Electronic Supplementary Material (ESI) for Polymer Chemistry

Supporting Information

Isoindigo Dye Incorporated Copolymers with Naphthalene and Anthracene: Promising Materials for Organic Field Effect Transistors and Organic Photovoltaics

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Synthesis of 6, 6'-dibromoisoindigo:

To a suspension of 6-bromooxindole (4.26 g, 1.88 mmol) and 6-bromoisatin (4.00 g, 1.88 mmol) in AcOH (120 mL) was added conc. HCl (37%) solution (1.0 mL). The mixture was refluxed for 24 h. The mixture was allowed to cool and filtered. The solid material was washed with water, ethanol, and ether. After drying under vacuum, brown 6,6'-dibromoisoindigo (6.0 g, 75%) was obtained.

Synthesis of 6,6'-dibromo-N,N'-(2-octyldodecanyl)-isoindigo (1):

To a solution of 6,6'-dibromoisoindigo (1.02 g, 2.42 mmol), potassium carbonate (1.00 g, 7.26 mmol) in dimethylformamide (DMF) (80 mL), 1-iodo-2-octyldodecane (2.38 g, 5.82 mmol) was added under nitrogen. The mixture was stirred for 24 h at 100°C and then the solvent was removed under reduced pressure. The residues were purified by silica gel chromatography with eluting (hexane: dichloromethane; 5:1) to give 6,6'-dibromo-N,N'-(2-octyldodecanyl)-isoindigo as a deep-red solid. (1.5 g, 63 %). 1H NMR (CDCl3, 300 MHz, ppm) δ: 9.04-9.00 (d, 2H), 7.15-

7.11 (dd, 2H), 6.87 (d, 2H), 3.70-3.60 (m, 4H), 1.87 (m, 2H), 1.40-1.10 (m, 48H), 0.95-0.86 (m, 12H). 13C NMR(CDCl3, 100 MHz, ppm): δ 169.00, 146.27, 132.57, 131.06, 126.65, 125.10, 120.44, 111.55, 44.74, 36.11, 31.89, 31.84, 31.56, 29.95, 29.61, 29.59, 29.56, 29.50, 29.31, 29.25, 26.37, 22.65, 14.06, 14.04.

Synthesis of 2,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxabrolan-2-yl)naphthalene (2): 2,6-Dibromo-naphthalene (3.00 g, 10.49 mmol), bis(pinacolato)diboron (6.45 g, 25.18 mmol), $PdCl_2$(dppf) (1.85 g, 2.40 mmol), and potassium acetate (KOAc) (6.15 g, 61.52 mmol) were added in Schlenk flask and kept under vacuum for 10 min. Under an argon flow anhydrous 1, 4-dioxane (40 mL) was added to above mixture and the mixture was stirred at room temperature for 30 min before it was heated at 80°C and stirred for 20 h. The resulting mixture was quenched by adding water and extracted with ethyl acetate (100 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and filtered. After removing the solvent, a dark red solid was obtained, which was purified by silica gel chromatography by using 3 % ethyl acetate in hexane as eluent to give the title compound (**4**) as a white solid (2.5 g, 62 %). ^{1}H NMR (400 MHz, CDCl3): δ 8.35 (s, 2H), 7.85-7.84 (dd, 4H), 1.39 (s, 24H). ^{13}C NMR (100 MHz, CDCl3): δ 136.39, 134.73, 130.75, 128.08, 84.36, 25.32.

