

## Supporting Information

# Visible and Near-infrared Organic photosensitizers comprising isoindigo derivatives as chromophores: synthesis, optoelectronic properties and factors limiting their efficiency in dye solar cells

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## I. Instruments and methods

UV-vis absorption spectra were recorded in solution on a Cary 60 (wavelength range: 190 to 1100 nm; 1.5 nm fixed spectral bandwidth, full spectrum Xenon pulse lamp single source), Agilent.

Electrochemical studies of the synthesized molecules were carried out in a one compartment, three-electrode electrochemical cell equipped with a flat platinum working electrode (7 mm<sup>2</sup>), a platinum wire counter electrode, and a silver wire pseudo-reference electrode, whose potential was checked using the Fc<sup>+</sup>/Fc couple as an internal standard. The electrolyte consisted of 0.2 M tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>) solution in dichloromethane containing 2 × 10<sup>-3</sup> M of the dye. Cyclic voltammetry measurements were conducted with a sweep rate of 100 mV.s<sup>-1</sup>.

## II. Dyes Sensitized Solar Cells fabrication and characterizations

### Fabrication

The devices were prepared as followed: the various layers of TiO<sub>2</sub> films were screen printed. The electrode total active area was 0.36 cm<sup>2</sup>. A first layer (12 μm) of transparent titania was deposited with a TiO<sub>2</sub> nanoparticles paste (Ti-Nanoxide HT/SP) purchased from Solaronix, Switzerland. To further increase the light-harvesting capacity of these devices, a reflective layer (Solaronix' Ti-Nanoxide R/SP) of 4 μm was added on top. The total thickness of the titania working electrode was around 17 μm. In order to optimize adhesion, titania layer porosity and specific area a pre and post TiCl<sub>4</sub> treatment was performed. After sintering at 500°C and cooling down to 80°C, the sintered TiO<sub>2</sub> electrodes were sensitized by immersion in a solution of the dye in indicated solvent with or without chenodeoxycholic acid (CDCA) for 18 h, and then assembled using a thermally platinized FTO/glass (TCO 22-7, Solaronix) counter electrode. The working and counter electrodes were separated by a 25 μm thick hot melt gasket (Meltonix 1170-25, Solaronix) and sealed by heating. The heating was minimized to avoid dye thermal degradation. The cell was then filled with a volatile electrolyte (Solaronix Iodolyte HI-30) through a pre-drilled hole using a vacuum pump. The electrolyte injection hole on the thermally platinized FTO glass counter electrode was finally sealed with a thin glass cover. Devices using a non-volatile ionic liquid based electrolyte (Solaronix Mosalyte TDE-250) were prepared following the previously described procedure. The devices were characterized using a Solaronix SolarSim 150 previously calibrated. The current–voltage characteristics of the cell measured under AM 1.5G, 100% sun, were obtained by applying external potential bias to the cell and by measuring the generated photocurrent with a Keithley model 2400 digital source meter (Keithley, USA). The devices were masked prior to measurement according to a procedure previously described to attain an illuminated active area of 0.16 cm<sup>2</sup>.

### Charge Extraction

As the name indicates, with this technique, we extract and measure the charge accumulated in the system under operating conditions. The Charge Extraction (CE) measurements were carried out with a system similar to that employed by O'Regan et al.<sup>1</sup> The cells were simultaneously in open-circuit and illuminated with LEDs until they reach to the steady state. Right after, the LEDs were switched off and the cells were short-circuited. Under these conditions, all the accumulated charges under open-circuit conditions can be collected, allowing the measurement to calculate the electron density.<sup>2</sup> By changing the LEDs intensity, the electron density can be

estimated as a function of the cell voltage. The obtained value determines the conduction band edge shift of the semiconductor. The CE system consists in six white LEDs that generate pulses controlled by the Trigger (TGP, from Thurlby Thandar Instruments). The voltage decay is measured by an oscilloscope TDS 2022 from Tektronix©.

### **Transient Photovoltage**

Transient photovoltage (TPV) measurements were also carried out with a system similar to the one employed by O'Regan et al.<sup>1</sup> This technique provides information on the electron recombination rate between the photoinjected electrons in the semiconductor band and the redox couple presents in the electrolyte under operating conditions. In TPV measurements, a constant background voltage is applied to the cells with a set of white LEDs until they reach to a steady state condition. Afterwards, an ultra-short laser pulse (660 nm, 10 mW) is applied and induces extra-injected electrons in the conduction band of the TiO<sub>2</sub>. Those extra charges recombine with the oxidized electrolyte due to the open circuit conditions, producing a transient decay. By modifying the voltage (changing the illumination intensity of the white LEDs) it is possible to record different transient decays. The TPV equipment is the same used for CE measurements.

### **Laser-Transient Absorption Spectroscopy**

The measurement of Laser-Transient Absorption Spectroscopy (L-TAS) measurements were similar to those carried out previously in our group.<sup>3</sup> It provides us information about the electron injection constant by monitoring the formation of the dye cation species (D<sup>+</sup>) which appears after the electron injection. L-TAS can determinate both the undesired charge recombination of these electrons in the semiconductor with the oxidized dye and the regeneration of the dye cation by the redox electrolyte.<sup>4</sup> A sample is irradiated constantly at a determinate wavelength, which corresponds to the maximum absorption wavelength of the excited state of the sample. At the same time, it is excited with a short light pulse, producing a change in the sample optical density. The change in optical density is monitored during a short period to record the variations.

The L-TAS experiments were carried as follow. On the one hand, we used sensitized films and added carefully on top of the film the electrolyte. The wet film is covered with a thin microscopy cover slide and the experiment is carried out. After the L-TAS experiment, the film is rinsed with solvent to remove the electrolyte and we check that the initial decay is recovered. On the other hand, we also fabricated complete devices using very thin FTO. These devices are also used for L-TAS measurements and the decays with/without electrolyte are recorded.

### **References related to photophysical characterizations:**

1. (a) O'Regan, B. C.; Bakker, K.; Kroeze, J.; Smit, H.; Sommeling, P.; Durrant, J. R., Measuring Charge Transport from Transient Photovoltage Rise Times. A New Tool To Investigate Electron Transport in Nanoparticle Films. *The Journal of Physical Chemistry B* 2006, 110 (34), 17155-17160; (b) O'Regan, B. C.; Scully, S.; Mayer, A. C.; Palomares, E.; Durrant, J., The Effect of Al<sub>2</sub>O<sub>3</sub> Barrier Layers in TiO<sub>2</sub>/Dye/CuSCN Photovoltaic Cells Explored by Recombination and DOS Characterization Using Transient Photovoltage Measurements. *The Journal of Physical Chemistry B* 2005, 109 (10), 4616-4623.
2. Duffy, N. W.; Peter, L. M.; Rajapakse, R. M. G.; Wijayantha, K. G. U., Investigation of the Kinetics of the Back Reaction of Electrons with Tri-Iodide in Dye-Sensitized Nanocrystalline Photovoltaic Cells. *The Journal of Physical Chemistry B* 2000, 104 (38), 8916-8919.

3. Zewdu, T.; Clifford, J. N.; Hernandez, J. P.; Palomares, E., Photo-induced charge transfer dynamics in efficient TiO<sub>2</sub>/CdS/CdSe sensitized solar cells. *Energy & Environmental Science* 2011, 4 (11), 4633-4638.
4. (a) Haque, S. A.; Tachibana, Y.; Willis, R. L.; Moser, J. E.; Grätzel, M.; Klug, D. R.; Durrant, J. R., Parameters Influencing Charge Recombination Kinetics in Dye-Sensitized Nanocrystalline Titanium Dioxide Films. *The Journal of Physical Chemistry B* 2000, 104 (3), 538-547; (b) Tachibana, Y.; Moser, J. E.; Grätzel, M.; Klug, D. R.; Durrant, J. R., Subpicosecond Interfacial Charge Separation in Dye-Sensitized Nanocrystalline Titanium Dioxide Films. *The Journal of Physical Chemistry* 1996, 100 (51), 20056-20062.

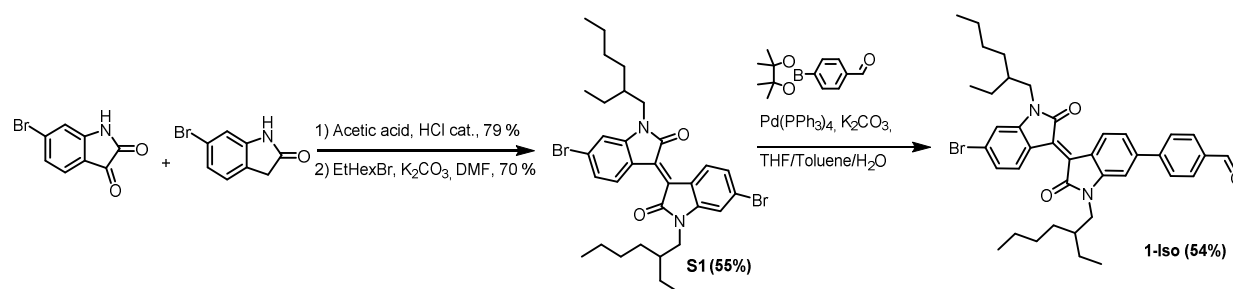
### III. Synthesis

#### Materials

4-formylphenylboronic acid, 4-bromobenzaldehyde, tri-*tert*-butyl phosphonium tetrafluoroborate, palladium acetate (II) pivalic acid, potassium carbonate, tetrakis(triphenylphosphine)palladium(0), tris(dibenzylideneacetone)dipalladium(0), 2-cyanoacetic acid, piperidine, Zinc, n-BuLi [2.5 M solution in Tetrahydrofuran (THF)], n-BuLi [1.6 M solution in n-hexane], trimethyltin chloride solution [1 M solution in THF] were purchased from Aldrich, Acros Organics or TCI chemicals and used as received. N-Bromo-Succinimide (NBS) was purchased from Fisher Chemicals, tri(*o*-tolyl)phosphine and di-*tert*-butyl(methyl)phosphonium tetrafluoroborate from Strem Chemicals, 2-octylthiophene from Alfa Aesar, 3,4-diaminothiophene from Janssen Chemica. The solvents, such as anhydrous toluene, chloroform and acetonitrile from Aldrich were used as received. THF was used after distillation under sodium and benzophenone. Spectroscopic grade solvents from Aldrich were used for spectral measurements.

#### Synthesis of Isoindigo core:

Figure S1- Synthetic route for 1-Iso



#### Synthesis of 6,6'-dibromo-1,1'-bis(2-ethylhexyl)-[3,3'-biindolinylidene]-2,2'-dione (S1) was synthesized according to the literature<sup>1</sup>:

1) To a suspension of 6-bromooxindole (4.69 g, 22.12 mmol, 1 eq) and 6-bromoisatin (5 g, 22.12 mmol, 1 eq) in acetic acid (150 mL), conc. HCl solution (0.1 ml) was added and heated under reflux for 48h. The mixture was allowed to cool at room temperature and was precipitated in water (1L) then filtrated. The solid material was washed with water, methanol and ethyl acetate and provide 6,6'-dibromoisoidigo (7.383 g, 79%) as a brown solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ = 11.07 (s, 1H), 8.91 (d, 1H, J<sub>1</sub>=8.5Hz), 7.15 (d, 1H, J<sub>1</sub>=8.5Hz), 6.97 (s, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ = 170.32, 147.26, 134.03, 132.34, 127.01, 125.36, 122.63, 113.92.

2) To a suspension of 6,6'-dibromoisoidigo (3 g, 7.14 mmol, 1 eq) and potassium carbonate (4.94 g, 35.71 mmol, 5 eq) in anhydrous dimethylformaldehyde (DMF) (150 mL), 1-bromo-2-

ethylhexyl (4.14 g, 3.81 ml, 21.43 mmol, 3 eq) was injected through a septum under nitrogen. The mixture was stirred overnight at 100°C and then poured into water (200 mL). The organic phase was extracted with dichloromethane, washed with brine and dried over MgSO<sub>4</sub>. After removal of the solvent under reduced pressure, the deep-red solids were purified by silica chromatography, eluting with (CH<sub>2</sub>Cl<sub>2</sub>: Hexane = 1:1) to give 6,6'-dibromo-N,N'-(2-ethylhexyl)-isoindigo (**S1**) (3.1 g, 70 %)

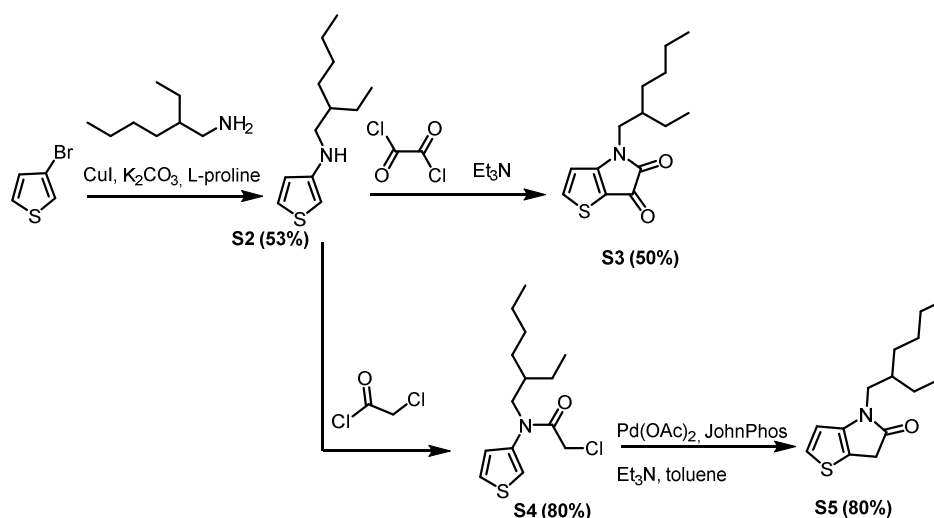
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ = 9.00 (d, J = 8.7 Hz, 2H), 7.13 (dd, J<sub>1</sub> = 8.7 Hz, J<sub>2</sub> = 1.5 Hz, 2H), 6.81 (d, J = 1.5 Hz, 2H), 3.60-3.48 (m, 4H), 1.90-1.72 (m, 2H), 1.43-1.20 (m, 16H), 0.95-0.82 (m, 12H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ = 168.25, 146.33, 132.71, 131.16, 126.82, 125.27, 120.53, 111.69, 44.53, 37.58, 30.73, 28.72, 24.15, 23.20, 14.19, 10.79.

