

Supporting Information

Investigating their crystalline nature, charge transport properties and photovoltaic performances of ladder-type small molecules

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1. Materials and Measurements.

All reactions and operations were carried out under argon atmosphere with the use of standard Schlenk techniques. All chemicals, unless otherwise specified, were purchased from Aldrich and used as received. Indacenodithieno[3,2-b]thiophene (IDTT), IDTT-CHO, IDTT-di-Tin, IDT-di-Tin, 5'-bromo-[2,2'-bithiophene]-5-carbaldehyde were synthesized according to a previously reported procedure.¹⁻⁴

The ¹H and ¹³C NMR spectra were collected on a Bruker AVANCE III 500M spectrometer operating at 500 and 125 MHz in deuterated chloroform solution with TMS as reference, respectively. UV-Vis spectra were measured using a Perkin-Elmer Lambda-9 spectrophotometer. Cyclic voltammetry of small molecular film was conducted in acetonitrile with 0.1 M Bu₄NPF₆ using a scan rate of 100 mV S⁻¹. ITO, Ag/AgCl and Pt wire were used as working electrode, reference electrode and counter electrode, respectively. The differential scanning calorimetry (DSC) was carried out on a TA Q200 instrument under purified nitrogen gas flow with a temperature ramp rate of 10 °C/min. AFM images under tapping mode were taken on a Veeco multimode AFM with a Nanoscope III controller.

2. FET fabrication and testing.

Field-effect transistors were fabricated through the top-contact and bottom-gate

geometry. Heavily doped p-type silicon <100> substrates with a 300 nm thermal oxide layer were purchased from Montco Silicon Technologies INC. After cleaning the substrate by sequential ultrasonication in acetone and isopropyl alcohol for 15 min followed by air plasma treatment, the oxide layer was passivated with a thin divinyltetramethyldisiloxane-bis(benzocyclobutene) (BCB) buffer layer. Small molecule thin films were spin-coated from a 0.5 wt % DCB solution. Interdigitated source and drain electrodes ($W=1000\ \mu\text{m}$, $L=20/30\ \mu\text{m}$) were defined by evaporating a Au (40 nm) through a shadow mask from the resistively heated Mo boat at 10^{-7} Torr. OFET characterization was carried out in a N_2 -filled glovebox using an Agilent 4155B semiconductor parameter S6 analyzer. The field-effect mobility was calculated in the saturation regime from the linear fit of $(I_{\text{ds}})^{1/2}$ vs V_{gs} . The threshold voltage (V_{t}) was estimated as the x intercept of the linear section of the plot of $(I_{\text{ds}})^{1/2}$ vs V_{gs} . The sub threshold swing was calculated by taking the inverse of the slope of I_{ds} vs V_{gs} in the region of exponential current increase.

3. Solar cell fabrication and testing.

To fabricate the conventional solar cells, ITO-coated glass substrates ($15\ \Omega/\text{sq.}$) were cleaned with detergent, de-ionized water, acetone, and isopropyl alcohol. A thin layer (ca. 40 nm) of PEDOT:PSS (Baytron® P VP Al 4083, filtered at $0.45\ \mu\text{m}$) was first spin-coated on the pre-cleaned ITO-coated glass substrates at 5,000 rpm and baked at $140\ ^\circ\text{C}$ for 10 minutes under ambient conditions. The substrates were then transferred into an argon-filled glove-box. Subsequently, the small molecule:PC₇₁BM active layer (1:2 wt, 80~90 nm, prepared by dissolving the small molecule in o-dichlorobenzene and filtered with a $0.2\ \mu\text{m}$ PTFE filter) was spin-coated on the PEDOT:PSS layer from a homogeneously blended solution. The substrates were annealed at $110\ ^\circ\text{C}$ for 10 minutes. After the fullerene surfactant was spin-coated onto the BHJ layer, the substrates were annealed at $110\ ^\circ\text{C}$ for 5 minutes prior to electrode deposition. At the final stage, the substrates were pumped down to high vacuum ($< 2 \times 10^{-6}$ Torr), and silver (100 nm) was thermally evaporated onto the

active layer through shadow masks to define the active area ($10.08 \times 10^{-2} \text{ cm}^2$) of the devices. The current-voltage (I-V) characteristics of unencapsulated photovoltaic devices were measured under ambient using a Keithley 2400 source-measurement unit. An Oriel xenon lamp (450 Watt) with an AM1.5 G filter was used as the solar simulator. A Hamamatsu silicon solar cell with a KG5 color filter, which is traced to the National Renewable Energy Laboratory (NREL), was used as the reference cell. To calibrate the light intensity of the solar simulator, the power of the xenon lamp was adjusted to make the short-circuit current (ISC) of the reference cell under simulated sun light as high as it was under the calibration condition. The spectral mismatches resulting from the test cells, the reference cell, the solar simulator, and the AM1.5 were calibrated with mismatch factors (M). According to Shrotriya et al. The mismatch factor is defined as

