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Supporting Information

Improved Structural Order by Side-Chain Engineering of Organic Small Molecules for Photovoltaic Applications.

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General methods

All reactions were performed under a dry atmosphere of argon using standard Schlenk tube techniques. All chemicals were used as received from commercial sources without further purification unless otherwise stated. THF was distilled from sodium and benzophenone under an Ar atmosphere. The 300, 400 (^{1}H) and 75, 100 MHz (^{13}C) NMR spectra were recorded at room temperature using perdeuterated solvents as internal standards on a Bruker Advance spectrometer. Chromatographic purifications were performed using 40-63 μm silica gel. TLC was performed on silica gel plates coated with fluorescent indicator.

Spectroscopic Measurements

Absorption spectra in solution and in thin films were recorded on a Shimadzu UV-2600 spectrophotometer. In solid state, the absorption spectra were measured on thin films drop-casted on glass substrates from a 0.5 mg/mL chloroform solution of TPD-TAT dyes.

XRD Measurements

Powder XRD patterns were obtained with a linear monochromatic Cu Kα1 beam (λ=1.5405 Å) obtained using a sealed-tube generator equipped with a bent quartz monochromator and a curved Inel CPS 120 counter gasfilled detector; periodicities up to 70 Å can be measured, and the sample temperature controlled to within ±0.01 °C from 20 to 200 °C. The sample was filled in Lindemann capillaries and exposure times were of 6 h.

DSC Measurements

DSC measurements were performed with a TA Instruments Q1000 instrument, operated at a scanning rate of 5 °C min^{-1} on heating and on cooling.

Polarized Optical Microscopy

Optical textures were observed with a Leitz Orthoplan polarizing microscopy equipped with a Mettler FP82 hot stage and a FP80 unit.

Devices Preparation

Field effect mobility measurements. Top contact-bottom gate (TC-BG) organic field-effect transistors (OFETs) were fabricated on silicon substrates with 200 nm thermal silicon oxide (SiO_2) on fronts as gate dielectric. The source and drain contacts were thermal evaporated on top of the active layer, and composed of 120 nm thick silver on top of a 7 nm thick Molybdenum trioxide (MoO_3) layer (Fig. S1).

The resistivity of the wafer is around 0.01 – 0.02 Ω.cm and the thickness is 675±25 μm.

The substrates were cut by YAG laser into the dimension of 15 × 20 mm.

The channel length and channel width are summarized in the table S1.

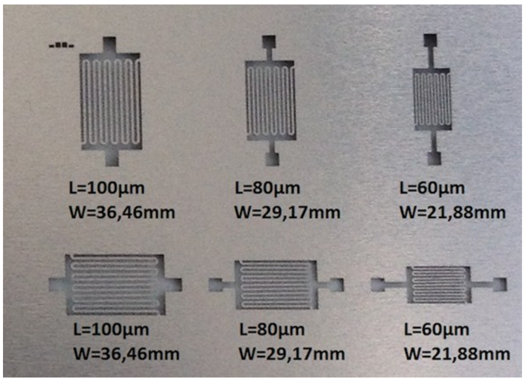

Figure S1. Scheme of a substrate including six OFETs of variable dimensions.

Channel length L (µm)	Channel width W (mm)	W/L
60	21.6	360
80	28.8	360
100	36	360

Table S1. OFETs dimensions.

The substrates were cleaned in acetone and isopropyl alcohol and subsequently for 15 minutes in an ultra-violet ozone system. Then, hexamethyldisilazane (HMDS) was spin coated (500 rpm for 5 s and then 4000 rpm for 50 s) under nitrogen ambient and followed by an annealing step at 135°C for 10 minutes. Finally, 5 mg/ml concentrated anhydrous chloroform solutions of TPD_x-TAT_x dyes were spin-coated (3000rpm for 60s). The top electrodes (7nm MoO_3 and 120 nm Ag) were thermal evaporated on the top of the active layer under vacuum ($<10^{-6}$ mbar). Both, the FET elaboration and characterizations were performed in nitrogen ambient. The transistor output and transfer characteristics were recorded using a Keithley 4200 semiconductor characterization system. The charge carrier mobility was extracted in the saturation regime using the usual formalism on FET devices annealed at the same temperature as the optimized photovoltaic devices.

