Supporting Information

Enhanced Solid-state Order and Field-Effect Hole Mobility Through Control of Nanoscale Polymer Aggregation

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I. General methods

For the molecular weight determination of polymers, samples were dissolved in HPLC grade chloroform at a concentration of 1 mg/mL. The resulting solution was briefly heated and then allowed to return to room temperature prior to filtering through a 0.45 μ m polytetrafluoroethylene (PTFE) filter. Size-exclusion chromatography (SEC) was performed with HPLC grade chloroform at an elution rate of at 1.0 mL/min through three PLgel Mixed-C columns at room temperature. The particle size in the columns was 5 μ m and the columns were maintained at room temperature. The SEC system consisted of a Waters 2695 Separation Module and a Waters 486 Tunable Absorption Detector. The apparent molecular weights and polydispersities (M_w/M_n) were determined with a calibration based on linear polystyrene standards using Millennium software from Waters.

UV-vis-NIR spectral data were measured at room temperature with a Varian Cary 50 Conc spectrophotometer. Thin-film measurements were collected by spin-coating a chloroform solution of the polymer on to an octyltrichlorosilane (OTS) functionalized quartz substrate. Films were subjected to the same conditions as those outlined for the optimized OFET devices prior to UV-vis analysis.

Cyclic voltammograms were collected using a Solartron 1285 potentiostat under the control of CorrWare II software. A standard three-electrode cell based on a Pt wire working electrode, a silver wire pseudo-reference electrode (calibrated vs. Fc/Fc^+), and a Pt wire counter electrode was purged with nitrogen and maintained under a nitrogen atmosphere during all measurements. Acetonitrile was purchased anhydrous from Aldrich and tetrabutylammonium hexafluorophosphate (0.1 M) was used as the supporting electrolyte. Polymer films were drop cast onto a Pt wire working electrode from a 1% (w/w) chloroform solution and dried under nitrogen prior to measurement.

Polymer solubility (milligrams per milliliter) in chloroform was determined by making a saturated solution (> 40 mg/mL) of each material and allowing the solutions to stir overnight at 60 °C. The hot solutions were then filtered through a 0.2 μ m PTFE syringe filter to remove undissolved polymer. A known volume of the filtered solution was transferred to a tared glass vial, evaporated to dryness, and the weight was determined.

The topography of the active layers were imaged using a Veeco Multimode V atomic force microscope (AFM) operated in tapping mode under ambient conditions using aluminum coated silicon cantilevers (Veeco; TAP150Al, $f_0 = 122-169$ kHz, k = 5N/m). The average root mean square roughness (R_{RMS}) of the films was obtained from a minimum of five distinct AFM images gathered from three independently fabricated devices. R_{RMS} values were gathered over a 1 μ m x 1 μ m image. AFM images were analyzed using the WSxM 5.0 software.¹

Grazing-incidence X-ray scattering (GIXD) experiments were conducted at the Stanford Synchotron Radiation Lightsource (SSRL) on beamline 11-3. Samples were prepared following the same procedure for fabricating OFET devices using the optimized device conditions and were irradiated at a fixed incident angle of approximately 0.1°. The GIXD patterns were recorded with a 2-D image detector (MAR345 image plate detector) using an X-ray energy of 12.71 keV ($\lambda = 0.975$ Å). To maximize the intensity from the sample, the incident angle was carefully chosen such that the X-ray beam penetrated the sample completely but did not interact significantly with the silicon substrate. Typical exposure times were between 30 and 900 s.

Differential scanning calorimetry was performed on each of the polymers using 2-6 mg of material in a TA Instruments DSC Q200. Samples were scanned from 50 to 250°C at a rate of 5° C/min.

¹H NMR spectra of the polymer samples in chloroform-*d* were obtained using a Bruker AV-500 instrument with an inverse probe at 40 °C.

Dynamic light scattering (DLS) was performed using a Zetasizer Nano ZS (Malvern Instruments). Samples were measured from 0.5 mg/mL solutions in chloroform using a 1-cm-path-length quartz cuvette and averaged over a minimum of five separately prepared samples.

II. Synthetic procedures

Synthetic methods, including monomer syntheses, were adapted from previously reported procedures described in our earlier work on furan-containing polymers for solar cell applications.^{2,3} All commercially available reagents obtained from suppliers were used without further purification. Unless otherwise noted, all reactions were carried out under nitrogen with standard Schlenk techniques, and glassware used in dry reactions was flame dried under high-vacuum prior to use. Tetrahydrofuran (THF), dimethylformamide (DMF), and toluene were purified and dried by passing through two columns of neutral alumina, under nitrogen, prior to use. Flash chromatography was performed using Silicycle SiliaFlash @ P60 (particle size 40-63 μ m, 230-400 mesh) silica gel.