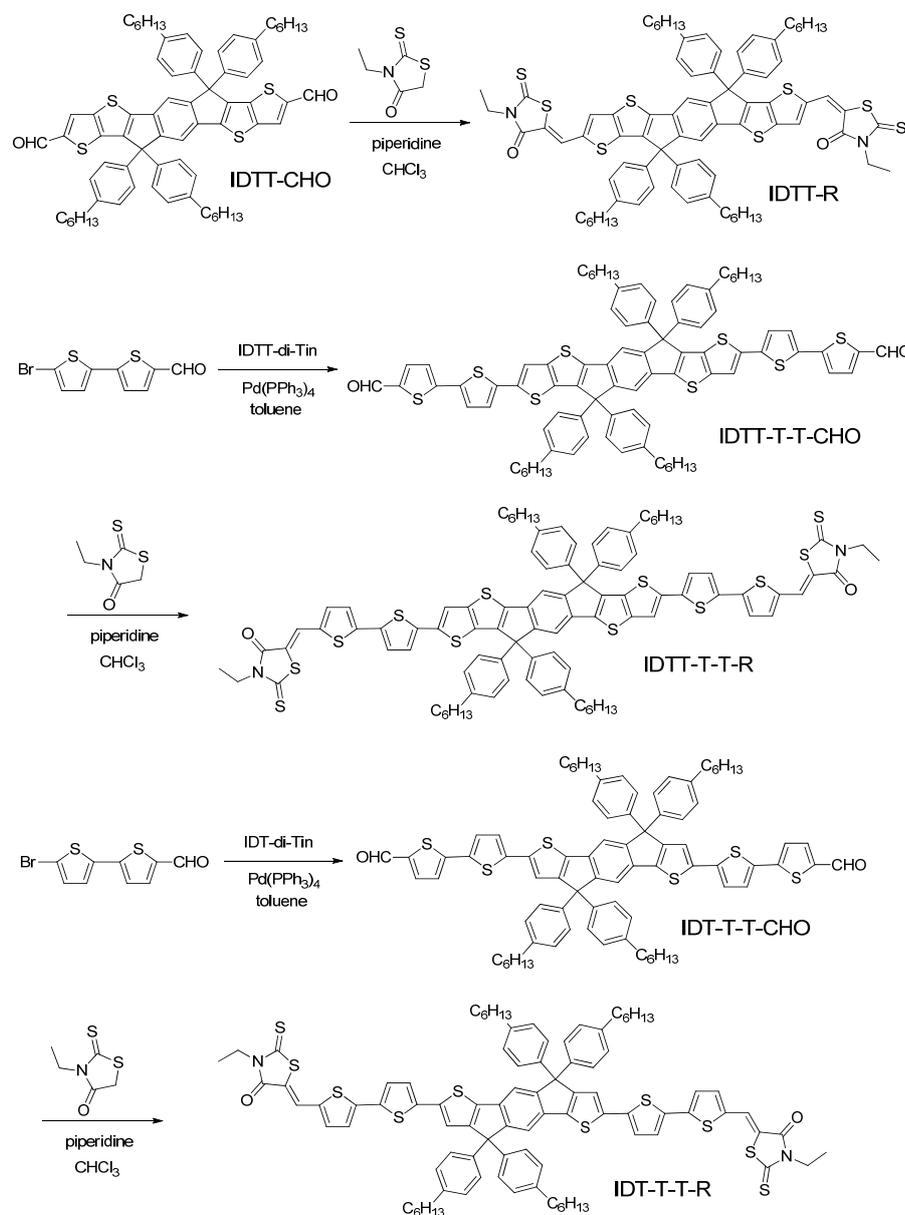
$$M = \frac{\int_{\lambda_1}^{\lambda_2} E_{Ref}(\lambda) S_R(\lambda) d\lambda \int_{\lambda_1}^{\lambda_2} E_S(\lambda) S_T(\lambda) d\lambda}{\int_{\lambda_1}^{\lambda_2} E_{Ref}(\lambda) S_T(\lambda) d\lambda \int_{\lambda_1}^{\lambda_2} E_S(\lambda) S_R(\lambda) d\lambda}$$

