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Alkylated indacenodithieno[3,2-b]thiophene-based all donor ladder-type conjugated polymers for organic thin film transistors

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General.

All chemicals were purchased from commercial suppliers and used as received unless otherwise specified. 2,5-bis(trimethylstannyl)thiophene,[1] 2,5-bis(trimethylstannyl)thieno[3,2-*b*]thiophene[1] and 2,6-bis(trimethylstannyl)dithieno[3,2-*b*:2',3'-*d*]thiophene[2] were synthesised according to previous reports. ^{1}H NMR spectra were recorded on BRUKER 400 spectrometer with $CDCl_3$ as solution at room temperature. Number-average (M_n) and weight-average (M_w) molecular weight were determined by Agilent Technologies 1200 series GPC running in chlorobenzene at 80 °C, and calibrated against narrow polydispersity polystyrene standards. UV-Vis spectra were recorded on a UV-1601 Shimadzu UV-vis spectrometer. Flash chromatography (FC) was performed on silica gel (Merck Kieselgel 60 F254 230-400 mesh). Photo Electron Spectroscopy in Air (PESA) measurements were recorded with a Riken Keiki AC-2 PESA spectrometer with a power setting of 5 nW and a power number of 0.5. Samples for PESA were prepared on glass substrates by spin-coating. Thermogravimetric analysis (TGA) was carried out using a PerkinElmer Pyris 1 TGA machine, with heating from 50 to 700 °C at a heating rate of 20 °C/min under N_2. Differential scanning calorimetry (DSC) measurements were conducted under nitrogen at scan rate of 20 °C/min with a TA DSC-Q20 instrument. The molecular packing was characterized by wide-angle X-ray diffraction (XRD, PANalytical X'Pert Pro MPD) using the Cu Kα radiation. θ/2θ scans were performed at room temperature to the films drop cast from the corresponding polymer solutions onto silicon substrates.

OTFT device fabrication and characterisation.

Top gate/bottom contact devices were fabricated on glass substrates using Au (40 nm) source-drain electrodes and CYTOP dielectric. Au electrodes were treated with pentafluorobenzene thiol (PFBT) SAM to increase the work function. Polymers were dissolved in chlorobenzene at a concentration of 10 mg/ml, and spin coated at 2000 rpm for 60 s. The obtained polymer film was annealed at 200 °C for 30 min, before spin coating of 900 nm CYTOP dielectric followed by drying at 100 °C for 30 min. Al gate electrodes (40 nm) were then evaporated under vacuum using shadow masks. The channel width and length of the transistors are 1000 μm and 40 μm, respectively. Transistor characterization was carried out under nitrogen using a Keithley 4200 parameter analyzer. Linear mobility was calculated according to the equation below:

$$\mu_{lin} = \frac{L}{WC_iV_D}\left(\frac{\partial I_{D\,lin}}{\partial V_G}\right)$$

And saturation mobility was extracted from the slope of $I_D^{1/2}$ vs. V_G:

$$\mu_{sat} = \frac{2L}{WC_i}\left(\frac{\partial \sqrt{I_{D\,sat}}}{\partial V_G}\right)^2$$

Transistor trap density was calcultaed according to the equation below:[3]

$$N_{tr} = \frac{C_i}{e^2}\left(\frac{eS}{kTln(10)} - 1\right)$$

Synthesis of copolymers. To a 20 mL glass vial was charged 3,9-dibromo-5,11-dihydro-5,5,11,11-tetrahexadecyl-s-indaceno[1,2-b:5,6-b']dithieno[3,2-b]thiophene

(0.50 mmol), bis(trimethyl stannyl)-monomer (0.50 mmol), $Pd_2(dba)_3$ (0.01mmol), (o-tol)$_3$P (0.04 mmol) and chlorobenzene (12 mL). This mixture was degassed with argon for 20 min. The vial was sealed then and placed in a microwave reactor and heated sequentially at 140 °C (2 min), 160 °C (2 min), and 180 °C (20 min). After cooling to 50 °C, the product mixture was poured into a mixture of methanol (100 mL) and conc. HCl (5 mL). The precipidate was collected by filtration and washed with water to give a crude product. This polymer was further purified by washing via Soxhlet xxtraction with methanol (24 h), acetone (24 h), hexane (24 h) then chloroform. Remaining palladium residues were removed by vigorously stirring the chloroform fraction with aqueous sodium diethyldithiocarbamate for 2 hours at 60 °C. The organic phase was then separated, washed with water, concentrated under reduced pressure and again precipitated in methanol, filtered off and dried under vacuum to afford the polymer.

