An Alternating 5, 5-Dimethylcyclopentadiene and Diketopyrrolopyrrole Copolymer Prepared at Room Temperature for High Performance Organic Thin-Film Transistors

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EXPERIMENTAL SECTION

General: All reactions were carried out in oven-dried glassware under Ar using solvents and reagents as commercially supplied, unless otherwise stated. 5,5-dimethylcyclopenta-1,3-diene-1,4-diyl bis(trifluoromethanesulfonate)¹ and 2,5-bis(2-octyldodecyl)-3,6-bis(5-(4,4,5,5-tetramethyl-1,3,2-

dioxaborolan-2-yl)thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione² were synthesised by the reported methods. The ¹H NMR spectrum was recorded on a Bruker AV-400 (400 MHz), using the residual solvent resonance of d_2 -1,1,2,2-tetrachloroethane and is given in ppm. Elemental Analysis was performed in a Thermo Scientific (Calro Erba) Elemental Analyser, configured for % C, H, and N. Number-average (M_n) and weight-average (M_n) molecular weight were determined by a Agilent Technologies 1200 series GPC running in chlorobenzene at 80 °C, using two PL mixed B columns in series, and calibrated against narrow polydispersity poly(styrene) standards. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry was performed on a Bruker ultrafleXtreme MALDI-TOF analyzer. Anthracene (or 2,5-dihydroxybenzoic acid) and myoglobin were used as the matrix and calibration internal standard, respectively. Thermal gravimetric analysis (TGA) was performed on a TA Instruments Discovery thermogravimetric analyzer at a heating rate of 20 °C/min to 700 °C. Differential scanning calorimetry (DSC) was performed on a TA Instruments Discovery differential calorimeter at a scan rate of 20 °C/min from *ca.* -20 °C to 270 °C. UV-vis spectra were recorded on a Cary-5000 spectrophotometer. Photo Electron Spectroscopy in Air (PESA) measurements was recorded with a Riken Keiki AC-2 PESA spectrometer with a power setting of 10 nW and a power number of 0.5. Samples for PESA were prepared on glass substrates by spin-coating.

Measurement of UV stability of PDPPCp and PDPPT:

For measuring the UV stability of the polymer, dilute solutions of **PDPPCp** and **PDPPT** in chlorobenzene were prepared and the UV-vis absorption spectra were recorded. The solutions were then stored on a bench top in ambient air and light for 24 hours, before the spectra were recorded again.

GIWAXS:

GIWAXS measurements were performed at the SAXS/WAXS beamline at the Australian Synchrotron.³ Two-dimensional scattering patterns were recorded on a Dectris Pilatus 1M detector with 11 keV photons used to probe the samples. An angle of incidence close to the critical angle ($\sim 0.13^\circ$) was used. The total exposure time was 3 s, with the reported images a composite of three separate 1 s exposures taken with different lateral detector offsets to fill in the regions missed by gaps in the detector. A silver behenate standard was used to calibrate the sample-to-detector distance. Results were analysed using NIKA 2D⁴ implemented in IgorPro.

OTFT (organic field effect transistor) device fabrication.

PDPPCp solutions were prepared by dissolving the polymer in chlorobenzene at a concentration of 10 mg/ml. Transistors were prepared by first thermally evaporating Au (40 nm) onto glass substrates through a shadow mask to form bottom source/drain (S/D) electrodes, that were then treated with self-assembled monolayer (SAM) of pentafluorobenzenethiol (PFBT) to improve the work function. The SAM treatment step was carried out by immersing the substrates with patterned Au electrodes in a solution containing 1:1000 of PFBT in ethanol for 30 min before rinsing off with plenty of ethanol to remove the excess materials and annealing at 100 °C for 15 min. Polymer was then spin coated at 1000 rpm for 60 s on top of the substrates with PFBT-treated bottom electrodes. The obtained films were then thermally annealed at 120 or 200 °C for 30 min under nitrogen. A layer of 900-nm CYTOP (Asahi Glass) dielectric was then deposited on top of the polymer layer by spin coating at 2000 rpm for 60 s followed by an annealing step at 100 °C for 30 min. The transistor structure was then completed by thermally evaporating 50 nm Al gate electrodes through a shadow mask, resulting in the bottom contact, top contact architecture. The channel width and length of the final transistors were 1000 µm and 30 or 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:

$$\mu_{\rm lin} = \frac{L}{WC_{\rm i}V_{\rm D}} \left(\frac{\partial I_{\rm D\,lin}}{\partial V_{\rm G}}\right)$$

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

$$\mu_{\text{sat}} = \frac{2L}{WC_{\text{i}}} \left(\frac{\partial \sqrt{I_{\text{D sat}}}}{\partial V_{\text{G}}} \right)^2$$

To insert a copper(I) thiocyante (CuSCN) thin layer between polymer film and Au electrodes instead of PFBT SAM, CuSCN was dissolved in diethyl sulfide at a concentration of 5 mg/mL and spin cast onto the substrates with pre-patterned Au electrodes at 5000 rpm for 60s. The obtained CuSCN thin film was annealed at

100 °C for 30 min under nitrogen. Polymer solution was then spin cast and annealed following the same procedures mentioned above for PFBT devices.

Polymer Synthesis

Poly{2,5-*bis*(2-octyldodecyl)-3,6-*di*(*thiophen*-2-*yl*)*pyrrolo*[3,4-*c*]*pyrrole*-1,4(2H,5H)*dione-alt*-5,5-*dimethylcycopenta*-1,3-*dien*-1,4-*diyl*}(**PDPPCp**).

5,5-dimethylcyclopenta-1,3-diene-1,4-diyl bis(trifluoromethanesulfonate) (92.2 mg, 0.236 mmol),

2,5-bis(2-octyldodecyl)-3,6-bis(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thioph en-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (262.9 mg, 0.236 mmol), Pd(dba)₂ (13.6 mg, 0.0236 mmol), and P(Cy)₃ (26.5 mg, 0.0946 mmol) were added into an oven-dried 20 mL high pressure microwave reactor tube. The tube was sealed and flushed with Ar, then degassed toluene (2 mL), THF (2 mL) and degassed aqueous 4.4 M KF (0.35 mL) were added. The mixture was thoroughly degassed under Ar, and then the argon inlet was removed. Then reaction was stirred at RT for 3 days. The polymer was precipitated in methanol (100 mL), and filtered through a Soxhlet thimble. The polymer was extracted using a Soxhlet apparatus with methanol, acetone, hexane and chloroform. The chloroform solution was concentrated in vacuo and re-precipitated into methanol. Vacuum filtration followed by drying under vacuum afforded **PDPPCp** as a dark-green solid (182 mg, yield: 87%). ¹H NMR (1,1,2,2-tetrachloroethane-*d*₄, 400MHz), δ (ppm): 9.05 (broad, 2H), 7.39 (broad, 2H), 7.01 (broad, 2H), 4.05 (broad, 4H), 2.00 (broad, 2H), 1.64 (broad, 6H), 1.37-1.23 (broad, 64H), 0.84 (broad, 12H). Anal. Calcd.: (C₆₁H₉₄N₂O₂S₂)_n: C, 77.00 ; H, 9.96; N, 2.94; Found: C, 76.94; H, 10.04; N, 3.02.

UV-Vis of PDPPCp:

In accordance with other DPP copolymers, absorbance bands in the high-energy region (*ca*. $\lambda = 350-450$ nm) are attributed to the π - π * transitions of the polymer backbone while those in the low-energy region (*ca*. 550 to 1000 nm) are ascribed to intramolecular charge transfer (ICT) from the electron-rich 5,5-dimethylCp unit to the electron-deficient DPP unit.⁵ The optical band gap of **PDPPCp** was estimated from the onset of film absorption to be *ca*. 1.31 eV, a value that is comparable to congeners bearing thiophene (*ca*. 1.30 eV)⁶ or selenophene (1.29 eV)⁷ in lieu of 5,5-dimethylCp.