SCLC mobility measurements. SCLC devices were elaborated to investigate the out-of-plane mobility. Indium Tin Oxide (ITO) coated glass was used as substrate. PEDOT:PSS was used as the hole injection electrode to extracted hole mobility. A 120 nm thick silver on top of a 7 nm thick Molybdenum trioxide (MoO_3) layer as the top electrode for measuring the hole mobility. The top electrode surface ranged from 2.25×10^{-3} mm^2 to 0.25 mm^2.

The substrates were cleaned in acetone, isopropyl alcohol and deionized water at 45°C for 15 minutes, respectively; then under ultra-violet ozone for 30 minutes. PEDOT:PSS was spin-coated on the top of ITO layer and then dried at 140°C for 30 minutes. Then 20 mg mL^{-1} chloroform solution of TPD_x-TAT_x was spin-coated in nitrogen-filled glovebox. Different thicknesses were achieved by different spin speeds. Then top electrodes were thermal evaporated on the top of the active layer under pressure. Devices were then measured in glovebox by the same Keithley 4200 semiconductor characterization system as OFET measurements. Mobility values are extracted using the Mott-Gurney law:

$$J_{SCLC} = \frac{9}{8}\varepsilon_0 \varepsilon_r \mu \frac{V^2}{L^3}$$

Where J is the current density, $\boldsymbol{\varepsilon}_0$ is the vacuum permittivity while $\boldsymbol{\varepsilon}_r$ is the dye dielectric constant, μ is the mobility, V is the voltage and L is the thickness of the active layer.

Photovoltaic conversion measurements. Bulk heterojunction devices were elaborated using the different synthesized molecules as electron donor and $PC_{71}BM$ as electron acceptor. Inverted solar cells using polyethyleneimine, 80% ethoxylated (PEIE) as an interfacial layer were elaborated. The standard device structure was the following: ITO/PEIE(5 nm)/ TPD_x-TAT_x:$PC_{71}BM$/MoO_3(7 nm)Ag(120 nm). Indium Tin Oxide coated glass with a surface resistance lower than 20 Ω/sq was used as transparent substrate.

Substrates were cleaned sequentially by ultrasonic treatments in acetone, isopropyl alcohol, and deionized water. After an additional cleaning for 30 minutes under ultra-violet generated ozone, PEIE (M_W=70000 g/mol) was spin coated (5000 rpm, 60s) to obtain a 5 nm thick layer and thermally annealed for 10 minutes at 100°C under nitrogen atmosphere. The chloroform solutions of TPD_x-TAT_x:$PC_{71}BM$ were stirred for at least 24 hours at RT before spin-coating. The TPD_x-TAT_x solution concentrations were of 5 mg.mL^{-1} or 7.5 mg.mL^{-1} and 1,8-diiodoctane (DIO) was tested as additive with concentrations ranging from 0 to 0.4% vol. The relative TPD_x-TAT_x:$PC_{71}BM$ weight ratio was varied from 1:1 to 1:5. The active layer spin coating conditions were the following: a first 120 seconds step (speed: 2000 rpm, acceleration: 600 rpm.s^{-1}) followed by a second 60 seconds step (speed: 2500 rpm, acceleration: 600 rpm.s^{-1}). A post-deposition thermal annealing process (for 10 minutes at 80°C) was added before the anode thermal evaporation. A MoO_3 (7 nm)/Ag (120 nm) bi-layer was used as anode. Each device contained four 12 mm^2 diodes, the surface of each diode being carefully defined by a shadow mask. Current versus Voltage (J-V) characteristics were measured using a source measurement unit Keithley 2400 under darkness and under AM1.5G (100 mW.cm^2) illumination. The standard illumination was provided by a Class A Lot Oriel solar simulator (550 W filtered Xe lamp) and the illumination power was calibrated using a reference silicon solar cell. Calibrated silicon reference cells were used to monitor the incident and the reflected light power for each wavelength. The photovoltaic cells elaboration after substrate preparation and the characterizations were performed in nitrogen ambient.

Density Functional Theory (DFT) calculations

DFT.calculations using density functional theory at the B3LYP/6-311+G* level of theory in vacuum have been performed using SPARTAN 10[1]. In order to keep a reasonable computing time, a smaller molecule with a single TAT unit and a thiophene-thienopyrroledione (TPD) dye has been considered (Figure S2). The alkyl side-chains circled in red in Figure S2 have been changed from methyl to octyl (C8) and ramified 2-ethylhexyl chains (EH). For all configurations, the dihedral angle between the TAT moiety and the dye (green planes in Figure S2).