Synthesis of 2,8-bis(4,4,5,5-tetramethyl-1,3,2-dioxabrolan-2-yl)anthracene (3):2,8-Dibromo-anthracene (2.00 g, 6.46 mmol), bis(pinacolato)diboron (4.16 g, 16.16 mmol), $PdCl_2$(dppf) (0.164 g, 26.38 mmol), and potassium acetate (KOAc) (2.5 g, 26.38 mmol) were added in Schlenk flask and kept under vacuum for 10 min. Under an argon flow anhydrous 1, 4-dioxane (40 mL) was added to above mixture and the mixture was stirred at room temperature for 30 min before it was heated at 80 °C and stirred for 20 h. The resulting mixture was quenched by adding water and extracted with ethyl acetate (100 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and filtered. After removing the solvent, a dark red solid was obtained, which was purified by silica gel chromatography by using 3 % ethyl acetate in hexane as eluent to give the title compound (**4**) as a white solid (2.0 g, 71 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.55 (s, 2H), 8.44 (s, 2H), 8.01 (dd, 2H), 7.76 (dd, 2H), 1.39 (s, 24H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 137.68, 133.12, 132.23, 129.50, 127.80, 127.54, 84.38, 25.34.

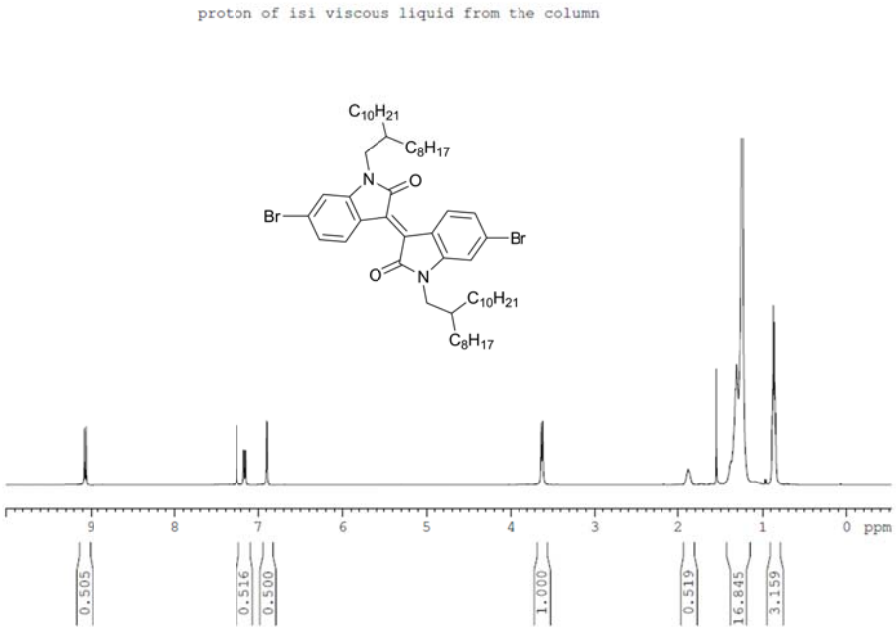


Figure S1. ^{1}H NMR of 36,6'-dibromo-N,N'-(2-octyldodecanyl)-isoindigo in $CDCl_3$ (**1**).

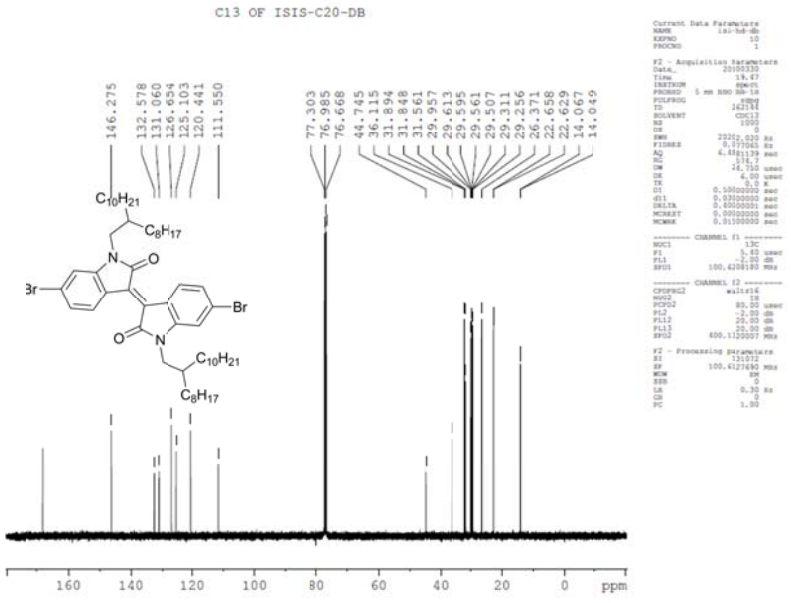


Figure S2. ^{13}C spectrum of 6,6'-dibromo-N,N'-(2-octyldodecanyl)-isoindigo in $CDCl_3$ (**1**).

