

Supporting Information

LUMO's modulation by electron withdrawing unit modification in amorphous TAT dumbbell-shaped molecules

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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 (^1H) 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-2101 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 TAT-based dyes.

XRD Measurements

Powder XRD patterns were obtained with a linear monochromatic Cu $\text{K}\alpha_1$ beam ($\lambda=1.5405 \text{ \AA}$) 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 \AA can be measured, and the sample temperature controlled to within $\pm 0.01 \text{ }^\circ\text{C}$ from 20 to 200 $^\circ\text{C}$. 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 $^\circ\text{C min}^{-1}$ on heating and on cooling.

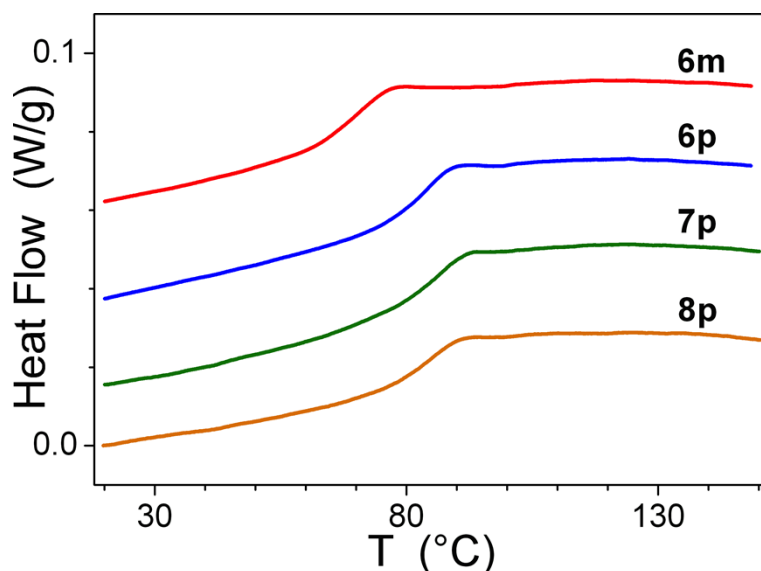


Figure S1: DSC spectra of compounds **6m** and **6p-8p**

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. Bottom contact field-effect transistors (FETs) were elaborated on commercially available pre-patterned test structures whose source and drain contacts were composed of a 30 nm thick gold layer on top of a 10 nm thick Indium Tin Oxide (ITO) layer. A 230 nm thick silicon oxide was used as gate dielectric and n-doped ($3 \times 10^{17} \text{ cm}^{-3}$) silicon crystal as gate electrode. The channel length and channel width were 20 μm and 10 mm, respectively. The test structures were cleaned in acetone and isopropyl alcohol and subsequently for 30 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 130°C for 10 minutes. Finally, 5 mg/mL anhydrous chloroform of dyes **6m** and **6-8p** solutions were spin coated

(1250 rpm for 60s and 2250 rpm for 60s) to complete the FET devices. The samples were then left overnight under vacuum ($<10^{-6}$ mbar) to remove residual solvent traces. 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.

Photovoltaic conversion measurements. Bulk heterojunction devices were elaborated using the different synthesized molecules as electron donor and PC₇₁BM 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)/dye **6m** or **6p-8p**:PC₇₁BM/MoO₃(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 chlorobenzene dye **6m** or dye **6p-8p**:PC₇₁BM solutions were stirred for at least 24 hours at 50°C before spin-coating. An extra stirring for 15 minutes at 100°C was added just before the active layer deposition. The dye **6m** or dye **6p-8p** concentration of the solution was 5 mg.mL. The relative dye **6m** or dye **6p-8p**:PC₇₁BM 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) followed by a second 60 seconds step (speed: 2500 rpm, acceleration: 600 rpm/s). A post-deposition thermal annealing process (for 10 or 15 minutes from 100 to 120°C) was added before the anode thermal evaporation. A MoO₃ (7 nm)/Ag (120 nm) bi-layer was used as anode. Each device contained four 12 mm² 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.cm²) 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. External Quantum Efficiency (EQE) measurements were performed using a home-made setup including a 150 W Lot Oriel Xe solar simulator as a light source, a Jobin-Yvon microHR monochromator and several focusing lenses to obtain a 2 mm diameter monochromatic light beam on the solar cell under investigation. 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.

Materials

All reagents, N-bromosuccinimide, Bis(pinacolato)diboron, oxo-indole, 6-bromo-isatin, phosphoryl trichloride, were used directly as obtained commercially unless otherwise noted. Compounds 3¹, 4², 5³ and 10,15-dihydro-5H-diindolo[3,2-a:3',2'-c]carbazole⁴ were obtained according to the respective references.