IDTT-T: Red solid. Yield (79%). GPC (chlorobenzene, 80 °C): Mn = 48200 g/mol, Mw = 108000 g/mol; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (br, 2H, Ar-H), 7.32 (br, 2H, Ar-H), 7.17 (br, 2H, Ar-H), 1.81-2.38 (m, 8H, CH2), 0.97-1.45 (br, 104H), 0.71-0.96 (br, 20H, CH_2 and CH_3). Anal. Calcd.: $(C_{88}H_{138}S_5)_n$: C, 77.92; H, 10.26; Found: C, 77.39; H, 10.82.

IDTT-TT: Red solid. Yield (87%). GPC (chlorobenzene, 80 ºC): Mn = 74400 g/mol, Mw = 152000 g/mol; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (br, 2H, Ar-H), 7.37 (br, 2H, Ar-H), 7.32 (br, 2H, Ar-H), 1.67-2.39 (m, 8H, CH_2), 0.95-1.42 (br, 104H), 0.70-0.93 (br, 20H, CH_2 and CH_3). Anal. Calcd.: $(C_{90}H_{138}S_6)_n$: C, 76.53; H, 9.85; Found: C, 76.36; H, 9.74.

IDTT-DTT: Red solid. Yield (90 %). GPC (chlorobenzene, 80 ºC): Mn = 109000 g/mol, Mw = 186000 g/mol; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (br, 2H, Ar-H), 7.43 (br, 2H, Ar-H), 7.33 (br, 2H, Ar-H), 1.78-2.45 (m, 8H, CH_2), 0.96-1.49 (br, 104H), 0.61-0.95 (br, 20H, CH_2 and CH_3). Anal. Calcd.: $(C_{92}H_{138}S_7)_n$: C, 75.24; H, 9.47; Found: C, 75.17; H, 9.61.

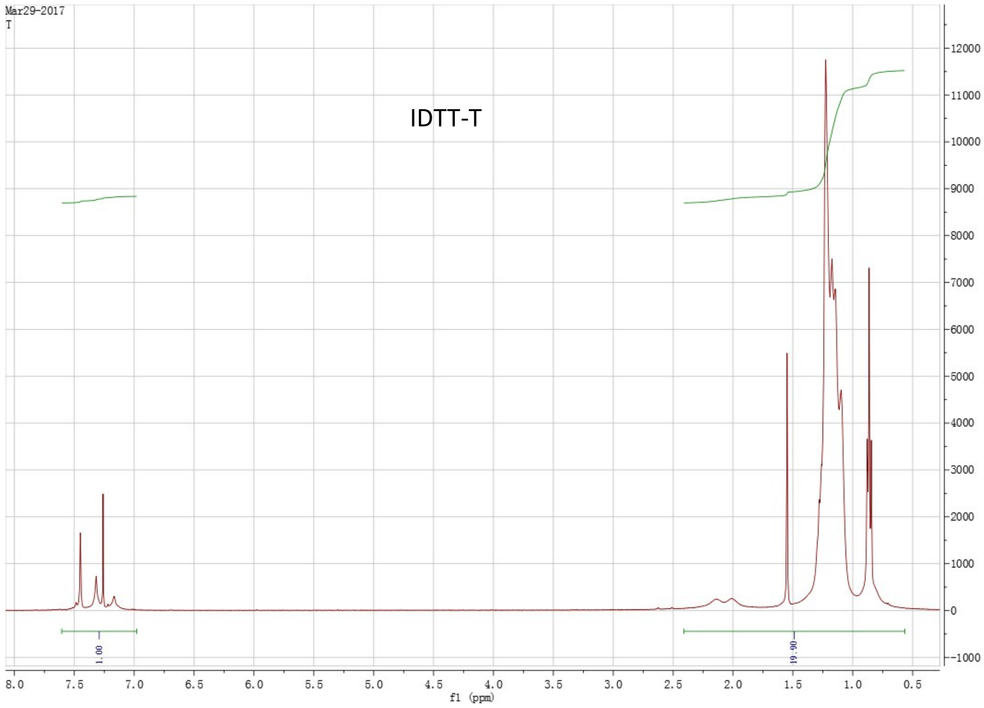


Figure S1. ^{1}H NMR spectra of IDTT-T in $CDCl_3$ at RT.