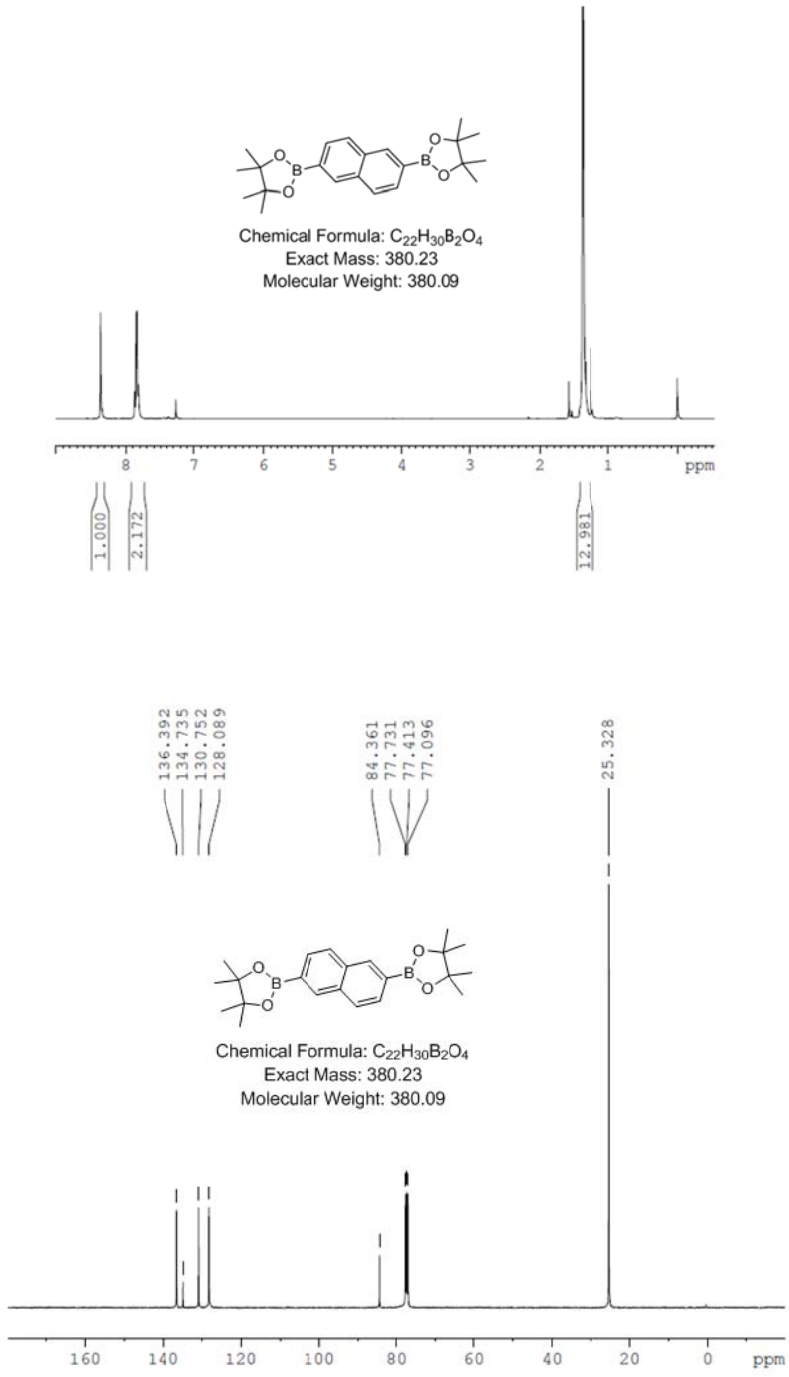


Figure S3. ^{1}H NMR and ^{13}C spectrum of 2,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxabrolan-2-yl)naphthalene (**2**) in $CDCl_3$.

