. for C26H42FN2OS[79]Br[81]Br+ = 609.1343 [M+H]+; found: 609.1344

FO10: ¹H NMR (400 MHz, CDCl₃) δ 4.12 (d, J = 5.1 Hz, 2H), 1.85 (p, J = 6.0 Hz, 1H), 1.66 – 1.52 (m, 2H), 1.52 – 1.20 (m, 40H), 0.88 (t, J = 6.8 Hz, 6H). ¹⁹F NMR (377 MHz, CDCl₃) δ -111.25. ¹³C NMR (101 MHz, CDCl₃) δ 158.10, 155.53, 150.14, 149.75, 149.56, 149.20 (d), 106.07 (d), 98.82, 98.58, 78.26 (d), 39.23, 32.07, 31.13, 30.12, 29.85, 29.82, 29.78, 29.51, 26.97, 22.84, 14.27. HRMS (APCI): m/z calcd. for C30H50FN2OS[79]Br[81]Br+ = 665.1969 [M+H]+; found: 665.1968

General procedure for the preparation of the polymers



Both monomers (0.5 mmol, 1 eq.), $Pd_2(dba)_3 \cdot CHCl_3$ (0.01 mmol, 0.02 eq.) and $P(o-tol)_3$ (0.04 mmol, 0.08 eq.) were placed in an oven-dried 20 mL microwave vial and flushed with nitrogen three times. Dry chlorobenzene (CB) (10 mL) was degassed for approx. 30 min and added to the reaction vial via syringe. The reaction mixture was degassed properly for 20 min. The vial was transferred to a microwave reactor and heated stepwise to 180 °C (120 °C for 2 min, 140 °C for 2 min, 160 °C for 2 min) and the temperature was kept for 40 min. Afterwards, the blue viscous solution was precipitated into methanol, followed by filtration to isolate the crude polymer. Purification was carried out using Soxhlet extraction with methanol, acetone, hexane and chloroform (in that order). The chloroform fraction was concentrated to approx. 10 mL and precipitated in methanol. The suspension was stirred for 20 min and the polymer was isolated as a blue solid.

Scale up of FO6-T

Both monomers (4 mmol, 1 eq.), $Pd_2(dba)_3 \cdot CHCl_3$ (0.08 mmol, 0.02 eq.) and $P(o-tol)_3$ (0.32 mmol, 0.08 eq.) were placed in an oven-dried 100 mL 2N-RBF and flushed with nitrogen three times. Dry chlorobenzene (CB) (60 mL) was degassed for approx. 30 min and added to the reaction vial *via* syringe.

The reaction mixture was degassed properly for 20 min. The reaction mixture was heated to reflux and left overnight while stirring. Afterwards, the blue viscous solution was precipitated into methanol, followed by filtration to isolate the crude polymer. Purification was carried out using Soxhlet extraction with methanol, acetone, hexane and chloroform (in that order). The chloroform fraction was concentrated and precipitated in methanol. The suspension was stirred for 20 min and the polymer was isolated as a blue solid (1.81 g, 95 %).

Elemental Analysis

Elemental Analysis was performed by the London Metropolitan University Elemental Analysis Service.

Polymer	Expected			Found		
	C (%)	H (%)	N (%)	C (%)	H (%)	N (%)
FO4-T	62.82	6.95	6.66	64.32	6.14	6.36
FO6-T	65.51	7.82	5.88	66.29	7.04	5.67
FO8-T	67.63	8.51	5.26	68.44	8.47	4.97
FO10-T	69.34	9.07	4.76	70.05	8.57	4.61
FO6-2T	64.48	7.03	5.01	65.47	6.51	4.76
FO8-2T	66.41	7.70	4.56	68.60	7.85	3.89
FO10-2T	68.02	8.26	4.17	66.95	6.95	4.36
FO6-TT	63.12	7.00	5.26	63.02	6.34	5.02
FO8-TT	65.27	7.70	4.76	66.05	7.21	4.46
FO10-TT	67.04	8.28	4.34	67.90	7.58	4.12

Table S1: Elemental analysis results and comparison to expected values for the respective atoms.

NMR spectroscopy



Figure S1: ¹H NMR (400 MHz) spectrum of FO2 recorded in CDCl_{3.}



Figure S2: ¹⁹F NMR (376 MHz) of FO2 recorded in CDCl_{3.}



Figure S3: ¹³C NMR (100 MHz) spectrum of FO2 recorded in CDCl₃.