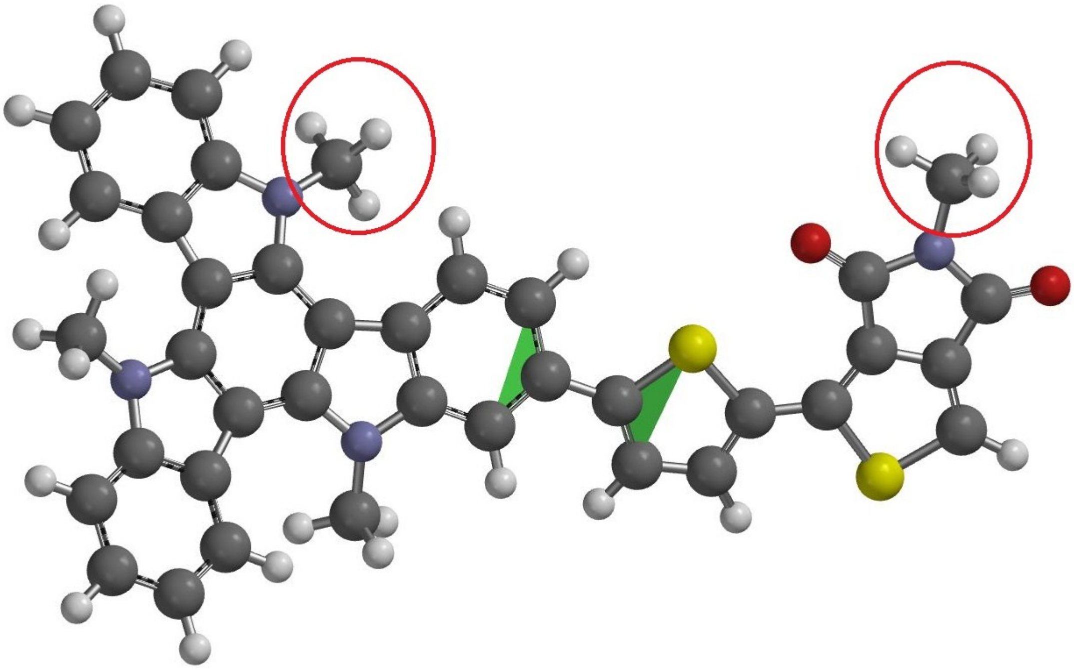

Figure S2. Chemical structure of the molecule used for DFT calculations.

For every alkyl-chain combination considered, the TAT-dye dihedral angle is constant and equal to 22° and the conformation of the molecule stays unchanged. Therefore, the steric hindrance induced by the alkyl chains is negligible, as far as single isolated molecules are concerned, in agreement with the very similar UV-vis spectra measured in solution for the four molecules.

Materials and synthesis

All reagents, N-bromosuccinimide, Bis(pinacolato)diboron, oxo-indole, 6- bromo-isatin, phosphoryl trichloride, were used directly as obtained commercially unless otherwise noted. 2-(trimethylstannyl)thiophene,[2] 1,3-Dibromo-5-alkylthieno[3,4-*c*]pyrrole-4,6-dione[3] and compounds **5** and **6**[4] were obtained according to the respective references.