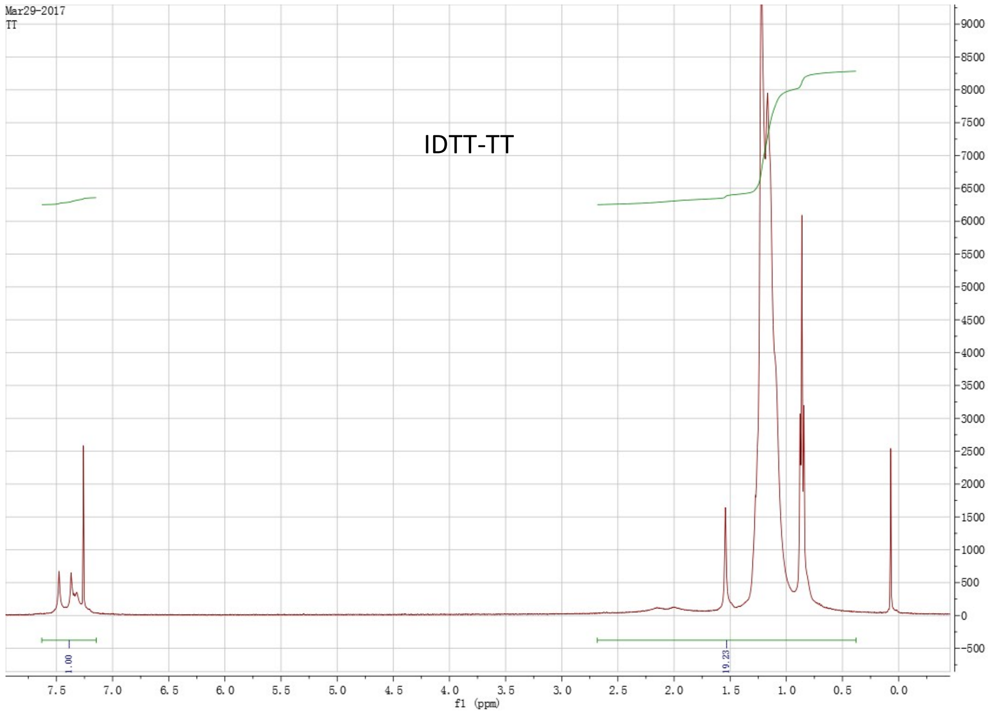


Figure S2. ^{1}H NMR spectra of IDTT-TT in $CDCl_3$ at RT.