Figure S1. ¹H NMR spectra of **PDPPCp**.



Figure S2. (a) Crude ¹H NMR spectrum of

2,5-bis(2-octyldodecyl)-3,6-bis(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thioph en-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (DPP-boronic ester) after stirring under the polymerization conditions for 3 days [in the absence of
5,5-dimethylcyclopenta-1,3-diene-1,4-diyl bis(trifluoromethanesulfonate)] (b) Crude ¹H NMR spectrum of DPP-boronic ester after stirring for 3 days under the polymerization conditions but in the absence of Pd(dba)₂ and
5,5-dimethylcyclopenta-1,3-diene-1,4-diyl bis(trifluoromethanesulfonate; (c) ¹H NMR spectrum of DPP-boronic ester.



Figure S3. (a) TGA thermogram of **PDPPCp** (heating rate of 20 °C/min under air; (b) DSC heating and cooling traces (second cycle) of **PDPPCp** at a scanning speed of 20 °C/min (endo up).



Figure S4. UV-vis spectra of **PDPPCp** and **PDPPT** in dilute chlorobenzene before and after exposure to ambient conditions for 24 h.



Figure S5. The structures of **DPPCp**, **DPPT** and **DPPBz** trimers.



Figure S6. Energy-minimized conformation (B3LYP/6-31G*) of methyl substituted DPPT (a) and DPPBz (b) trimers.



Figure S7. Transfer (a) and output (b) characteristics of BC/TG configuration OFET device with PDPPCp/Au-PFBT annealed at 120 °C. (c) Mobility calculation based on first derivative of the linear regime transfer curve and first derivative of the square root of the saturation regime transfer curve. (d) Device structure.



Figure S8 Transfer (a) and output (b) characteristics of BC/TG configuration OFET device with PDPPCp/Au-CuSCN annealed at 120 °C. (c) Mobility calculation based on first derivative of the linear regime transfer curve and first derivative of the square root of the saturation regime transfer curve. (d) Device structure.



Figure S9 GIWAXS integrated cake slices from 2D GIWAXS diffraction pattern in (a) and out of plane (b). Pole figure showing the orientation distribution for the (100) peak of
PDPPCp annealed at 120 °C and 200 °C (c). The gap in the plots around 0 is due to the inability of the GIWAXS geometry to measure near-specular at the (100) Bragg angle as a result of the fixed incident angle. Chi is the angle away from surface normal.



Figure S10. AFM phase images of **PDPPCp** (a) on glass surface and annealed at 120 °C; (b) on CuSCN surface and annealed at 120 °C; and (c) on CuSCN surface and annealed at 200 °C. Scan size: $1 \times 1 \ \mu m^2$.



Figure S11. AFM topography (a) and phase (b) images of CuSCN thin film on glass. Scan size: $1\times1~\mu m^2.$



Figure S12. AFM topography images of **PDPPCp** on glass surface and CuSCN surface and annealed at 120 °C before (a, b) and after spin-coating CYTOP solvent CT180 (c, d). Scan size: $1 \times 1 \ \mu m^2$.

| Annealing temperature | Alkyl Stacking | | | π-stacking | |
|--------------------------|-----------------|-------------------|------------------------------|-----------------|-------------------|
| | Spacing (nm) | Coherence (nm) | Orientation (S *) | Spacing (nm) | Coherence (nm) |
| 120 °C | 2.114(1) | 13.7(2) | -0.3520097 | 0.430(1) | 3(1) |
| 200 °C | 2.156(1) | 18.1(2) | -0.3584352 | 0.426(1) | 6(1) |

Table S1. Summary of GIWAXS data based on PDPPCp annealed at 120 and 200 °C.

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