Preparative experimental part

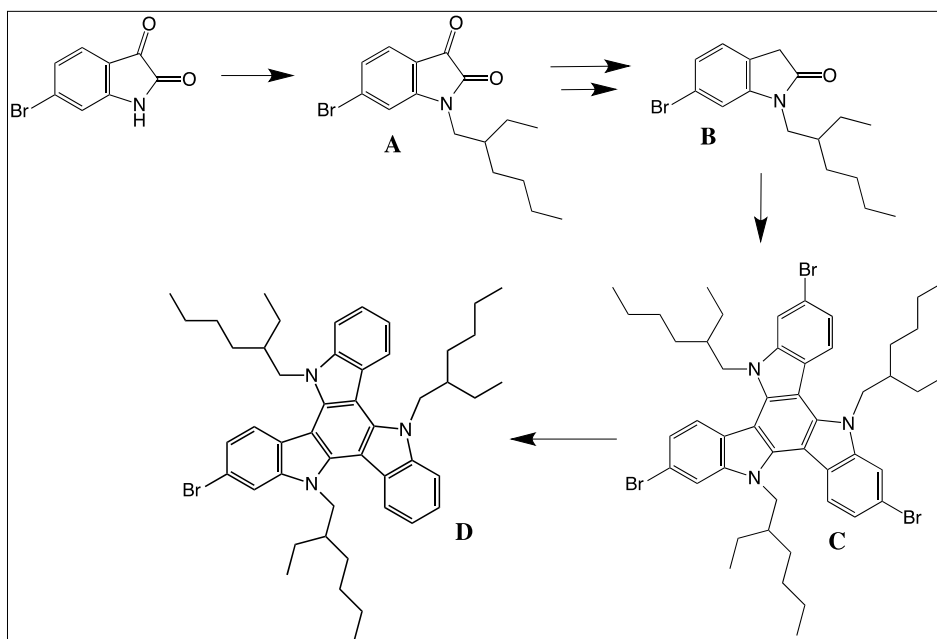


Figure S2: Synthetic pathway for compound **D**

6-bromo-1-(2-ethylhexyl)indoline-2,3-dione (compound A): In a Schlenk tube, compounds 6-bromoindatin (12.5 g, 54.4 mmol), and sodium hydride (980 mg, 81.6 mmol) were dissolved in a mixture of dimethylformamide and tetrahydrofuran (40 mL of each) under argon. The mixture was heated at 60°C for 30 min before adding of the 1-bromo-2-ethylhexyl (11.4 mL, 81.6 mmol). The mixture was then stirred at 60°C for 2 days. The solution was cooled down to room temperature, and the solvent evaporated to dryness. The crude was dissolved in CH_2Cl_2 and was washed with water (3X90 mL) and dried over MgSO_4 and concentrated under reduced pressure. The purification was carried out by chromatography on flash silica as static phase with CH_2Cl_2 as mobile phase and afforded **A** (8.3 g, 24.4 mmol) as an orange oil (45%).

^1H NMR (CDCl_3 , 300 MHz): 0.93 (t, 6H, $^3J = 5.3$ Hz; CH_3), 1.32-1.39 (m, 8H, CH_2), 1.81 (t, 1H, $^3J = 6.0$ Hz; CH), 3.59 (d, 2H, $^3J = 7.7$ Hz; CH_2), 7.04 (d, 1H, $^4J = 1.4$ Hz; ArH), 7.29 (dd, 1H, $^3J = 7.1$ Hz; $^4J = 1.4$ Hz; ArH), 7.46 (d, 1H, $^3J = 7.9$ Hz; ArH); ^{13}C NMR (CDCl_3 , 75 MHz): 10.5, 14.0, 23.0, 23.9, 28.4, 30.5, 37.2, 44.6, 114.0, 116.3, 126.3, 126.8, 133.5, 152.2, 158.3, 182.3.

6-bromo-1-(2-ethylhexyl)indolin-2-one (compound B): In a Schlenk tube, **compounds A** (8.0 g, 23.6 mmol) and hydrazine monohydrate (50 mL) were stirred at reflux for 2 hours under argon. The solution was cooled down to room temperature, and the 50 mL of ethyl acetate was added. The solution was washed with water (3X60 mL) and dried over MgSO₄ and concentrated under reduced pressure. The crude product was then mix with a solution of hydrochloric acid 6N (200 mL) and stirred at 60°C for 2h30. The solution was cooled down to room temperature, and the 100 mL of dichloromethane was added. The solution was washed with water (3X100 mL) and dried over MgSO₄ and concentrated under reduced pressure. The purification was carried out by chromatography on flash silica as static phase with CH₂Cl₂ as mobile phase and afforded **B** (6.35 g, 19.9 mmol) as a yellow oil (83%).

¹H NMR (CDCl₃, 300 MHz): 0.94 (t, 6H, ³J = 7.4 Hz; CH₃), 1.30-1.39 (m, 8H, CH₂), 1.81 (t, 1H, ³J = 6.1 Hz; CH), 3.47 (s, 2H, CH₂), 3.56 (d, 2H, ³J = 7.7 Hz; CH₂), 6.94 (d, 1H, ⁴J = 1.4 Hz; ArH), 7.10 (d, 1H, ³J = 7.8 Hz; ArH), 7.16 (dd, 1H, ³J = 7.8 Hz ; ⁴J = 1.6 Hz; ArH); ¹³C NMR (CDCl₃, 75 MHz): 10.6, 14.0, 23.0, 23.9, 28.5, 30.5, 35.3, 37.2, 44.3, 111.9, 121.3, 123.4, 124.8, 125.6, 146.4, 175.0.