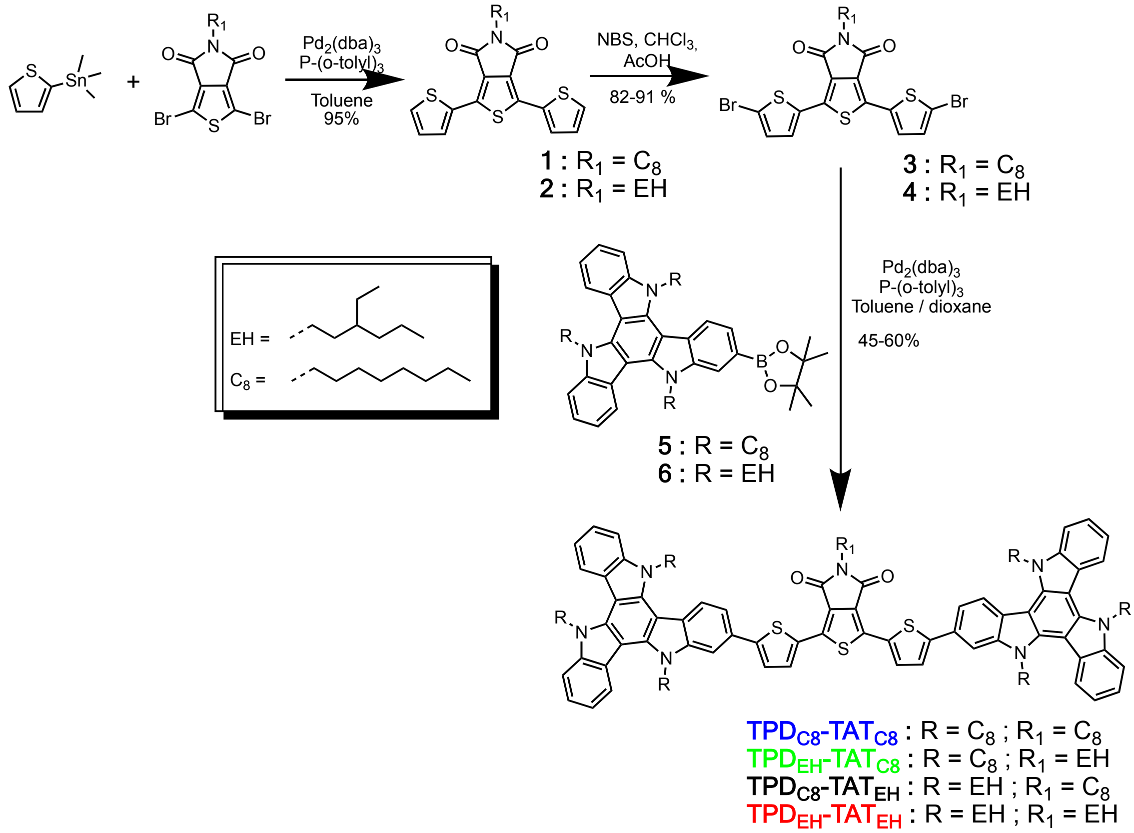

Figure S3. Synthetic route towards the preparation of the TPD_x-TAT_x molecules

5-octyl-1,3-di(thiophen-2-yl)-4*H*-thieno[3,4-*c*]pyrrole-4,6(5*H*)-dione (1):

A flame dried Schlenck was charged with Octyl-4*H*-thieno[3,4-*c*]pyrrole-4,6(5*H*)-dione (1.0 eq). Anhydrous and degassed toluene (0.1M) was added under inert gas followed by 2-(trimethylstannyl)thiophene (2.2 eq). Finally, the $Pd_2(dba)_3$ (2 mol%) and $P(o\text{-tolyl})_3$ (8 mol%) were added in one portion and the mixture was stirred 18 hours at 120°C. After cooling to room temperature the reaction mixture was filtered through a pad of celite and the toluene solution was evaporated under reduced pressure. Then, the crude material was purified by column chromatography (silica gel, CH_2Cl_2/PE: 30/70), providing the compound 1 as a yellow solid, (MW = 429.62 $g.mol^{-1}$), with 81% of yield.

^{1}H NMR ($CDCl_3$, 300MHz): δ = 8.00 (dd, 2H, *J* = 3.7 Hz, *J* = 1.0 Hz), 7.4 (dd, 2H, *J* = 5.0 Hz, J = 1.0 Hz), 7.14 (t, 2H, *J* = 3.7 Hz), 3.65 (t, 2H, *J* = 7.2 Hz), 1.68 (m, 2H), 1.29 (m, 10H), 0.89 (t, 3H, *J* = 6.7 Hz). **^{13}C NMR** ($CDCl_3$, 75MHz): δ = 162.7, 136.6, 132.6, 130.0, 128.7, 128.5, 38.7 31.9, 29.3, 28.6, 27.1, 22.8, 14.2.

5-(2-ethylhexyl)-1,3-di(thiophen-2-yl)-4*H*-thieno[3,4-*c*]pyrrole-4,6(5*H*)-dione (2):

A flame dried Schlenck was charged with Ethylhexyl-4*H*-thieno[3,4-*c*]pyrrole-4,6(5*H*)-dione (1.0 eq). Anhydrous and degassed toluene (0.1M) was added under inert gas followed by 2-(trimethylstannyl)thiophene (2.2 eq). Finally, the $Pd_2(dba)_3$ (2 mol%) and $P(o\text{-}tolyl)_3$ (8 mol%) were added in one portion and the mixture was stirred 18 hours at 120°C. After cooling to room temperature the reaction mixture was filtered through a pad of celite and the toluene solution was evaporated under reduced pressure. Then, the crude material was purified by column chromatography (silica gel, CH_2Cl_2/PE: 30/70), providing the compound 2 as a yellow solid, (MW = 429.62 g.mol^{-1}), with 82% of yield.