### Synthesis of 4-(6'-bromo-1,1'-bis(2-ethylhexyl)-2,2'-dioxo-[3,3'-biindolinylidene]-6-yl)benzaldehyde (**1-Iso**) was synthesized according to the literature<sup>2</sup>:

Under argon, 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde (162 mg, 698 μmol, 0.75 eq), (E)-6,6'-dibromo-1,1'-bis(2-ethylhexyl)-[3,3'-biindolinylidene]-2,2'-dione (600 mg, 931 μmol, 1eq), Tetrakis (triphenyl phosphine) palladium (48 mg, 5% mol), potassium carbonate (257 mg, 1.86 mmol, 2 eq) were dissolved in toluene (5 mL), water (3.7 mL) and THF (20 mL). The solution was vigorously stirred and heated at 80°C overnight. The reaction was quenched with HCl solution (2M) and the organic phase was extracted with chloroform and washed with water and brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under vacuum. The crude solid was chromatographed on silica gel using n-hexane/diethyl ether (9/1) as eluent to afford **1-Iso** as a red solid (266 mg, 57%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ = 10.12 (s, 1H), 9.30 (d, 1H, J<sub>1</sub>=8.3Hz), 9.13 (d, 1H, J<sub>1</sub>=8.3Hz), 7.89 (ABQ, 4H, J<sub>1</sub>=8.4Hz, ΔvAB= 73 Hz), 7.37 (dd, 1H, J<sub>1</sub>=8.4Hz, J<sub>2</sub>=1.7Hz), 7.24 (dd, 1H, J<sub>1</sub>=8.4Hz, J<sub>2</sub>=1.7Hz), 7.04 (d, 1H, J<sub>1</sub>=1.5Hz), 6.96 (d, 1H, J<sub>1</sub>=1.5Hz), 3.84-3.61 (m, 4H), 1.91 (m, 2H), 1.50-1.25 (m, 16H), 1.00-0.92 (m, 12H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ = 191.68, 168.44, 168.17, 146.31, 146.23, 145.98, 143.62, 135.82, 133.05, 132.53, 131.04, 130.36, 127.60, 126.63, 125.11, 121.79, 121.32, 120.50, 111.55, 106.81, 44.41, 44.30, 40.83, 37.71, 37.47, 30.74, 30.61, 28.76, 28.60, 24.17, 24.02, 23.81, 23.06, 20.77, 17.48, 17.28, 14.63, 14.06, 10.76, 10.65.

### Synthesis of Thienoisatin and Thieno-oxindole:

Figure S2- Synthetic routes for thienoisatin and thieno-oxindole



**Synthesis of N-(2-ethylhexyl) thiophene-3-amine (S2) was synthesized according to the literature<sup>3</sup>:**

3-bromothiophene (5.75 ml, 61.34 mmol), ethylhexylamine (11.05 ml, 67.47 mmol), copper(I) iodide (1.17 g, 6.13 mmol), potassium carbonate (1.17 g, 6.13 mmol) and L-proline (1.17 g, 6.13 mmol) were stirred in 20 ml of DMSO at 80°C overnight. The mixture was quenched with water and extracted with diethyl ether, dried on Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated via rotary evaporation. The crude product was purified with silica gel chromatography (Hexane) to give N-(2-ethylhexyl) thiophene-3-amine (**S2**) (8.45 g, 65%) as a brownish oil that turns red quickly on exposure to air and light. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ = 7.14 (dd, 1H, J<sub>1</sub>=5.3Hz, J<sub>2</sub>=3.2Hz), 6.62 (dd, 1H, J<sub>1</sub>=5.3Hz, J<sub>2</sub>=3.2Hz), 5.92 (dd, 1H, J<sub>1</sub>=3Hz, J<sub>2</sub>=1.6Hz), 3.57 (m, 1H), 2.98 (d, 2H), 1.55 (m, 1H), 1.27-1.44(m, 8H), 0.86-0.94 (m, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ = 149.14, 124.98, 119.93, 94.79, 53.41, 49.47, 39.24, 31.42, 29.05, 24.58, 23.10, 14.09, 10.97.

**Synthesis of 4-(2-ethylhexyl)-4H-thieno[3,2-b]pyrrole-5,6-dione (S3) was synthesized according to the literature<sup>3</sup>:**

A dry round bottom flask was charged with oxalyl chloride (6.09 g, 47.97 mmol, 4.11 mL, 1.2 equiv.) in dichloromethane (30 mL) and a stir bar and cooled to 0 °C. To this flask, a solution of N-(2-ethylhexyl)thiophene-3-amine (8.45 g, 39.98 mmol, 1.0 equiv.) in dry dichloromethane (20 mL) was added dropwise over 15 min via addition funnel. After addition was complete, the reaction mixture was allowed to stir for 30 min at room temperature before dropwise addition of a solution of triethylamine (4 mL) in dichloromethane (10 mL). The mixture was allowed to stir at room temperature for 12 h, after which it was poured into water, extracted three times with dichloromethane, dried on Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated via rotary evaporation. The residue was purified via flash silica gel chromatography (15% EtOAc/hexanes) to provide 4-(2-ethylhexyl)-4H-thieno[3,2-b]pyrrole-5,6-dione (**S3**) (5.37 g, 61% yield) of a bright orange oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ = 7.98 (d, 1H, J<sub>1</sub>=4.9Hz, 6.75 (d, 1H, J<sub>1</sub>=4.9Hz), 3.53 (d, 2H, J<sub>1</sub>=2Hz), 1.73 (m, 1H), 1.29-1.30 (m, 8H), 0.89-0.92 (m, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ = 172.94, 165.46, 161.71, 143.74, 113.1, 111.04, 46.05, 38.27, 30.454, 28.54, 23.82, 22.92, 13.69, 10.49. Anal. calcd for C<sub>14</sub>H<sub>19</sub>NO<sub>2</sub>S: C, 63.36; H, 7.22; N, 5.28; O, 12.06; S, 12.08. Found: C, 63.56; H, 7.12; N, 5.21; S, 12.02%.

**Synthesis of 2-chloro-N-(2-ethylhexyl)-N-(thiophen-3-yl)acetamide (S4) was synthesized according to the literature<sup>4</sup>:**

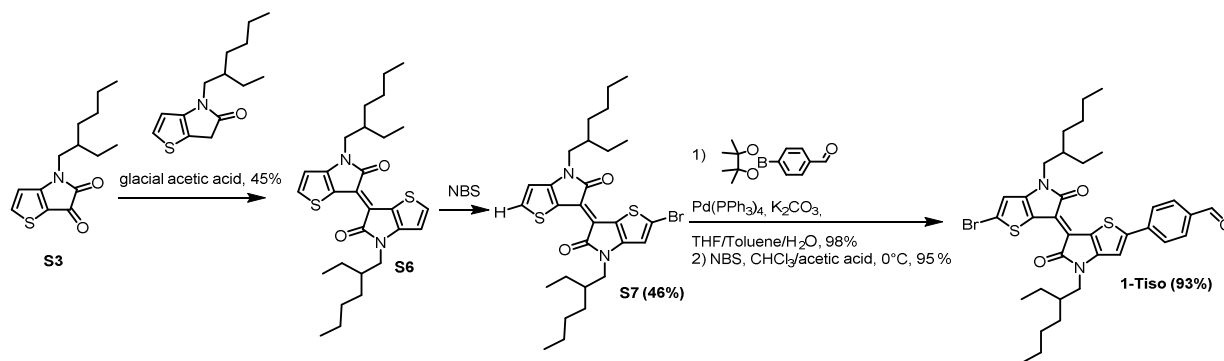
A dry round bottom flask was charged with N-(2-ethylhexyl)thiophene-3-amine (7.13 g, 33.73 mmol, 1.0 equiv.) and distilled dichloromethane (80 mL), and set to stir at 0 °C. To this flask, a solution of chloroacetyl chloride (4.19 g, 37.11 mmol, 2.96 mL, 1.1 equiv.) in dichloromethane (20 mL) was added dropwise over 15 min via addition funnel. The reaction mixture was allowed to warm to room temperature and stir overnight. Upon completion, the reaction mixture was concentrated by rotary evaporation and purified via flash silica gel chromatography (10% EtOAc/hexanes) to provide 2-chloro-N-(2-ethylhexyl)-N-(thiophen-3-yl)acetamide (**S4**) (7.795 g, 80%) of dark red oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ = 7.38 (dd, J<sub>1</sub>=5.2Hz, J<sub>2</sub>=3.2 Hz, 1H), 7.19 (dd, J<sub>1</sub>=3.2Hz, J<sub>2</sub>=1.2 Hz, 1H), 6.95 (dd, J<sub>1</sub>=5.2Hz, J<sub>2</sub>=1.2 Hz, 1H), 3.88 (s, 2H), 3.60 (d, J = 7.6 Hz, 2H), 1.54-1.48 (m, 1H), 1.29-1.15 (m, 8H), 0.89-0.84 (m, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ = 166.9, 140.1, 126.9, 126.1, 122.0, 53.3, 42.2, 36.4, 26.45, 22.90, 22.86, 14.34, 14.31.

**Synthesis of 4-(2-ethylhexyl)-4,6-dihydro-5H-thieno[3,2-b]pyrrol-5-one (S5) was synthesized according to the literature<sup>4</sup>:**

A Schlenk tube was charged with palladium (II) acetate (163.79 mg, 730  $\mu\text{mol}$ , 6 mol %), 2-(di-tert-butylphosphino)biphenyl (JohnPhos, 435 mg, 1.46 mmol, 12 mol%) and 2-chloro-N-(2-ethylhexyl)-N-(thiophen-3-yl)acetamide (3.5 g, 12.16 mmol, 1 equiv.). The tube was evacuated and backfilled with nitrogen three times, and dry triethylamine (1.85 mg, 18.24 mmol, 2.55 mL, 1.5 equiv.) and degassed (freeze-pump-thaw) toluene (20 ml) were added. The reaction mixture was allowed to stir at 100 °C for 3 h. Upon completion, it was diluted with ethyl acetate, filtered through a Celite plug and concentrated by rotary evaporation. The residue was purified by flash silica gel chromatography (10% EtOAc/hexanes) to provide 4-(2-ethylhexyl)-4,6-dihydro-5H-thieno[3,2-b]pyrrol-5-one (**S5**) (2.437 g, 80%) of a brown oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  = 7.24 (d, 1H,  $J_1=5.1\text{Hz}$ ), 6.74 (d, 1H,  $J_1=5.1\text{Hz}$ ), 3.58 (s, 2H), 3.55 (dd, 2H,  $J_1=7.4\text{Hz}$ ,  $J_2=2.2\text{Hz}$ ) 1.73 (m, 1H), 1.38-1.26 (m, 8H), 0.89-0.92 (m, 6H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  = 177.65, 147.25, 126.29, 114.03, 111.90, 111.78, 45.73, 38.27, 36.24, 30.54, 28.67, 23.89, 23.02, 14.07, 10.61.

### Synthesis of Thienoisindigo et benzo-thieno-isindigo derivatives

Figure S3- Synthetic route for 1-Tiso



### Synthesis of 1,1'-bis(2-ethylhexyl)-[3,3'-biindolinylidene]-2,2'-dione (**S6**) was synthesized according to the literature<sup>4</sup>:

A dry flask was charged with 4-(2-ethylhexyl)-4,6-dihydro-5H-thieno[3,2-b]pyrrol-5-one (384 mg, 1.53 mmol, 1.0 equiv.), 4-(2-ethylhexyl)-4H-thieno[3,2-b]pyrrole-5,6-dione (405 mg, 1.53 mmol, 1.0 equiv.) in glacial acetic acid (20 mL). The reaction mixture was allowed to stir at 110°C overnight. Upon cooling, the mixture was poured into water, extracted three times with chloroform, dried on  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated via rotary evaporation. The residue was purified via flash silica gel chromatography (10% diethyl ether/hexanes) to provide 280 mg (51% yield) of **S6** as a dark purple solid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  = 7.52 (d, 2H,  $J_1=5.2\text{Hz}$ ), 6.79 (d, 2H,  $J_1=5.2\text{Hz}$ ), 3.69 (m, 4H), 1.85 (m, 2H), 1.42-1.28 (m, 16H), 0.93-0.86 (m, 12H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  = 171.31, 151.55, 134.21, 121.07, 114.22, 111.35, 45.82, 38.50, 30.57, 28.65, 23.95, 23.01, 14.03, 10.66.

### Synthesis of (E)-2-bromo-4,4'-bis(2-ethylhexyl)-[6,6'-bithieno[3,2-b]pyrrolylidene]-5,5'(4H,4'H)-dione (**S7**):

To a solution of (E)-4,40-bis(2-hexyldecyl)-[6,60-bithieno[3,2-b] pyrrolylidene]-5,50(4H,40 H)-dione (280 mg, 561  $\mu\text{mol}$ ) in chloroform (25 ml) was added N-bromosuccinimide (99 mg, 0.56 mmol, 1.0 eq) at 0°C overnight. Upon completion the reaction mixture was washed with HCl 2M and water and dried over  $\text{Na}_2\text{SO}_4$  before it was purified over a silica column with a Hexane/diethyl ether 90/10 eluent to give the desired product **S7** (366 mg, 46% yield).  $^1\text{H}$  NMR

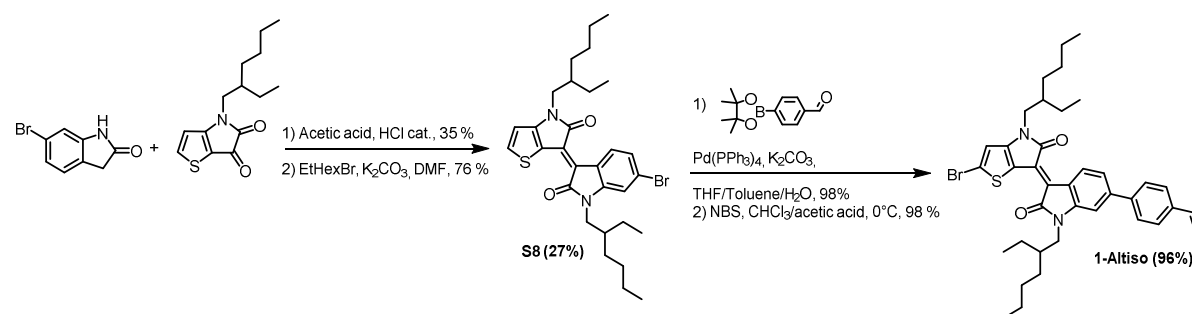
(CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 7.54 (d, 2H,  $J_1=5.2$ Hz), 6.82 (s, 1H), 6.77 (d, 2H,  $J_1=5.2$ Hz), 3.64 (m, 4H), 1.78 (m, 2H), 1.40-1.24 (m, 16H), 0.93-0.86 (m, 12H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 170.81, 170.39, 152.14, 150.44, 150.29, 139.82, 123.66, 120.38, 119.84, 115.87, 114.95, 108.66, 45.90, 38.53, 31.58, 30.52, 28.62, 28.59, 23.91, 23.04, 22.64, 14.10, 14.03, 10.62. Anal. calcd for C<sub>28</sub>H<sub>37</sub>BrN<sub>2</sub>O<sub>2</sub>S<sub>2</sub>: C, 58.22; H, 6.46; N, 4.84; O, 5.54; S, 11.10. Found: C, 61.94; H, 7.09; N, 4.44; S, 10.49.

### Synthesis of 4-(2'-bromo-4,4'-bis(2-ethylhexyl)-5,5'-dioxo-4,4',5,5'-tetrahydro-[6,6'-bithieno[3,2-b]pyrrolylidene]-2-yl)benzaldehyde (1-Tiso):

1) Under argon, 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde (166.9 mg, 719  $\mu$ mol, 1.5 eq), (E)-2-bromo-4,4'-bis(2-ethylhexyl)-[6,6'-bithieno[3,2-b]pyrrolylidene]-5,5'(4H,4'H)-dione (277 mg, 479  $\mu$ mol, 1eq), Tetrakis (triphenyl phosphine) palladium (23 mg, 5% mol), potassium carbonate (132.5 mg, 1.86 mmol, 2 eq) were dissolved in toluene (5 mL), water (3.7 mL) and THF (20 mL). The solution was vigorously stirred and heated at 80°C overnight. The reaction was quenched with HCl solution (2M) and the organic phase was extracted with chloroform and washed with water and brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under vacuum. The crude solid was chromatographed on silica gel using n-hexane/DCM (9/1) as eluent to afford the desired compound as a blue solid (288 mg, 98%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 10.01 (s, 1H), 7.88 (m, 4H), 7.51 (d, 2H,  $J_1=5.2$ Hz), 6.86 (s, 1H), 6.74 (d, 2H,  $J_1=5.2$ Hz), 3.71 (d, 2H,  $J=7.4$ Hz), 3.64 (d, 2H,  $J=7.4$ Hz), 1.87-1.81 (m, 2H), 1.42-1.26 (m, 16H), 0.96-0.86 (m, 12H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 191.16, 170.81, 170.39, 152.14, 150.44, 150.29, 139.82, 135.75, 130.46, 125.87, 123.66, 120.38, 119.84, 115.87, 114.95, 108.66, 45.90, 38.53, 31.58, 30.52, 28.62, 28.59, 23.91, 23.04, 22.64, 14.10, 14.03, 10.62. Anal. calcd for C<sub>35</sub>H<sub>42</sub>N<sub>2</sub>O<sub>3</sub>S<sub>2</sub>: C, 69.73; H, 7.02; N, 4.65; O, 7.96; S, 10.64. Found: C, 69.86; H, 6.81; N, 4.55; S, 10.41.