2,7,12-tribromo-5,10,15-tris(2-ethylhexyl)-10,15-dihydro-5H-diindolo[3,2-a:3',2'-c]carbazole

(compound C): 6-bromo-1-(2-ethylhexyl)indolin-2-one (4.84 g, 14.99 mmol) was dissolved in 16 ml POCl₃ and the solution was heated to reflux for 3h. The solution was neutralized with aq. NaOH and the precipitate was filtered and washed with water (3X50 mL). The purification was carried out by chromatography on flash silica as static phase with a mixture of petroleum ether/toluene (95/5) as mobile phase and afforded compound **C** (1.13 g) as a pale yellow oil (24%).

¹H NMR (CDCl₃, 300 MHz): 0.41-0.52 (m, 9H; CH₃), 0.62-1.26 (m, 33H; CH₂), 1.93 (m, 3H; CH₂), 4.69 (m, 6H; CH₂), 7.42-7.45 (d-d, 3H, ³J = 8.5 Hz, ⁴J = 1.6 Hz; Ar H), 7.68 (d, 3H, ⁴J = 1.5Hz; Ar H), 8.01 (d, 3H, ³J = 8.6 Hz; Ar H); ¹³C NMR (CDCl₃, 75 MHz): 10.1, 10.2, 13.9, 22.9, 23.0, 28.2, 29.8, 38.1, 50.7, 103.5, 114.5, 116.4, 122.2, 122.8, 123.3, 139.0, 142.1.

2-bromo-5,10,15-tris(2-ethylhexyl)-10,15-dihydro-5H-diindolo[3,2-a:3',2'-c]carbazole (compound D): Compound C (1.15 g, 1.25 mmol) was dissolved in 20 THF/MeOH (7/3) and NiCl₂·6H₂O (0.59 g, 2.5 mmol) was added. The mixture was heated to 60°C and NaBH₄ (0.85 mg, 22.5 mmol) was added in six portions. The reaction was monitored by TLC and quenched with H₂O. The organic phases were extracted with CHCl₃, dried over MgSO₄ and concentrated under reduced pressure. The purification was carried out by chromatography on flash silica as a stationary phase with a mixture of petroleum ether/toluene (95/5) as a mobile phase and afforded compound D (0.17 g) as a pale yellow oil (17%).

¹H NMR (CDCl₃, 300 MHz): 0.41-0.52 (m, 9H; CH₃), 0.62-1.26 (m, 33H; CH₂), 2.05 (m, 3H; CH₂), 4.96 (m, 6H; CH₂), 7.33 (t, 2H, ³J = 7.5 Hz; Ar H), 7.43 (t, 3H, ³J = 7.5 Hz; Ar H), 7.61 (d, 2H, ³J = 9.8 Hz; Ar H), 7.73 (d, 1H, ⁴J = 1.6 Hz; Ar H), 8.10 (d, 1H, ³J = 8.5 Hz; Ar H), 8.28 (t, 2H, ³J = 7.7 Hz; Ar H); ¹³C NMR (CDCl₃, 75 MHz): 10.1, 10.2, 10.2, 10.3, 10.3, 14.0, 21.6, 22.9, 23.0, 23.0, 28.2, 28.3, 28.3, 28.4, 29.9, 38.1, 50.7, 111.6, 114.3, 119.7, 122.3, 122.4, 123.2, 123.6, 125.4, 128.4, 129.2, 138.0, 141.2, 142.2.

