Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Effect of Side Chain Length on Film Structure and Electron Mobility of Core-Unsubstituted Pyromellitic Diimides and Enhanced Mobility of the Dibrominated Core Using the Optimized Side Chain

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Experimental Section

General

^{1}H NMR spectra were recorded with a Bruker Avance 400 MHz spectrometer. Elemental analyses were performed by Atlantic Mircolab (Norcross, Georgia). DSC measurements were carried out with a TA Instruments DSC Q20 at a heating and cooling rate of 5 °C/min, with a nitrogen flow of 50 mL/min. The electrochemical measurements were carried out in dichloromethane solutions under nitrogen with 0.1M tetrabutylammonium hexafluorophosphate (NBu_4PF6) as the supporting electrolyte at room temperature using an EG&G Instruments 263A potentiostat/galvanostat. The cyclic voltammograms were obtained at a scan rate of 100 mV/s. A platinum disk and platinum wire were used as the working and counter electrode, respectively; Ag/AgCl in 3 M NaCl aqueous solution was used as the reference electrode. UV-vis absorption spectra were collected in dichloromethane solutions using a Varian Cary 50 Bio UV-Vis spectrophotometer. X-ray diffraction scans were acquired in the Bragg-Brentano (θ-2θ) geometry using a Phillips X-pert Pro X-ray diffraction system. The X-ray wavelength is 1.54 Å (Cu Kα). Scan step size was 0.02° and time per step was 2 seconds. Si/SiO_2 substrates were made from heavily-doped silicon wafers (Si Tech) with 300nm thermal oxide (Process Specialties) on top.

Synthesis

N, N'-Bis(1H,1H-perfluoropentyl)pyromellitic diimide (4-1-PyDI) was prepared as reported previously.[1] Other PyDI derivatives were synthesized using the same procedure of 4-1-PyDI: pyromellitic dianhydride was reacted with corresponding amines in DMF overnight at 110^{o}C, and the white solid obtained after filtration was further purified by sublimation under high vacuum.

N, N'-Bis(1H,1H-perfluorobutyl)pyromellitic diimide (3-1-PyDI) ^{1}HNMR (400MHz, $CDCl_3$): 8.46(s, 2H), 4.45(t, *J* = 15.0 Hz, 4H). Elemental analysis: Calcd for $C_{18}H_6F_{14}N_2O_4$, C, 37.26; H, 1.04; F, 45.84; N, 4.83. Found: C, 37.47; H, 1.00; F, 44.57; N, 4.92.

N,N'-Bis(1H,1H-perfluorohexyl)pyromellitic diimide (5-1-PyDI) ^{1}HNMR (400MHz, $CDCl_3$): 8.47(s, 2H), 4.46(t, *J* = 15.2 Hz, 4H). Elemental analysis: Calcd for $C_{22}H_6F_{22}N_2O_4$, C, 33.87; H, 0.78; F, 53.57; N, 3.59. Found: C, 33.93; H, 0.59; F, 53.58; N, 3.68.

N,N'-Bis(1H,1H-perfluoroheptyl)pyromellitic diimide (6-1-PyDI) ^{1}HNMR (400MHz, $CDCl_3$): 8.46(s, 2H), 4.44(t, *J* = 15.2 Hz, 4H). Elemental analysis: Calcd for $C_{24}H_6F_{26}N_2O_4$, C, 32.75; H, 0.69; F, 56.11; N, 3.18. Found: C, 33.63; H, 0.52; F, 56.20; N, 3.15.

N,N'-Bis(1H,1H-perfluorooxtyl)pyromellitic diimide (7-1-PyDI) ^{1}HNMR (400MHz, $CDCl_3$): 8.46(s, 2H), 4.45(t, J = 15.2 Hz, 4H). Elemental analysis: Calcd for $C_{26}H_6F_{30}N_2O_4$, C, 31.86; H, 0.62; F, 58.14; N, 2.86. Found: C, 31.69; H, 0.41; F, 57.89; N, 2.90.