2) To a solution of (E)-4-(4,4'-bis(2-ethylhexyl)-5,5'-dioxo-4,4',5,5'-tetrahydro-[6,6'-bithieno[3,2-b]pyrrolylidene]-2-yl)benzaldehyde (288 mg, 477  $\mu$ mol) in chloroform (25 ml) was added N-bromosuccinimide (85 mg, 0.48 mmol, 1.0 eq) at 0°C overnight. Upon completion the reaction mixture was washed with HCl 2M and water and dried over Na<sub>2</sub>SO<sub>4</sub> before it was purified over a silica column with a Hexane/DCM 60/40 eluent to give the desired **1-Tiso** (309 mg, 95% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 10.01 (s, 1H), 7.88 (m, 4H), 7.09 (s, 1H), 6.82 (s, 1H), 3.71 (d, 2H,  $J=7.4$ Hz), 3.64 (d, 2H,  $J=7.4$ Hz), 1.87-1.81 (m, 2H), 1.42-1.26 (m, 16H), 0.96-0.86 (m, 12H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 191.16, 170.81, 170.39, 152.14, 150.44, 150.29, 139.82, 135.75, 130.46, 125.87, 123.66, 120.38, 119.84, 115.87, 114.95, 108.66, 45.90, 38.53, 31.58, 30.52, 28.62, 28.59, 23.91, 23.04, 22.64, 14.10, 14.03, 10.62. Anal. calcd for C<sub>35</sub>H<sub>41</sub>BrN<sub>2</sub>O<sub>3</sub>S<sub>2</sub>: C, 61.66; H, 6.06; N, 4.11; O, 7.04; S, 9.41. Found: C, 61.20; H, 5.89; N, 3.96; S, 9.19.

**Figure S4- Synthetic route for 1-Altiso**





**Synthesis of (Z)-6-(6-bromo-1-(2-ethylhexyl)-2-oxoindolin-3-ylidene)-4-(2-ethylhexyl)-4,6-dihydro-5H-thieno[3,2-b]pyrrol-5-one (S8) was synthesized according to the literature<sup>5</sup>:**

1) A dry round bottom flask was charged with 4-(2-ethylhexyl)-4H-thieno[3,2-b]pyrrole-5,6-dione (1.25 g, 4.72 mmol, 1.0 equiv.), 6-bromooxindole (1 g, 4.72 mmol, 1 equiv.), glacial acetic acid (25 mL), a stir bar and 3 drops of conc. HCl. The reaction mixture was allowed to stir at reflux (125 °C), until all of the starting dione was consumed. Upon cooling to room temperature, the mixture was poured into water, extracted three times with chloroform, dried on Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated via rotary evaporation. The residue was purified via flash silica gel chromatography (10% ethyl acetate/hexanes) to provide (Z)-6-(6-bromo-2-oxoindolin-3-ylidene)-4-(2-ethylhexyl)-4,6-dihydro-5H-thieno[3,2-b]pyrrol-5-one (633 mg, 56% yield) as a dark red solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ = 10.57 (s, 1H), 8.79 (d, 1H, J<sub>1</sub>=8.5Hz), 7.5 (d, 1H, J<sub>1</sub>=5.2Hz), 6.93 (dd, 1H, J<sub>1</sub>=8.5Hz, J<sub>2</sub>=1.8Hz), 6.80 (d, 1H, J<sub>1</sub>=1.8Hz), 6.62 (d, 1H, J<sub>1</sub>=5.2Hz), 3.57 (d, 2H, J<sub>1</sub>=2Hz), 1.79 (m, 1H), 1.34-1.26 (m, 8H), 0.89-0.95 (m, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ = 171.25, 170.24, 153.55, 142.85, 137.20, 129.95, 129.55, 124.75, 124.58, 121.15, 120.45, 114.69, 112.81, 110.99, 45.73, 38.57, 31.55, 30.627, 28.73, 23.99, 2261, 14.06.

2) A dry round bottom flask was charged with (Z)-6-(6-bromo-2-oxoindolin-3-ylidene)-4-(2-ethylhexyl)-4,6-dihydro-5H-thieno[3,2-b]pyrrol-5-one (633 mg, 1.38 mmol, 1.0 equiv.), 2-ethylhexylbromide (798 mg, 4.13 mmol, 3 equiv.), DMF (20 mL) and a stir bar. The flask was stirred at 100 °C for 5 min to ensure all of the starting material was solubilized. Lastly potassium carbonate (952 mg, 6.89 mmol, 5 equiv.) was added in portion, and the reaction mixture was allowed to stir at 100 °C for 2 h until all starting material was consumed. Upon cooling to room temperature, the mixture was poured into water, extracted three times with chloroform, dried on Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated via rotary evaporation. The residue was purified via flash silica gel chromatography (10% dichloromethane/hexanes) to provide (Z)-6-(6-bromo-1-(2-ethylhexyl)-2-oxoindolin-3-ylidene)-4-(2-ethylhexyl)-4,6-dihydro-5H-thieno[3,2-b]pyrrol-5-one **S8** as a pink solid (852 mg, 62% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ = 9.14 (d, 1H, J<sub>1</sub>=8.5Hz), 7.59 (d, 1H, J<sub>1</sub>=5.2Hz), 7.22 (dd, 1H, J<sub>1</sub>=8.5Hz, J<sub>2</sub>=1.8Hz), 6.97 (d, 1H, J<sub>1</sub>=1.8Hz), 6.75 (d, 1H, J<sub>1</sub>=5.2Hz), 3.71-3.64 (m, 4H), 1.84 (m, 2H), 1.41-1.29 (m, 16H), 0.89-0.95 (m, 12H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ = 170.80, 169.25, 153.28, 145.20, 136.84, 130.172, 129.85, 125.11, 124.90, 121.73, 120.09, 114.78, 111.52, 111.07, 45.88, 44.40, 38.51, 37.51, 30.64, 30.58, 28.71, 28.69, 24.03, 24.01, 23.08, 23.04, 10.71, 10.66.

**Synthesis of 4-(3-(2-bromo-4-(2-ethylhexyl)-5-oxo-4,5-dihydro-6H-thieno[3,2-b]pyrrol-6-ylidene)-1-(2-ethylhexyl)-2-oxoindolin-6-yl)benzaldehyde (1-Altiso):**

1) Under argon, 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde (170 mg, 735 μmol, 1.5 eq), (Z)-6-(6-bromo-1-(2-ethylhexyl)-2-oxoindolin-3-ylidene)-4-(2-ethylhexyl)-4,6-dihydro-5H-thieno[3,2-b]pyrrol-5-one (280 mg, 490 μmol, 1eq), Tetrakis (triphenyl phosphine) palladium (28 mg, 5% mol), potassium carbonate (135 mg, 980 μmol, 2 eq) were dissolved in toluene (5 mL), water (0.5 mL) and THF (15 mL). The solution was vigorously stirred and heated at 80 °C overnight. The reaction was quenched with HCl solution (2M) and the organic phase was extracted with Chloroform and washed with water and brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under vacuum. The crude solid was chromatographed on silica gel using n-hexane/ethyl acetate (9/1) as eluent to afford the desired product as a dark pink solid (286 mg, 98%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ = 10.08 (s, 1H), 9.34 (d, 1H, J<sub>1</sub>=8.3Hz), 7.89 (ABQ, 4H, J<sub>1</sub>=8.4Hz, Δν<sub>AB</sub>= 73 Hz), 7.60 (d, 1H, J<sub>1</sub>=5.2Hz), 7.37 (dd, 1H, J<sub>1</sub>=8.2Hz, J<sub>2</sub>=1.8Hz), 7.08 (d, 1H, J<sub>1</sub>=1.8Hz), 6.76 (d, 1H, J<sub>1</sub>=5.2Hz), 3.79 (m, 2H), 3.67 (m, 2H), 1.94 (m, 2H), 1.85 (m, 2H), 1.41-1.29 (m, 16H), 0.89-0.95 (m, 12H). <sup>13</sup>C NMR (CDCl<sub>3</sub>,

100 MHz):  $\delta$  = 191.74, 170.81, 169.52, 153.24, 146.70, 144.92, 141.98, 136.82, 135.62, 130.35, 129.21, 127.64, 121.48, 121.37, 111.05, 106.78, 45.87, 44.29, 38.52, 37.76, 30.71, 30.65, 28.72, 24.18, 24.02, 23.09, 23.05, 14.09, 10.83, 10.68. Anal. calcd for C<sub>36</sub>H<sub>44</sub>N<sub>2</sub>O<sub>3</sub>S: C, 74.46; H, 7.43; N, 4.69; O, 8.04; S, 5.37. Found: C, 71.99; H, 7.38; N, 4.12; S, 4.87.

2) Under argon, (Z)-4-(1-(2-ethylhexyl)-3-(4-(2-ethylhexyl)-5-oxo-4,5-dihydro-6H-thieno[3,2-b]pyrrol-6-ylidene)-2-oxoindolin-6-yl)benzaldehyde (150 mg, 251.3  $\mu$ mol, 1 eq) was solubilized in chloroform (20 ml) at 0°C. N-bromosuccinimide (49.2 mg, 276.5  $\mu$ mol, 1.1 eq) was added in three portions over 15 min. The reaction mixture was allowed to stir overnight at ambient temperature. The mixture was extracted with chloroform and washed with HCl 2M, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated by rotary evaporation. The crude product was purified via silica gel chromatography (1:1 dichloromethane/hexane) to provide (Z)-4-(3-(2-bromo-4-(2-ethylhexyl)-5-oxo-4,5-dihydro-6H-thieno[3,2-b]pyrrol-6-ylidene)-1-(2-ethylhexyl)-2-oxoindolin-6-yl)benzaldehyde (**1-Altiso**) as a purple solid (317 mg, 98%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 10.08 (s, 1H), 9.27 (d, 1H, J<sub>1</sub>=8.3Hz), 7.88 (ABQ, 4H, J<sub>1</sub>=8.4Hz,  $\Delta$ vAB= 73 Hz), 7.35 (dd, 1H, J<sub>1</sub>=8.2Hz, J<sub>2</sub>=1.8Hz), 7.06 (d, 1H, J<sub>1</sub>=1.8Hz), 6.79 (s, 1H), 3.77 (m, 2H), 3.62 (m, 2H), 1.91 (m, 2H), 1.80 (m, 2H), 1.46-1.25 (m, 16H), 0.89-0.95 (m, 12H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 191.68, 169.89, 169.56, 151.79, 146.57, 144.89, 142.10, 135.67, 130.35, 130.07, 129.50, 129.18, 129.07, 127.59, 126.15, 121.67, 121.47, 121.38, 115.27, 114.54, 106.89, 45.89, 44.37, 38.53, 37.78, 30.73, 30.60, 28.74, 28.67, 24.18, 23.98, 23.08, 14.08, 10.80, 10.64. Anal. calcd for C<sub>37</sub>H<sub>43</sub>BrN<sub>2</sub>O<sub>3</sub>S: C, 65.77; H, 6.41; N, 4.15; O, 7.10; S, 4.75; Br, 11.82. Found: C, 64.91; H, 6.28; N, 3.95; S, 4.58.

### Synthesis of aldehyde derivatives

#### Synthesis of (E)-4-(6'-(5-(4-(diphenylamino)phenyl)-4-octylthiophen-2-yl)-1,1'-bis(2-ethylhexyl)-2,2'-dioxo-[3,3'-biindolinylidene]-6-yl)benzaldehyde (**3-Iso**):

Under argon, 4-(3-octylthiophen-2-yl)-N,N-diphenylaniline (200 mg, 909.8  $\mu$ mol) was dissolved in distilled THF (10 mL) then n-BuLi (2.5M, 218  $\mu$ L, 545  $\mu$ mol) was added at -78°C. The solution was stirred for an hour at -60°C before adding Bu<sub>3</sub>SnCl (185  $\mu$ L, 682.3  $\mu$ mol) at -78°C. The solution was allowed to reach room temperature and stirred for 2 hours. The reaction was quenched with a saturated solution of ammonium chloride and the organic phase was extracted with diethyl ether, dried with Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The resulting oil was engaged without any further purification in a Stille coupling reaction with (E)-4-(6'-bromo-1,1'-bis(2-ethylhexyl)-2,2'-dioxo-[3,3'-biindolinylidene]-6-yl)benzaldehyde (200 mg, 298.6  $\mu$ mol), Pd<sub>2</sub>dba<sub>3</sub> (10.9 mg, 11.9  $\mu$ mol) and P(o-tolyl)<sub>3</sub> (7.27 mg, 23.9  $\mu$ mol) dissolved in anhydrous toluene (15 mL) and refluxed for 24 hours. The mixture was then poured into HCl (2 M). The organic phase was extracted with CHCl<sub>3</sub>, washed with HCl (2 M), dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The crude solid was purified by chromatography on silica gel using diethyl ether/*n*-hexane 3:7 as eluent to afford **3-Iso** as a dark solid. (263 mg, 255  $\mu$ mol, 86%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 10.08 (s, 1H), 9.22 (ABQ, 2H, J<sub>1</sub>=8.3Hz,  $\Delta$ vAB= 25.02 Hz), 7.89 (ABQ, 4H, J<sub>1</sub>=8.3Hz,  $\Delta$ vAB= 77.14 Hz), 7.35-7.27 (m, 9H), 7.16 (m, 4H), 7.10 (m, 2H), 7.08-7.04 (m, 2H), 7.00 (dd, 2H, J<sub>1</sub>=9Hz, J<sub>2</sub>=1.6Hz), 3.75 (m, 4H), 2.70 (m, 2H), 1.91 (m, 2H), 1.71-1.60 (m, 5H), 1.48-1.26 (m, 23H), 0.99-0.86 (m, 15H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 191.68, 168.66, 168.56, 147.47, 147.44, 146.48, 145.99, 145.66, 143.32, 142.86, 140.94, 139.77, 139.40, 138.39, 135.74, 133.27, 131.25, 130.49, 130.35, 130.09, 129.92, 129.78, 129.38, 128.98, 128.40, 127.85, 127.56, 127.13, 124.82, 123.33, 122.87, 122.13, 121.11, 120.68, 118.84, 106.60, 104.65, 44.26, 44.18, 37.81, 37.78, 31.91, 31.03, 30.88, 30.81, 29.57, 29.43, 29.28, 29.01, 28.94, 28.84, 24.34, 24.23, 23.10, 22.69, 14.13, 14.11, 10.86, 10.81. Anal. calcd for C<sub>69</sub>H<sub>77</sub>N<sub>3</sub>O<sub>3</sub>S: C, 80.58; H, 7.55; N, 4.09; O, 4.67; S, 3.12. Found: C, 80.31; H, 7.42; N, 4.01; S, 2.96.