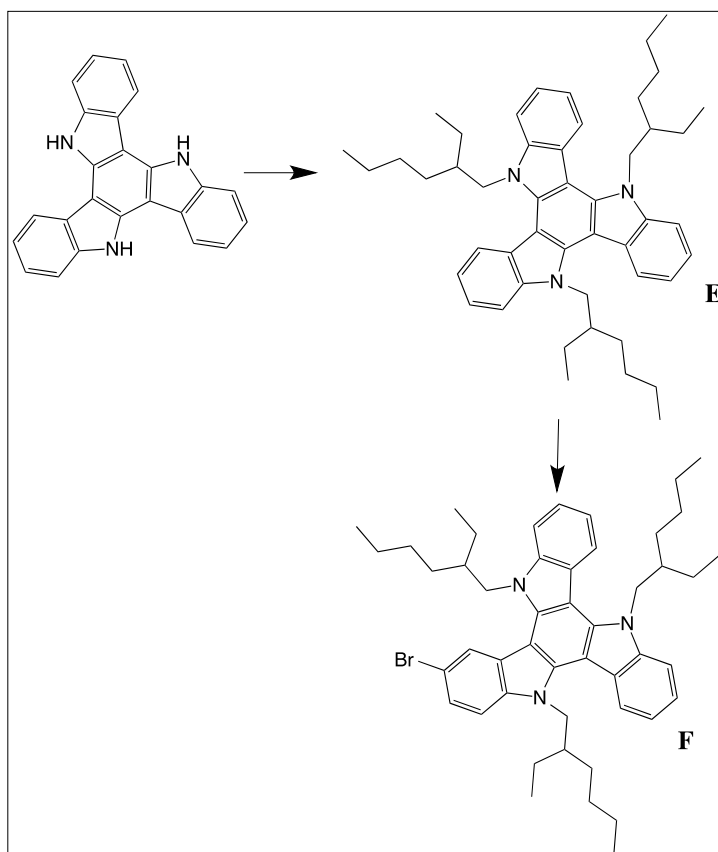


Figure S3: Synthetic pathway for compound **G**

5,10,15-tris(2-ethylhexyl)-10,15-dihydro-5H-diindolo[3,2-*a*:3',2'-*c*]carbazole (compound E): A suspension of compounds 10,15-dihydro-5H-diindolo[3,2-*a*:3',2'-*c*]carbazole (3.5 g, 10.13 mmol) and NaH (60% in mineral oil) (3.0 g, 11.83 mmol) in 90 ml DMF/THF (50/50) was stirred during 30 min. After addition of 2-ethylhexyl bromide (13 ml, 70.94 mmol), the mixture was heated at 70°C overnight. The solution was cooled down to room temperature, and the solvent evaporated to dryness. The crude product was dissolved in CH₂Cl₂ and was washed with water (3X150 mL), the organic phases was dried over MgSO₄ and concentrated under reduce pressure. The purification was carried out by chromatography on flash silica as static phase with a mixture of petroleum ether/CH₂Cl₂ (95/5) as mobile phase and afforded compound **E** (6.9 g) as a pale yellow oil (quantitative).

^1H NMR (CDCl_3 , 300 MHz): 0.41-0.52 (m, 9H; CH_3), 0.62-1.26 (m, 33H; CH_2), 2.05 (m, 3H; CH_2), 4.96 (m, 6H; CH_2), 7.31 (t, 3H, $^3\text{J} = 8.0$ Hz; Ar H), 7.40 (t, 3H, $^3\text{J} = 8.0$ Hz; Ar H), 7.62 (d, 3H, $^3\text{J} = 8.6$ Hz; Ar H), 8.29 (d, 3H, $^3\text{J} = 8.6$ Hz; Ar H); ^{13}C NMR (CDCl_3 , 75 MHz): 10.2, 10.3, 13.9, 22.9, 28.3, 29.9, 38.1, 50.7, 103.8, 111.5, 119.6, 122.3, 122.4, 123.7, 139.3, 141.2.

3-bromo-5,10,15-tris(2-ethylhexyl)-10,15-dihydro-5H-diindolo[3,2- α :3',2'-c]carbazole (compound F): **Compound E** (5.65 g, 8.28 mmol) was dissolved in 95 ml CHCl_3/DMF (90/5) and placed in dark. NBS was then added portion wise and the reaction was monitoring with TLC. The solution was quenched with H_2O and the organic phases was extracted with CHCl_3 . Dried over MgSO_4 and concentrated under reduce pressure. The purification was carried out by chromatography on flash silica as static phase with a mixture of petroleum ether/toluene (95/5) as mobile phase and afforded compound **F** (3.74 g) as a pale yellow oil (59%).

^1H NMR (CDCl_3 , 300 MHz): 0.41-0.52 (m, 9H; CH_3), 0.62-1.26 (m, 33H; CH_2), 2.05 (m, 3H; CH_2), 4.96 (m, 6H; CH_2), 7.34 (t, 2H, $^3\text{J} = 8.4$ Hz; Ar H), 7.44 (t, 3H, $^3\text{J} = 7.5$ Hz; Ar H), 7.61 (d-d, 2H, $^3\text{J} = 8.9$, $^4\text{J} = 1.6$ Hz; Ar H), 7.73 (d, 1H, $^4\text{J} = 1.8$ Hz; Ar H), 8.09 (d, 1H, $^3\text{J} = 9.5$ Hz; Ar H), 8.28 (t, 2H, $^3\text{J} = 8.7\text{Hz}$; Ar H); ^{13}C NMR (CDCl_3 , 75 MHz): 10.1, 10.2, 10.2, 10.3, 10.3, 14.0, 21.6, 22.9, 23.0, 23.0, 28.2, 28.3, 28.3, 28.4, 29.9, 38.1, 50.7, 111.6, 114.3, 119.7, 122.3, 122.4, 123.2, 123.6, 125.4, 128.4, 129.2, 138.0, 141.2, 142.2.

2-boronate-5,10,15-triazatruxene (compound 1): In a Schlenk tube compounds **compound D** (4.5 g, 5.91 mmol), bis(pinacolato)diboron (3.0 g, 11.83 mmol) and potassium acetate (3.48 g, 35.46 mmol) were dissolved in dioxane (120 mL). Argon was bubbled through the mixture for 45 min, then $[\text{Pd}(\text{dppf})_2\text{Cl}_2 \cdot \text{CH}_2\text{Cl}_2]$ (45 mg) was added and the mixture was stirred at 100°C for 1day. The solution was cooled down to room temperature, and the solvent evaporated to dryness. The crude was dissolved in CH_2Cl_2 and was washed with water (3X150 mL) and dried over MgSO_4 and concentrated under reduced pressure. The purification was carried out by chromatography on flash silica as static phase with a mixture of petroleum ether/ CH_2Cl_2 (60/40) as mobile phase and afforded (4.0 g) as a pale yellow oil (83%).