Poly(2,5-bis(2-butyloctyl)-3-(furan-2-yl)-6-(5-(thiophen-2-yl)furan-2-yl)pyrrolo[3,4c]pyrrole-1,4(2H,5H)-dione) (PDPP2FT-BO)



A 50-mL Schlenk tube was charged with **1-BO** (180.0 *m*g, 0.236 *m*mol) and **2** (96.71 mg, 0.236 *m*mol), and the tube was evacuated and refilled with N₂ three times. Chlorobenzene (7 mL) was added to the tube, and the resulting solution was degassed by bubbling N₂ for 30 min while an oil bath was preheated to 90 °C. Upon removing the degassing needle, Pd₂(dba)₃ (2 mol %, 4.72 μ mol, 4.32 *m*g), P(*o*-tol)₃ (8 mol %, 18.88 μ mol, 5.75 *m*g were added to the solution, and the Schlenk tube was immediately heated at 90

°C. After 5 min, the mixture was stirred for additional 24 h at 110 °C. The reaction mixture was allowed to cool to 55 °C before chloroform (30 mL) and a palladium scavenger, N,N-diethylphenylazothioformamide (CAS# 39484-81-6, 20 mol%), were added. The resulting mixture was stirred for 3 h at 55°C and precipitated into methanol (200 mL). The precipitates

were filtered through a Soxhlet thimble and purified via Soxhlet extraction. The polymer was washed for 12 h with methanol, washed for 8 h with hexanes and extracted with chloroform. The chloroform solution was then precipitated into methanol (150 mL), and the suspension was filtered through a 20 μ m Nylon membrane to afford **PDPP2FT-BO** as a dark solid (148 mg, M_n = 55 kDa, M_w = 87 kDa, PDI = 1.6).

Poly(2,5-dihexadecyl-3-(furan-2-yl)-6-(5-(thiophen-2-yl)furan-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione) (PDPP2FT-C16)



Followed the same synthetic procedure as for **PDPP2FT-BO**. Instead, used **1-C16** (150 mg, 0.171 mmol), **2** (70.25 mg, 0.171 mmol), Pd₂(dba)₃ (2 mol %, 3.43 μ mol, 3.14 mg), P(*o*-tol)₃ (8 mol %, 13.72 μ mol, 4.17 mg) and chlorobenzene (5.6 mL). The precipitates were filtered through a Soxhlet thimble and purified via Soxhlet extraction. The polymer was washed for 12 h with

methanol, 2 h with hexanes and 2 h in dichloromethane, and it was extracted with chloroform. The chloroform solution was then precipitated into methanol (200 mL), and the suspension was filtered through a 20 μ m Nylon membrane to afford **PDPP2FT-C16** as a dark solid (123 mg, M_n = 52 kDa, M_w = 80 kDa, PDI = 1.6).

Poly(3-([2,2'-bifuran]-5-yl)-2,5-bis(2-butyloctyl)-6-(furan-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione) (PDPP3F-BO)



Followed the same synthetic procedure as for **PDPP2FT-BO**. Instead, used **1-BO** (18.24 mg, 0.168 mmol), **3** (66.2 mg, 0.168 mmol), $Pd_2(dba)_3$ (2 mol %, 3.36 µmol, 3.08 mg), $P(o-tol)_3$ (8 mol %, 13.45 µmol, 4.09 mg) and chlorobenzene (5 mL). The precipitates were filtered through a Soxhlet thimble and purified via Soxhlet extraction. The polymer was washed for 12 h with methanol and 8 h with hexanes, and it was extracted with chloroform. The chloroform solution was then precipitated into

methanol (200 mL), and the suspension was filtered through a 20 μ m Nylon membrane to afford **PDPP2FT-C16** as a dark solid (103 mg, $M_n = 46$ kDa, $M_w = 77$ kDa, PDI = 1.6).

Poly(3-([2,2'-bifuran]-5-yl)-6-(furan-2-yl)-2,5-dihexadecylpyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione) (PDPP3F-C16)



Followed the same synthetic procedure as for **PDPP2FT-BO**. Instead, used **1-C16** (154.686 mg, 0.177 mmol), **3** (69.6 mg, 0.177 mmol), Pd₂(dba)₃ (2 mol %, 3.54 μ mol, 3.24 mg), P(*o*-tol)₃ (8 mol %, 14.14 μ mol, 4.31 mg) and chlorobenzene (5.4 mL). The precipitates were filtered through a Soxhlet thimble and purified via Soxhlet extraction. The polymer was washed for 12 h with

methanol, 2 h with hexanes and 14 h in dichloromethane, and it was extracted with chloroform. The chloroform solution was then precipitated into methanol (200 mL), and the suspension was filtered through a 20 μ m Nylon membrane to afford **PDPP2FT-C16** as a dark solid (132 mg, M_n = 59 kDa, M_w = 92 kDa, PDI = 1.6).