N,N'-Bis(1H,1H-perfluorononyl)pyromellitic diimide (8-1-PyDI) ^{1}HNMR (400MHz, $CDCl_3$): 8.46(s, 2H), 4.45(t, J = 15.2 Hz, 4H). Elemental analysis: Calcd for $C_{28}H_6F_{34}N_2O_4$, C, 31.13; H, 0.56; F, 59.79; N, 2.59. Found: C, 30.97; H, 0.51; F, 59.87; N, 2.67.

N,N'-Bis(1H,1H-perfluoroundecanyl)pyromellitic diimide (10-1-PyDI) ^{1}HNMR (400MHz, $CDCl_3$): 8.46(s, 2H), 4.45(t, J = 15.2 Hz, 4H). Elemental analysis: Calcd for $C_{32}H_6F_{42}N_2O_4$, C, 30.02; H, 0.47; F, 62.32; N, 2.19. Found: C, 30.28; H, 0.36; F, 62.09; N, 2.25.

N,N'-Bis(3-(perfluoroctyl)propyl)pyromellitic diimide (8-3-PyDI) Elemental analysis: Calcd for $C_{32}H_{14}F_{34}N_2O_4$, C, 33.82; H, 1.24; F, 56.84; N, 2.47. Found: C, 34.07; H, 1.14; F, 56.93; N, 2.50.

N,N'-Bis(1H,1H-perfluoropentyl)-3,6-dibromopyromellitic diimide (Br2-4-1-PyDI). 1H,1H-perfluoropentyl amine (1.59g) was added into a solution of 3,6-diibromopyromellitic dianhydride[2] (0.8g) in dry THF (20mL) under nitrogen environment. The mixture was stirred at room temperature overnight. After removing the solvent under reduced pressure, anhydrous sodium acetate (0.70g) and acetic anhydride (15mL) were added. The mixture was heated at 100^0C under nitrogen for 3 hours. After pouring ice water, the precipitate was collected by filtration (1.55g, 87%) and purified by sublimation under high vacuum. ^{1}HNMR (400MHz, $CDCl_3$): 4.44(t, J = 15.2 Hz, 4H). Elemental analysis: Calcd for $C_{20}H_4F_{18}N_2O_4Br_2$, C, 28.66; H, 0.48; F, 40.81; N, 3.34. Found: C, 28.75; H, 0.30; F, 40.91; N, 3.44.

Device Fabrication and Characterization

Heavily-doped silicon with 300 nm thermal oxide dielectric layer on top was coated with octadecyltrimethoxysilane (OTS) or hexamethyldisilazane (HMDS) self-assembled monolayer. Thin-film transistors in top-contact/bottom-gate configuration were fabricated on the silicon substrate using thermally evaporated PyDIs (45nm) and gold (50nm) as the semiconducting layer and electrode, respectively. The channel widths were 6 mm, and the channel lengths were 250µm. Device characterization was performed using a Keithley 4200 Semiconductor Parameter Analyzer in a Janis Research ST-500-1 vacuum triaxial probe station. The transistor mobility μ was extracted from the $(I_D)^{1/2}$-V_G plot and the following equation:

$$I_D = \frac{W}{2L}\mu\, C_i(V_G - V_{TH})^2$$

where W and L are the device channel width and length, C_i is the capacitance of the 3000Å SiO_2 dielectric (1.15×10^{-9} F/cm^2), and V_{TH} is the threshold voltage.

Single Crystal Growth

Single crystals were grown by loading source material in a 5-inch long inner quartz tube (16 mm inner diameter/18 mm outer diameter) that was then put into another long outer quartz tube. All the tubes were pre-cleaned with HPLC grade acetone. The source was heated at 300°C for 3 hours in a flow of 99.999% pure He at 100 cm^3/min.