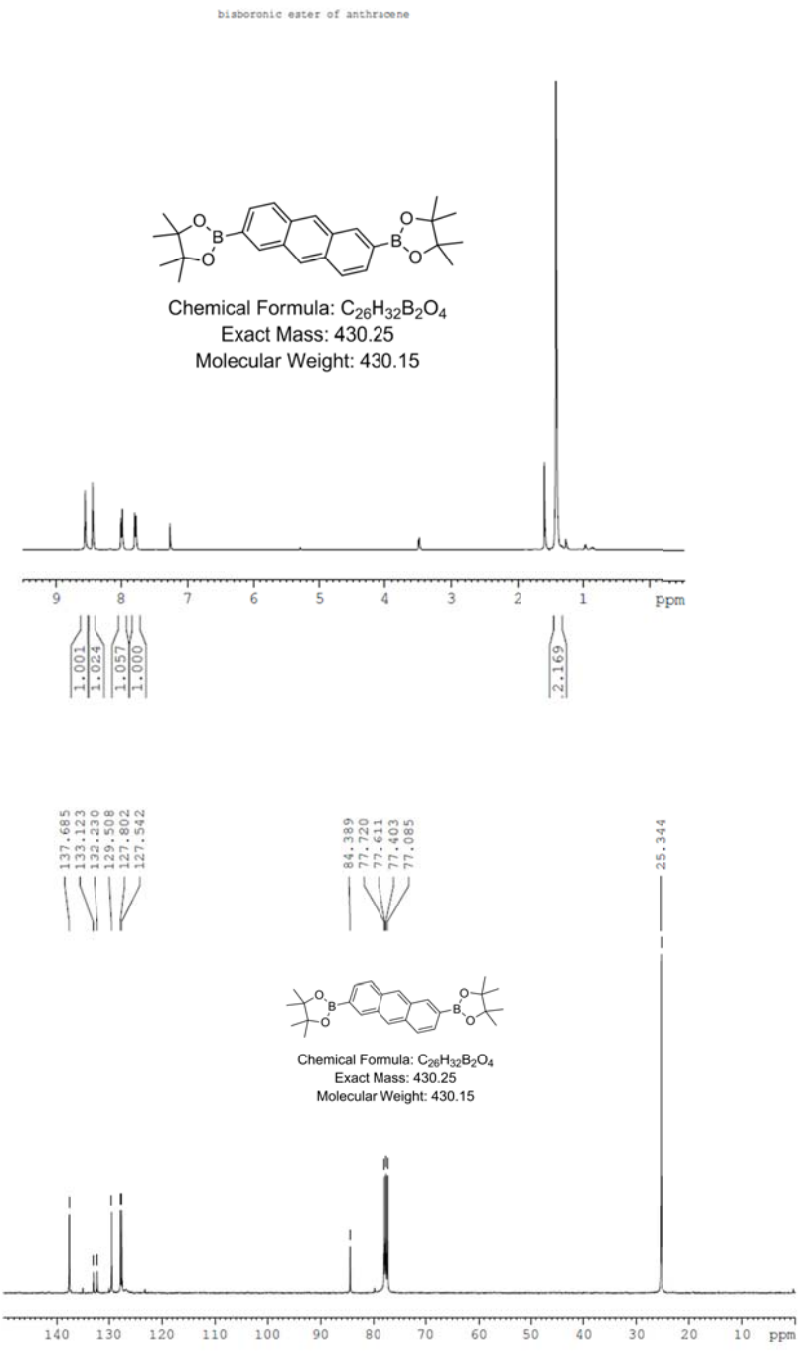
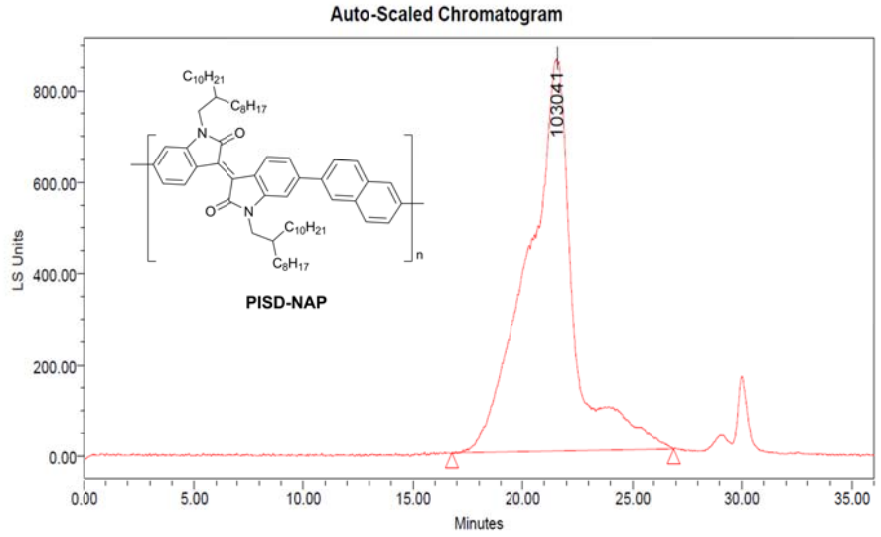