^{1}H NMR ($CDCl_3$, 300MHz): δ = 8.02 (dd, 2H, *J* = 3.7 Hz, *J* = 0.9 Hz), 7.4 (dd, 2H, *J* = 5.0 Hz, *J* = 0.9 Hz), 7.14 (t, 2H, *J* = 3.9 Hz), 3.57 (d, 2H, *J* = 7.2 Hz), 1.84 (m, 1H), 1.32 (m, 8H), 0.92 (m, 6H). **^{13}C NMR** ($CDCl_3$, 75MHz): δ = 160.1, 136.6, 132.6, 130.1, 128.7, 128.6, 42.7, 38.4, 30.8, 24.1, 23.2, 14.2, 10.6.

1,3-bis(5-bromothiophen-2-yl)-5-octyl-*4H*-thieno[3,4-*c*]pyrrole-4,6(5*H*)-dione (3):

Compound 1 (0.002 mol, 1 eq) was added under dark and Ar in a mixture of $CHCl_3$ (31 mL) and acetic acid (31 mL). This solution was cooled to 0°C then NBS (2 eq) was added in several portion. After complete addition the mixture was stirred at room temperature for 24 hours then quenched with water and extracted with CHCl3. The organic was washed with water and dried on Na_2SO_4 before evaporation of solvent. Purification was carried out by column chromatography (silica gel, CH_2Cl_2/PE: 20/80), providing the compound 3 as a yellow solid, (MW = 587.41 g.mol^{-1}) with 63% of yield.

^{1}H NMR (CDCl3, 300MHz): δ = 7.66 (d, 2H, *J* = 4.0 Hz), 7.07 (d, 2H, *J* = 4.0 Hz), 3.55 (d, 2H, *J* = 7.2 Hz), 1.84 (m, 1H), 1.32 (m, 8H), 0.92 (m, 6H). **^{13}C NMR** (CDCl3, 75MHz): δ = 162.3, 135.6, 133.9, 131.3, 130.0, 128.8, 116.9, 53.6, 38.4, 30.8, 24.1, 23.2, 14.2, 10.6.

1,3-bis(5-bromothiophen-2-yl)-5-(2-ethylhexyl)-*4H*-thieno[3,4-*c*]pyrrole-4,6(5*H*)-dione (4):

Compound 2 (0.002 mol, 1 eq) was added under dark and Ar in a mixture of $CHCl_3$ (31 mL) and acetic acid (31 mL). This solution was cooled to 0°C then NBS (2 eq) was added in several portion. After complete addition the mixture was stirred at room temperature for 24 hours then quenched with water and extracted with CHCl3. The organic was washed with water and dried on Na_2SO_4 before evaporation of solvent. Purification was carried out by column chromatography (silica gel, CH_2Cl_2/PE: 20/80), providing the compound 4 as a yellow solid, (MW = 587.41 g.mol^{-1}) with 57% of yield.

^{1}H NMR ($CDCl_3$, 300MHz): δ = 7.64 (d, 2H, *J* = 4.2 Hz), 7.07 (d, 2H, *J* = 4.2 Hz), 3.63 (t, 2H, *J* = 7.2 Hz), 1.64 (m, 2H), 1.30 (m, 10H), 0.89 (t, 3H, *J* = 7.3 Hz). **^{13}C NMR** ($CDCl_3$, 75MHz): δ = 162.5, 135.3, 133.9, 131.3, 129.9, 128.8, 116.9, 53.6, 38.8, 32.0, 31.9, 29.3(x2), 28.6, 27.1, 22.8, 14.2.

General method for Suzuki-Miyaura cross-coupling: In a Schlenk tube the dioxoborolan derivative (1.5 eq), the dibromo derivative (1 eq) and Cs_2CO_3 (4 eq) were dissolved in dioxane. Argon was bubbled through the mixture for 45 min, then $P(Cy)_3$ (0.08 eq) and $Pd_2(dba)_3$ (0.03 eq) was added and the mixture was stirred at 110°C for 1 day. The solution was cooled down to room temperature and filtered through a pad of celite. The solvent was evaporated to dryness and the crude was dissolved in CH_2Cl_2 and was washed with water. Organic was extracted and dried over Na_2SO_4 and concentrated under reduced pressure. The purification was carried out by column chromatography (silica gel, CH_2Cl_2/PE: 30/70).