where $E_{Ref}(\lambda)$ is the reference spectral irradiance (AM1.5), $E_S(\lambda)$ is the source spectral irradiance, $S_R(\lambda)$ is the spectral responsivity of the reference cell, and $S_T(\lambda)$ is the spectral responsivity of the test cell, each as a function of wavelength (λ). The spectral responsivities of the test cells and the reference cell were calculated from the corresponding external quantum efficiencies (EQE) by the relationship

$$S(\lambda) = \frac{q\lambda}{hc} EQE(\lambda)$$

where the constant term q/hc equals 8.0655×10^5 for wavelength in units of meters and $S(\lambda)$ in units of AW^{-1} . The Hamamatsu solar cell was also used as the detector for determining the spectral irradiance of the solar simulator. To minimize the spectral transformation, the irradiance spectrum has been calibrated with the spectral responsivity of the Hamamatsu cell and the grating efficiency curve of the monochromator (Oriel Cornerstone 130).

4. Synthesis.



Scheme S1. Synthetic route of IDTT-R, IDTT-T-T-R and IDT-T-T-R.

Synthesis of IDTT-R.

IDTT-CHO (200 mg, 0.19 mmol) and 3-ethyl rhodanine (300 mg, 1.86 mmol) were dissolved in a dry CHCl₃ (30 mL) solution, and then three drops of piperidine was added to the mixture. The resulting solution was stirred and refluxed for 12 h under argon. The reaction mixture was extracted with CH₂Cl₂ (50 mL × 2), the organic layer

was washed with water and dried over anhydrous Na_2SO_4 . After removal of solvent, the crude product was purified by silica gel using a mixture of petroleum/dichloromethane (2:1) as eluent. The crude solid was recrystallized from methanol and CHCl_3 mixture three times to afford IDTT-R as a black solid (217 mg, 86%).

^1H NMR (400 MHz, Chloroform-*d*) δ : 7.86 (s, 2 H), 7.58 (m, 4 H), 7.18-7.12 (m, 16 H), 4.18 (q, $J = 7.1$ Hz, 4 H), 2.57 (t, $J = 7.8$ Hz, 8 H), 1.60 (m, 8 H), 1.36 – 1.25 (m, 30 H), 0.86 (t, $J = 6.8$ Hz, 12 H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ : 191.8, 167.2, 154.5, 147.7, 146.7, 143.1, 142.3, 139.3, 139.3, 139.1, 136.4, 128.7, 127.8, 127.1, 125.9, 119.9, 117.7, 63.0, 40.0, 35.6, 31.7, 31.2, 29.2, 22.6, 14.1, 12.3. HRMS (MALDI-TOF) m/z : calcd. for $\text{C}_{80}\text{H}_{85}\text{N}_2\text{O}_2\text{S}_8$, 1361.437; found, 1361.417.

Synthesis of IDTT-T-T-CHO.

A solution of 5'-bromo-[2,2'-bithiophene]-5-carbaldehyde (195 mg, 0.71 mmol) and IDTT-di-Tin (400 mg, 0.30 mmol) in dry toluene (20 mL) was degassed twice with argon followed by the addition of $\text{Pd}(\text{PPh}_3)_4$ (41 mg, 0.036 mmol). After being stirred at 100°C for 48 h under argon, the reaction mixture was poured into water (100 mL) and extracted with CH_2Cl_2 (50 mL \times 2). The organic layer was washed with water and dried over anhydrous Na_2SO_4 . After removal of solvent, the crude product was purified by silica gel using a mixture of petroleum/dichloromethane (1:1) as eluant to afford IDTT-T-T-CHO (405 mg, 97%) as a red solid.