**Synthesis of 2-cyano-3-(4-((E)-6'-(5-(4-(diphenylamino)phenyl)-4-octylthiophen-2-yl)-1,1'-bis(2-ethylhexyl)-2,2'-dioxo-[3,3'-biindolinylidene]-6-yl)phenyl)acrylic acid (3-Altiso):**

Under argon, (E)-4-(6'-(5-(4-(diphenylamino)phenyl)-4-octylthiophen-2-yl)-1,1'-bis(2-ethylhexyl)-2,2'-dioxo-[3,3'-biindolinylidene]-6-yl)benzaldehyde (175 mg, 170.16  $\mu\text{mol}$ ), cyanoacetic acid (144.74 mg, 1.70 mmol), were dissolved in a mixture of acetonitrile (6 mL) and chloroform (4 mL). A catalytic amount of piperidine was added and the solution was refluxed for 3 hours. Solvent was removed under reduced pressure and the solid dissolved in chloroform. The organic phase was washed with HCl solution (2 M), dried on  $\text{Na}_2\text{SO}_4$  and concentrated. The crude solid was purified by chromatography on silica gel using DCM, DCM/MeOH 98:2 and DCM/MeOH/Acetic acid 90:5:5 as eluent to afford **3-Altiso** as a black solid (185 mg, 169  $\mu\text{mol}$ , 98%).  $^1\text{H}$  NMR (THF d8, 400 MHz):  $\delta$  = 9.39 (dd, 2H,  $J_1=8.5\text{Hz}$ ,  $J_2=22.4\text{ Hz}$ ), 8.29 (s, 1H), 8.03 (ABQ, 4H,  $J_1=8.3\text{Hz}$ ,  $\Delta\nu_{\text{AB}}=101.95\text{ Hz}$ ), 7.45 (s, 1H), 7.45-7.35 (m, 3H), 7.31-7.26 (m, 5H), 7.21 (s, 1H), 7.14-7.02 (m, 9H), 3.78 (m, 4H), 2.70 (m, 2H), 1.97 (m, 2H), 1.51-1.25 (m, 30H), 1.01-0.86 (m, 15H).  $^{13}\text{C}$  NMR (THF d8, 100 MHz):  $\delta$  = 169.24, 169.16, 153.74, 148.60, 147.15, 146.95, 145.32, 143.44, 142.04, 140.59, 140.03, 139.03, 133.47, 132.76, 132.36, 131.99, 131.82, 131.46, 130.64, 130.25, 128.97, 128.27, 128.16, 125.72, 124.22, 123.72, 123.15, 121.85, 121.15, 119.05, 107.03, 105.07, 44.61, 44.50, 38.86, 38.71, 32.93, 31.94, 31.81, 31.66, 30.54, 30.46, 30.31, 29.86, 29.77, 29.61, 24.07, 23.62, 14.51, 11.17, 11.06.

HRMS (ESI):  $[\text{M}]^+ = 1094.5741$  (0 ppm) (calcd. for  $\text{C}_{72}\text{H}_{78}\text{N}_4\text{O}_4\text{S}$ : 1094.57383).

**Synthesis of (E)-4-(2'-(5-(4-(diphenylamino)phenyl)-4-octylthiophen-2-yl)-4'-(2-ethylbutyl)-4-(2-ethylhexyl)-5,5'-dioxo-4,4',5,5'-tetrahydro-[6,6'-bithieno[3,2-b]pyrrolylidene]-2-yl)benzaldehyde (3-Tiso):**

Under argon, 4-(3-octylthiophen-2-yl)-N,N-diphenylaniline (93 mg, 211.53  $\mu\text{mol}$ ) was dissolved in distilled THF (10 mL) then n-BuLi (1.5 M, 152  $\mu\text{L}$ , 243.26  $\mu\text{mol}$ ) was added at  $-78^\circ\text{C}$ . The solution was stirred for an hour at  $-60^\circ\text{C}$  before adding  $\text{Bu}_3\text{SnCl}$  (69.2  $\mu\text{L}$ , 317.3  $\mu\text{mol}$ ) at  $-78^\circ\text{C}$ . The solution was allowed to reach room temperature and stirred for 2 hours. The reaction was quenched with a saturated solution of ammonium chloride and the organic phase was extracted with diethyl ether, dried with  $\text{Na}_2\text{SO}_4$ , filtered and concentrated under reduced pressure. The resulting oil was engaged without any further purification in a Stille coupling reaction with (E)-4-(2'-bromo-4,4'-bis(2-ethylhexyl)-5,5'-dioxo-4,4',5,5'-tetrahydro-[6,6'-bithieno[3,2-b]pyrrolylidene]-2-yl)benzaldehyde (115 mg, 168.7  $\mu\text{mol}$ ),  $\text{Pd}_2\text{dba}_3$  (3.9 mg, 4.23  $\mu\text{mol}$ ) and  $\text{P}(\text{o-tolyl})_3$  (2.58 mg, 8.46  $\mu\text{mol}$ ) dissolved in anhydrous toluene (15 mL) and refluxed for 24 hours. The mixture was then poured into HCl (2 M). The organic phase was extracted with  $\text{CHCl}_3$ , washed with HCl (2 M), dried over  $\text{Na}_2\text{SO}_4$  and concentrated under reduced pressure. The crude solid was purified by chromatography on silica gel using diethyl ether/n-hexane 3:7 as eluent to afford **3-Tiso** as a greenish solid. (135 mg, 129.7  $\mu\text{mol}$ , 77%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  = 9.96 (s, 1H), 7.82 (q, 4H,  $J_1=8.3\text{Hz}$ ), 7.31-7.26 (m, 7H), 7.15 (m, 4H), 7.09-7.04 (m, 4H), 7.02 (s, 1H), 6.70 (s, 1H), 3.69-3.63 (m, 4H), 2.64 (t, 2H,  $J_1=7.3\text{Hz}$ ), 1.85 (m, 2H), 1.68-1.60 (m, 5H), 1.42-1.23 (m, 23H), 0.94-0.87 (m, 15H).  $^{13}\text{C}$  NMR

(CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 191.20, 171.12, 170.80, 152.66, 151.19, 148.94, 147.60, 147.48, 147.09, 140.09, 139.81, 139.33, 135.51, 134.82, 130.98, 130.48, 129.71, 129.50, 128.91, 127.84, 127.50, 125.68, 124.99, 123.51, 122.80, 120.87, 118.36, 116.62, 113.54, 108.54, 106.96, 45.96, 45.90, 38.64, 32.02, 30.98, 30.66, 29.69, 29.54, 29.38, 29.11, 28.76, 28.71, 27.96, 26.96, 24.04, 23.19, 22.80, 17.64, 14.25, 14.19, 13.72, 10.79. Anal. calcd for C<sub>65</sub>H<sub>73</sub>N<sub>3</sub>O<sub>3</sub>S<sub>3</sub>: C, 75.03; H, 7.07; N, 4.04; O, 4.61; S, 9.24. Found: C, 71.85; H, 7.06; N, 3.58; S, 8.25.

**Synthesis of 4-(6'-(6-(diphenylamino)-4,4-bis(4-hexylphenyl)-4H-indeno[1,2-b]thiophen-2-yl)-1,1'-bis(2-ethylhexyl)-2,2'-dioxo-[3,3'-biindolinylidene]-6-yl)benzaldehyde (2-Iso):**

Under argon, 4,4-dioctyl,N-N'-diphenyl-4H-indeno[1,2-b]thiophen-6-amine (308 mg, 467  $\mu$ mol) was dissolved in distilled THF (20 mL) then n-BuLi (1.5M, 383  $\mu$ L, 537  $\mu$ mol, 1.15 eq) was added at -78 °C. The solution was stirred for an hour at -60 °C before adding trimethyltin chloride solution (1M, 700  $\mu$ L, 700  $\mu$ mol, 1.5 eq) at -78 °C. The solution was allowed to reach room temperature and stirred for 2 hours. The reaction was quenched with a saturated solution of ammonium chloride and the organic phase was extracted with pentane, washed with water and dried on Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under vacuum. The resulting oil was engaged without any further purification in a Stille coupling with (Z)-4-(3-(2-bromo-4-(2-ethylhexyl)-5-oxo-4,5-dihydro-6H-thieno[3,2-b]pyrrol-6-ylidene)-1-(2-ethylhexyl)-2-oxoindolin-6-yl)benzaldehyde (250 mg, 373  $\mu$ mol, 0.8 eq), Pd<sub>2</sub>dba<sub>3</sub> (8.55 mg, 9.33  $\mu$ mol, 0.02 eq) and P(o-tolyl)<sub>3</sub> (5.68 mg, 18.66  $\mu$ mol, 0.04 eq) in anhydrous toluene (20 ml) and refluxed overnight. The mixture was then poured into HCl (2M). The organic phase was extracted with chloroform, washed with water, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. The crude solid was chromatographed on silica using Diethyl ether/n-hexane: 3/7 as eluent to afford **2-Iso** as a brown solid (366 mg, 78.6%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 10.08 (s, 1H), 9.21 (ABQ, 2H, J<sub>1</sub>=8.3Hz,  $\Delta$ vAB=26.83 Hz), 7.89 (ABQ, 4H, J<sub>1</sub>=8.3Hz,  $\Delta$ vAB=76.74 Hz), 7.33-7.27 (m, 4H), 7.23-7.18 (m, 5H), 7.11-6.95 (m, 17H), 3.75 (m, 4H), 2.56 (m, 4H), 1.90 (m, 2H), 1.58 (m, 2H), 1.45-1.29 (m, 22H), 0.98-0.86 (m, 18H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 191.70, 168.72, 168.59, 156.17, 155.15, 147.54, 146.54, 146.40, 146.00, 145.85, 145.67, 142.88, 142.13, 141.55, 141.50, 139.03, 135.73, 133.18, 131.32, 131.14, 130.48, 130.35, 130.02, 129.18, 128.303, 127.79, 127.59, 124.24, 122.92, 122.88, 122.17, 122.03, 121.14, 120.72, 120.62, 120.07, 118.71, 106.63, 104.39, 63.33, 44.26, 44.14, 37.79, 35.56, 31.75, 31.40, 30.89, 30.80, 30.35, 29.14, 28.90, 28.82, 24.31, 24.22, 23.09, 22.62, 14.10, 10.87, 10.80. Anal. calcd for C<sub>86</sub>H<sub>93</sub>N<sub>3</sub>O<sub>3</sub>S: C, 82.72; H, 7.51; N, 3.36; O, 3.84; S, 2.57. Found: C, 82.70; H, 7.54; N, 3.35; S, 2.42.

**Synthesis of 4-(3-(2-(6-(diphenylamino)-4,4-bis(4-hexylphenyl)-4H-indeno[1,2-b]thiophen-2-yl)-4-(2-ethylhexyl)-5-oxo-4,5-dihydro-6H-thieno[3,2-b]pyrrol-6-ylidene)-1-(2-ethylhexyl)-2-oxoindolin-6-yl)benzaldehyde (2-Altiso):**

Under argon, 4,4-dioctyl,N-N'-diphenyl-4H-indeno[1,2-b]thiophen-6-amine (200 mg, 303  $\mu$ mol) was dissolved in distilled THF (10 mL) then n-BuLi (2.5M, 151  $\mu$ L, 364  $\mu$ mol, 1.2eq) was added at -78 °C. The solution was stirred for an hour at -60 °C before adding tributyltin chloride (123  $\mu$ L, 455  $\mu$ mol, 1.5 eq) at -78 °C. The solution was allowed to reach room temperature and stirred for 2 hours. The reaction was quenched with a saturated solution of ammonium chloride and the organic phase was extracted with pentane, washed with water and dried on Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under vacuum. The resulting oil was engaged without any further purification in a Stille coupling with (Z)-4-(3-(2-bromo-4-(2-ethylhexyl)-5-oxo-4,5-dihydro-6H-thieno[3,2-b]pyrrol-6-ylidene)-1-(2-ethylhexyl)-2-oxoindolin-6-yl)benzaldehyde (150 mg, 222  $\mu$ mol, 1 eq) and Pd(Ph<sub>3</sub>)<sub>4</sub> (11.45 mg, 11  $\mu$ mol, 5% mol). The products were dissolved in anhydrous toluene (20mL) and refluxed overnight. The mixture was then poured into HCl (2M). The organic phase was extracted with chloroform, washed with

water, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. The crude solid was chromatographed on silica using DCM/n-hexane : 3/7 and then 1/1 as eluent to afford **2-Altiso** as a dark solid (145 mg, 52%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ = 10.08 (s, 1H), 9.28 (d, 1H, J<sub>1</sub>=8.3Hz), 7.89 (ABQ, 4H, J<sub>1</sub>=8.4Hz, Δv<sub>AB</sub>= 73 Hz), 7.39 (s, 1H), 7.37 (dd, 1H, J<sub>1</sub>=8.2Hz, J<sub>2</sub>=1.8Hz), 7.28 (d, 1H, J<sub>1</sub>=8.2Hz), 7.24 (s, 1H), 7.21 (m, 2H), 7.20 (m, 2H), 7.09-7.01 (m, 15H), 6.95 (dd, 1H, J<sub>1</sub>=8.2Hz, J<sub>2</sub>=1.8Hz), 6.76 (s, 1H), 3.79 (m, 2H), 3.67 (d, 2H, J<sub>1</sub>=7.7Hz), 2.56 (t, 4H, J<sub>1</sub>=7.7Hz), 1.94 (m, 1H), 1.87 (m, 1H), 1.59(m, 4H), 1.48-1.26 (m, 28H), 0.89-0.95 (m, 18H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ = 191.76, 170.79, 169.78, 156.31, 155.28, 153.91, 149.33, 147.47, 146.84, 146.68, 144.38, 142.61, 141.55, 141.34, 141.21, 138.93, 135.53, 130.92, 130.36, 129.40, 129.22, 128.61, 128.35, 127.77, 127.58, 124.36, 123.06, 122.74, 121.88, 121.84, 121.67, 121.32, 120.17, 119.66, 106.73, 106.11, 63.23, 45.84, 44.36, 38.51, 37.82, 35.57, 31.76, 31.41, 30.77, 30.57, 29.11, 28.81, 28.63, 27.87, 26.87, 24.22, 23.98, 23.10, 22.63, 17.55, 14.12, 13.62, 10.93, 10.67. Anal. calcd for C<sub>84</sub>H<sub>91</sub>N<sub>3</sub>O<sub>3</sub>S<sub>2</sub>: C, 80.41; H, 7.31; N, 3.35; O, 3.83; S, 5.11. Found: C, 79.19; H, 7.37; N, 3.12; S, 4.71.