TPD_{C8}-TAT_{C8}: Dark red solid (MW = 1789.65 g.mol^{-1}), Yield = 50%.

^{1}H NMR ($CDCl_3$, 300 MHz): 8.49 (d, 2H, *J* = 6.5 Hz), 8.46 (d, 2H, *J* = 3.8 Hz), 8.42 (d, 2H, *J* = 7.4 Hz), 8.21 (d, 2H, *J* = 8.5 Hz), 7.83 (s, 2H), 7.66 (d, 2H, *J* = 8.0 Hz), 7.54 (m, 12H), 7.31 (d, 2H, *J* = 3.9 Hz), 4.75 (m, 12H), 3.89 (t, 2H, *J* = 6.7 Hz), 1.98 (m, 14H), 1.25 (m, 70H), 1.01 (m, 21H). **^{13}C NMR** (C_6D_6, 75 MHz): 162.6, 148.6, 141.8, 141.6, 141.4, 140.2, 139.6, 138.9, 135.9, 131.8, 131.7, 129.1, 124.0, 124.0, 123.9, 123.2, 122.1, 120.1, 118.3, 111.0, 110.8, 107.6, 104.0, 103.9, 103.8, 47.0, 38.8, 32.4, 32.2, 32.1, 32.1, 30.2, 30.1, 29.8, 29.6, 29.5, 29.4, 29.2, 27.6, 27.0, 27.0, 26.9, 23.2, 23.1, 23.0, 14.4, 14.3. **Maldi-TOF m/z**: 1789.06.

TPD_{EH}-TAT_{C8}: Red solid (MW = 1789.65 g.mol^{-1}), Yield = 40%.
^{1}H NMR (C_6D_6, 400 MHz): 8.39 (d, 2H, *J* = 4.7 Hz), 8.34 (d, 2H, *J* = 3.8 Hz), 8.31 (s, 2H), 8.11 (d, 2H, *J* = 8.4 Hz), 7.73 (s, 2H), 7.58 (d, 2H, *J* = 8.2 Hz), 7.45 (m, 12H), 7.21 (d, 2H, *J* = 3.9 Hz), 4.63 (m, 12H), 3.70 (d, 2H, *J* = 7.1 Hz), 2.14 (m, 1H), 1.86 (m, 12H), 1.49 (m, 10H), 1.15 (m, 61H), 1.01 (t, 3 H, *J* = 7.2 Hz), 0.91 (m, 18H). **^{13}C NMR** (C_6D_6, 100 MHz): 163.0, 148.6, 141.7, 141.6, 141.4, 140.1, 139.6, 138.9, 135.9, 131.9, 131.7, 128.9, 128.7, 124.0, 123.9, 123.8, 123.2, 122.1, 122.1, 120.1, 118.2, 110.9, 110.8, 107.8, 107.6, 104.0, 103.9, 103.8, 47.0, 39.0, 32.2, 32.1, 32.1, 31.3, 30.2, 30.1, 29.6, 29.5, 29.5, 29.4, 29.1, 27.0, 27.0, 26.9, 23.6, 23.1, 23.0, 14.5, 14.5, 14.4, 14.4, 10.9. **Maldi-TOF m/z**: 1789.09.

TPD_{C8}-TAT_{EH}: Orange-red solid (MW = 1789.65 g.mol^{-1}), Yield = 53%.
^{1}H NMR (C_6D_6, 300 MHz): 8.55 (d, 2H, *J* = 7.5 Hz), 8.41 (s, 2H), 8.39 (d, 2H, *J* = 7.6 Hz), 8.22 (d, 2H, *J* = 8.4 Hz), 7.86 (s, 2H), 7.68 (d, 2H, *J* = 8.2 Hz), 7.55-7.43 (m, 12H), 7.33 (d, 2H, *J* = 3.8 Hz), 4.77 (m, 12H), 3.77 (d, 2H, *J* = 7.2 Hz), 2.11 (m, 7H), 1.07-0.68 (m, 77H), 0.45 (m, 21H). **^{13}C NMR** (C_6D_6, 75 MHz): 163.1, 149.2, 141.9, 141.7, 141.5, 140.4, 139.8, 139.1, 136.1, 131.9, 131.8, 129.1, 128.7, 124.2, 124.0, 123.9, 123.0, 119.9, 118.0, 112.0, 111.8, 108.9, 104.3, 104.1, 104.1, 50.6, 39.0, 38.5, 38.4, 38.3, 31.3, 30.4, 30.2, 29.1, 28.87, 28.6, 28.5, 28.4, 24.5, 23.6, 23.2, 23.2, 14.4, 14.3, 14.1, 10.8, 10.4, 10.3, 10.2, 10.1, 10.0. **Maldi-TOF m/z**: 1789.06.