^1H NMR (500 MHz, Chloroform-*d*) δ : 9.84 (s, 2 H), 7.63 (d, $J = 4.0$ Hz, 4 H), 7.53 (s, 2 H), 7.41 (s, 2 H), 7.24 (d, $J = 3.8$ Hz, 2 H), 7.22 – 7.19 (m, 10 H), 7.12 (d, $J = 8.2$ Hz, 8 H), 7.08 (d, $J = 3.8$ Hz, 2 H), 2.58 (t, $J = 7.5$ Hz, 8 H), 1.61-1.57 (m, 8 H), 1.38 – 1.25 (m, 24 H), 0.87 (t, $J = 6.5$ Hz, 12 H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ : 182.3, 153.6, 146.6, 146.3, 143.9, 142.2, 141.9, 141.6, 139.9, 139.5, 137.3, 137.1, 136.0, 133.2, 128.6, 128.0, 126.9, 124.4, 124.0, 117.4, 117.0, 100.0, 62.9, 35.6, 31.7, 31.2, 29.2, 22.6, 14.1. MS (MALDI) m/z : calcd. for $\text{C}_{86}\text{H}_{83}\text{O}_2\text{S}_8$, 1403.4; found, 1403.9.

Synthesis of IDTT-T-T-R.

IDTT-T-T-CHO (200 mg, 0.14 mmol) and 3-ethyl rhodanine (229 mg, 1.42 mmol) were dissolved in a dry CHCl_3 (40 mL) solution, and then three drops of piperidine was added to the mixture. The resulting solution was stirred and refluxed for 12 h under argon. The reaction mixture was extracted with CH_2Cl_2 (50 mL \times 2), the organic layer was washed with water and dried over anhydrous Na_2SO_4 . After removal of solvent, the crude product was purified by silica gel using CHCl_3 as eluent. The crude solid was recrystallized from methanol and CHCl_3 mixture three times to afford IDTT-T-T-R as a black solid (202 mg, 84%).

^1H NMR (500 MHz, Chloroform-*d*) δ : 7.83 (s, 2 H), 7.51 (s, 2 H), 7.41 (s, 2 H), 7.32 (d, $J = 4.0$ Hz, 2 H), 7.23-7.18 (m, 12 H), 7.12-7.11 (m, 10 H), 4.19 (q, $J = 7.5$ Hz, 4 H), 2.57 (t, $J = 7.5$ Hz, 8 H), 1.64 – 1.50 (m, 8 H), 1.35 – 1.26 (m, 30 H), 0.86 (t, $J = 6.5$ Hz, 12 H). MS (MALDI) m/z : calcd. for $\text{C}_{96}\text{H}_{92}\text{N}_2\text{O}_2\text{S}_{12}$, 1688.4; found, 1688.3.

Synthesis of IDT-T-T-CHO.

A solution of 5'-bromo-[2,2'-bithiophene]-5-carbaldehyde (532 mg, 1.95 mmol) and IDT-di-Tin (1.00 g, 0.81 mmol) in dry toluene (40 mL) was degassed twice with argon followed by the addition of $\text{Pd}(\text{PPh}_3)_4$ (113 mg, 0.098 mmol). After being stirred at 100 °C for 48 h under argon, the reaction mixture was poured into water (100 mL) and extracted with CH_2Cl_2 (100 mL \times 2). The organic layer was washed with water and dried over anhydrous Na_2SO_4 . After removal of solvent, the crude product was purified by silica gel using a mixture of petroleum/dichloromethane (1:1) as eluant to afford IDT-T-T-CHO (1.03 g, 98%) as a red solid.

^1H NMR (500 MHz, Chloroform-*d*) δ : 9.83 (s, 2 H), 7.61 (d, $J = 4.0$ Hz, 2 H), 7.47 (s, 2 H), 7.26-7.23 (m, 10 H), 7.18 (d, $J = 3.9$ Hz, 2 H), 7.16 (s, 2 H), 7.13 (d, $J = 8.3$ Hz, 8 H), 7.09 (d, $J = 3.8$ Hz, 2 H), 2.61 (t, $J = 7.5$ Hz, 8 H), 1.63 (m, 8 H), 1.35 (m, 24 H), 0.91 (t, $J = 6.5$ Hz, 12 H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ : 182.2, 156.8, 153.5, 146.7, 141.7, 14.4, 141.4, 141.0, 139.8, 138.9, 137.3, 135.1, 134.1, 128.4, 127.8, 126.9, 124.0, 123.8, 120.2, 117.3, 63.1, 35.5, 31.7, 31.3, 29.1, 22.6, 14.1. HRMS (MALDI) m/z :

calcd. for $C_{82}H_{83}O_2S_6$, 1291.4712; found, 1291.4615.

Synthesis of IDT-T-T-R.