Figure S4. ^{1}H NMR and ^{13}C spectrum of 2,8-bis(4,4,5,5-tetramethyl-1,3,2-dioxabrolan-2-yl)anthracene in (**3**) $CDCl_3$.

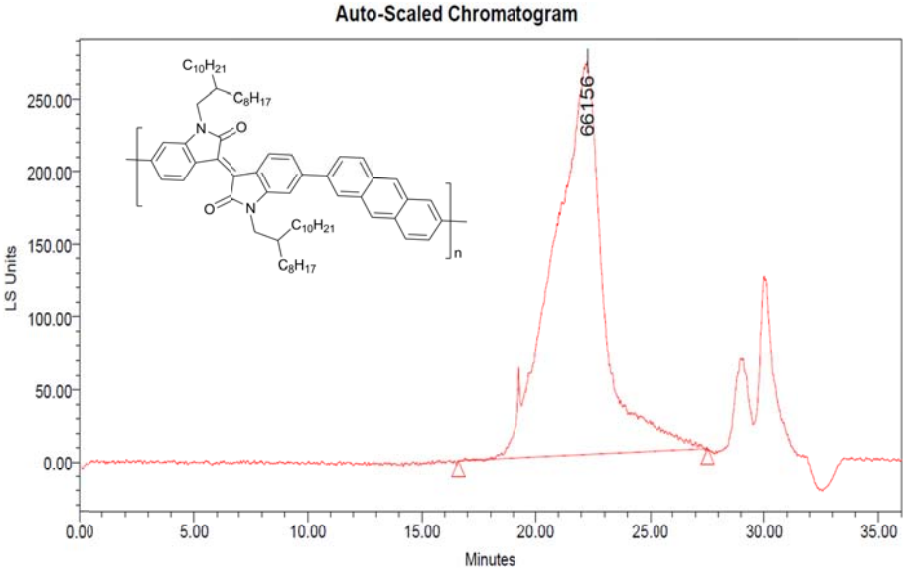
(a)



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		74190	215969	103041	488760	816419		2.911032		

(b)



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		55276	132786	66156	285258	524891		2.402241		

Figure S5. GPC elution curve and molecular weight of (a) **PISD-NAP** and (b) **PISD-ANT** using THF as eluent and PMMA as standards at a column temperature of 40°C.