**Synthesis of 4-(2'-(6-(diphenylamino)-4,4-bis(4-hexylphenyl)-4H-indeno[1,2-b]thiophen-2-yl)-4,4'-bis(2-ethylhexyl)-5,5'-dioxo-4,4',5,5'-tetrahydro-[6,6'-bithieno[3,2-b]pyrrolylidene]-2-yl)benzaldehyde (2-Tiso):**

Under argon, 4,4-dioctyl,N-N'-diphenyl-4H-indeno[1,2-b]thiophen-6-amine (151 mg, 228.8 μmol) was dissolved in distilled THF (10 mL) then n-BuLi (1.5 M, 241 μL, 263.12 μmol) was added at -78°C. The solution was stirred for an hour at -60°C before adding Bu<sub>3</sub>SnCl (74 μL, 343.19 μmol) at -78°C. The solution was allowed to reach room temperature and stirred for 2 hours. The reaction was quenched with a saturated solution of ammonium chloride and the organic phase was extracted with diethyl ether, dried with Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The resulting oil was engaged without any further purification in a Stille coupling reaction with (E)-4-(2'-bromo-4,4'-bis(2-ethylhexyl)-5,5'-dioxo-4,4',5,5'-tetrahydro-[6,6'-bithieno[3,2-b]pyrrolylidene]-2-yl)benzaldehyde (125 mg, 183.04 μmol), Pd<sub>2</sub>dba<sub>3</sub> (4.2 mg, 4.58 μmol) and P(o-tolyl)<sub>3</sub> (2.8 mg, 9.15 μmol) dissolved in anhydrous toluene (15 mL) and refluxed for 24 hours. The mixture was then poured into HCl (2 M). The organic phase was extracted with CHCl<sub>3</sub>, washed with HCl (2 M), dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The crude solid was purified by chromatography on silica gel using DCM/n-hexane 2:8 as eluent to afford **2-Tiso** as a greenish solid. (157 mg, 124.5 μmol, 68%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz): δ = 9.99 (s, 1H), 7.86 (m, 4H), 7.36 (s, 1H), 7.33 (d, 1H, J<sub>1</sub>=8.2Hz), 7.25 (m, 1H), 7.16 (d, 1H, J<sub>1</sub>=2Hz), 7.13 (s, 1H), 7.11-7.02 (m, 14H), 6.98 (dd, 1H, J<sub>1</sub>=8.2Hz, J<sub>2</sub>=2Hz), 6.85 (s, 1H), 3.71-3.66 (m, 4H), 2.58 (t, 4H, J=7.6Hz), 1.86 (m, 2H), 1.60 (m, 4H), 1.45-1.29 (m, 22H), 0.97-0.87 (m, 18H). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 100 MHz): δ = 191.43, 171.41, 171.10, 156.56, 155.52, 153.17, 151.91, 149.33, 147.91, 147.52, 147.12, 142.50, 142.23, 141.79, 140.32, 139.88, 136.07, 131.25, 130.70, 129.65, 128.79, 128.09, 126.05, 124.81, 123.55, 123.06, 122.07, 121.29, 120.92, 120.59, 118.63, 116.70, 113.78, 109.18, 107.19, 63.65, 46.20, 39.06, 39.01, 35.88, 32.16, 31.90, 31.02, 30.95, 29.50, 29.12, 29.04, 24.39, 23.51, 23.04, 14.28, 10.85. Anal. calcd for C<sub>82</sub>H<sub>89</sub>N<sub>3</sub>O<sub>3</sub>S<sub>3</sub>: C, 78.12; H, 7.12; N, 3.33; O, 3.81; S, 7.63. Found: C, 77.05; H, 6.97; N, 3.25; S, 7.65.

**Synthesis of the dyes**

**Synthesis of (Z)-4-(3-(2-(5-(4-(diphenylamino)phenyl)-4-octylthiophen-2-yl)-4-(2-ethylhexyl)-5-oxo-4,5-dihydro-6H-thieno[3,2-b]pyrrol-6-ylidene)-1-(2-ethylhexyl)-2-oxoindolin-6-yl)benzaldehyde (TPAT8-Iso):**

Under argon, (E)-4-(6'-(5-(4-(diphenylamino)phenyl)-4-octylthiophen-2-yl)-1,1'-bis(2-ethylhexyl)-2,2'-dioxo-[3,3'-biindolinylidene]-6-yl)benzaldehyde (175 mg, 170.16 μmol),

cianoacetic acid (144.74 mg, 1.70 mmol), were dissolved in a mixture of acetonitrile (6 mL) and chloroform (4 mL). A catalytic amount of piperidine was added and the solution was refluxed for 3 hours. Solvent was removed under reduced pressure and the solid dissolved in chloroform. The organic phase was washed with HCl solution (2 M), dried on Na<sub>2</sub>SO<sub>4</sub> and concentrated. The crude solid was purified by chromatography on silica gel using DCM, DCM/MeOH 98:2 and DCM/MeOH/Acetic acid 90:5:5 as eluent to afford **TPAT8-Iso** as a black solid (185 mg, 169 μmol, 98%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ = 9.39 (dd, 2H, J<sub>1</sub>=8.5Hz, J<sub>2</sub>= 22.4 Hz), 8.29 (s, 1H), 8.03 (ABQ, 4H, J<sub>1</sub>=8.3Hz, ΔvAB= 101.95 Hz), 7.45 (s, 1H), 7.45-7.35 (m, 3H), 7.31-7.26 (m, 5H), 7.21 (s, 1H), 7.14-7.02 (m, 9H), 3.78 (m, 4H), 2.70 (m, 2H), 1.97 (m, 2H), 1.51-1.25 (m, 30H), 1.01-0.86 (m, 15H). <sup>13</sup>C NMR (THF d8, 100 MHz): δ = 169.24, 169.16, 153.74, 148.60, 147.15, 146.95, 145.32, 143.44, 142.04, 140.59, 140.03, 139.03, 133.47, 132.76, 132.36, 131.99, 131.82, 131.46, 130.64, 130.25, 128.97, 128.27, 128.16, 125.72, 124.22, 123.72, 123.15, 121.85, 121.15, 119.05, 107.03, 105.07, 44.61, 44.50, 38.86, 38.71, 32.93, 31.94, 31.81, 31.66, 30.54, 30.46, 30.31, 29.86, 29.77, 29.61, 24.07, 23.62, 14.51, 11.17, 11.06.

**Synthesis of (E)-2-cyano-3-(4-((Z)-3-(2-(5-(4-(diphenylamino)phenyl)-4-octylthiophen-2-yl)-4-(2-ethylhexyl)-5-oxo-4,5-dihydro-6H-thieno[3,2-b]pyrrol-6-ylidene)-1-(2-ethylhexyl)-2-oxoindolin-6-yl)phenyl)acrylic acid (TPAT8-Altiso):**

Under argon, (Z)-4-(3-(2-(5-(4-(diphenylamino)phenyl)-4-octylthiophen-2-yl)-4-(2-ethylhexyl)-5-oxo-4,5-dihydro-6H-thieno[3,2-b]pyrrol-6-ylidene)-1-(2-ethylhexyl)-2-oxoindolin-6-yl)benzaldehyde (230 mg, 222.3 μmol), cyanoacetic acid (94.6 mg, 1.11 mmol), were dissolved in a mixture of acetonitrile (6 mL) and chloroform (4 mL). A catalytic amount of piperidine was added and the solution was refluxed for 3 hours. Solvent was removed under reduced pressure and the solid dissolved in chloroform. The organic phase was washed with HCl solution (2 M), dried on Na<sub>2</sub>SO<sub>4</sub> and concentrated. The crude solid was purified by chromatography on silica gel using DCM, DCM/MeOH 98:2 and DCM/MeOH/Acetic acid 90:5:5 as eluent to afford TPAT8-Altiso as a greenish solid (204 mg, 185 μmol, 84%). <sup>1</sup>H NMR (THF-d, 400 MHz): δ = 9,31 (d, 1H, J<sub>1</sub>=8.3Hz), 8.29 (s, 1H), 8.03 (ABQ, 4H, J<sub>1</sub>=8.3Hz, ΔvAB=101.03 Hz), 7.44 (m, 2H), 7.36 (m, 2H), 7.30-7.26 (m, 5H), 7.13-7.02 (m, 8H), 7.00 (s, 1H), 3.84 (m, 2H), 3.72 (m, 2H), 2.71 (t, 2H, J<sub>1</sub>=7.3Hz), 2.02 (m, 1H), 1.93 (m, 1H), 1.50-1.26 (m, 28H), 0.99-0.87 (m, 15H). <sup>13</sup>C NMR (THF-d, 100 MHz): δ= 171.02, 169.92, 163.65, 154.79, 153.62, 148.95, 148.48, 148.28, 145.58, 145.54, 141.69, 140.46, 139.98, 135.60, 132.14, 130.28, 130.02, 129.73, 129.41, 128.68, 128.24, 128.02, 125.59, 124.08, 123.28, 122.54, 121.12, 120.32, 116.21, 114.56, 107.34, 106.93, 104.33, 46.01, 44.49, 39.30, 38.53, 32.68, 31.58, 31.40, 31.27, 30.53, 30.44, 30.30, 30.18, 30.04, 29.59, 29.33, 29.30, 23.85, 23.79, 23.36, 14.25, 10.85, 10.74. HRMS (ESI): [M]<sup>+</sup>= 1100.5306 (0 ppm) (calcd. for C<sub>70</sub>H<sub>76</sub>N<sub>4</sub>O<sub>4</sub>S<sub>2</sub>: 1100.53025).

**Synthesis of (E)-2-cyano-3-(4-((E)-2'-(5-(4-(diphenylamino)phenyl)-4-octylthiophen-2-yl)-4,4'-bis(2-ethylhexyl)-5,5'-dioxo-4,4',5,5'-tetrahydro-[6,6'-bithieno[3,2-b]pyrrolylidene]-2-yl)phenyl)acrylic acid (TPAT8-Tiso):**

Under argon, (E)-4-(2'-(5-(4-(diphenylamino)phenyl)-4-octylthiophen-2-yl)-4'-(2-ethylbutyl)-4-(2-ethylhexyl)-5,5'-dioxo-4,4',5,5'-tetrahydro-[6,6'-bithieno[3,2-b]pyrrolylidene]-2-yl)benzaldehyde (120 mg, 115.3 μmol), cyanoacetic acid (98 mg, 1.15 mmol), were dissolved in a mixture of acetonitrile (6 mL) and chloroform (4 mL). A catalytic amount of piperidine was added and the solution was refluxed for 3 hours. Solvent was removed under reduced pressure and the solid dissolved in chloroform. The organic phase was washed with HCl

solution (2 M), dried on Na<sub>2</sub>SO<sub>4</sub> and concentrated. The crude solid was purified by chromatography on silica gel using DCM, DCM/MeOH 98:2 and DCM/MeOH/Acetic acid 90:5:5 as eluent to **TPAT8-Tiso** as a greenish solid (113 mg, 102 μmol, 84%). <sup>1</sup>H NMR (THF-d, 400 MHz): δ = 8.20 (s, 1H), 8.07 (m, 2H), 7.96-7.86 (m, 2H), 7.40-7.25 (m, 8H), 7.13-7.03 (m, 8H), 3.75 (m, 4H), 2.70 (t, 2H, J<sub>1</sub>=7.3Hz), 1.92 (m, 2H), 1.69 (m, 5H), 1.41-1.26 (m, 23H), 0.99-0.89 (m, 15H). <sup>13</sup>C NMR (THF-d, 100 MHz): δ = 153.98, 153.12, 152.77, 150.72, 148.95, 148.90, 148.81, 147.63, 140.88, 140.82, 140.06, 139.66, 136.36, 132.49, 130.74, 130.37, 128.89, 128.66, 126.68, 126.00, 124.45, 123.80, 121.44, 121.36, 119.58, 119.47, 117.56, 117.53, 116.94, 114.85, 109.71, 108.11, 46.70, 46.62, 39.92, 39.84, 33.00, 31.86, 30.60, 30.50, 30.34, 29.97, 29.76, 29.11, 28.98, 28.86, 27.87, 24.11, 23.67, 18.41, 14.53, 14.49, 14.02, 11.14. HRMS (ESI): [M]<sup>+</sup> = 1106.4863 (0 ppm) (calcd. for C<sub>68</sub>H<sub>74</sub>N<sub>4</sub>O<sub>4</sub>S<sub>3</sub>: 1106.48667).

**Synthesis of 2-cyano-3-(4-((E)-6'-(6-(diphenylamino)-4,4-bis(4-hexylphenyl)-4H-indeno[1,2-b]thiophen-2-yl)-1,1'-bis(2-ethylhexyl)-2,2'-dioxo-[3,3'-biindolinylidene]-6-yl)phenyl)acrylic acid (TPAF-Iso):**

Under argon, 4-(7-(6-(diphenylamino)-4,4-bis(4-hexylphenyl)-4H-indeno[1,2-b]thiophen-2-yl)benzo[c][1,2,5]thiadiazol-4-yl)benzaldehyde (230 mg, 184 μmol, 1 eq), cyanoacetic acid (157 mg, 1.84 mmol, 5eq), were dissolved in a mixture of acetonitrile (12 mL) and chloroform (8 mL). A catalytic amount of piperidine was added and the solution was refluxed for 3 hours. Solvent was removed under reduced pressure and the solid dissolved in chloroform. The organic phase was washed with HCl solution (2M), dried on Na<sub>2</sub>SO<sub>4</sub> and concentrated. The crude solid was chromatographed on silica using DCM first then DCM/MeOH : 90/5 and then DCM/MeOH/Acetic acid : 90/5/5 as eluent to afford the corresponding dye **TPAF-Iso** as a dark black solid (162.5 mg, 67 %). <sup>1</sup>H NMR (THF d8, 400 MHz): 8.03 (dd, 2H, J<sub>1</sub>=8.4Hz, J<sub>2</sub>=11.3Hz), 8.30 (s, 1H), 8.03 (ABQ, 4H, J<sub>1</sub>=8.4Hz, Δν<sub>AB</sub>= 50.8 Hz), 7.59 (s, 1H), 7.40-7.30 (m, 3H), 7.20-6.95 (m, 21H), 3.80 (m, 4H), 2.55 (m, 4H), 1.62-1.29 (m, 34H), 0.98-0.86 (m, 18H). <sup>13</sup>C NMR (THF d8, 100 MHz): δ = 169.49, 157.80, 156.46, 153.59, 148.91, 147.71, 147.24, 147.20, 145.49, 143.73, 142.95, 142.40, 139.90, 132.50, 131.95, 131.61, 130.25, 129.28, 128.98, 128.49, 124.01, 123.35, 123.30, 122.13, 121.38, 121.19, 119.22, 107.26, 105.12, 44.81, 44.67, 44.63, 39.04, 38.92, 36.64, 32.97, 32.81, 32.01, 31.84, 30.34, 29.93, 29.79, 24.26, 23.75, 14.68, 11.37, 11.25. HRMS (ESI): [M]<sup>+</sup> = 1314.6986 (0 ppm) (calcd. for C<sub>89</sub>H<sub>94</sub>N<sub>4</sub>O<sub>4</sub>S: 1314.69903).