^1H NMR (CDCl_3 , 300 MHz): 0.85 (t, 9H, $3\text{J} = 7.6$ Hz; CH_3), 1.27-1.42 (m, 18H; CH_2), 1.49 (s, 12H; CH_3), 4.93 (t, 4H, $^3\text{J} = 7.6$ Hz; CH_2), 5.03 (t, 2H, $^3\text{J} = 7.6$ Hz; CH_2), 7.35-7.41 (m, 2H; Ar H), 7.46-7.51 (m, 2H; Ar

H), 7.66 (d, 2H, $^3J = 7.9$ Hz; Ar H), 7.85 (d, 1H, $^3J = 8.2$ Hz; Ar H), 8.15 (s, 1H, Ar H), 8.31-8.34 (m, 3H; Ar H); ^{13}C NMR (CDCl_3 , 75 MHz): 14.0, 22.5, 22.6, 22.7, 25.0, 25.1, 26.3, 26.4, 26.5, 29.8, 30.1, 31.4, 31.5, 31.6, 46.9, 47.1, 83.8, 103.2, 103.3, 110.5, 117.1, 119.7, 120.8, 121.5, 121.7, 122.8, 123.4, 123.5, 123.6, 126.1, 127.8, 131.4, 134.8, 138.9, 139.4, 139.7, 140.6, 141.0, 141.1.

3-boronate-5,10,15-triazatruxene (compound 2): The synthetic method is identical to that reported for the synthesis of the **compound 1** except that **compound F** was used as starting and commercially available material.

^1H NMR (CDCl_3 , 300 MHz): 0.42-0.49 (m, 9H; CH_3), 0.63-1.01 (m, 33H; CH_2), 1.44 (s, 12H; CH_3), 2.05 (m, 3H; CH_2), 4.96 (m, 2H; CH_2), 7.31-7.37 (m, 2H; Ar H), 7.40-7.46 (m, 2H; Ar H), 7.61 (d, 2H, $^3J = 7.8$ Hz; Ar H), 7.79 (d, 1H, $^3J = 7.5$ Hz; Ar H), 8.09 (s, 1H, Ar H), 8.28 (d, 3H, $^3J = 7.8$; Ar H); ^{13}C NMR (CDCl_3 , 75 MHz): 10.3, 13.9, 14.0, 22.9, 23.1, 25.0, 25.1, 28.3, 28.4, 28.5, 29.5, 29.8, 29.9, 30.0, 30.5, 38.1, 50.8, 83.8, 103.8, 103.9, 111.6, 117.9, 119.6, 119.7, 121.5, 122.3, 122.5, 123.7, 123.8, 124.9, 125.8, 126.1, 127.8, 131.4, 134.9, 139.4, 139.7, 139.8, 140.9, 141.2.

General method for Suzuki-Miyaura cross-coupling: In a Schlenk tube the boronate compound (220 mg, 0.304 mmol), the dibromo thiophene-electron withdrawing-thiophene compound (0.88 mmol) and Cs_2CO_3 (182 mg, 1.32 mmol) were dissolved in dioxane. Argon was bubbled through the mixture for 45 min, then $\text{P}(\text{Cy})_3$ and $\text{Pd}_2(\text{dba})_3$ (10 mg) was added and the mixture was stirred at 110°C for 1 day. The solution was cooled down to room temperature, and the solvent evaporated to dryness. The crude was dissolved in CH_2Cl_2 and was washed with water (3X30 mL) and dried over MgSO_4 and concentrated under reduced pressure. The purification was carried out by chromatography on flash silica as static phase with a mixture of petroleum ether/ CH_2Cl_2 (70/30) as mobile phase and afforded the desire compound as a powder.

Compound 6m: Using **compound 3** as dibromo derivative. ^1H NMR (CDCl_3 , 300 MHz): 0.52-0.65 (m, 18H; CH_3), 0.78-1.04 (m with grease, 66H; CH_2), 2.06 (m broad, 6H; CH), 4.96 (m, 12H; CH_2), 7.32-7.53 (m, 8H; Ar H), 7.52 (d, 2H, $^3J = 3.9$ Hz; Ar H), 7.59 (d, 4H, $^3J = 8.01$ Hz; Ar H), 7.67 (dd, 2H, $^3J = 8.3$ Hz, 4J

= 1.41 Hz; Ar H), 7.82 (s, 2H; Ar H), 7.86 (s, 2H; Ar H), 8.17 (d, 2H, $^3J = 3.9$ Hz; Ar H), 8.23-8.33 (m, 6H; Ar H); ^{13}C NMR (CDCl_3 , 75 MHz): 10.2, 10.3, 10.3, 10.4, 14.1, 22.9, 23.1, 28.4, 28.5, 28.6, 30.0, 30.1, 38.2, 50.7, 103.7, 103.9, 108.5, 111.5, 117.9, 119.6, 122.4, 122.5, 123.6, 125.2, 125.7, 128.5, 128.9, 138.1, 138.9, 139.4, 140.0, 141.1, 141.2, 141.6; Exact mass: 1658.96; molecular weight: 1660.46, Maldi-TOF m/z : 1659.93.