Figure S4: ¹H NMR (400 MHz) spectrum of FO4 recorded in CDCl_{3.}



Figure S5: ¹⁹F NMR (376 MHz) of FO4 recorded in CDCl_{3.}



Figure S6: ¹³C NMR (100 MHz) spectrum of FO4 recorded in CDCl₃.



Figure S7: ¹H NMR (400 MHz) spectrum of FO6 recorded in CDCl_{3.}



Figure S8: ¹⁹F NMR (376 MHz) spectrum of FO6 recorded in CDCl_{3.}



Figure S9: ¹³C NMR (100 MHz) spectrum of FO6 recorded in CDCl₃.



Figure S10: ¹H NMR (400 MHz) spectrum of FO8 recorded in CDCl_{3.}



Figure S11: ¹⁹F NMR (376 MHz) spectrum of FO8 recorded in CDCl₃.



Figure S12: ¹³C NMR (100 MHz) spectrum of FO8 recorded in CDCl₃.



Figure S13: ¹H NMR (400 MHz) spectrum of FO10 recorded in CDCl_{3.}



Figure S14: ¹⁹F NMR (376 MHz) spectrum of FO10 recorded in CDCl₃.



Figure S15: ¹³C NMR (100 MHz) spectrum of FO10 recorded in CDCl₃.



Figure S16: ¹H NMR (400 MHz) (top) and ¹⁹F NMR (spectra of FO4-T recorded in CDCl₃ at 55 °C.



Figure S17: ¹H NMR (top) and ¹⁹F NMR spectra of **FO6-T** recorded in CDCl₃ at 55 °C.



Figure S18: ¹H NMR (top) and ¹⁹F NMR spectra of FO8-T recorded in CDCl₃ at 55 $^{\circ}$ C.



Figure S19: 1H NMR (top) and 19F NMR spectra of FO10-T recorded in CDCl3 at 55 °C.



Figure S20: ¹H NMR (top) and ¹⁹F NMR spectra of FO6-2T recorded in CDCl₃ at 55 °C.



Figure S21: ¹H NMR (top) and ¹⁹F NMR spectra of FO8-2T recorded in CDCl₃ at 55 °C.



Figure S22: ¹H NMR (top) and ¹⁹F NMR spectra of FO10-2T recorded in CDCl₃ at 55 °C.



Figure S23: ¹H NMR (top) and ¹⁹F NMR spectra of FO8-TT recorded in CDCl₃ at 55 °C.



Figure S24: ¹H NMR (top) and ¹⁹F NMR spectra of FO10-TT recorded in CDCl₃ at 55 °C.

Solubility Limit Determination

The limit of the solubility of selected polymers was determined *via* a standard calibration curve method.² UV/vis absorption measurements of polymer solutions in chloroform of different concentrations (0.01 mg/mL to 0.05 mg/mL) were performed and the calibration curve constructed. Saturated solutions of the polymers were prepared in chloroform by continually adding material to the solution, and subsequent centrifuging of the solutions (20 min, 10000 rpm), an aliquot of the solution was used to prepare a diluted sample for UV/vis absorption measurement. The concentration of the saturated solution was then determined by using the linear equation of the standard calibration curve.



Figure S25: Absorption measurements of the polymers for the determination of the solubility limit. Measurements were taken at five different concentrations as indicated in the graph.



Figure S26: Absorption at a certain wavelength (indicated in plot) at different concentrations.

Polymer	Abs at λ_{max}	Slope	Intersect	Conc. in aliquot	Solubility	limit
				(mg/mL)	(mg/mL)	
FO4-T	1.31	44.52	0.0210	0.0290	14.5	
FO6-T	1.52	44.06	-0.3239	0.0418	41.8	
FO6-2T	0.94	35.76	-0.0745	0.0285	2.9	
FO8-2T	1.27	40.97	-0.0435	0.0321	8.0	
FO10-2T	1.01	46.51	-0.0134	0.0219	11.0	
FO6-TT	1.27	31.20	-0.1119	0.0442	4.4	
FO8-TT	0.87	42.71	-0.0573	0.0217	10.8	
FO10-TT	2.07	51.68	0.0103	0.0398	39.8	

Table S2: Absorption measurements and linear equation values for each polymer. The solubility limit was calculated from the absorption measurement of the diluted aliquot of the prepared saturated solutions.