**Synthesis of (E)-2-cyano-3-(4-((Z)-3-(2-(6-(diphenylamino)-4,4-bis(4-hexylphenyl)-4H-indeno[1,2-b]thiophen-2-yl)-4-(2-ethylhexyl)-5-oxo-4,5-dihydro-6H-thieno[3,2-b]pyrrol-6-ylidene)-1-(2-ethylhexyl)-2-oxoindolin-6-yl)phenyl)acrylic acid (TPAF-Altiso):**

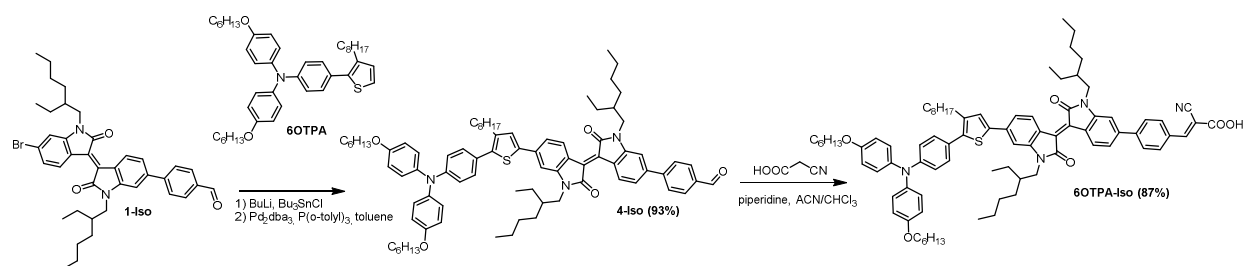
Under argon, (Z)-4-(3-(2-(6-(diphenylamino)-4,4-bis(4-hexylphenyl)-4H-indeno[1,2-b]thiophen-2-yl)-4-(2-ethylhexyl)-5-oxo-4,5-dihydro-6H-thieno[3,2-b]pyrrol-6-ylidene)-1-(2-ethylhexyl)-2-oxoindolin-6-yl)benzaldehyde (138 mg, 109.98 μmol), cyanoacetic acid (46.77 mg, 1mmol, 5eq), were dissolved in a mixture of acetonitrile (6mL) and chloroform (4mL). A catalytic amount of piperidine was added and the solution was refluxed for 3 hours. Solvent was removed under reduced pressure and the solid redissolved in chloroform. The organic phase was washed with HCl solution (2M), dried on Na<sub>2</sub>SO<sub>4</sub> and concentrated. The crude solid was chromatographed on silica using DCM, DCM/MeOH 98:2 and then DCM/MeOH/Acetic acid 90:5:5 as eluent to afford the corresponding dye **TPAF-Altiso** as a green solid (70 mg, 48%). <sup>1</sup>H NMR (THF-d8, 400 MHz): δ = 9.31 (d, 1H, J<sub>1</sub>=8.3Hz), 8.29 (s, 1H), 8.14 (m, 2H), 7.89 (m, 2H), 7.53 (s, 1H), 7.43 (d, 1H, J<sub>1</sub>=8.3Hz), 7.35 (d, 1H, J<sub>1</sub>=8.3Hz), 7.27 (s, 1H), 7.22-7.18 (m, 4H), 7.16 (m, 1H), 7.13-7.10 (m, 4H), 7.06-7.04 (m, 9H), 6.99-6.93 (m, 3H), 3.83 (m, 2H), 3.72 (d, 2H, J<sub>1</sub>=7.7Hz), 2.56 (t, 4H, J<sub>1</sub>=7.7Hz), 2.01 (m, 1H), 1.94 (m, 1H), 1.59(m, 4H), 1.48-1.29

(m, 28H), 0.98-0.86 (m, 18H).  $^{13}\text{C}$  NMR (THF-d<sub>8</sub>, 100 MHz):  $\delta$  = 168.41, 167.30, 154.72, 153.48, 152.14, 146.95, 145.74, 144.82, 142.89, 140.17, 139.68, 139.37, 138.98, 137.63, 129.55, 129.46, 129.14, 127.18, 126.95, 126.68, 126.24, 125.91, 125.36, 122.30, 121.01, 120.92, 120.08, 119.92, 119.43, 118.45, 118.19, 117.42, 111.94, 104.41, 104.26, 61.47, 43.43, 41.89, 36.59, 35.90, 33.56, 29.88, 29.73, 28.77, 28.61, 27.80, 27.25, 26.70, 26.65, 21.89, 21.21, 21.17, 20.66, 11.61, 8.23, 8.10. HRMS (ESI):  $[\text{M}]^{+} = 1320.6554$  (0 ppm) (calcd. for  $\text{C}_{87}\text{H}_{92}\text{N}_4\text{O}_4\text{S}_2$ : 1320.65545).

### Synthesis of (E)-2-cyano-3-(4-((E)-2'-(6-(diphenylamino)-4,4-bis(4-hexylphenyl)-4H-indeno[1,2-b]thiophen-2-yl)-4,4'-bis(2-ethylhexyl)-5,5'-dioxo-4,4',5,5'-tetrahydro-[6,6'-bithieno[3,2-b]pyrrolylidene]-2-yl)phenyl)acrylic acid (TPAF-Tiso):

Under argon, (E)-4-(2'-(6-(diphenylamino)-4,4-bis(4-hexylphenyl)-4H-indeno[1,2-b]thiophen-2-yl)-4,4'-bis(2-ethylhexyl)-5,5'-dioxo-4,4',5,5'-tetrahydro-[6,6'-bithieno[3,2-b]pyrrolylidene]-2-yl)benzaldehyde (150 mg, 119  $\mu\text{mol}$ ), cyanoacetic acid (101 mg, 1.19 mmol), were dissolved in a mixture of acetonitrile (6mL) and chloroform (4mL). A catalytic amount of piperidine was added and the solution was refluxed for 3 hours. Solvent was removed under reduced pressure and the solid redissolved in chloroform. The organic phase was washed with HCl solution (2M), dried on  $\text{Na}_2\text{SO}_4$  and concentrated. The crude solid was chromatographed on silica using DCM, DCM/MeOH 98:2 and then DCM/MeOH/Acetic acid 90:5:5 as eluent to afford the corresponding dye **TPAF-Tiso** as a green solid (118 mg, 75 %).  $^1\text{H}$  NMR (THF-d<sub>8</sub>, 400 MHz):  $\delta$  = 8.17 (s, 1H), 7.94 (m, 2H), 7.69 (m, 2H), 7.43 (s, 1H), 7.28 (m, 1H), 7.20 (m, 5H), 7.14 (m, 5H), 7.06 (m, 8H), 6.99-6.92 (m, 4H), 3.71 (m, 4H), 2.58 (t, 4H,  $J=7.6\text{Hz}$ ), 1.94 (m, 2H), 1.60 (m, 4H), 1.40-1.31 (m, 22H), 0.97-0.87 (m, 18H).  $^{13}\text{C}$  NMR (THF-d<sub>8</sub>, 100 MHz):  $\delta$  = 168.65, 168.42, 154.49, 153.25, 150.88, 149.83, 147.22, 145.78, 144.74, 139.79, 139.39, 138.04, 136.68, 129.61, 129.43, 129.19, 127.17, 126.25, 125.97, 123.31, 122.31, 120.94, 120.19, 118.86, 118.10, 115.96, 114.54, 111.71, 106.57, 104.62, 61.41, 43.68, 43.48, 36.71, 36.65, 33.56, 29.88, 29.75, 28.71, 28.64, 27.24, 26.75, 26.69, 21.92, 21.89, 21.19, 20.66, 11.64, 11.62, 8.10. HRMS (ESI):  $[\text{M}]^{+} = 1326.6125$  (0 ppm) (calcd. for  $\text{C}_{85}\text{H}_{90}\text{N}_4\text{O}_4\text{S}_3$ : 1326.61187).

### Synthesis of 6OTPA-Iso



**Figure S5- Synthetic route for 6OTPA-Iso**

4-(hexyloxy)-N-(4-(hexyloxy)phenyl)-N-(4-(3-octylthiophen-2-yl)phenyl)aniline was synthesized according to the literature (D. Joly, L. Pellejà, S. Narbey, F. Oswald, T. Meyer, Y. Kervella, P. Maldivi, J. N. Clifford, E. Palomares and R. Demadrille, *Energy Environ. Sci.*, 2015, **8**, 2010–2018.)



**Synthesis of (E)-4-(6'-(5-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)-4-octylthiophen-2-yl)-1,1'-bis(2-ethylhexyl)-2,2'-dioxo-[3,3'-biindolinylidene]-6-yl)benzaldehyde (4-Iso):**

Under argon, 4-(hexyloxy)-N-(4-(hexyloxy)phenyl)-N-(4-(3-octylthiophen-2-yl)phenyl)aniline (300 mg, 468.76  $\mu\text{mol}$ ) was dissolved in distilled THF (10 mL) then n-BuLi (1.6M, 352  $\mu\text{L}$ , 563  $\mu\text{mol}$ ) was added at  $-78^\circ\text{C}$ . The solution was stirred for an hour at  $-78^\circ\text{C}$  before adding  $\text{Bu}_3\text{SnCl}$  (191  $\mu\text{L}$ , 703  $\mu\text{mol}$ ) at  $-78^\circ\text{C}$ . The solution was allowed to reach room temperature and stirred for 2 hours. The reaction was quenched with a saturated solution of ammonium chloride and the organic phase was extracted with diethyl ether, dried with  $\text{Na}_2\text{SO}_4$ , filtered and concentrated under reduced pressure. The resulting oil was engaged without any further purification in a Stille coupling reaction with (E)-4-(6'-bromo-1,1'-bis(2-ethylhexyl)-2,2'-dioxo-[3,3'-biindolinylidene]-6-yl)benzaldehyde (200 mg, 298.6  $\mu\text{mol}$ ),  $\text{Pd}(\text{dba})_3$  (10.9 mg, 11.9  $\mu\text{mol}$ ) and  $\text{P}(\text{o-tolyl})_3$  (7.27 mg, 23.9  $\mu\text{mol}$ ) dissolved in anhydrous toluene (15 mL) and refluxed for 24 hours. The mixture was then poured into HCl (2 M). The organic phase was extracted with  $\text{CHCl}_3$ , washed with HCl (2 M), dried over  $\text{Na}_2\text{SO}_4$  and concentrated under reduced pressure. The crude solid was purified by chromatography on silica gel using diethyl ether/n-hexane 3:7 as eluent to afford the desired product as a black solid. (340 mg, 298.54 mmol, 93%).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  = 10.08 (s, 1H), 9.24 (d, 1H,  $J_1=8.4\text{Hz}$ ), 9.17 (d, 1H,  $J_1=8.4\text{Hz}$ ), 7.99 (m, 2H), 7.79 (m, 2H), 7.32 (dd, 1H,  $J_1=8.4\text{Hz}$ ,  $J_2=1.7\text{Hz}$ ), 7.29 (s, 1H), 7.28 (dd, 1H,  $J_1=8.4\text{Hz}$ ,  $J_2=1.7\text{Hz}$ ), 7.27 (m, 1H), 7.25 (m, 1H), 7.10 (m, 4H), 7.0 (d, 1H,  $J_1=1.6\text{Hz}$ ), 6.97 (d, 1H,  $J_1=1.6\text{Hz}$ ), 6.94 (m, 2H), 6.85 (m, 2H), 3.95 (t, 4H,  $J_1=6.5\text{Hz}$ ), 1.90 (m, 2H), 1.79 (m, 4H), 1.66 (m, 2H), 1.49-1.26 (m, 44H), 0.99-0.86 (m, 21H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  = 191.66, 168.68, 168.56, 155.77, 148.42, 146.50, 145.98, 145.62, 143.29, 142.83, 140.50, 140.30, 139.91, 139.38, 138.52, 135.70, 133.32, 131.12, 130.43, 130.32, 130.01, 129.54, 128.95, 128.37, 127.55, 127.11, 126.96, 125.57, 125.43, 122.13, 121.10, 120.55, 119.48, 118.79, 115.34, 106.59, 104.62, 68.28, 44.25, 44.15, 37.79, 37.75, 31.89, 31.60, 31.02, 30.86, 30.78, 29.56, 29.41, 29.32, 29.26, 29.12, 28.98, 28.90, 28.81, 25.76, 24.30, 24.20, 23.07, 22.66, 22.61, 14.12, 14.10, 14.07, 14.02, 10.84, 10.78.

Anal. calcd for  $\text{C}_{81}\text{H}_{101}\text{N}_3\text{O}_5\text{S}$ : C, 79.18; H, 8.29; N, 3.42; O, 6.51; S, 2.61. Found: C, 77.14; H, 8.54; N, 2.75; S, 2.27.

**Synthesis of (E)-3-(4-((E)-6'-(5-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)-4-octylthiophen-2-yl)-1,1'-bis(2-ethylhexyl)-2,2'-dioxo-[3,3'-biindolinylidene]-6-yl)phenyl)-2-cyanoacrylic acid (6OTPA-Iso):**

Under argon, (E)-4-(6'-(5-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)-4-octylthiophen-2-yl)-1,1'-bis(2-ethylhexyl)-2,2'-dioxo-[3,3'-biindolinylidene]-6-yl)benzaldehyde (180 mg, 146.43  $\mu\text{mol}$ ), cyanoacetic acid (62.30 mg, 733  $\mu\text{mol}$ , 5 eq), were dissolved in a mixture of acetonitrile (6 mL) and chloroform (4 mL). A catalytic amount of piperidine was added and the solution was refluxed for 3 hours. Solvent was removed under reduced pressure and the solid dissolved in chloroform. The organic phase was washed with HCl solution (2 M), dried on  $\text{Na}_2\text{SO}_4$  and concentrated. The crude solid was purified by chromatography on silica gel using DCM, DCM/MeOH 98:2 and DCM/MeOH/Acetic acid 90:5:5 as eluent to afford the desired product as black solid (166 mg, 87%).

$^1\text{H}$  NMR (THF d8, 400 MHz):  $\delta$  = 9.32 (m, 2H), 8.35 (m, 1H), 8.05 (m, 2H), 7.73 (m, 2H), 7.34 (s, 1H), 7.24-7.17 (m, 4H), 7.09-7.06 (m, 5H), 6.91 (m, 2H), 6.87 (m, 5H), 3.97 (t, 4H,  $J_1=6.4\text{Hz}$ ), 1.98-1.92 (m, 2H), 1.79 (m, 4H), 1.67 (m, 2H), 1.55-1.33 (m, 44H), 1.04-0.90 (m, 21H).  $^{13}\text{C}$  NMR (THF d8, 100 MHz):  $\delta$  = 168.17, 168.12, 156.07, 148.50, 145.98, 145.77,

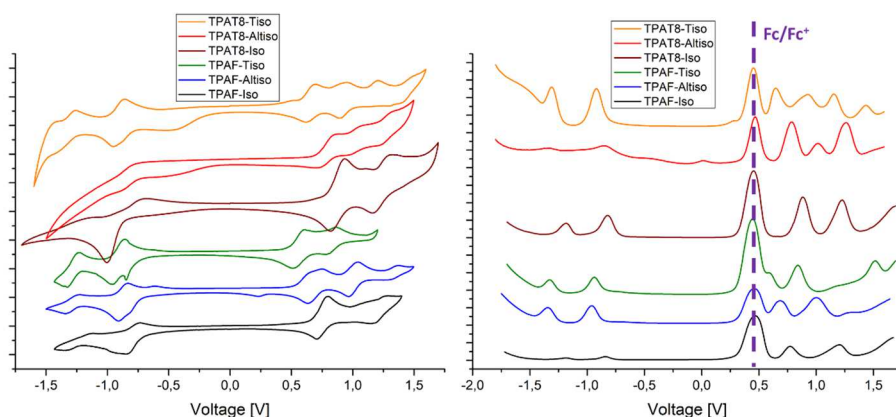
142.21, 140.66, 140.34, 139.36, 138.98, 137.85, 132.21, 130.95, 130.76, 130.41, 129.30, 126.81, 125.76, 121.96, 120.72, 119.83, 119.33, 117.77, 115.16, 105.64, 103.78, 67.87, 43.64, 43.54, 37.89, 37.80, 31.90, 31.61, 30.90, 30.74, 29.63, 29.57, 29.44, 29.35, 29.27, 28.89, 28.84, 28.69, 25.76, 23.02, 22.57, 22.53, 13.55, 13.50, 13.47, 13.37, 10.22, 10.15.

HRMS (ESI):  $[M]^+ = 1294.7511$  (0 ppm) (calcd. for  $C_{84}H_{102}N_4O_6S$ : 1294.75146).