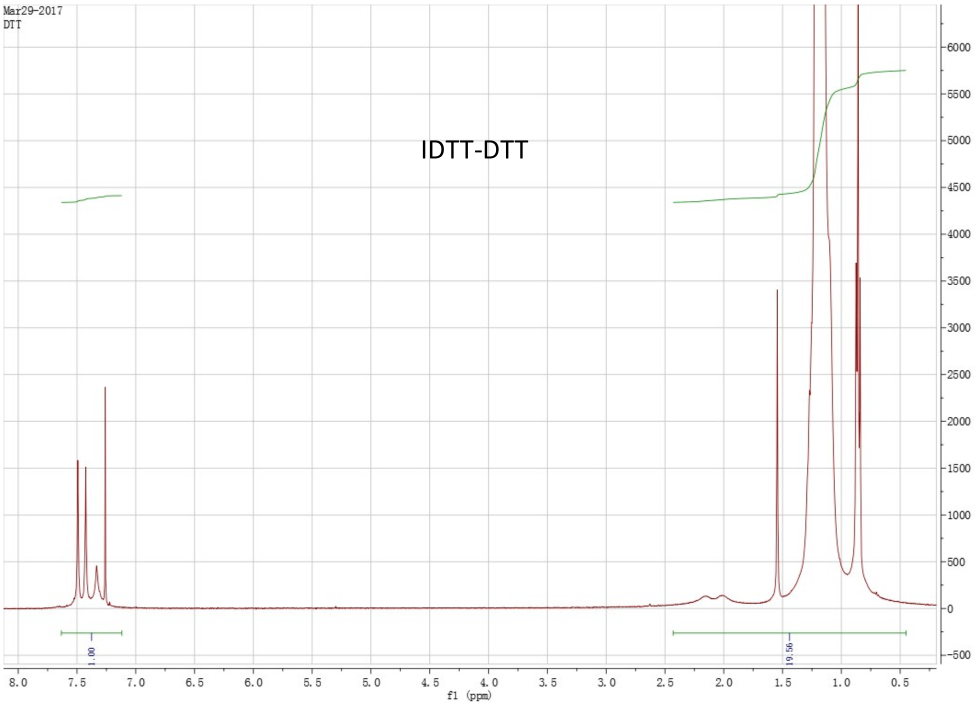


Figure S3. ^1H NMR spectra of IDTT-DTT in $CDCl_3$ at RT.

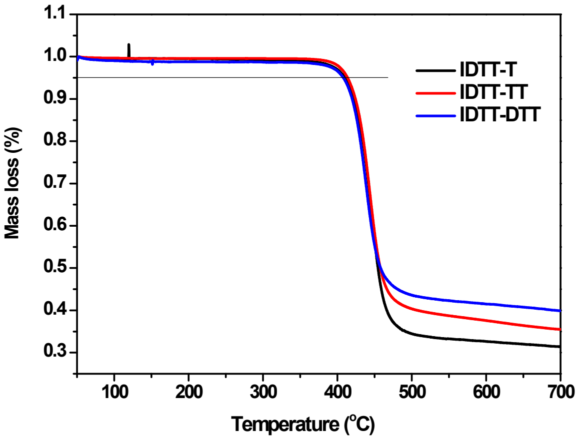


Figure S4. TGA plots of IDTT-T, IDTT-TT and IDTT-DTT with a heating rate of 20 ºC/min under nitrogen.