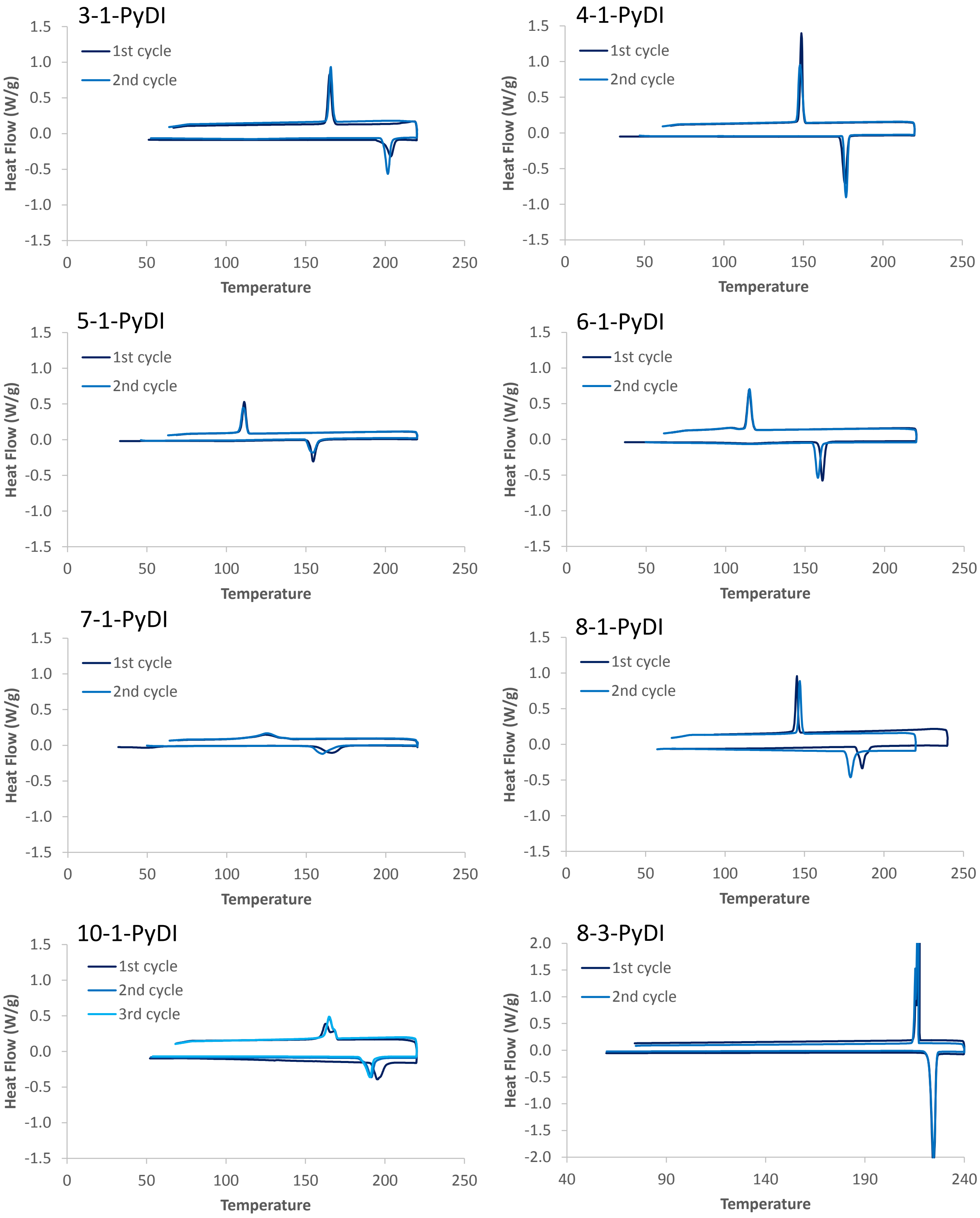


Figure S1 DSC Thermograms of the PyDI derivatives (exothermic up).

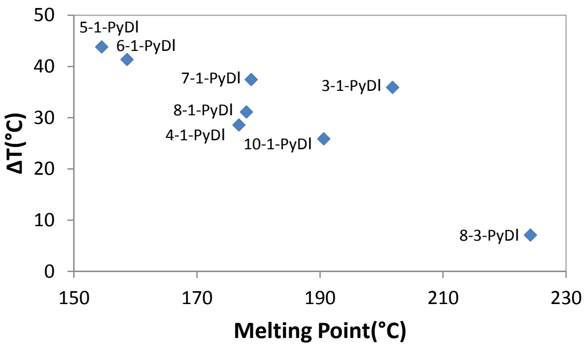


Figure S2 Hystereses from DSC Thermograms of the PyDI derivatives.