IDT-T-T-CHO (273 mg, 0.23 mmol) and 3-ethyl rhodanine (371 mg, 2.3 mmol) were dissolved in a dry $CHCl_3$ (50 mL) solution, and then three drops of piperidine was added to the mixture. The resulting solution was stirred and refluxed for 12 h under argon. The reaction mixture was extracted with CH_2Cl_2 (50 mL \times 2), the organic layer was washed with water and dried over anhydrous Na_2SO_4 . After removal of solvent, the crude product was purified by silica gel using a mixture of petroleum/chloroform (2:1) as eluent. The crude solid was recrystallized from methanol and $CHCl_3$ mixture three times to afford IDT-T-T-R as a black solid (288 mg, 79%).

1H NMR (400 MHz, Chloroform-*d*) δ : 7.80 (s, 2 H), 7.42 (s, 2 H), 7.29 (d, J = 4.0 Hz, 2 H), 7.21-7.18 (m, 10 H), 7.17 (d, J = 4.0 Hz, 2 H), 7.13 (s, 2 H), 7.12-7.08 (m, 10 H), 4.17 (q, J = 7.2 Hz, 4 H), 2.58 (t, J = 7.5 Hz, 8 H), 1.59 (m, 8 H), 1.38-1.26 (m, 30 H), 0.88 (t, J = 6.5 Hz, 12 H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ : 191.8, 167.2, 156.8, 153.5, 145.1, 141.7, 141.4, 141.1, 139.4, 139.0, 136.4, 135.3, 135.1, 134.2, 128.4, 127.9, 126.2, 124.9, 124.7, 124.1, 120.5, 120.2, 117.4, 63.1, 39.9, 35.6, 31.7, 31.3, 29.1, 22.6, 14.1, 12.3. HRMS (MALDI) m/z : calcd. for $C_{92}H_{93}N_2O_2S_{10}$, 1577.4439; found, 1577.4323.

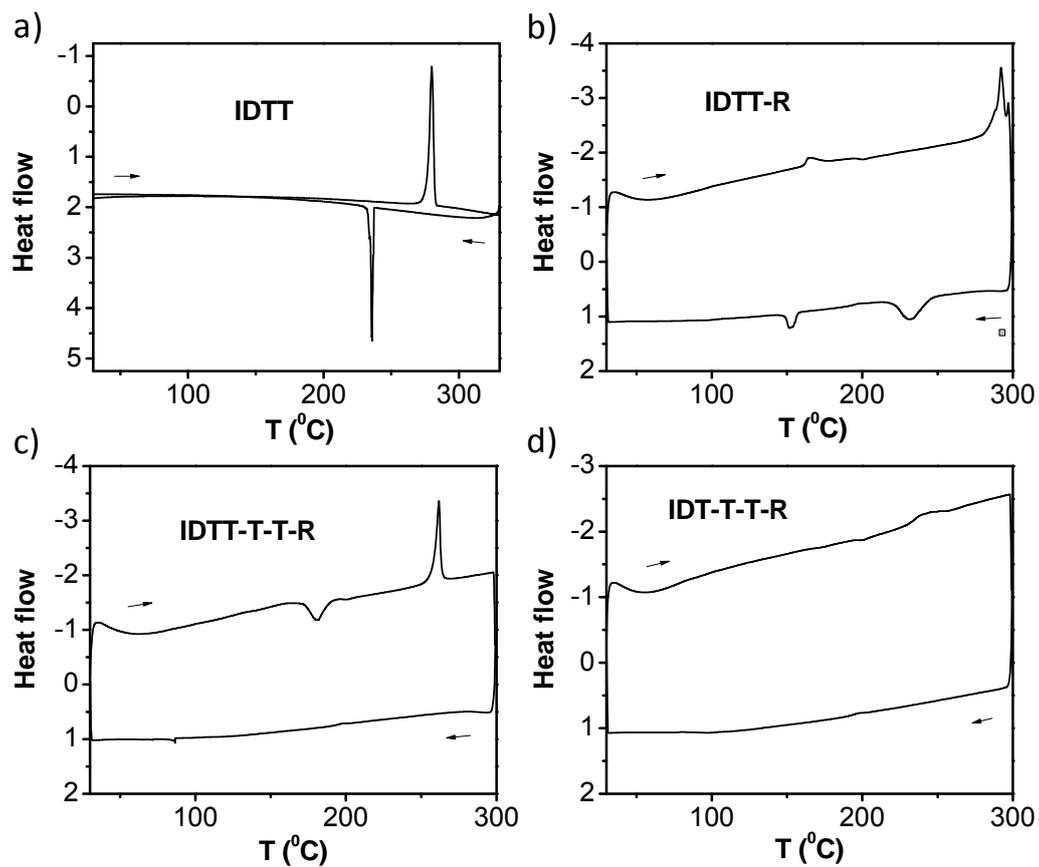


Figure S1. DSC curves of a) IDTT; b) IDTT-R; c) IDTT-T-T-R; d) IDT-T-T-R.