Thermogravimetric Analysis (TGA)



Figure S27: TGA for polymers FO10-T, FO10-2T and FO10-TT

Differential scanning calorimetry (DSC)



Figure S28: DSC heating (top) and cooling curves for the polymers a) FOR-T, b) FOR-2T and c) FOR-TT with a heating rate of 10 $^{\circ}$ C/min.

Optoelectronic characterisation



Figure S29: Photoluminescence spectra of polymers in solution in CHCl₃ a) **FOR-T** polymers c) **FOR-2T** polymers e) **FOR-TT** polymers and in thin film b) **FOR-T** polymers, d) **FOR-2T** polymers and f) **FOR-TT** polymers. The solutions were prepared at a 5 μ M concentration and thin films were prepared from a 10 mg/mL solution and spin coated on glass slides.



Figure S30: Normalised absorption of polymers at different concentrations in chloroform to investigate in solution behaviour.



Figure S31: Normalised absorption of polymers a) **FO6-2T**, b) **FO8-2T**, c) **FO10-2T** and d) **FO10-TT** at temperatures varying from 20 °C to 80 °C in chlorobenzene.

Determination of energy levels



Figure S32: Cyclic voltammograms of polymer films in an acetonitrile-[n-Bu₄N]PF₆ solution (0.1 M) at a scan rate of 100 mVs⁻¹; the potentials were measured against an Ag/Ag⁺ reference electrode and referenced using Ferrocene (Fc/Fc⁺) as a standard. a) **FOR-T**, b) **FOR-2T** and c) **FOR-TT**.

OTFTs

Transfer and output characteristics of the FO6-T, FO8-T, FO8-2T and FO8-TT as measured in the ptype region.



Figure S33: Transfer and output characteristics of a) FO6-T and b) FO8-T OTFTs in bottom contact, top gate device configuration as measured for devices with channel length 30 nm and width of 1000 nm.



Figure S34: Transfer and output characteristics of a) FO8-2T and b) FO8-TT OTFTs in bottom contact, top gate device configuration as measured for devices with channel length 30 nm and width of 1000 nm.

Table S3: OTFTs parameters summary including linear and saturation mobility, and threshold voltage. The latter was calculated from the slope of the second derivative of the drain current. An average of 10 devices measured by material.

OSCs	Linear mobility	Saturation mobility	Threshold
	(cm ² /Vs)	(cm ² /Vs)	Voltage (V)
FO6-T	0.02±0.01	0.04±0.01	- 22
FO8-T	0.018±0.003	0.039 ± 0.02	- 18

FO8-2T	0.02±0.01	0.06 ± 0.02	- 19
FO8-TT	0.02±0.01	$0.038 {\pm} 0.007$	- 8

Photovoltaic Properties



Figure S35: Statistic bar plot for the PCEs of all polymers FOX-T, FOX-2T and FOX-TT



Figure S36: Light-intensity-dependent J–V measurements of OPVs from FO6-T:Y6 and FO8-T:Y6 blends.



Figure S37: EQE of FO6-T with two different acceptors Y6 and L8BO in a conventional structure architecture

Charge carrier mobility measurements

Hole Mobilities

Table S4: Calculated hole mobilities for the polymers and the polymer blends with Y6

Polymer	Active layer thickness	Mobility (cm ² /Vs)
FO8-T	95nm	1.55x10 ⁻⁴
FO8-TT	110nm	4.95x10 ⁻⁴
FO6-T	75nm	1.08x10 ⁻⁴
FO8-2T	160nm	1.76x10 ⁻⁴
FO8-T:Y6	100nm	2.32x10 ⁻⁵
FO8-TT:Y6	120nm	7x10 ⁻⁵
FO6-T:Y6	95nm	3.43x10 ⁻⁵
FO8-2T:Y6	250nm	1.10x10 ⁻⁴

The J-V curves for every condition used to extract the respective mobilities are reported below.



Figure S38: J-V curves and the linear fit for devices based on different polymers a) to d) and the blends of the polymers with the acceptor Y6 e) to h).

Electron Mobilities

	Active layer thickness	Mobility (cm ² /Vs)
Y6	70nm	1.15x10 ⁻⁴
FO8-T:Y6	100nm	2.2x10 ⁻⁴
FO8-TT:Y6	120nm	5.1x10 ⁻⁴
FO6-T:Y6	95nm	7.3x10 ⁻⁵
FO8-2T:Y6	250nm	5.5x10 ⁻³

Table S5: Determined Electron mobilities for the polymer blends with Y6



Figure S39: J-V curves of the polymers and Y6 including the linear fits for determining the electron mobilities is shown.