Compound 6p: Using **compound 3** as dibromo derivative. ^1H NMR (CDCl_3 , 300 MHz): 0.58-0.62 (m, 18H; CH_3), 0.78-1.04 (m with grease, 66H; CH_2), 2.27 (m broad, 6H; CH), 4.97 (m broad, 12H, $^3J = 7.9$ Hz; CH_2), 7.58-7.69 (m, 16H; Ar H), 7.98 (d, 2H, $^3J = 8.0$ Hz; Ar H), 8.21 (s, 2H; Ar H), 8.37 (d, 2H, $^3J = 3.7$ Hz; Ar H), 8.46-8.54 (m, 4H; Ar H), 8.6-8.61 (m, 2H; Ar H); ^{13}C NMR (CDCl_3 , 75 MHz): 10.4, 10.4, 14.0, 14.1, 22.9, 23.1, 28.4, 28.5, 30.0, 30.1, 38.1, 50.7, 103.7, 103.9, 108.5, 111.5, 117.9, 119.6, 122.4, 122.5, 123.6, 125.2, 125.7, 128.5, 128.9, 138.1, 138.9, 140.0, 141.1, 141.2, 141.6, 147.1, 152.8; Exact mass: 1658.96; molecular weight: 1660.46, Maldi-TOF m/z : 1659.94

Compound 7p: Using **compound 4** as dibromo derivative. ^1H NMR (CDCl_3 , 300 MHz): 0.46-0.52 (m, 18H; CH_3), 0.65-1.03 (m with grease, 66H; CH_2), 2.04 (m broad, 6H; CH), 4.83 (m broad, 12H, $^3J = 7.9$ Hz; CH_2), 7.31-7.49 (m, 10H; Ar H), 7.57-7.68 (m, 6H; Ar H), 7.77 (s, 1H; Ar H), 7.84 (s, 1H; Ar H), 8.08 (d, 1H, $^3J = 3.7$ Hz; Ar H), 8.16 (d, 2H, $^3J = 7.9$ Hz; Ar H), 8.24 (d, 2H, $^3J = 8.1$ Hz; Ar H), 8.31 (d, 2H, $^3J = 7.7$ Hz; Ar H), 8.57 (d, 1H, $^3J = 4.0$ Hz; Ar H), 8.80 (s, 1H; Ar H); ^{13}C NMR (CDCl_3 , 100 MHz): 10.2, 10.3, 13.8, 13.9, 13.9, 13.9, 13.9, 22.8, 22.9, 23.0, 23.2, 28.2, 28.2, 28.3, 28.3, 28.4, 28.5, 29.8, 30.0, 38.0, 50.4, 50.5, 103.5, 103.5, 103.6, 103.7, 103.7, 108.3, 108.5, 111.3, 111.5, 117.6, 117.7, 119.5, 119.6, 120.0, 122.2, 122.4, 123.3, 123.4, 123.4, 123.7, 124.1, 127.9, 128.0, 129.1, 133.2, 135.2, 138.7, 138.7, 139.3, 139.4, 139.8, 140.0, 140.3, 141.0, 141.0, 141.3, 141.4, 145.6, 147.2, 148.0, 150.5, 154.6; Exact mass: 1659.95; molecular weight: 1661.45, Maldi-TOF m/z : 1660.98.

Compound 8p: Using **compound 5** as dibromo derivative. ^1H NMR ($\text{C}_2\text{D}_2\text{Cl}_4$, 400 MHz): 0.56-0.69 (m, 18H; CH_3), 0.71-1.12 (m with grease, 66H; CH_2), 2.12 (m broad, 6H; CH), 4.99 (m broad, 12H, $^3J = 7.9$ Hz; CH_2), 7.38-7.43 (m, 5H; Ar H), 7.48-7.53 (m, 6H; Ar H), 7.68-7.73 (m, 8H; Ar H), 7.93 (s, 1H; Ar H),

8.33-8.38 (m, 6H; Ar H). ^{13}C NMR ($\text{C}_2\text{D}_2\text{Cl}_4$, 100 MHz): 10.2, 10.2, 10.3, 10.3, 10.4, 10.4, 13.9, 13.9, 13.9, 13.9, 22.8, 22.9, 23.3, 23.3, 23.5, 28.4, 28.4, 28.5, 28.5, 28.6, 28.7, 29.8, 30.2, 30.3, 38.4, 38.5, 50.9, 104.0, 104.2, 108.3, 111.5, 111.6, 112.5, 118.0, 119.8, 122.3, 122.5, 122.7, 123.5, 123.9, 126.0, 128.2, 134.0, 138.8, 139.5, 140.0, 141.3, 141.4, 141.8; Exact mass: 1664.91; molecular weight: 1666.49, Maldi-TOF m/z: 1665.90.

