

Supplementary Information

An alternating copolymer based on dithienothiophene and diketopyrrolopyrrole units for thin-film transistors and organic solar cells

Kang Yee Seah, Jun Li, Kok-Haw Ong, Siew-Lay Lim, Hoi-Ka Wong, Zhi-Kuan Chen

Institute of Materials Research and Engineering (IMRE), Agency for Science, Technology, and Research (A*STAR), 3 Research Link, Singapore 117602

Instrumentation and characterization:

¹H NMR data were acquired on a Bruker DPX 400 MHz spectrometer. Differential scanning calorimetry (DSC) was carried out under nitrogen on a TA Instrument DSC Q100 instrument (scanning rate of 10 °C min⁻¹). Thermogravimetric analysis (TGA) was carried out using a TGA Q500 instrument (heating rate of 10 °C min⁻¹). Molecular weight determinations were carried out in hot trichlorobenzene solution on a Shimadzu Prominence CBM-20A series HPLC using Agilent PLGel Olexis (300 x 7.5mm) column with polystyrene calibration standards. UV-Vis-NIR spectra were recorded on a Shimadzu model 2501-PC.

OTFT devices Fabrication:

Top-contact, bottom-gate TFT test devices were prepared in ambient conditions (humidity level ~55- 60%) without taking any special precautions to exclude air, moisture and ambient light. A heavily n-doped silicon wafer with a 200-nm thermal silicon dioxide (SiO₂) was used as the substrate/gate electrode, with the SiO₂ layer serving as the gate dielectric. The SiO₂/Si substrate was first immersed in acetone and ultrasonicated for 10 minutes, withdrawn and blown dry with nitrogen gas. It was then immersed again in a piranha solution (60ml of H₂SO₄ : 30ml of H₂O₂) for 8 minutes, followed by rinsing with deionized water, and then re-immersed in a solution of octyltrichlorosilane (OTS-8) in toluene at 60 °C for 20 minutes. It was then rinsed with toluene

and then blown dry with nitrogen gas. The semiconductor layer was deposited on top of the OTS-8-modified SiO₂ surface by spin coating a solution at a concentration of 4 mg mL⁻¹ of PDPP-T-DTT in 1,2-dichlorobenzene (DCB) at 800 rpm for 240 seconds and vacuum dried for 30 min to give a thin film semiconductor layer. Subsequently, gold source/drain electrode pairs were deposited by thermal evaporation through a metal shadow mask to create a series of TFTs with channel length (L) of 150 μm and width (W) of 4 mm. Silicon oxide at the backside of the silicon wafer of the TFT device was removed with sandpaper to provide a conductive gate contact.

Organic Photovoltaic Device Fabrication:

For the BHJ solar cells, polymer was dissolved in DCB solution at a concentration of 8 mg mL⁻¹. Blends of polymer with PC₇₁BM were prepared in the mass ratio of 1:1, 1:2 and 1:4 in DCB. The patterned ITO glass substrates were first sonicated in a detergent bath for half an hour, followed by rinsing with de-ionized water for 20 min. This was succeeded by sonicating in an acetone and iso-propanol bath for 15 min and 20 min respectively. The cleaning step was concluded by drying the substrates in an oven at 80 °C for at least an hour. The substrates were subjected to UV-ozone treatment for 10 min before a 40 nm thick PEDOT:PSS was spin-coated onto the ITO surface. The polymer/PCBM solution was then spin-coated onto the PEDOT:PSS layer at 1000 rpm for 120 seconds and left standing to dry for 2 hours. A 10 nm thick calcium layer, followed by 100 nm of silver, were deposited onto the blend layer via thermal evaporation to form the cathode. The active area of the device is 9 mm². Current density-Voltage (J-V) measurements were carried out in an inert environment (MBraun glovebox, N₂ atmosphere) under 1 Sun (AM1.5G) conditions using a solar simulator (SAN-EI Electric XES-301S 300W Xe Lamp JIS Class AAA).