IV. DFT calculated structures of oligomers

Optimized molecular geometries of the representative trimer structures were obtained by performing DFT calculations (B3LYP/6-31G(d)) with Gaussian09.



Figure S1. Optimized molecular geometries of terthiophene diketopyrrolopyrrole (DPP3T), bifuran-thiophene diketopyrrolopyrrole (DPP2FT), and terfuran diketopyrrolopyrrole (DPP3F).

	$\begin{bmatrix} R & A & B \\ N & Y & X & N \\ N & O & O \\ R & R & R \\ R & R & R \\ R & R & R \\ R & R &$				
	Torsion A (θ)	Torsion B (θ)	Bond Length A (Å)	Bond Length E (Å)	
DPP3T	3.65°	2.11 °	1.436	1.440	
DPP2FT	0.10°	0.10°	1.426	1.433	
DPP3F	0.00 °	0.00 °	1.426	1.426	

Figure S2. Inter-ring torsions and bond lengths of optimized polymer structures. Due to the symmetry of the molecule, bond angles and bond lengths were averaged from structurally equivalent bonds and the averages are shown.

III. Supplemental polymer properties data



Figure S3. Cyclic voltammograms of PDPP2FT and PDPP3F films.



Figure S4. Differential scanning calorimetry curves of PDPP2FT and PDPP3F.

V. OFET fabrication and characterization procedures

Bottom gate/top contact field-effect transistors were fabricated on heavily doped silicon (Addison Engineering) substrates that contained a thermally grown silicon dioxide gate dielectric (300 nm). For optimal performance and reproducibility, it was imperative that the surface of the substrates was as clean as possible. Consequently, the Si/SiO_x substrates were subjected to several cleaning steps prior to spin-coating the polymer active layer. To remove surface bound particulates, the substrates were sonicated sequentially in detergent (Hellmanex III in nanopure water), nanopure water, acetone, and isopropyl alcohol (20 min each). The substrates were then submerged in a solution of nanopure water, ammonium hydroxide (14.8 M), and hydrogen peroxide (30% in water) at a 2:1:1 ratio for 15 min to remove organic impurities from the surface. Afterwards, the wafers were rinsed thoroughly with water and isopropyl alcohol, dried with a stream of nitrogen, and further treated with UV/ozone cleaning for 20 minutes. The surfaces were functionalized with octyltrichlorosilane (OTS) by submerging the substrates in a 40 mM solution in dry hexane for ~24 h, and then soaked in a dilute pyridine solution (0.1 mM) for 1 h. Finally, functionalized substrates were sonicated in toluene for 30 s to remove physisorbed molecules, rinsed with isopropyl alcohol, and dried with a light N₂ stream.

All solution preparation, film formation, and electrical characterization were performed under N_2 inside a glovebox. Polymer solutions were prepared in chloroform and allowed to stir at 60 °C overnight. The hot solutions filtered through a 0.45 μ m PTFE filter, then spin-coated on to a freshly prepared substrate at 2000 RPM for 1 s. Casting the film by this method mimics drop-casting as the film is allowed to dry slowly over a few seconds after the spin sequence is completed. However, contrary to drop-casting, pseudo-spincoating forms a uniform and comparatively thin (80 - 100 nm) polymer film (determined via profilometry, Veeco Dektak 150). The films were allowed to dry under ambient glovebox conditions for a minimum of 30 min prior to deposition of the top electrodes. Top performing devices were thermally annealed at 140 °C for 30 minutes, followed by 5 days of vacuum annealing at 110 °C (~ 1 mbar), prior to electrode deposition. Shorter annealing times led to lower hole mobilities. Gold electrodes (35 nm at 6 Å/s) were thermally deposited on top the films through a shadowmask with predefined features. Field effect characteristics were obtained using an HP 4155C semiconductor parameter analyzer. This work focuses principally on field-effect hole mobility because bottom gate OFET architectures using SiO₂ are typically better for hole transport and exposed hydroxyl groups on the gate dielectric are known to readily trap electrons.⁴ Mobility was calculated via the saturation regime model using the fitted slope of the linear portion of the transfer curve and the standard saturation regime equation.⁵ Transfer curves and mobility data were collected with drain-to-souce voltages (V_{DS}) between -40 and -100 V. Threshold voltage (V_{th}) was obtained from the zero crossing value of the linear fit. The on/off ratio ($I_{on/off}$) was determined from the ratio of the source-drain current (I_{DS}) at maximum source-drain bias ($V_{DS} = -100$ V) and while in the off state.