#### References related to synthesis:

1. W. Ying, F. Guo, J. Li, Q. Zhang, W. Wu, H. Tian and J. Hua, *ACS Appl. Mater. Interfaces*, 2012, **4**, 4215–4224.
2. D. Wang, W. Ying, X. Zhang, Y. Hu, W. Wu and J. Hua, *Dyes Pigments*, 2015, **112**, 327–334.
3. H. Kang, S. Y. An, B. Walker, S. Song, T. Kim, J. Y. Kim and C. Yang, *J Mater Chem A*, 2015, **3**, 9899–9908.
4. Y. Koizumi, M. Ide, A. Saeki, C. Vijayakumar, B. Balan, M. Kawamoto and S. Seki, *Polym Chem*, 2013, **4**, 484–494
5. M. Karakawa and Y. Aso, *RSC Adv.*, 2013, **3**, 16259

## IV. Cyclic Voltammetry and Differential Pulse Voltammetry Data

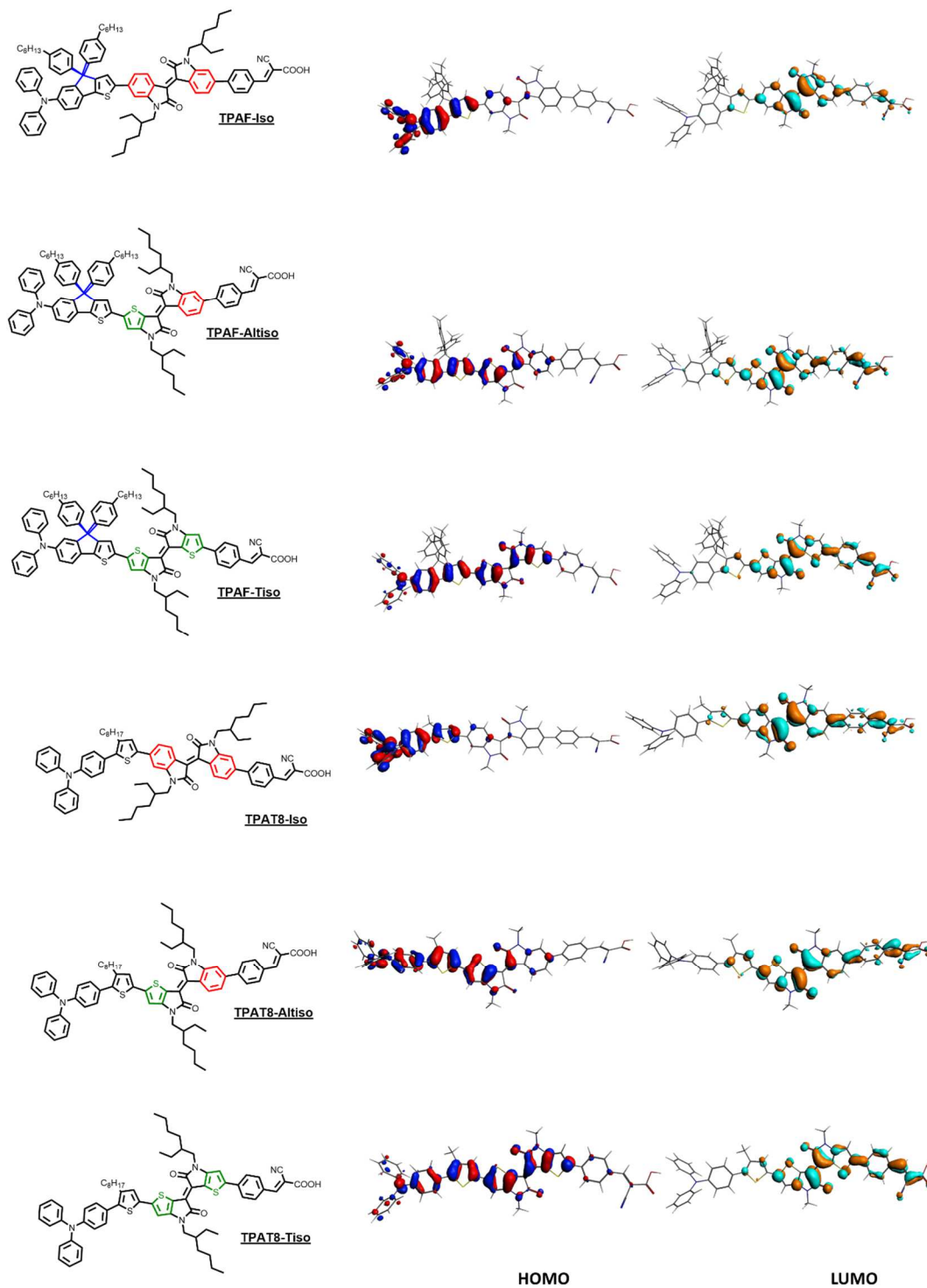


**Figure S6**– Dye voltammograms obtained by cyclic voltammetry (left) and differential pulse voltammetry (right). (Electrolyte:  $Bu_4NPF_6$  0,2 M in degassed anhydrous dichloromethane, scan speed:  $100\text{ mV}\cdot\text{s}^{-1}$ .)

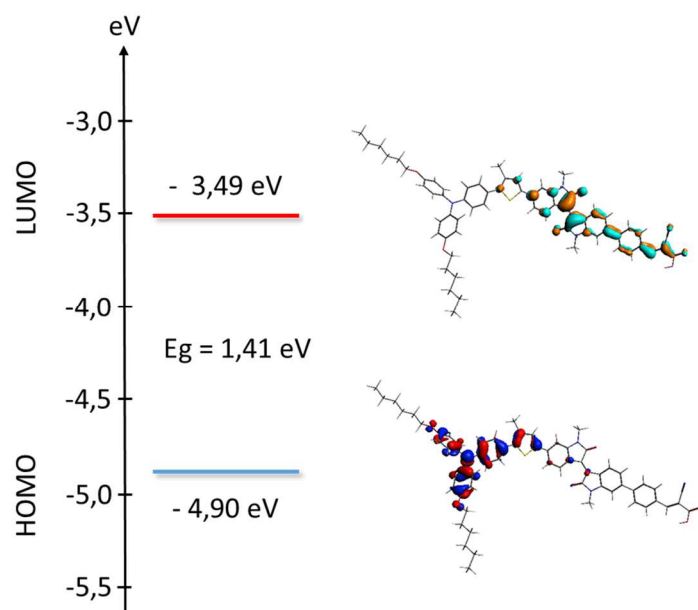
## V. DFT calculations and Bond Length Alternation determination

Density Functional Theory (DFT), implemented in ADF 2017, has been used to examine the frontier orbitals of every molecules. The estimated lowest energy conformations using Chem3D software were firstly submitted to a more accurate geometry optimization, using a combination of the Local Density Approximation VWN (Vosko, Wilk, Nusair) and the Generalized Gradient Approximation PBE (Perdew-Burke-Ernzerhof) functionals corrected for dispersion using Grimme methodology (Grimme 3) with the TZ2P basis sets (triple zeta + 2 polarization

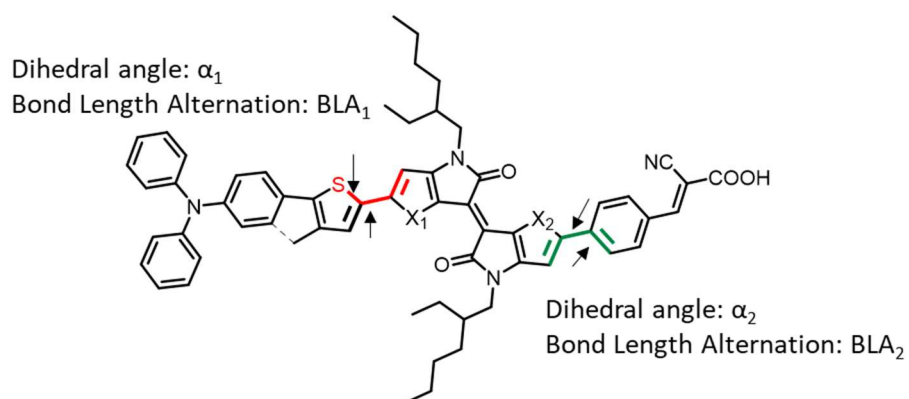
functions) in a solvent phase modeled through the COSMO model set for dichloromethane. Then, single-point calculations using the hybrid functional B3LYP (B3: Becke's 3-parameters,  $E_{\text{exchange}}$  functional + LYP: Lee, Yand, Parr,  $E_{\text{correlation}}$  functional) corrected with dispersion Grimme 3 with TZ2P sets in dichloromethane solvent phase were performed on the optimized conformations to modeled the HOMO and LUMO energy levels and their spatial localizations.<sup>1</sup>



**Figure S7a-** Frontier molecular orbital spatial repartition of the dyes calculated using hybrid B3LYP functional.



**Figure S7b-** Frontier molecular orbital spatial repartition of **6OTPA-Iso** calculated using hybrid B3LYP functional.



Dyes	$\alpha_1$ (°)	$BLA_1$ (Å)	$\alpha_2$ (°)	$BLA_2$ (Å)
TPAF-Iso	9.9	0.059	58.5	0.076
TPAF-Altiso	16.4	0.037	43.2	0.064
TPAF-Tiso	17.7	0.036	35.5	0.040
TPAT8-Iso	32.4	0.073	35.2	0.064
TPAT8-Altiso	32.5	0.046	39.4	0.061
TPAT8-Tiso	32.7	0.041	25.9	0.035

**Table S1-** Summary of the different dihedral angles and BLA (Bond Length Alternation) measurements of the 6 synthesized dyes calculated from DFT calculations.

**References related to DFT calculations and Bond Length Alternation determination:**

1. K. Burke and L. O. Wagner, *Int. J. Quantum Chem.*, 2013, **113**, 96–101.

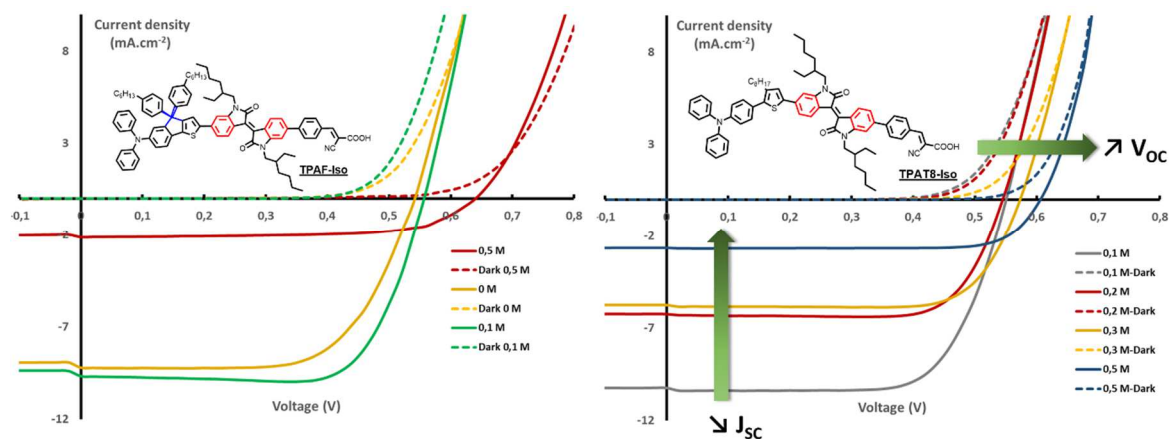
## VI. Optimization of TiO<sub>2</sub> thickness, tBP and CDCA ratio in solar cells.

### Optimization of TiO<sub>2</sub> thickness in TPAF-Iso and TPAF-Tiso based solar cells

Dye	Thickness(μm)	Voc (V)	Jsc (mA.cm <sup>-2</sup> )	FF	η (%)
TPAF-Iso	8+4 <sup>a</sup>	0.54	9.22	0.65	3.237
		0.51±0.05	8.38±0.85	0.65±0.01	2.75±0.49
	12+4 <sup>b</sup>	0.55	9.67	0.73	3.95
		0.55±0.01	9.38±0.29	0.74±0.01	3.84±0.22
TPAF-Tiso	8+4 <sup>a</sup>	0.36	1.75	0.44	0.28
		0.36±0.01	1.65±0.10	0.44±0.01	0.26±0.02
	12+4 <sup>b</sup>	0.40	3.17	0.55	0.70
		0.39±0.01	2.76±0.40	0.54±0.01	0.59±0.11

Photovoltaic parameters of solar cells obtained using the different fabrication conditions. Dyeing bath: dye/CDCA (a) 0.2/2mM, (b) 0.2/10mM, EtOH/CHCl<sub>3</sub> (4:1), electrode size 0.36 cm<sup>2</sup>, Electrolyte : BMII 0,5M, I<sub>2</sub> 0,03M, LiI 0.5M, Gthio 0.5M, tBP 0.1M. Irradiation 1 Sun, using a mask. First lines correspond to the results of the best cells, second lines correspond to the parameters obtained from two devices.”

### Optimization of tBP content in TPAF-Iso and TPAT8-Iso based solar cells



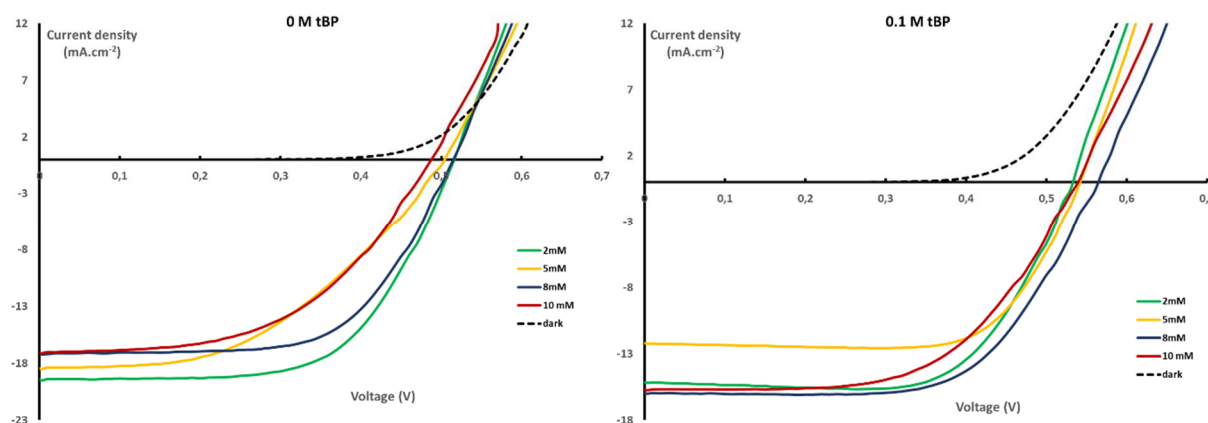
**Figure S8b-** IV curves of TPAF-Iso and TPAT8-Iso based solar cells obtained with different tBP ratio.

Dyes	[tBP] (mol.L <sup>-1</sup> )	V <sub>oc</sub> (V)	J <sub>sc</sub> (mA.cm <sup>-2</sup> )	FF	η (%)
TPAF-Iso	0	0.54	9.22	0.65	3.24
	0.1	0.56	9.67	0.74	3.94
	0.5	0.64	2.11	0.65	0.88
TPAT8-Iso	0.1	0.55	10.23	0.71	3.99
	0.2	0.54	6.23	0.75	2.55
	0.3	0.57	5.75	0.75	2.48
	0.5	0.61	2.65	0.79	1.27

Conditions : dye/CDCA 0.2/2mM, EtOH :CHCl<sub>3</sub> 4 :1, 12+4 μm. Electrolyte : BMII=0.5M, I<sub>2</sub>=0.03M, LiI=0.5M, Gthio=0.5M, tBP=X M

Photovoltaic parameters of TPAF-Iso and TPAT8-Iso based solar cells obtained with different tBP ratio.