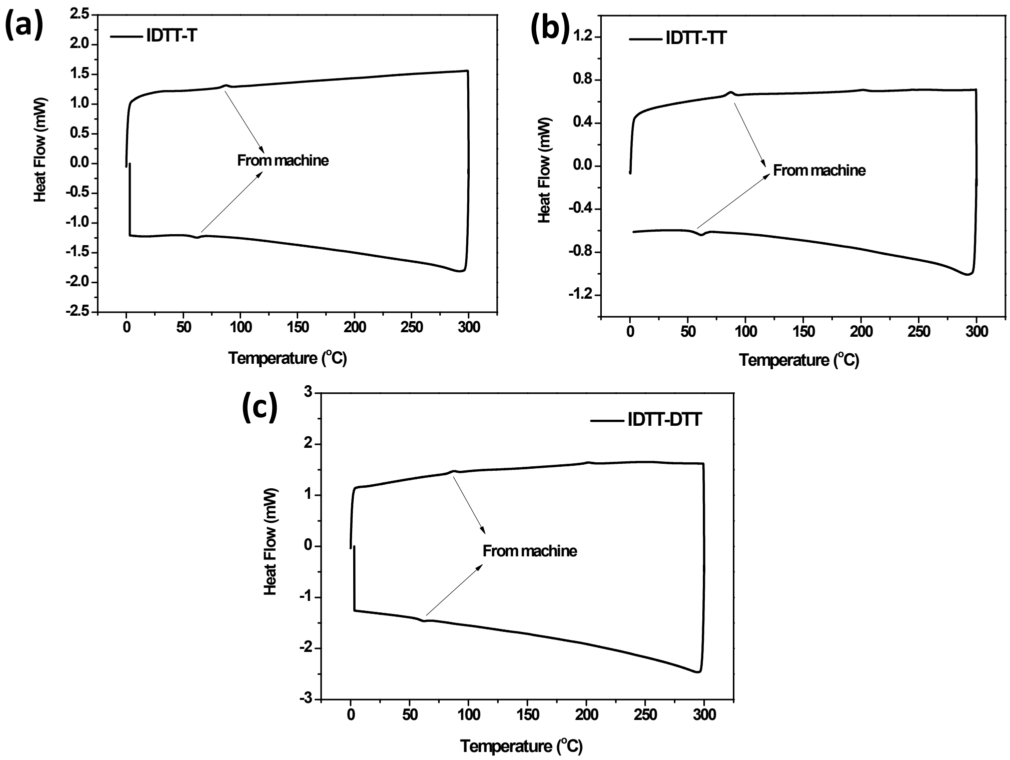
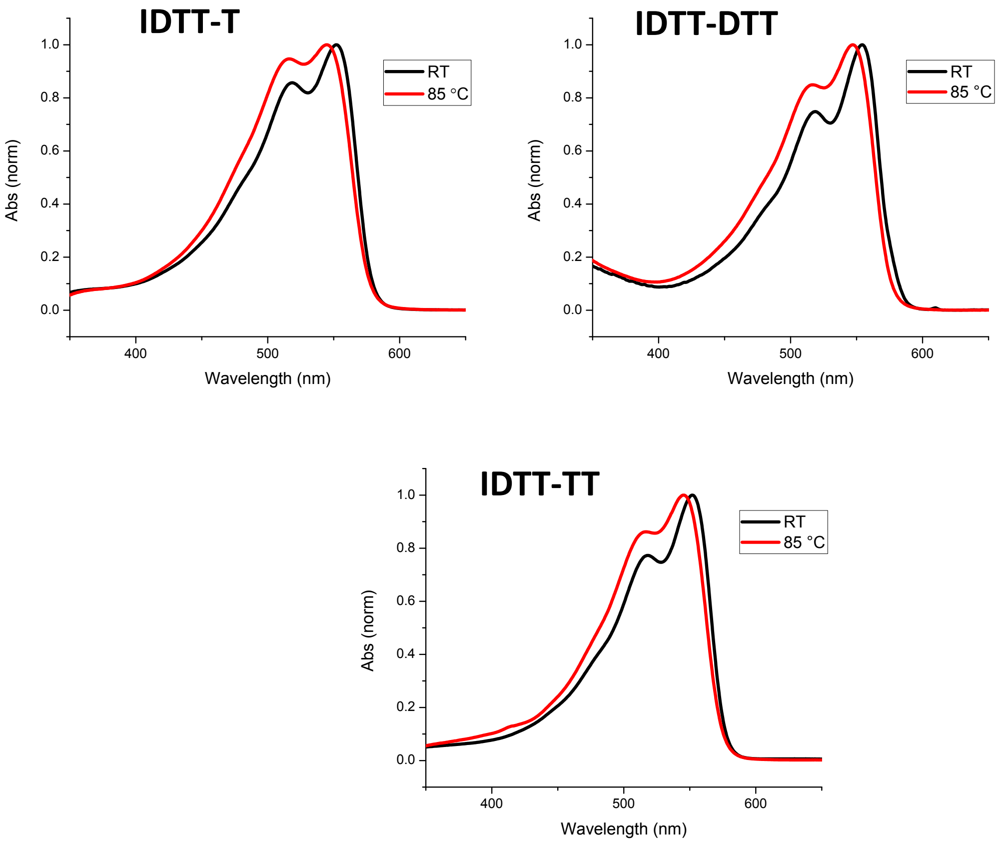


Figure S5. DSC trace (endo UP) of **IDTT-T** (a), **IDTT-TT** (b) and **IDTT-DTT** (c) recorded at a heating and cooling rate of 10 ºC/min under nitrogen.