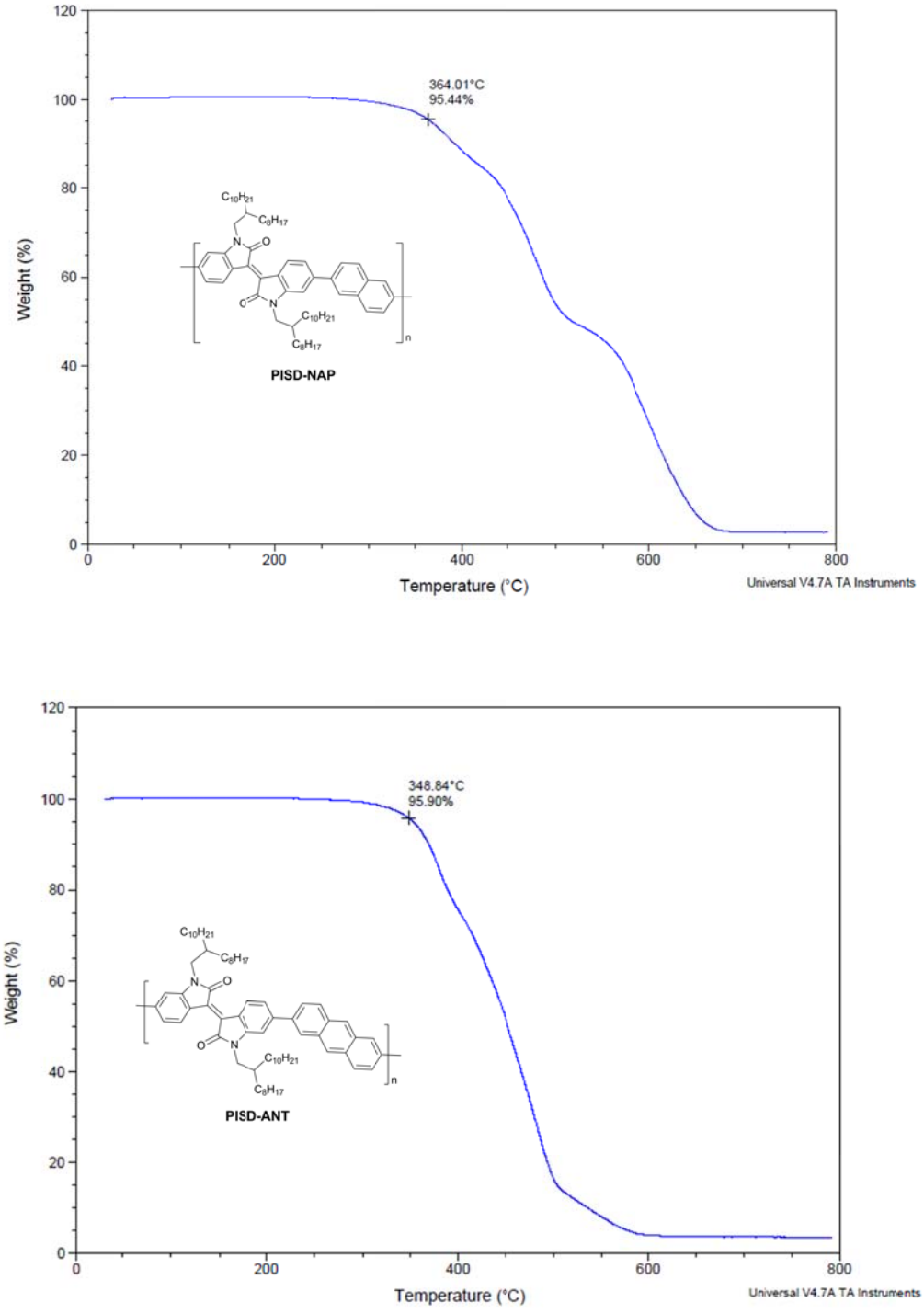


Figure S6. Thermogravimetric analysis (TGA) curves of (a) **PISD-NAP** and (b) **PISD-ANT** respectively.