VI. Extraction of GIXD packing parameters

To extract crystalline information from x-ray diffraction patterns, the 2D GIXD profiles were averaged over a polar angle (χ) for $\chi = 15 \pm 2^{\circ}$ and $\chi = 75 \pm 2^{\circ}$. Diffraction peaks in the cross-sectional scattering profile were then fitted to Lorentzian functions using peak fitting software (Fityk) and a standard least-squares model (Levenburg-Marquardt method), from which the peak center and full width at half max values were extracted.



Figure S5. Determining the extent of in-plane polymer packing. The relative ratio of in-plane to out-of-plane crystallites ($R_{in/out}$) is determined by integrating the scattering intensity at A (in-plane scattering) and dividing by the integrated out-of-plane scattering intensity (at B). Note that the scattering intensities at each χ is corrected by multiplying by $\cos(\chi)$.

To determine the degree of in-plane π -stacking for each polymer film, the ratio of inplane to out-of-plane scattering intensity ($R_{in/out}$) was calculated. To do this, a scattering intensity versus χ plot was attained by integrating the collective intensity of the π -stacking peak (q = peak max ± 0.2 Å⁻¹) over possible χ ($\chi = 0$ to 80°). After the scattering intensities at each χ were multiplied by the geometrical correction factor $\cos(\chi)$,⁶ the intensities were averaged over two polar angles, one for each polymer packing orientation. For in-plane polymer packing, the scattering intensity was integrated at the intersection of $\chi = 12 \pm 1^{\circ}$ and the π -stacking peak (area A, Figure S5). The out-of-plane contribution to the scattering profile was integrated at the peak max and $\chi = 78 \pm 1^{\circ}$ (area B, Figure S5). The ratio of the scattering intensity, $R_{in/out} = A/B$, defines the degree of in-plane π -stacking for each polymer film with larger ratios for films with more in-plane π -stacking.

VII. OFET fabrication on various self-assembled monolayers

To investigate the effect of polymer-substrate interactions on solid-state order and molecular packing, devices were fabricated on substrates functionalized with a variety of selfassembled monolayers as well as on bare, unfunctionalized SiO₂. Substrates were cleaned following the same cleaning procedure outlined in the OFET fabrication section. The surfaces octadecyltrichlorosilane functionalized with (ODTS), trichlorosilane were (TS), phenyltrichlorosilane (PTS), phenethyl-trichlorosilane (PETS), vinyltrichlorosilane (VTS), trifluoropropyltrichlorosilane (TFPTS), or perfluorooctyltrichlorosilane (PFOTS) by submerging the substrates in a 40 mM solution in hexane for 8 to 24 h. Functionalized substrates were sonicated in toluene for 30 s to remove physisorbed molecules, rinsed with isopropyl alcohol, and dried with a light N₂ stream. Surfaces were functionalized with hexamethyldisilazane (HMDS) by subjecting freshly cleaned wafers to HMDS vapor at 80°C for 5 hours.



Figure S6. GIXD of PDPP3F-BO and PDPP3F-C16 films on bare SiO₂, ODTS, HMDS, TS, and PTS functionalized surfaces.



Figure S7. GIXD of PDPP3F-BO and PDPP3F-C16 films on PETS, VTS, TFPTS, and PFOTS functionalized substrates.

VIII. Variable temperature UV-vis-NIR spectra

Variable temperature UV-vis-NIR absorption was performed with dilute polymer solutions (~ 0.02 mg/mL) in 1-cm-path-length quartz cuvettes using a Varian Cary 50 Bio spectrometer equipped with a Unisoku – CoolSpek UV (USP-203-B) temperature controller. The solutions were held at each respective temperature for 5 minutes prior to a spectral scan.



Figure S8. Variable temperature UV-vis-NIR spectra of PDPP2FT and PDPP3F in chloroform.

IX. Dynamic light scattering data of solution aggregates



Figure S9. Representative dynamic light scattering data for PDPP2FT and PDPP3F.

X. Effects of methanol additive on PDPP3F films



Figure S10. The effect of non-solvent additive (MeOH) on UV-vis-NIR absorption spectra (a) and GIXD (b) of PDPP3F-C16.



Figure S11. AFM height images (left column) and GIXD patterns (right column) of PDPP3F-BO films spun from solutions with 0%, 10%, 20%, and 30% (v/v) MeOH additive.

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