Cyclic Voltammetry

Potentials were determined by cyclic voltammetry in deoxygenated CH_2Cl_2 solutions, containing 0.1 M TBAPF_6 , at a solute concentration range of ca 1 mM and at rt. Potentials are given versus the saturated calomel electrode (SCE) and standardized vs ferrocene (Fc) as internal reference assuming that $E_{1/2}(\text{Fc}/\text{Fc}^+) = +0.38 \text{ V}$ ($\Delta E_p = 60 \text{ mV}$) vs SCE. The error in half-wave potential is $\pm 10 \text{ mV}$. Where the redox processes are irreversible, the peak potentials (E_{ap} or E_{cp}) are quoted. All reversible redox steps result from one-electron processes unless otherwise specified.

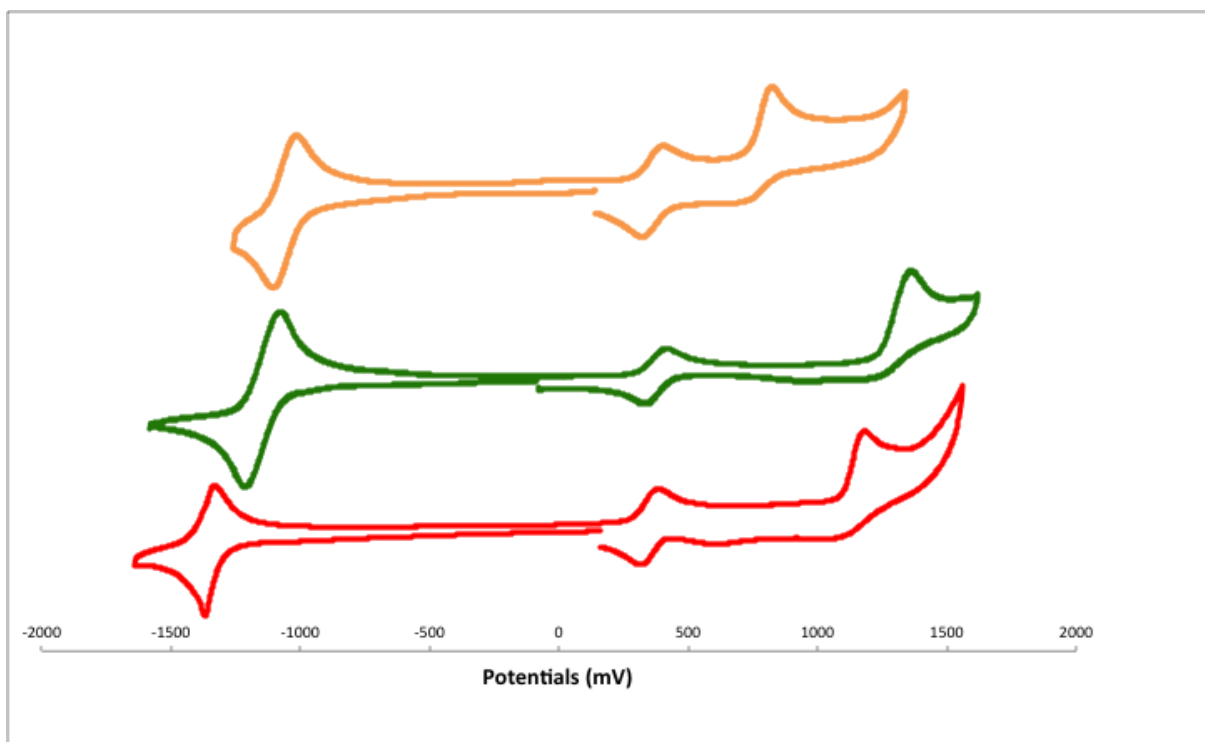


Figure S4: Cyclic voltammograms of the thiophene-based central chromophores in dichloromethane solution using TBAPF_6 as supporting electrolyte, compound 3 in red, compound 4 in green and compound 5 in orange, respectively.

Density Functional Theory

Density functional theory (DFT) calculations have been performed using SPARTAN 10 (www.wavefun.com) at the B3LYP/6-311+G* level of theory in vacuum.

