Supporting Information

Linking Design and Properties of Purine-Based Donor-Acceptor Chromophores as Optoelectronic Materials

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Synthesis of 6-bromo-9-ethylhexyl-purine

A solution of 6-bromopurine (3.000 g, 15.07 mmol) and potassium carbonate (6.25 g, 45.22 mmol) in DMF (100 mL) was prepared in a 250 mL 3-neck round-bottom flask equipped with a Teflon stir bar and the resulting mixture was stirred for 20 min. Ethylhexyl-bromide (5.36 mL, 30.15 mmol) was then added and the reaction mixture was stirred for 24 h. After 24 h, the reaction mixture was poured into DCM (50 mL), washed with H₂O (3×100 mL), and the combined organic layers were dried with MgSO4 and filtered. The crude product was purified by flash chromatography on silica gel using hexanes and ethyl acetate (4:1 v/v). The collected fractions were dried, yielding a white solid (68% yield). ¹H NMR (500 MHz, CDCl₃), δ (ppm): 0.85-0.95 (m) 1.20-1.36 (m), 1.62 (br singlet), 1.91-2.03 (m), 4.18 (d, 2H, CH₂), 8.08 (s, 1H, purine H), 8.70 (s, 1H, purine H). ¹³C NMR (500 MHz, CDCl₃), δ (ppm): 10.39, 13.93, 22.82, 23.67, 28.35, 30.31, 39.75, 47.89, 134.00, 143.07, 145.33, 150.92, 151.84. AccuTOF DART (ESI): calc'd [M+H⁺]: 310.079, found [M+H⁺]: 310.080.

General Stille Cross-Coupling Procedure

6-bromo-9-ethylhexyl-purine (2 equiv.), the distannyl monomer (1 equiv.), and Pd(PPh₃)₄ (5 mol. %) were added to a single-neck 15 mL round bottom flask equipped with a Teflon stir bar and sealed with a rubber septa. The atmosphere was rendered inert via three evacuation and refill cycles with argon. Degassed toluene was added via syringe under an argon atmosphere and the reaction flask was placed in an oil bath set to 100 °C and the mixture was stirred for 18-24 h. After the allotted reaction time, the toluene was removed and the crude mixture was dissolved in DCM. The crude mixture was then passed through a pad of celite to remove palladium. The filtrate was then concentrated in vacuo and the desired product was purified via column chromatography.

P-BDT-P: Mobile phase: 6:1 v/v hexanes:ethyl acetate. Orange solid. ¹H NMR (500 MHz, CDCl₃), δ (ppm): 0.88 (t), 0.94-0.98 (m), 1.08 (t), 1.24-1.40 (m), 1.41-1.52 (m), 1.55-1.84 (m), 1.91-1.97 (m), 2.00-2.05 (m), 4.21 (d), 4.40 (d) ,8.09 (s, 1H,), 8.99 (s, 1H, purine H), 9.27 (s, 1H, purine H). ¹³C NMR (500 MHz, CDCl₃), δ (ppm): 10.44, 11.41, 13.96, 14.19, 22.90, 23.17, 23.72, 23.87, 28.42, 29.29, 30.39, 30.50, 39.79, 40.79, 47.39,

75.55, 127.29, 129.88, 130.61, 134.01, 140.22, 145.05, 145.94, 149.79, 152.30, 152.42. AccuTOF DART (ESI): calc'd [M+H⁺]: 906.5376, found [M+H⁺]: 906.3566.

P-Th-P: Mobile phase: 2:1 v/v hexanes:ethyl acetate. Yellow powder. ¹H NMR (500 MHz, CDCl₃), δ (ppm): 0.88 (t), 0.94 (t), 1.24-1.39 (m), 2.01 (m), 4.21 (d), 8.10 (s), 8.77 (s, 1H, purine H), 8.94 (s, 1H, purine H). ¹³C NMR (500 MHz, CDCl₃), δ (ppm): 10.43, 13.97, 22.89, 23.71, 28.40, 30.36, 39.75, 47.40, 129.26, 133.37, 144.40, 144.93, 149.51, 152.42, 152.61. AccuTOF DART (ESI): calc'd [M+H⁺]: 544.3096, found [M+H⁺]: 544.3086.

P-TBTT-P: Mobile phase: 100% DCM. Red solid. ¹H NMR (500 MHz, CDCl₃), δ (ppm): 0.88 (t), 0.95 (t), 1.24-1.40 (m), 1.60 (s, br), 2.01 (m), 4.22 (d), 8.06 (s, 2H, purine H), 8.09 (s, 2H, purine H), 8.31 (d, 2 H, thiophene H) 8.73 (d, 2H, thiophene H), 8.94 (s, 2H, BT H). ¹³C NMR (500 MHz, CDCl₃), δ (ppm): 10.42, 13.97, 22.89, 23.71, 28.39, 30.36, 39.72, 47.39, 120.63, 126.08, 128.93, 129.20, 133.27, 140.89, 143.94 144.78, 149.49, 152.37, 152.44. AccuTOF DART (ESI): calc'd [M+H⁺]: 761.2990, found [M+H⁺]: 761.2956.

NMR Spectroscopy



Figure S1. ¹H NMR spectrum (500 MHz, 25 °C, CDCl₃) of 6-bromo-9-ethylhexylpurine; δ (ppm): 0.85-0.95 (m) 1.20-1.36 (m), 1.62 (br singlet), 1.91-2.03 (m), 4.18 (d, 2H, CH₂), 8.08 (s, 1H, purine H), 8.70 (s, 1H, purine H).