TPD_{EH}-TAT_{EH}: Orange solid (MW = 1789.65 g.mol^{-1}), Yield = 45%.
^{1}H NMR (C_6D_6, 400 MHz): 8.55 (d, 2H, *J* = 7.4 Hz), 8.42 (d, 2H, *J* = 3.7 Hz), 8.39 (d, 2H, *J* = 8.2 Hz), 8.23 (d, 2H, *J* = 8.4 Hz), 7.86 (s, 2H), 7.69 (d, 2H, *J* = 8.2 Hz), 7.50 (m, 12H), 7.33 (d, 2H, *J* = 3.8 Hz), 4.70 (m, 12H), 3.81 (t, 2H, *J* = 6.6 Hz), 2.11 (m, 6H), 1.85 (t, 2H, *J* = 6.0 Hz), 1.30 (m, 10H), 0.93 (m, 53H), 0.43 (m, 21H). **^{13}C NMR** (C_6D_6, 100 MHz): 162.7, 149.1, 141.9, 141.8, 141.6, 140.4, 139.8, 139.1, 136.0, 131.8, 129.3, 124.2, 124.0, 123.9, 123.0, 120.0, 118.0, 112.0, 111.8, 108.9, 104.4, 104.1, 50.6, 38.3, 32.3, 30.4, 30.2, 29.8, 29.7, 29.2, 28.8, 28.6, 27.6, 23.6, 23.2, 23.2, 23.1, 14.4, 14.3, 14.1, 10.4, 10.3, 10.2, 10.1. **Maldi-TOF m/z**: 1789.06.

Cyclic Voltammetry

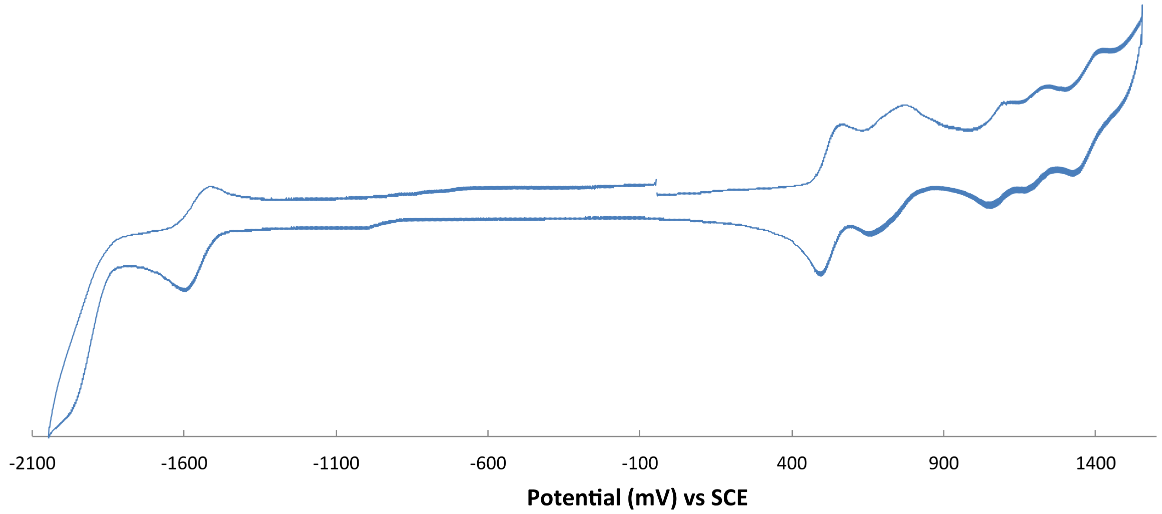

Figure S4. Cyclic voltamogram of TPD-TAT dyes in dichloromethane at rt. 1.5 mM substrate in 0.10 M Bu_4NPF_6.