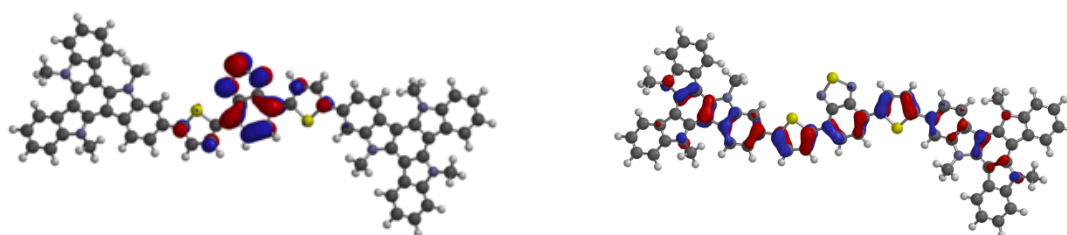


Figure S5: Calculated LUMO (left) and HOMO (right) levels for compound **6m**

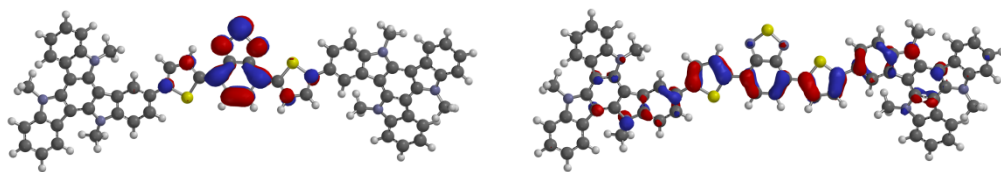


Figure S6: Calculated LUMO (left) and HOMO (right) levels for compound **6p**

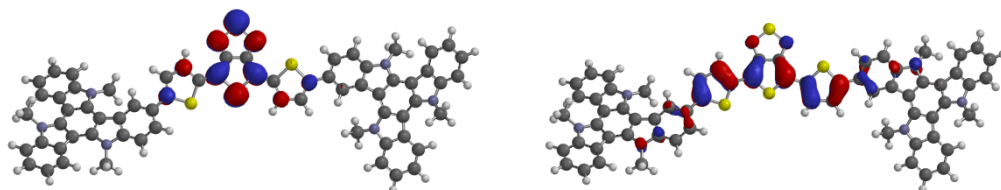


Figure S7: Calculated LUMO (left) and HOMO (right) levels for compound **8p**

Atomic Force Microscopy

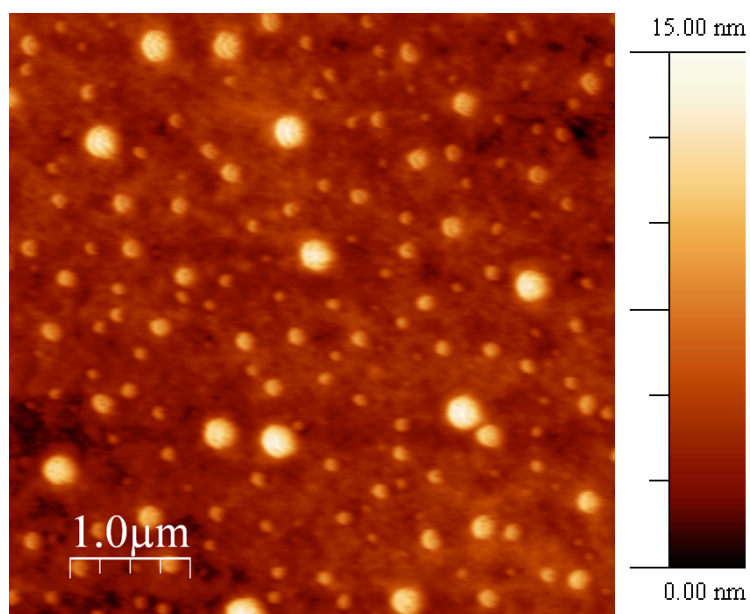


Figure S8: AFM height images ($1\ \mu\text{m} \times 1\ \mu\text{m}$) of **7p:PC₇₀BM** without DIO after annealing 10 min at 110°C.

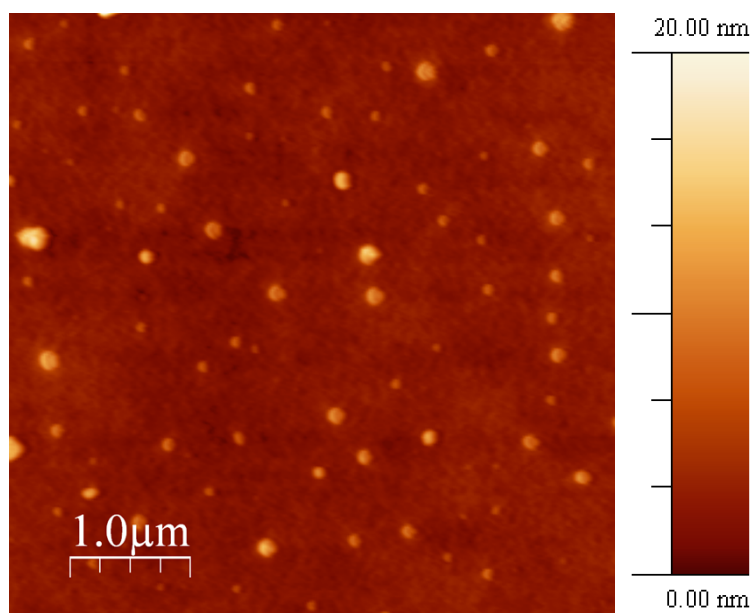


Figure S9: AFM height images ($1\ \mu\text{m} \times 1\ \mu\text{m}$) of **7p**:PC₇₀BM with 0.6 % vol. of DIO after annealing 10 min at 110°C.

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