Figures S6. UV/Vis spectra in CB solution at room temperature (black line) and 85 °C (red line)

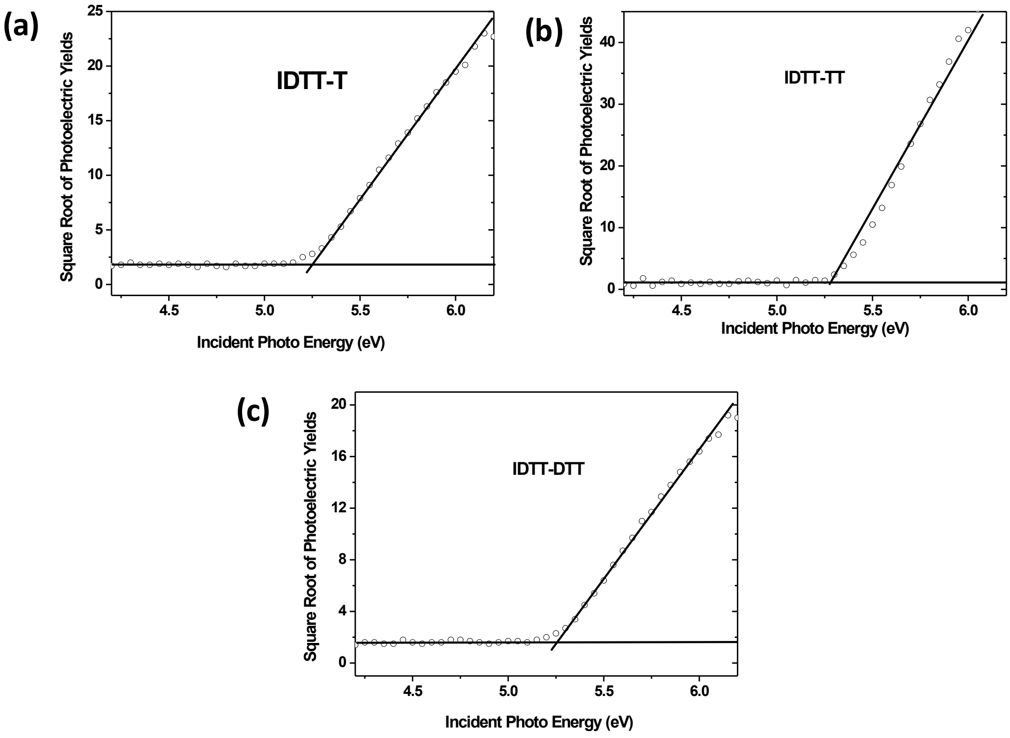


Figure S7. Photo electron spectroscopy in air of thin films of IDTT-T (a), IDTT-TT (b) and IDTT-DTT (c).

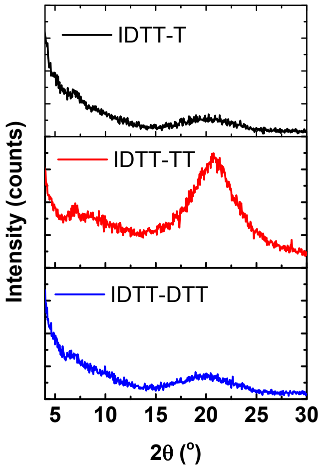


Figure S8. X-ray diffraction patterns of drop cast films of IDTT-T, IDTT-TT and IDTT-DTT after annealing at 200 °C.

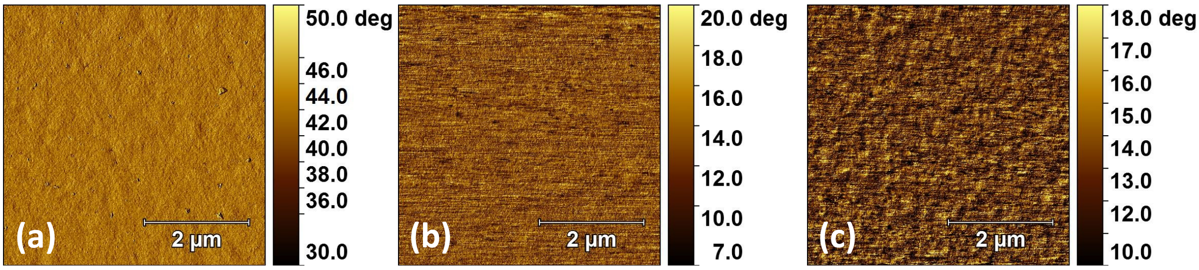


Figure S9. AFM phase images of thin film of IDTT- T (a), IDTT-TT (b), IDTT-DTT (c) after annealing at 200 °C.

References

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