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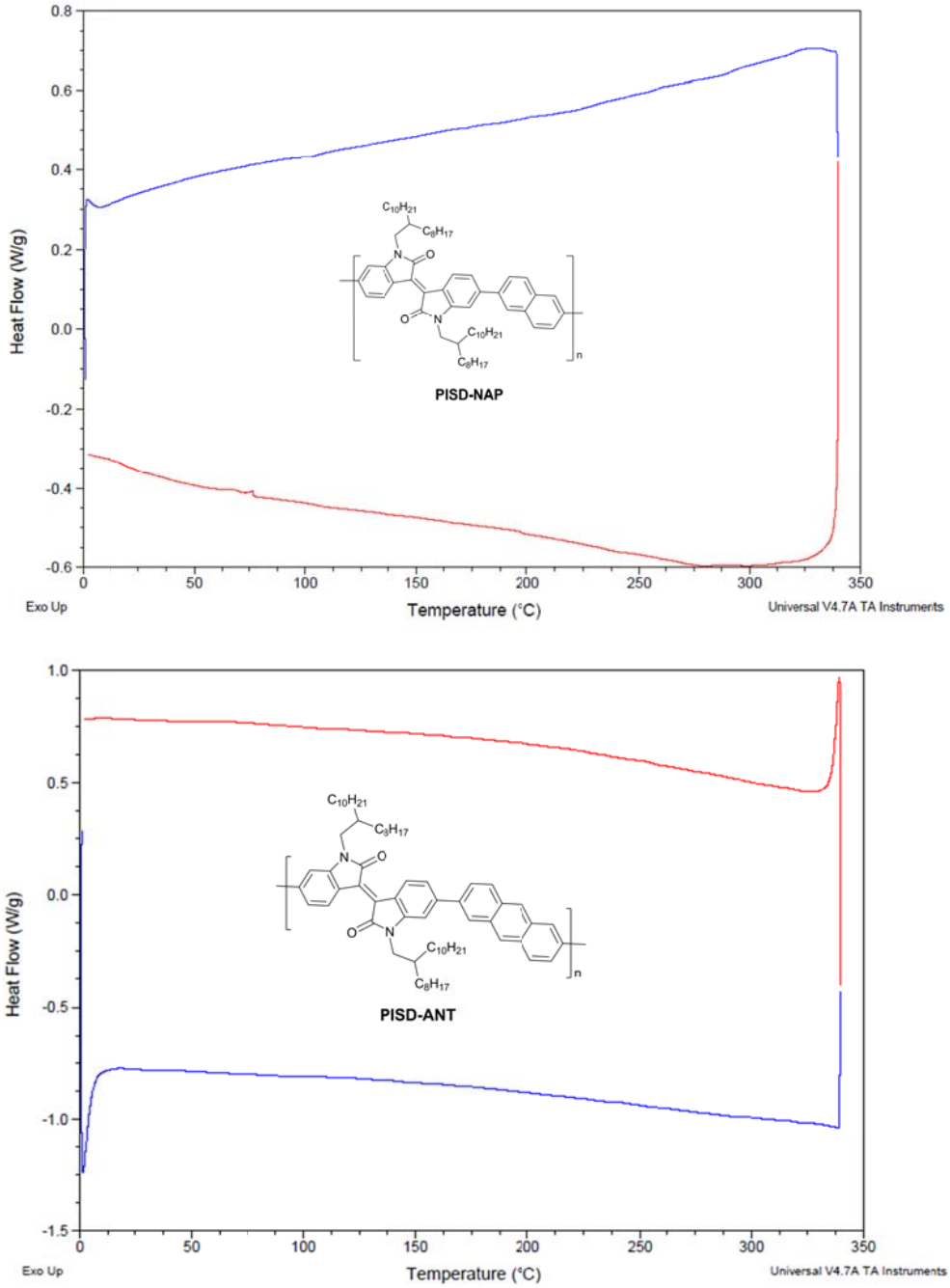

Figure S7. Differential scanning calarometry (DSC) graphs of (a) **PISD-NAP** and (b) **PISD-ANT** respectively.