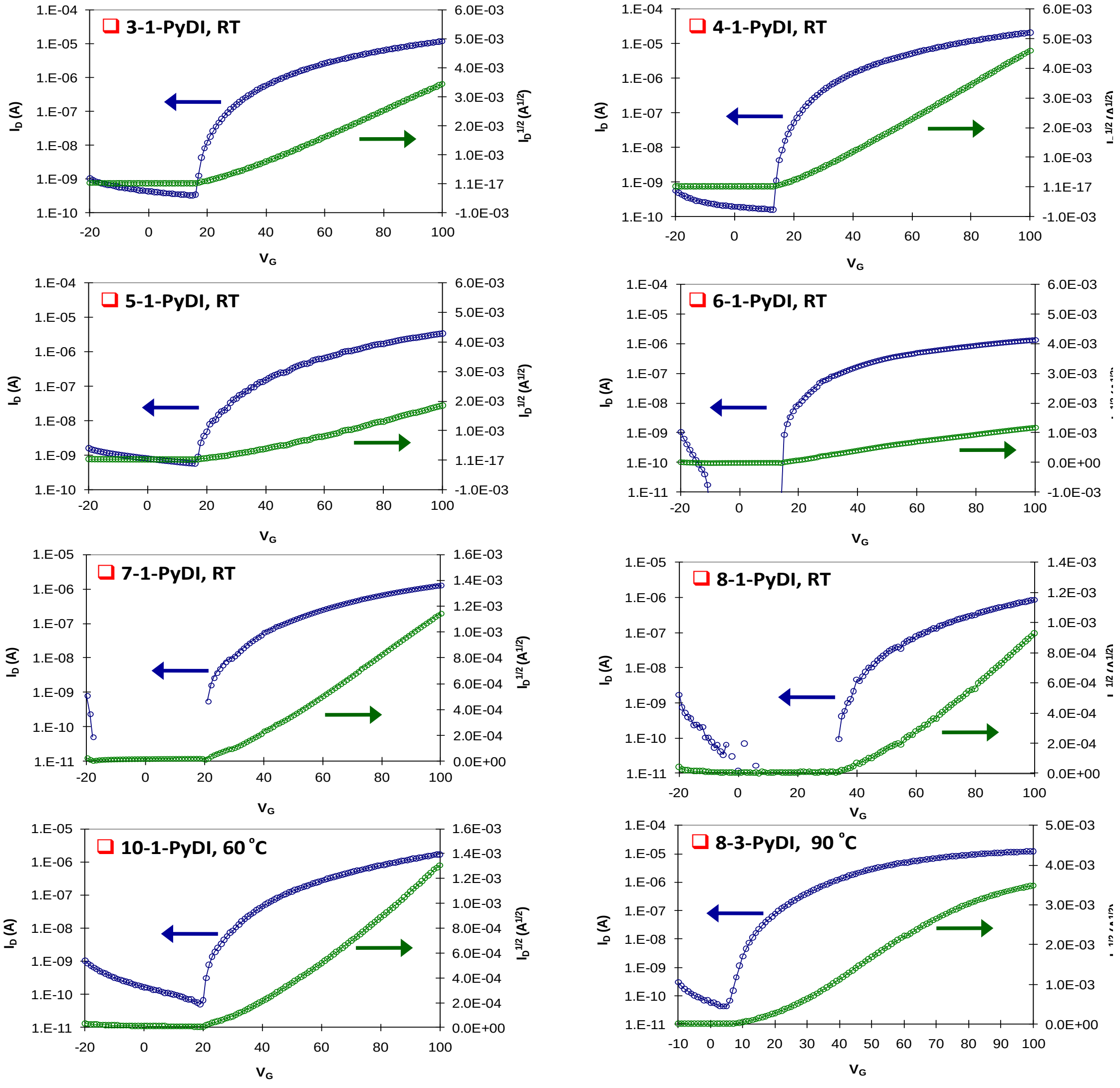


Figure S3 Transfer curves of transistors fabricated from series of PyDIs. Vd is kept constant at 100 V. The “most off” regions for 6-1, 7-1, and 8-1 compounds showed negative currents.