Figure S2. ¹³C NMR spectrum (500 MHz, 25 °C, CDCl₃) of 6-bromo-9ethylhexylpurine; δ (ppm): 10.39, 13.93, 22.82, 23.67, 28.35, 30.31, 39.75, 47.89, 134.00, 143.07, 145.33, 150.92, 151.84.



Figure S3. ¹H NMR spectrum (500 MHz, 25 °C, CDCl₃) of **P-BDT-P**; δ (ppm): 0.88 (t), 0.94-0.98 (m), 1.08 (t), 1.24-1.40 (m), 1.41-1.52 (m), 1.55-1.84 (m), 1.91-1.97 (m), 2.00-2.05 (m), 4.21 (d), 4.40 (d), 8.09 (s, 1H,), 8.99 (s, 1H, purine H), 9.27 (s, 1H, purine H).



Figure S4. ¹³C NMR spectrum (500 MHz, 25 °C, CDCl₃) of **P-BDT-P**; δ (ppm): 10.44, 11.41, 13.96, 14.19, 22.90, 23.17, 23.72, 23.87, 28.42, 29.29, 30.39, 30.50, 39.79, 40.79, 47.39, 75.55, 127.29, 129.88, 130.61, 134.01, 140.22, 145.05, 145.94, 149.79, 152.30, 152.42.



Figure S5. ¹H NMR spectrum (500 MHz, 25 °C, CDCl₃) of **P-TBTT-P**; δ (ppm): 0.88 (t), 0.95 (t), 1.24-1.40 (m), 1.60 (s, br), 2.01 (m), 4.22 (d), 8.06 (s, 2H, purine H), 8.09 (s, 2H, purine H), 8.31 (d, 2 H, thiophene H) 8.73 (d, 2H, thiophene H), 8.94 (s, 2H, BT H).



Figure S6. ¹³C NMR spectrum (500 MHz, 25 °C, CDCl₃) of **P-TBTT-P**; δ (ppm): 10.42, 13.97, 22.89, 23.71, 28.39, 30.36, 39.72, 47.39, 120.63, 126.08, 128.93, 129.20, 133.27, 140.89, 143.94 144.78, 149.49, 152.37, 152.44.



Figure S7. ¹H NMR spectrum (500 MHz, 25 °C, CDCl₃) of **P-Th-P**; δ (ppm): 0.88 (t), 0.94 (t), 1.24-1.39 (m), 2.01 (m), 4.21 (d), 8.10 (s), 8.77 (s, 1H, purine H), 8.94 (s, 1H, purine H).



Figure S8. ¹³C NMR spectrum (500 MHz, 25 °C, CDCl₃) of **P-Th-P**; δ (ppm): 10.43, 13.97, 22.89, 23.71, 28.40, 30.36, 39.75, 47.40, 129.26, 133.37, 144.40, 144.93, 149.51, 152.42, 152.61.

Thermogravimetric Analysis



Figure S9. Thermogravimetric analysis of **P-BDT-P** ramping 20 °C to 800 °C at a rate of 10 °C/min. The mass loss at T_d is consistent with loss of ethylhexyloxy side chains from BDT.



Figure S10. Thermogravimetric analysis of **P-TBTT-P** ramping 20 °C to 800 °C at a rate of 10 °C/min. The degradation event is attributed to loss of the purine functionalities to generate Compound **3** (see Scheme 1 in *Article*) because the ethylhexyl-functionalized purines contribute ~60% of the mass of **P-TBTT-P**.



Figure S11. Thermogravimetric analysis of **P-Th-P** ramping 20 °C to 800 °C at a rate of 10 °C/min.

UV-Vis Spectroscopy



Figure S12. UV-Vis spectra (from 325-600 nm) at various concentrations (2.5-20 μ M) of **P-BDT-P** in chloroform and the corresponding Beer's Law plots using the absorbance maximums.



Figure S13. UV-Vis spectra (from 325-600 nm) at various concentrations (2.5-20 μ M) of **P-TBTT-P** in chloroform and the corresponding Beer's Law plots using the absorbance maximums.



Figure S14. UV-Vis spectra (from 325-600 nm) at various concentrations (2.5-20 μ M) of **P-Th-P** in chloroform and the corresponding Beer's Law plots using the absorbance maximums.

Cyclic Voltammetry



Figure S15: Cyclic voltammogram of **P-BDT-P** (0.01 mmol) recorded at a scan rate of 100 mV/s in dichloromethane (5 mL), (nBu)₄NPF₆ (0.20 M), versus Fc/Fc⁺.



Figure S16: Cyclic voltammogram of **P-TBTT-P** (0.01 mmol) recorded at a scan rate of 100 mV/s in dichloromethane (5 mL), $(nBu)_4NPF_6$ (0.20 M), versus Fc/Fc⁺.



Figure S17. Cyclic voltammogram of **P-Th-P** (0.01 mmol) recorded at a scan rate of 100 mV/s in dichloromethane (5 mL), $(nBu)_4NPF_6$ (0.20 M), versus Fc/Fc⁺.

Frontier Molecular Orbital Plots



Figure S18. Frontier molecular orbital plots of P-BDT-P.



Figure S19. Frontier molecular orbital plots of P-TBTT-P.



Figure S20. Frontier molecular orbital plots of P-Th-P.