Synthetic procedure for PDPP-T-DTT:

The monomers were weighed and added to a reaction vial equipped with a magnetic stirrer. The vial was then transferred to a glovebox where tetrakis(triphenylphosphine)palladium(0) (4 mol%) and anhydrous chlorobenzene (20 mL) were added. The vial was then stirred at 120 °C for 72 hours using an oil bath. The reaction mixture was poured into 200 mL of methanol and 15 mL of concentrated hydrochloric acid and stirred overnight to remove the stannylated end-groups. The polymers were subjected to sequential Soxhlet extraction with methanol and hexane for 24 h each to remove the small molecules and oligomers. Then the polymer was Soxhlet extracted with chloroform, precipitated into methanol and filtered to obtain the final product (93% yield). ^1H NMR (1,1,2,2-tetrachloroethane- d_4 , 400 MHz, 120 °C) δ 8.85 (s, 2H), 7.36-7.22 (m, 6H), 4.11 (s, 4H), 3.05 (s, 4H), 2.079 (s, 2H), 1.92 (s, 4H), 1.56-1.36 (m, 80H), 0.96-0.95 (m, 18H). Anal. calcd. for $\text{C}_{84}\text{H}_{122}\text{N}_2\text{O}_2\text{S}_7$: C, 71.24; H, 8.68; N, 1.98; S, 15.85. Found C, 71.95; H, 8.89; N, 1.77; S, 15.73.

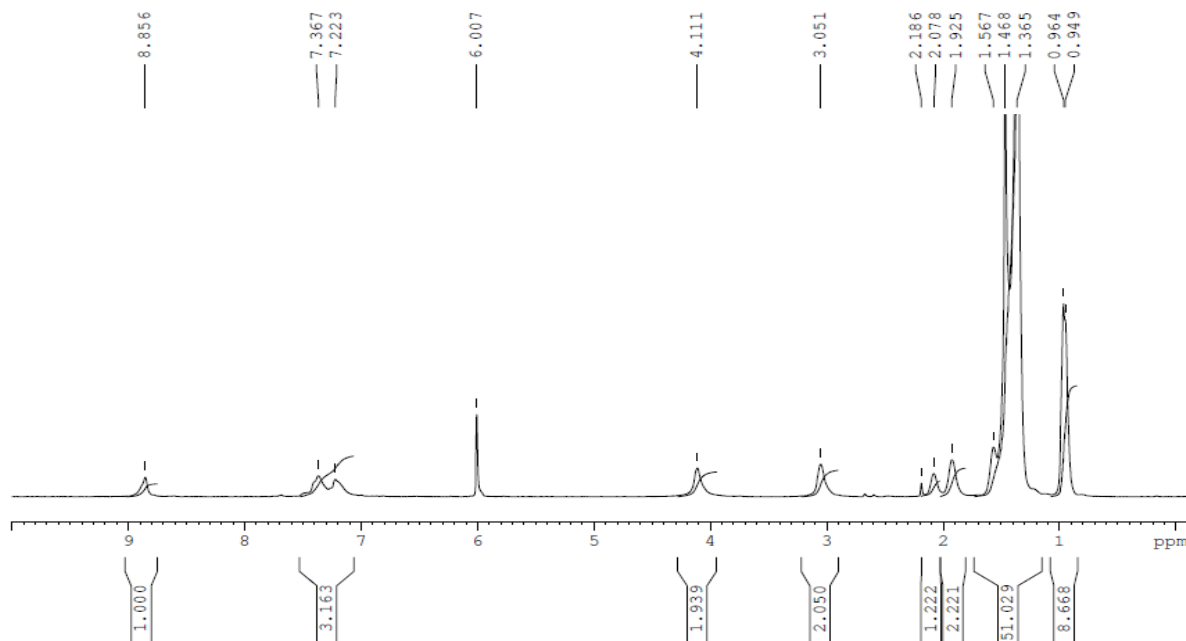


Figure S1. ^1H -NMR of PDPP-T-DTT.