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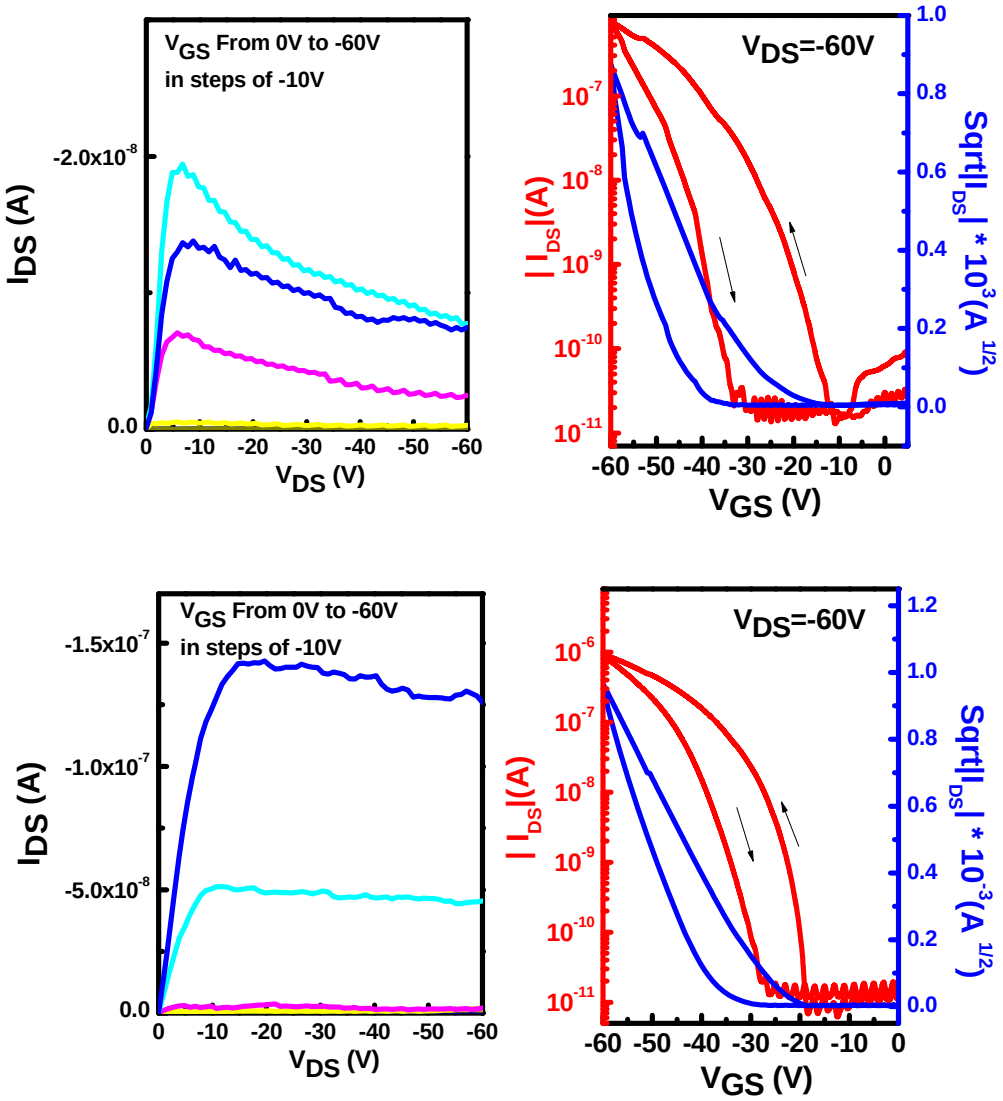

Figure S8. Field-effect transistor behavior of **PISD-NAP** and **PISD-ANT** polymers output characteristics (right) and transfer characteristics (left) for 60 nm thick film spin-coated from dichorobenzene (DCB) preannealed at 150° C(channel length 15µm, channel width = 4mm).