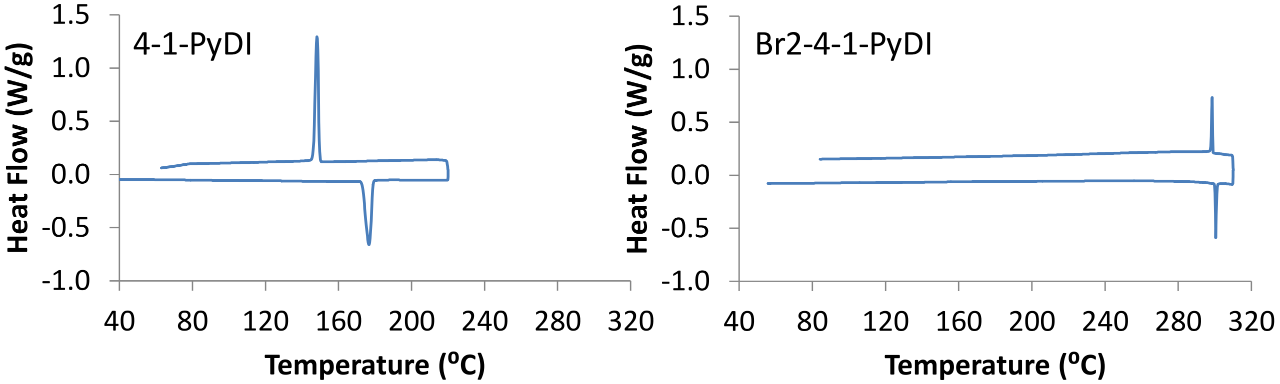


Figure S4 DSC Thermograms of 4-1-PyDI and Br2-4-1-PyDI (exothermic up).

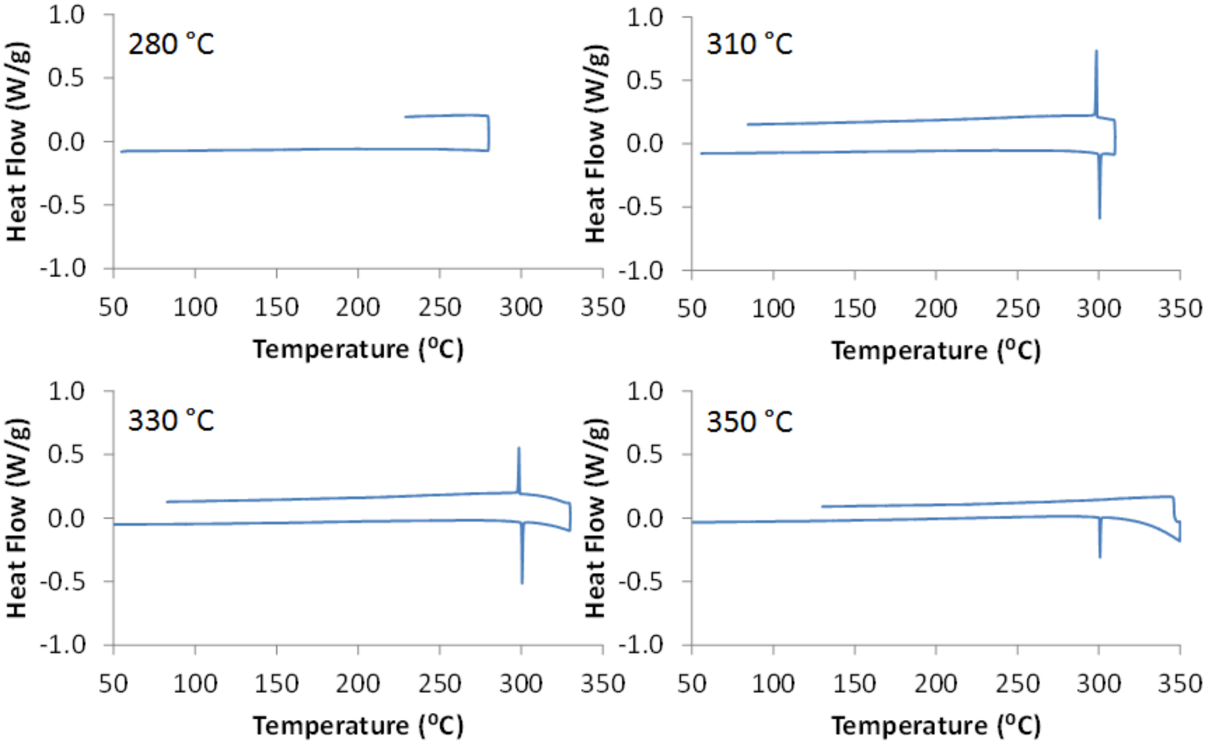


Figure S5 DSC of Br2-4-1-PyDI at different temperature range.