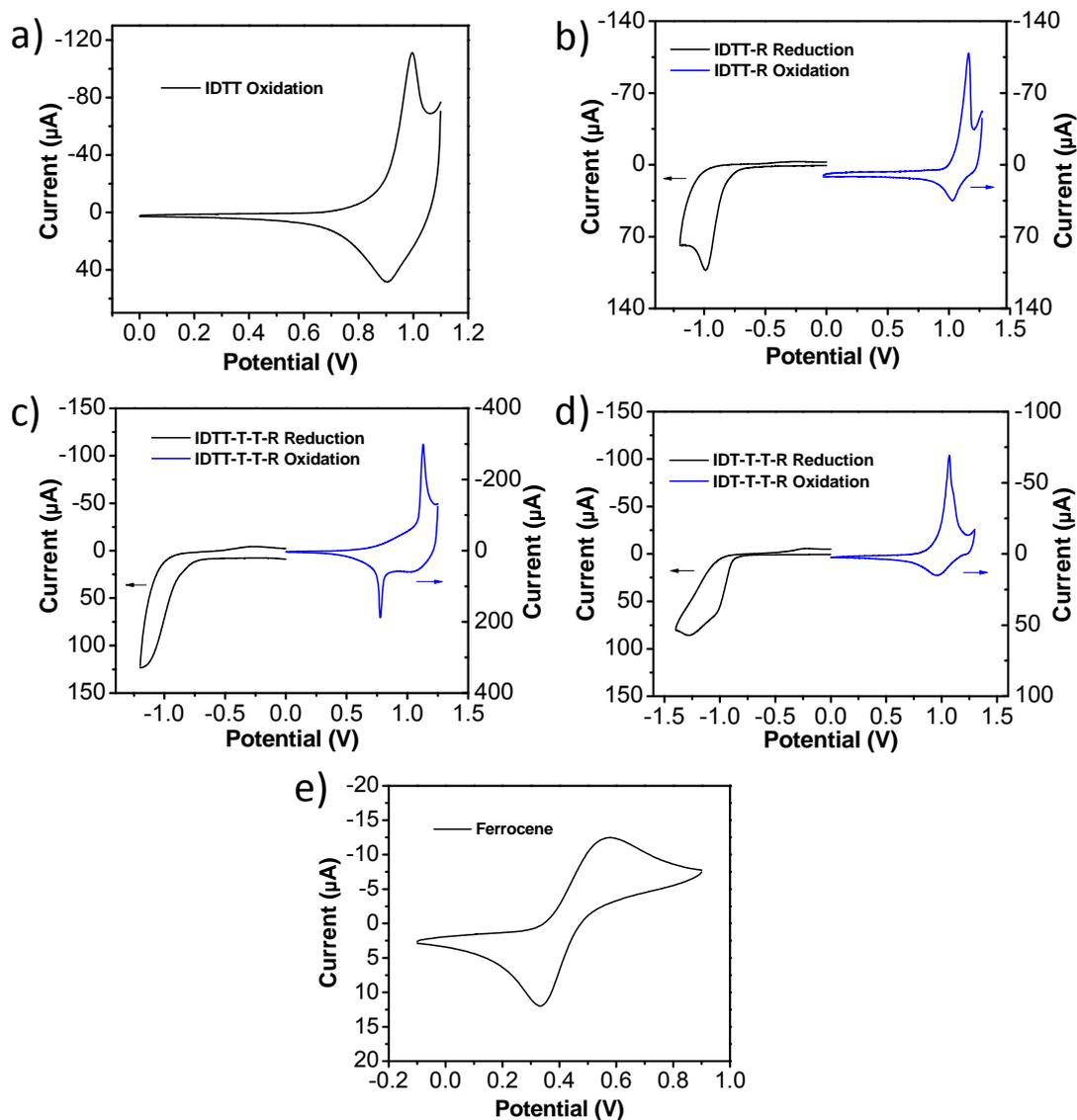


Figure S2. CV curves for a) IDTT; b) IDTT-R; c) IDTT-T-T-R; d) IDT-T-T-R and e) ferrocene in $\text{CH}_3\text{CN} / 0.1 \text{ M Bu}_4\text{NPF}_6$ at 100 mV s^{-1} .