XRD patterns

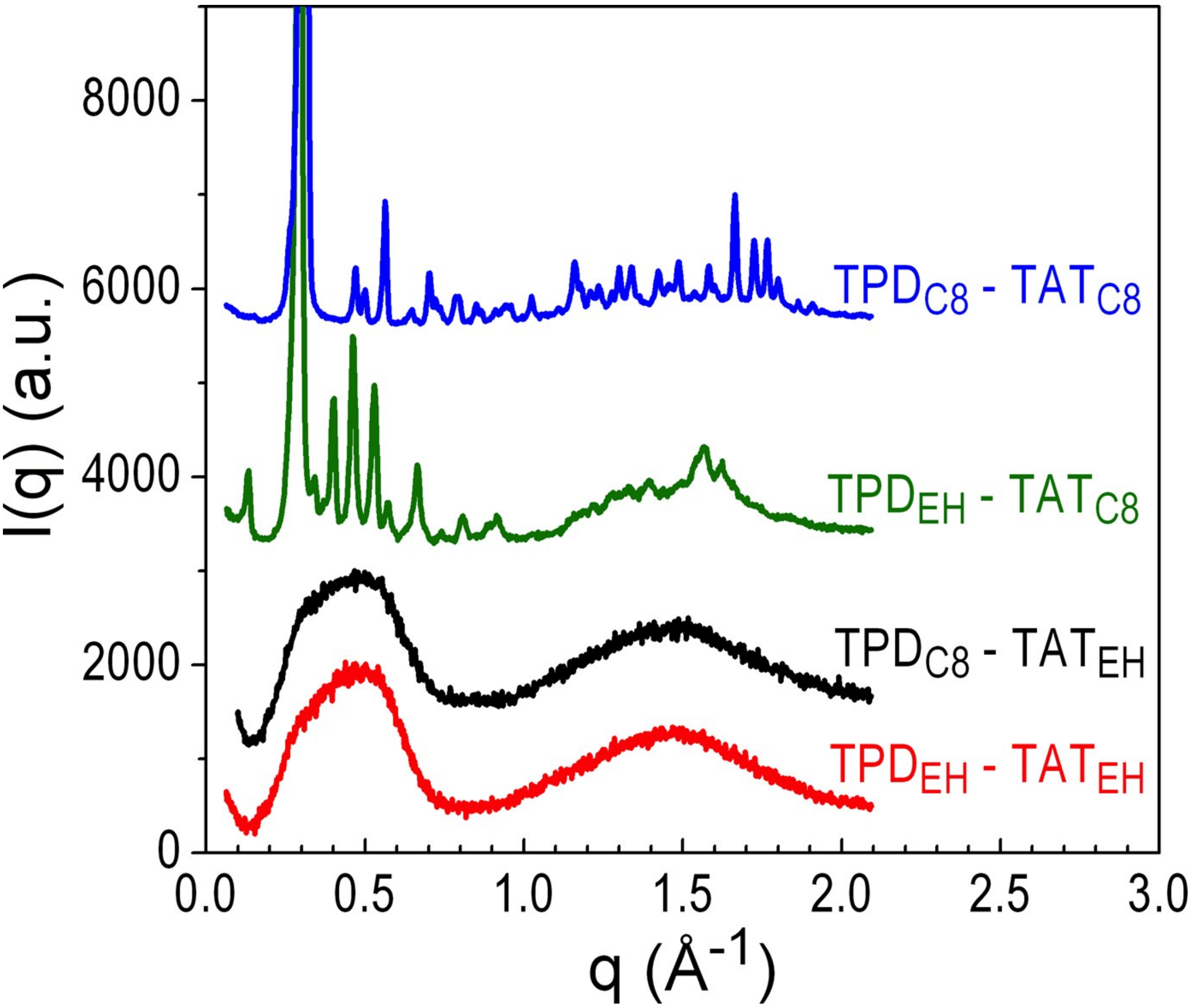

Figure S5. SAXS patterns of crystalline molecular organizations of TPD$_{C8}$-TAT$_{C8}$ at 150°C (blue curve), of TPD$_{EH}$-TAT$_{C8}$ at 130°C (green curve), and amorphous molecular organizations of TPD$_{C8}$-TAT$_{EH}$ at 95°C (black curve), and of TPD$_{EH}$-TAT$_{EH}$ at 95°C (red curve).

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[1] See *www.wavefun.com*

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[3] Y. Zhang, S. K. Hau, H.-L. Yip, Y. Sun, O. Acton and A. K.-Y. Jen, *Chem. Mater.*, 2010, **22**, 2696–2698.

[4] I. Bulut, P. Chávez, A. Mirloup, Q. Huaulmé, B. Heinrich, A. Hébraud, S. Méry, R. Ziessel, T. Heiser, P. Lévêque and N. Leclerc, *J. Mater. Chem. C*, 2016, **4**, 4296-4303.