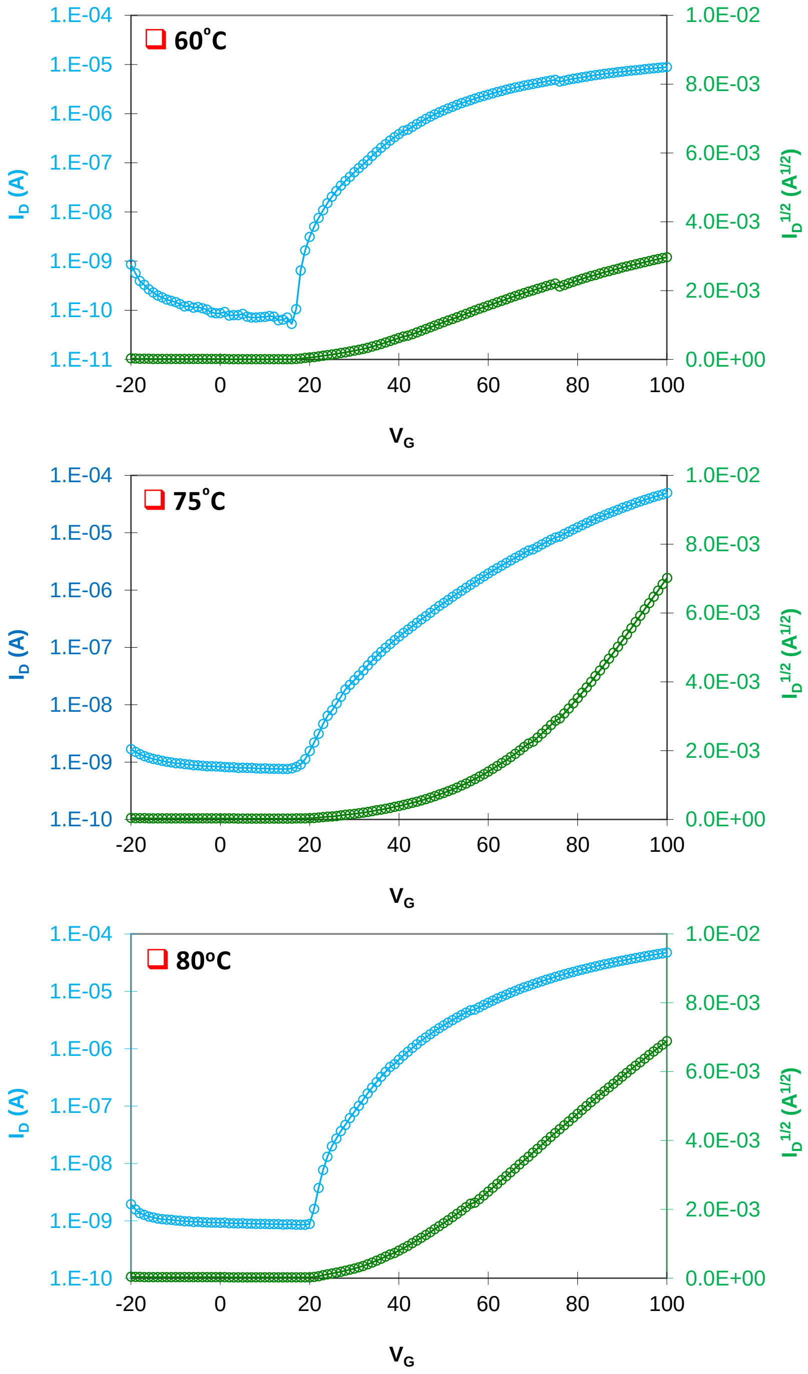


Figure S6 Transistor transfer curves of Br2-4-1-PyDI at different substrate temperature.