Table S1. Energy Level Parameters of IDTT, IDTT-R, IDTT-T-T-R and IDT-T-T-R.

| Small molecule | λ_{max} solution (nm) | λ_{max} film (nm) | $E_{\text{g, opt}}$ (eV) | $E_{\text{g, cv}}$ (eV) | HOMO (eV) | LUMO (eV) |
|----------------|---|-------------------------------------|-----------------------------|----------------------------|--------------|--------------|
| IDTT | 410 | 427 | 2.74 | --- | -5.24 | --- |
| IDTT-R | 569 | 586 | 1.96 | 1.87 | -5.40 | -3.53 |
| IDTT-T-T-R | 546 | 562 | 1.85 | 1.94 | -5.43 | -3.49 |
| IDT-T-T-R | 554 | 550 | 1.87 | 1.97 | -5.42 | -3.45 |

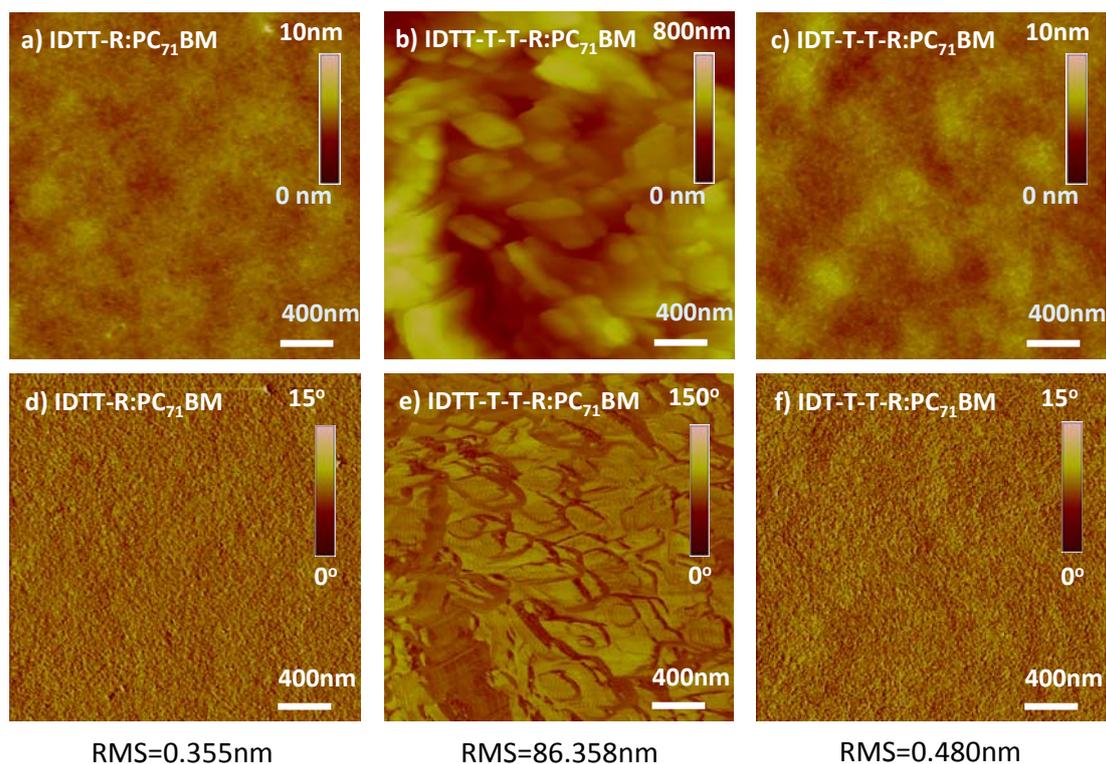


Figure S3. AFM (a–c) topography and (d–f) phase images of the IDTT-R:PC₇₁BM (1:2), IDTT-T-T-R:PC₇₁BM (1:2) and IDT-T-T-R:PC₇₁BM (1:2) blend films.

References

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