### Optimization of tBP content and CDCA ratio in 6OTPA-Iso based devices

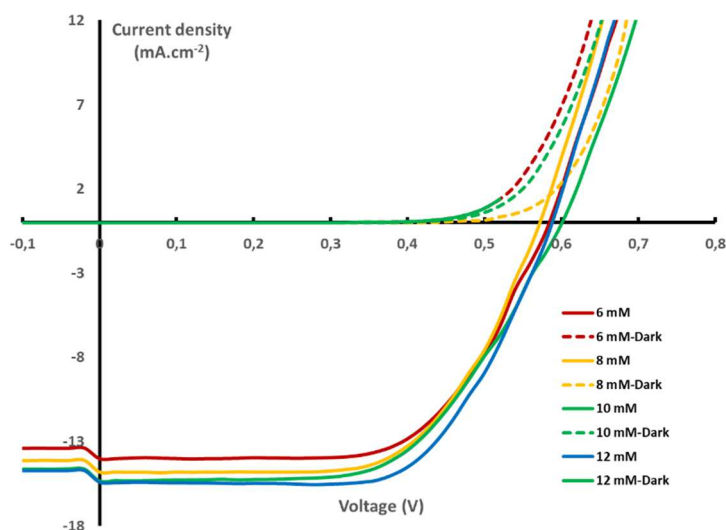


Dye	[tBP] (mol.L <sup>-1</sup> )	[CDCA] (mmol.L <sup>-1</sup> )	V <sub>oc</sub> (V)	J <sub>sc</sub> (mA.cm <sup>-2</sup> )	FF	η (%)
6OTPA-Iso	Electrolyte A 0	2	0.51	19.37	0.62	6.21
		5	0.50	18.41	0.46	4.30
		8	0.51	17.11	0.62	5.52
		10	0.49	17.04	0.52	4.28
	Electrolyte B 0.1	2	0.53	15.15	0.67	5.43
		5	0.54	12.22	0.71	4.74
		8	0.56	15.94	0.63	5.71
		10	0.54	15.70	0.58	4.91

Conditions : dye/CDCA 0.2/XmM. EtOH :CHCl<sub>3</sub> 1:1. 12+4 μm. Electrolyte : BMII 0.5M. I<sub>2</sub> 0.03M. LiI 0.5M. Gthio 0.5M. tBP 0.X M

**Figure S8d-** Photovoltaic parameters and IV curves of 6OTPA-Iso based solar cells obtained with different CDCA ratio and various tBP concentrations in the electrolyte.

## Optimization of CDCA ratio in TPAT8-Iso based devices



Dye	[CDCA] (mmol.L <sup>-1</sup> )	V <sub>OC</sub> (V)	J <sub>SC</sub> (mA.cm <sup>-2</sup> )	FF	η (%)
TPAT8-Iso	6	0.58	14.01	0.63	5.13
	8	0.57	14.13	0.66	5.31
	10	0.59	15.98	0.61	5.76
	12	0.59	15.41	0.64	5.80

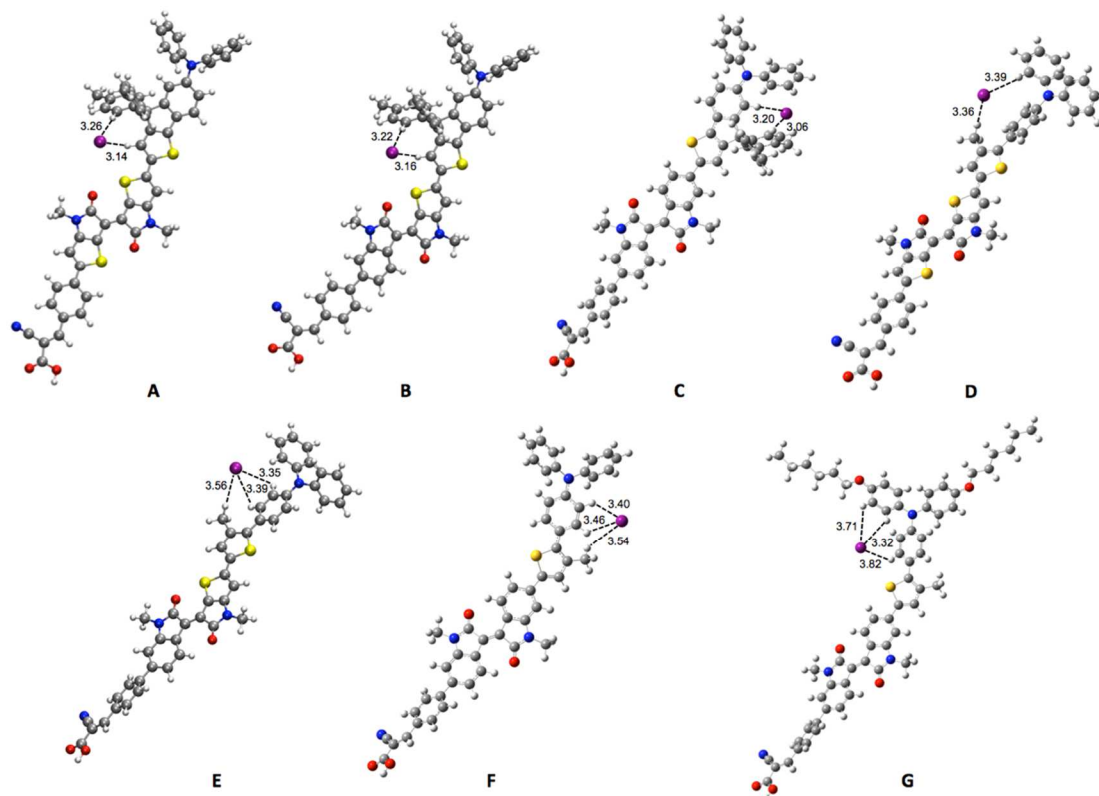
Conditions: dye/CDCA 0.2/XmM, EtOH :CHCl<sub>3</sub> 4 :1, 14+4 μm. Electrolyte : BMII 0.5M, I<sub>2</sub> 0.03M, LiI 0.5M, Gthio 0.5M, tBP 0.1M

**Figure S9-** Photovoltaic parameters and IV curves of TPAT8-Iso based solar cells obtained with different CDCA ratio.

## VII. Computational studies

**Table S2.** Interaction energies ( $E_{int.}$  in eV and (kcal mol<sup>-1</sup>)) between iodide and the oxidized dyes and z component of the dipole (in Debyes) of the oxidized dyes.

Dye	$E_{int.}$	Dipole(z)
TPAF_Tiso	-0.25 (-5.83)	88.07
TPAF_Altiso	-0.25 (-5.86)	109.95
TPAF_Iso	-0.30 (-6.84)	123.04
TPAT8_Tiso	-0.20 (-4.65)	78.58
TPAT8_Altiso	-0.21 (-4.73)	112.51
TPAT8_Iso	-0.20 (-4.58)	132.51
6OTPA_Iso	-0.21 (-4.94)	135.11



**Figure S10.** Computed interaction between iodide and TPAF\_Tiso (**A**), TPAF\_Altiso (**B**), TPAF\_Iso (**C**), TPAT8\_Tiso (**D**), TPAT8\_Altiso (**E**), TPAT8\_Iso (**F**) and OPA\_Iso (**G**). (Color code: C = gray, N = blue, O = red, S = yellow, I = purple, H = white; distances in Å).

### Computational details

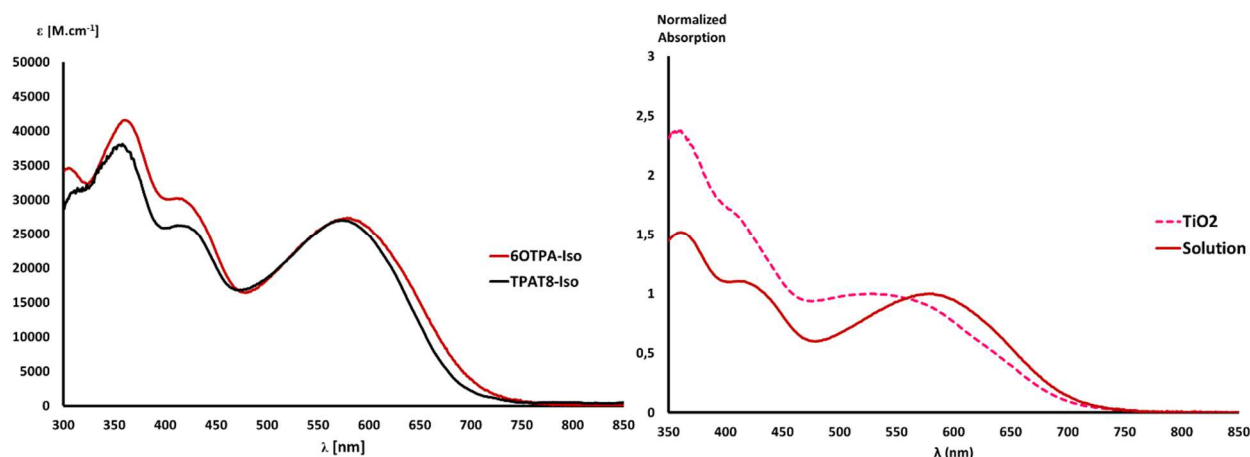
All the calculations have been carried out using the Gaussian09 software.<sup>1</sup> The HOMO/LUMO energies have been obtained after geometry optimizations of the neutral and cationic radical species of the studied dyes in gas phase using the B3LYP functional<sup>2</sup> in combination with the 6-31G\* basis set<sup>3</sup> for all atoms. This choice has been reported to produce a good agreement between the experimental and computed energies of frontier orbitals.<sup>4</sup> The dye/iodide interaction energies have been computed using the unrestricted formalism of the dispersion corrected M062X (D3) functional.<sup>5</sup> The geometries have been reoptimized in acetonitrile using the PCM method<sup>6</sup> and employing the SMD solvation model.<sup>7</sup> The cc-pVDZ basis set<sup>8</sup> was employed to describe all atoms except iodide, for which the aug-cc-pVDZ-PP basis set was used.<sup>9</sup> These settings have been employed before for describing this kind of interactions in similar systems.<sup>10</sup> To ensure that charges were distributed appropriately on the interacting pairs, a fragment guess was first generated specifying a negative charge on iodide and all subsequent calculations were performed reading their initial guess from a checkpoint file based off this fragment guess. The basis set superposition error (BSSE) for the dye-iodide interactions is considered to be negligible<sup>10</sup> and thus it was not computed for the species in this report.



**References related to computational studies:**

1. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian09, Revision D.01*, Gaussian, Inc.: Wallingford CT, **2009**.
2. (a) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H., *Chem. Phys. Lett.* **1989**, *157*, 200-206; (b) Becke, A. D., *J. Chem. Phys.* **1993**, *98*, 5648-5652; (c) Lee, C.; Yang, W.; Parr, R. G., *Phys. Rev. B* **1988**, *37*, 785-789.
3. (a) Ditchfield, R.; Hehre, W. J.; Pople, J. A., *J. Chem. Phys.* **1971**, *54*, 724-728; (b) Hehre, W. J.; Ditchfield, R.; Pople, J. A., *J. Chem. Phys.* **1972**, *56*, 2257-2261; (c) Hariharan, P. C.; Pople, J. A., *Theor. Chem. Acc.* **1973**, *28*, 213-222.
4. Burke, K.; Wagner, L. O., *Int. J. Quant. Chem.* **2013**, *113*, 96-101.
5. (a) Zhao, Y.; Truhlar, D. G., *Theor. Chem. Acc.* **2008**, *120*, 215-241; (b) Grimme, S., *J. Comp. Chem.* **2006**, *27*, 1787-1799; (c) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H., *J. Chem. Phys.* **2010**, *132*, 154104.
6. (a) Tannor, D. J.; Marten, B.; Murphy, R.; Friesner, R. A.; Sitkoff, D.; Nicholls, A.; Honig, B.; Ringnalda, M.; Goddard, W. A., *J. Am. Chem. Soc.* **1994**, *116*, 11875-11882; (b) Marten, B.; Kim, K.; Cortis, C.; Friesner, R. A.; Murphy, R. B.; Ringnalda, M. N.; Sitkoff, D.; Honig, B., *J. Phys. Chem.* **1996**, *100*, 11775-11788.
7. Marenich, A. V.; Cramer, C. J.; Truhlar, D. G., *J. Phys. Chem. B* **2009**, *113*, 6378-6396.
8. (a) Dunning Jr., T. H., *J. Chem. Phys.* **1989**, *90*, 1007-1023; (b) Woon, D. E.; Dunning Jr., T. H., *J. Chem. Phys.* **1993**, *98*, 1358-1371.
9. Peterson, K. A.; Figgen, D.; Goll, E.; Stoll, H.; Dolg, M., *J. Chem. Phys.* **2003**, *119*, 11113-11123.
10. Simon, S. J. C.; Parlange, F. G. L.; Swords, W. B.; Kellett, C. W.; Du, C.; Lam, B.; Dean, R. K.; Hu, K.; Meyer, G. J.; Berlinguette, C. P., *J. Am. Chem. Soc.* **2016**, *138*, 10406-10409.

## VIII Optoelectronic and photovoltaic data of 6OTPA-Iso dye



**Figure S11-** UV-Vis spectra of TPAT8-Iso and 6OTPA-Iso in dichloromethane and UV-Vis spectra grafted on TiO<sub>2</sub>.

	$\lambda_{\max\text{-UV}}^{\text{a,b}}$ [nm]	$\lambda_{\max\text{-Vis,NIR}}^{\text{a,b}}$ [nm]	$\epsilon^{\text{a}}$ [M <sup>-1</sup> .cm <sup>-1</sup> ]	$\lambda_{\text{onset}}^{\text{a,b}}$ [nm]	%A <sub>IR</sub> <sup>a</sup> (700nm)	$\Delta E_{\text{opt}}^{\text{c}}$ [eV]	HOMO <sup>d</sup> [eV]	LUMO <sup>d</sup> [eV]	$\Delta E_{\text{ele}}^{\text{c}}$ [eV] <sup>e</sup>
TPAT8-Iso	358 (355)	574 (546)	27000	686	1	1.8	-5.2	-3.4	1.8
6OTPA-Iso	363 (358)	579 (527)	27300	712	4	1.7	-5.1	-3.5	1.6

<sup>a</sup> Measured in CH<sub>2</sub>Cl<sub>2</sub> at room temperature at a concentration of 10<sup>-5</sup>M. <sup>b</sup> Parenthesis, measured after dyeing of 2 $\mu$ m thick TiO<sub>2</sub> films on glass substrate, in the presence of CDCA (dyeing solution 0.2mM Dye/ 2.0mM CDCA). <sup>c</sup> Calculated from optical absorption onset. <sup>d</sup> Values calculated from oxidative potential for the HOMO and reduction potential for the LUMO, measured by CV in CH<sub>2</sub>Cl<sub>2</sub> (2.10<sup>-3</sup>M) at room temperature, ferrocene/ferrocenium was used as the internal standard and measured at +0.48 V (-4.8 eV). <sup>e</sup> Using mean values obtained from electrochemical measurements with the following equation  $\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$ .

**Table S3:** Optical and electrochemical properties of TPAT8-Iso and 6OTPA-Iso

**Figure S12-** Photovoltaic parameters and IV curves of the best 6OTPA-Iso based solar cells.