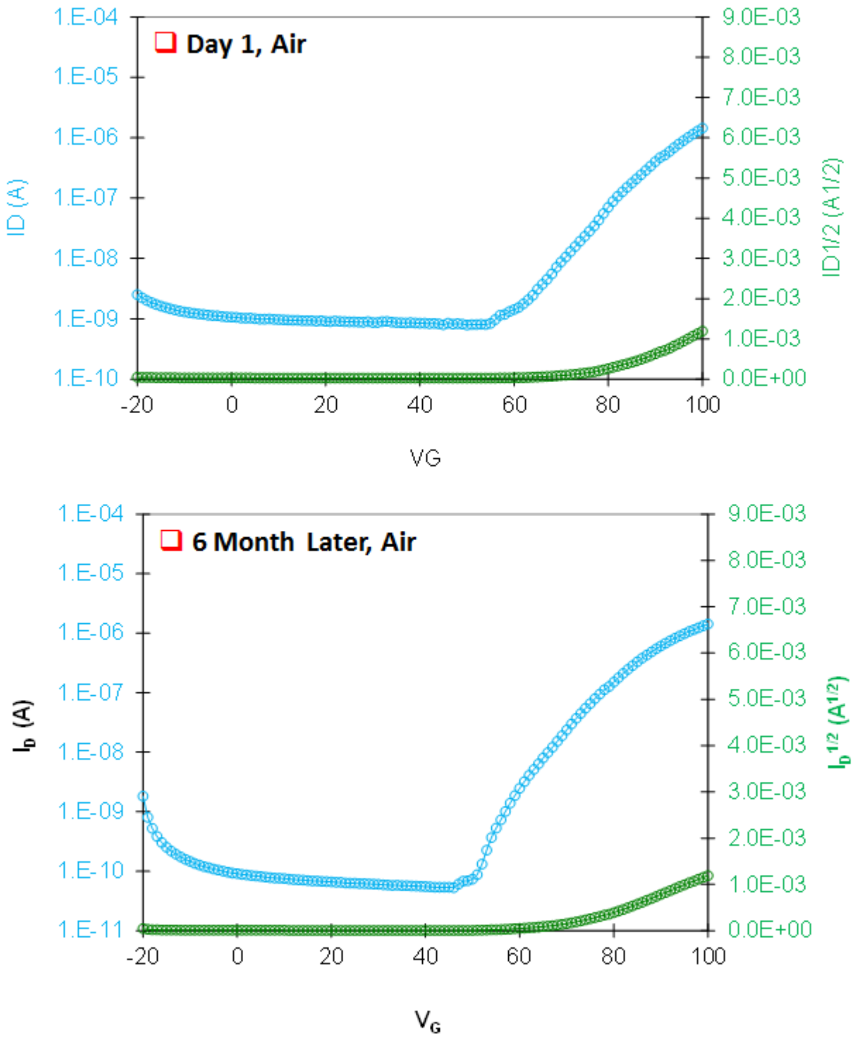


Figure S7 Transistor transfer curves of 75°C Br2-4-1-PyDI measured in air: day 1 and after six months.