PCE (%) Jsc (V) Voc (mA cm⁻²) FF FO6-T:Y12 24.90 0.82 0.61 12.64 5 Current Density (mA cm⁻²) FO6-T:Y12 0 -5 -10 -15 -20 -25

Table S6: Photovoltaic performance of devices based on FO6-T:Y12 prepared from xylene solutions (30 mg/ml) under AM1.5G illumination.

Figure 40: J-V curve of OSC device based on FO6-T:Y12 processed from xylene under AM1.5G illumination.

Voltage (V)

0.4

0.6

0.8

1.0

0.2

-30

0.0



Figure S41: Normalised PCE of FO6-T:Y6 device under 1 sun illumination over a total of 720 hours in N₂.



Figure S42: Normalised PCE of FO6-T:Y12 device under 1 sun illumination over a total of 720 hours in N_2 .



Figure S43. 2D GIWAXS images of neat FO6-T, neat Y6, FO6-T:Y6 blends and 1D line profiles.

As seen in Figure S39, the scattering pattern of the FO6-TY:Y6 blend consists of scattering from both FO6-T and Y6 as indicated by the azimuthal intensity distribution of $q \sim 0.3$ Å⁻¹ showing maxima in IP and OOP directions. The scattering features of the blend are dominated by the Y6 contribution indicating strong aggregation behaviour of Y6 and disruption of FO6-T packing with only (100) and (010) peaks of FO6-T being observed. The IP peak at $q \sim 0.3$ Å⁻¹ in blend film is likely to have contributions from both donor (D) and acceptor (A) peaks, resulting in peak shifting as compared to the IP plots of neat films. The OOP pi-pi (010) peak of A is significantly suppressed in the blend film.



Figure S44. 2D GIWAXS images of neat FO8-T, neat Y6, FO8-T:Y6 blends and 1D line profiles.

Similar observations as for the FO6-T:Y6 blend film, however the IP pi-pi (010) peak of FO8-T is completely suppressed in the blend film.



Figure S45 2D GIWAXS images of neat FO8-2T, neat Y6, FO8-2T:Y6 blends and 1D line profiles.

Scattering pattern consists of the blend scatterings from both FO8-2T and Y6. The scattering features are dominated by Y6 indicating strong aggregation behaviour of Y6 and disruption of FO8-2T packing with only (100), (100)' and (003) peaks of FO8-2T being observed.

Note that (010) peak of FO8-2T gets suppressed completely in blend film as indicated by the same pipi stacking peak position in blend film and neat Y6 film.



Figure S46 2D GIWAXS images of neat FO8-TT, neat Y6, FO8-TT:Y6 blends and 1D line profiles.

Scattering pattern of the blend consists of scattering feature from both FO8-TT and Y6.

The scattering features are dominated by the FO8-TT contribution indicating strong aggregation behavior of FO8-TT and disruption of Y6 packing with Y6 pi-pi stacking peak greatly suppressed.



Figure S47: Comparison of FO6-T and FO8-T 1D line plots. A clear shift of the (h00) peaks to longer q-positions can be observed.

Contact Angle Measurements

Table S7: Determined contact angles for droplets of water (DI), diiodomethane (DIM) and ethylene glycol (EG) on films on glass substrate. The Surface energy was determined according to according to Owens, Wendt, Rabel and Kaelble (OWRK) method.³ Flory Huggins parameter χ was determined following a published protocol.⁴

		Solvent			χ
	DI	DIM	EG	Surface Energy (mN/m)	(Polymer:Y6 blend)
FO4-T	102.60	56.06	36.90	39.09	0.528
FO6-T	105.27	51.01	37.5	42.29	0.226
FO8-T	96.27	59.42	33.78	37.13	0.783
FO10-T	100.32	57.44	34.53	38.4	0.611
FO6-TT	101.08	53.33	29.68	41.4	0.296
FO8-TT	104.79	50.78	25.13	44.15	0.112
FO10-TT	101	51.77	32.32	41.8	0.263
FO6-2T	100.95	59.49	29.86	38.12	0.647
FO8-2T	104.96	60.67	28.22	38.31	0.622
FO10-2T	106.97	62.65	32.08	36.86	0.823
Y6	96.21	35.09	32.58	48.7	

Synthetic Complexity (SC) Analysis

The analysis was conducted as outlined in recent works.^{5, 6} Consistency in retrieving and analysing the data was our main goal, we followed several rules and measures throughout the analysis. In the following protocol we will describe how each parameter was defined and analysed accordingly.