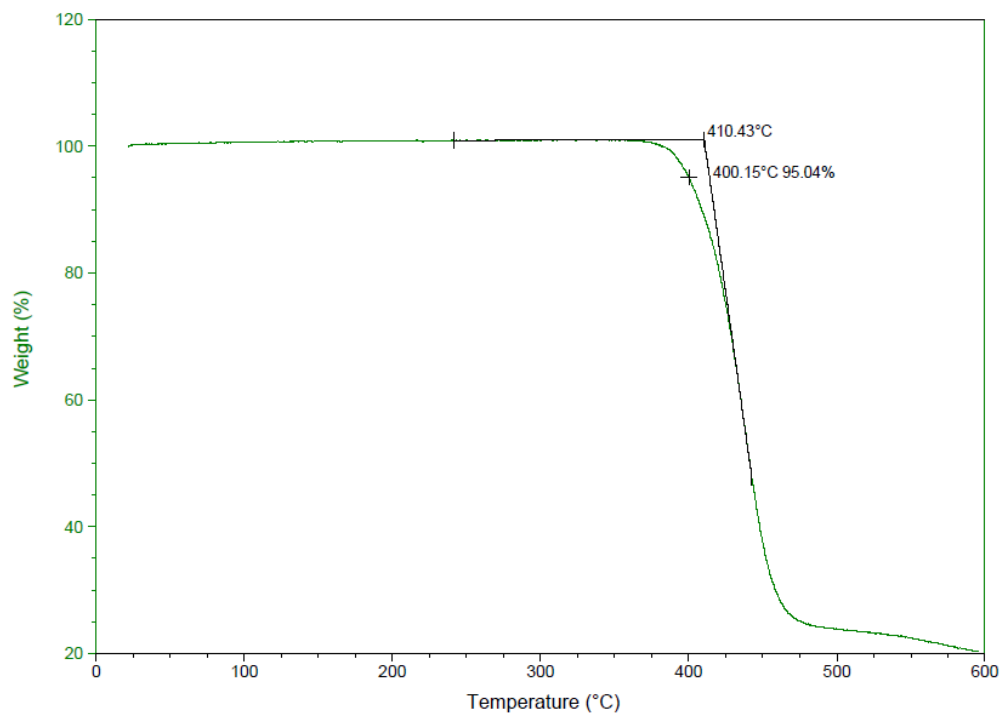


Figure S2. TGA thermogram of alternating PDPP-T-DTT with heating rate of 10 °C/min under nitrogen.

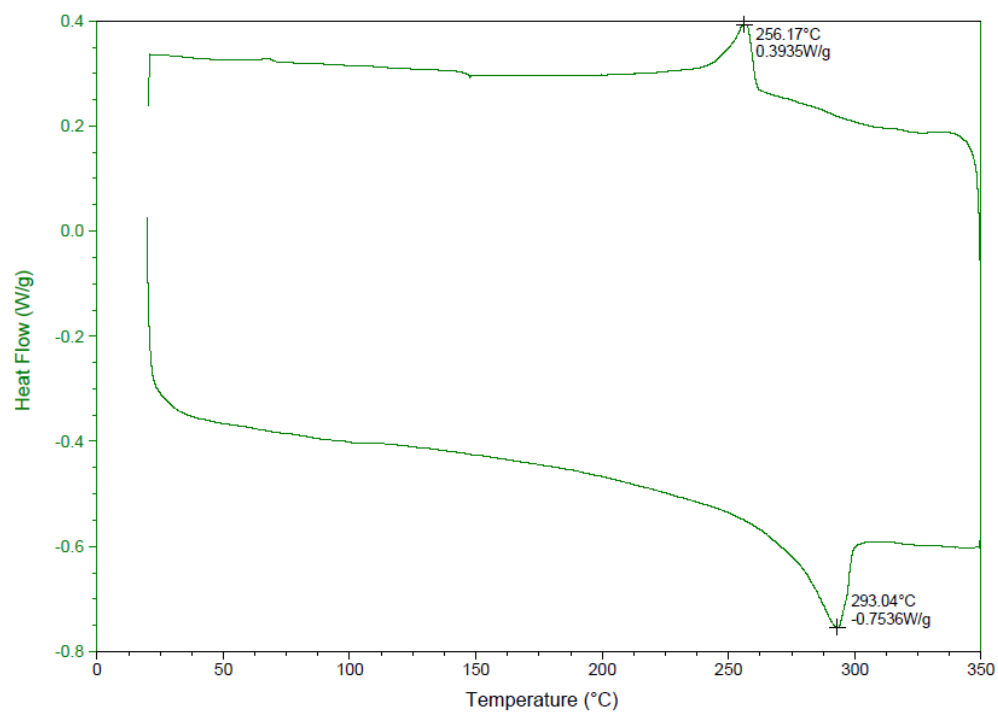


Figure S3. DSC thermogram of alternating PDPP-T-DTT with heating from room temperature to 350 °C and back to room temperature at a heating/cooling rate of 10 °C/min under nitrogen.