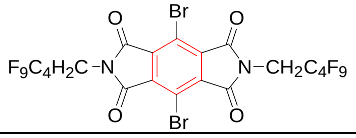
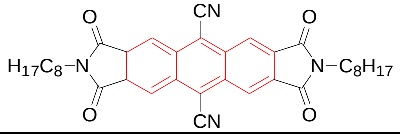
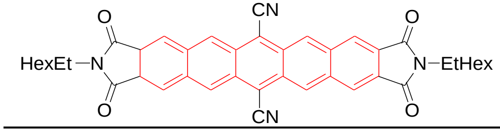
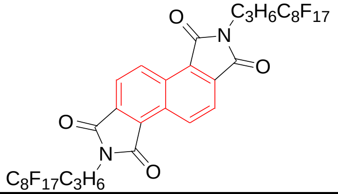
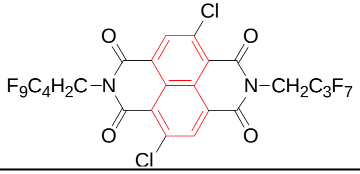
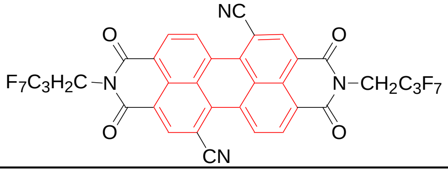
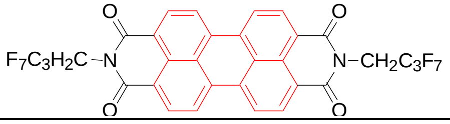
Compound	Mobility (cm^2/Vs)	Size of Conjugated Core (atoms)	LUMO	Bandgap (eV)	Number of Synthetic Steps	Reference
	0.2	6	-4.4	3.18	3	this work
	0.02	14	-4.3 (estimated)	2.58 (estimate)	5	(3)
	0.07*	22	-4.15	1.9	10	(4)
	0.52	10	N/A (low solubility)	N/A	4	(5)
	1.32	10	-4.01	2.91	5	(6)
	0.64	20	-4.5	2.3	3	(7)
	1.42	20	-3.85	N/A	1	(8)

Table S1 Highest electron mobility of different polycyclic aromatic hydrocarbon systems, along with their size of conjugated core, LUMO, bandgap, and number of synthetic steps. Mobilities are from devices made from vacuum process, except for the one marked with asterisk(*), which is from solution processes. The only compound that has a superior combination of mobility and high bandgap compared to the PyDI is the dichloro-NTCDI. As compared with the four somewhat dangerous steps to make the precursor anhydride for dichloro-NTCDI, PyDI can be obtained via a short and relatively benign reaction route.

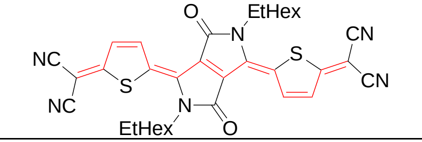
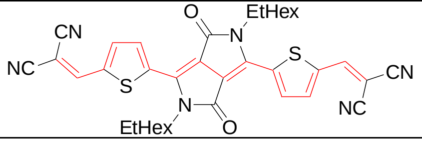
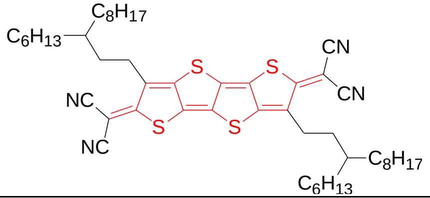
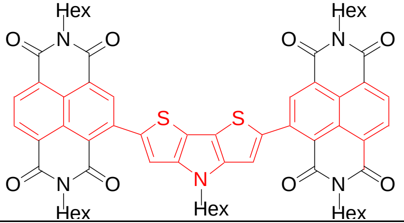
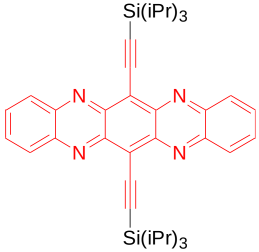
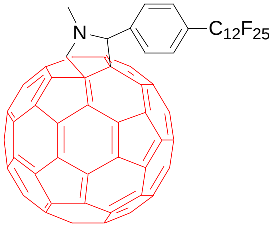
Compound	Mobility (cm^2/Vs)	Size of Conjugated Core (atoms)	LUMO	Bandgap (eV)	Number of Synthetic Steps	Reference
	0.50	14	-4.51	1.73	4	(9)
	0.39	16	-4.45	1.48	3	(10)
	0.43*	20	-4.30	1.8	6	(11)
	1.50*	31	-3.70	1.6	6	(12)
	1.87	26	-4.01	1.74	5	(13)
	0.25*	60	-3.63	N/A	4	(14)

Table S2 Highest electron mobility of different heterocyclic aromatic and fullerene systems, along with their size of conjugated core, LUMO, bandgap, and number of synthetic steps. Mobilities are from devices made from vacuum process, except for the ones marked with asterisk(*), which are from solution processes. High mobilities were demonstrated in many highly conjugated heterocyclic aromatic systems. However, their low bandgaps (< 2 eV) prohibit their use in wide bandgap applications, such as transparent displays and other transparent circuitry.

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