a) Number of Synthetic Steps (NSS)

From which starting material a synthesis of a polymer starts, is often difficult to define. For this analysis, the starting material for the synthesis of the polymers was defined as the material which the authors of the protocols we followed were using, if the molecule was commercially available and is comparable in cost. In our analysis, a synthetic step is defined as the process from the reaction occurring in the respective vessel followed by a work-up procedure. If a new reagent is added to the compound in a different vessel, the reaction was considered a separate step. The polymerisation step was included as well.

b) Reciprocal overall yield (RY)

The overall yield was calculated considering all individual yields that were given in the synthetic procedures.

c) Number of unit operations (NUO)

The synthetic procedures were analysed and the following operations in the work-up and purification protocol were counted as a unit operation: 1) Quenching/neutralisation, 2) Extraction, 3) Column chromatography, 4) Recrystallisation and 5) Distillation/Sublimation. It needs to be noted that removing the solvent in vacuo was counted as a distillation step.

d) Number of column chromatographies (NCC)

The number of column chromatographies was included as a separate parameter, as they are very inconvenient in an industrial setting. It needs to be noted, that the analysed protocols are based on lab scale syntheses, where column chromatography is a standard technique. If the preparation of the polymer were to be realised in an industrial setting, other possibilities might be feasible and would hence reduce the SC.

e) Number of hazardous chemicals (NHC)

All chemicals involved in the preparation of the polymers were taken into account, the following hazard statements were included: *H340*, *H341*, *H350*, *H351*, *H360*, *H361*, *H300*, *H304*, *H310*, *H330*, *H370*,

H371, H400, H410, H411, H260, H261, H220, H222, H224, H250, H290, H314, H318, H200, H20, H202, H203, H204, H205, H240, H241, H271.

The following formula was used to calculate the SC. The weighing parameters were adapted from Riccardo Po et al.⁶ in order to obtain a certain degree of reproducibility.

 $SC = 35 * NSS/NSS_{max} + 25* \log RY/\log RY_{max} + 15 * NUO/NUO_{max} + 15 * NCC/NCC_{max} + 10 * NHC/NHC_{max}$

Table S8: Synthetic complexity analysis: determined parameters for the respective polymers and result for synthetic complexity (SC)

D I	NGG	Yield	Quenching/		Column					
Polymer	NSS	(%)	neutralisation	Extraction	chromatography	Recrystallisation	Distillation/Sublimation	NUO	NHC	SC
PTQ10	6	28	4	4	1	2	3	14	23	7.9
PTVT-T	6	32	2	2	4	2	5	15	32	15.5
PB2	15	7	2	9	6	2	11	30	40	70.05
PM6	15	0.4	8	12	9	1	10	40	75	100.00
FO6-T	6	32	3	3	2	0	2	10	25	7.0
PDCBT	6	9	2	5	4	0	4	15	36	21.9

The synthetic route to each of the polymers in detail in the following graphs including the numbers corresponding to the respective unit operation (1 =Quenching/Neutralisation, 2 =Extraction, 3 =Column chromatography, 4 = Recrystallisation, 5 = Distillation/Sublimation).

Synthetic routes were retrieved from the literature. For the majority we used Riccardo Po et al, and made changes following more recent published work.⁶

PTQ10

1,4-dibromo-2,3-difluorobenzene can be used as starting material in the synthesis of PTQ10, as this is already a cheap building block for the synthesis.⁷



PM6









PTV-T





PDCBT



F06-T

Synthesis of precursor based on published protocols of J. Rech⁷ and R. Po⁶



Br S Br $(Me)_3Sn$ $Sr(Me)_3$

Batch-to-batch reproducibility

FO6-T (Batch A): M_n: 56 kDa, M_w: 205 kDa

FO6-T (Batch B): M_n: 55 kDa, M_w: 250 kDa

Table S9: Photovoltaic parameters of the two different FO6-T batches in blends with Y6 as the acceptor under the illumination of AM1.5G.

	V _{OC} (V)	J _{SC} (mA cm ⁻²)	Fill factor (%)	PCE (%)
FO6-T:Y6 Batch A	0.79	26.70	67	14.1
FO6-T:Y6 Batch B	0.79	26.42	66	13.7



Figure S48: OPV J-V characteristics based on FO6-T:Y6 processed from two different FO6-T batches

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