Supporting Information

Modulating Charge Transport Characteristics of Bis-azaisoindigo-based D-A Conjugated Polymers through Energy Level Regulation and Side Chain Optimization

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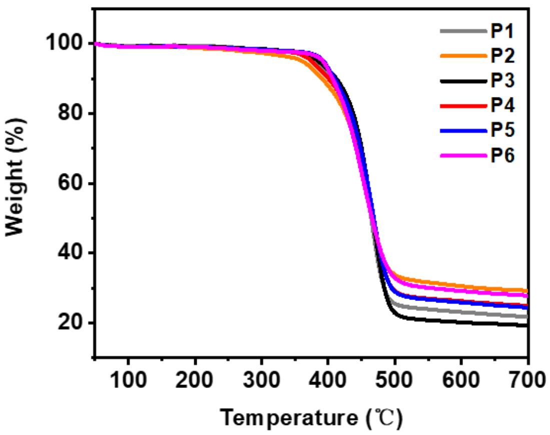


Figure S1. TGA curves of P1-P6.

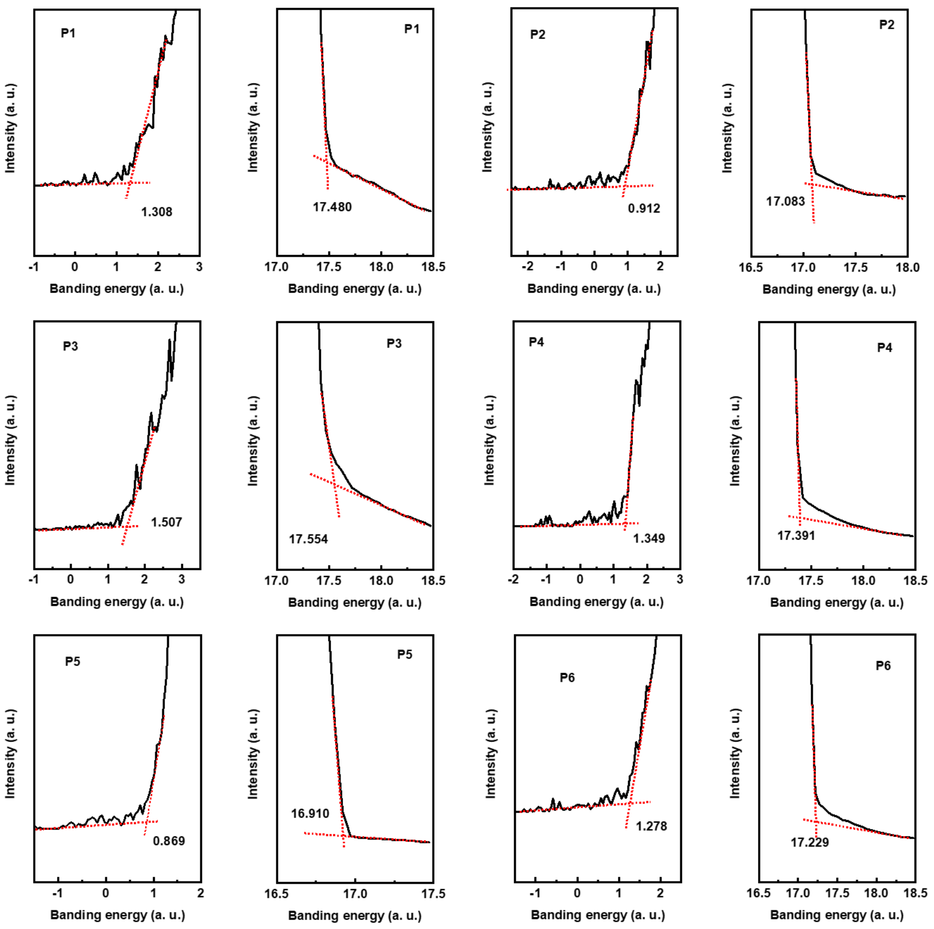


Figure S2. Ultraviolet photoelectron spectroscopy (UPS) spectra of P1-P6.

Table S1. GIXRD results of P1-P6.

Polymer	P1	P2	P3	P4	P5	P6
d-spacing (Å)	24.26	25.31	24.50	26.18	28.18	26.46
d-ππ (Å)	3.84	3.64	3.85	3.65	3.60	3.56

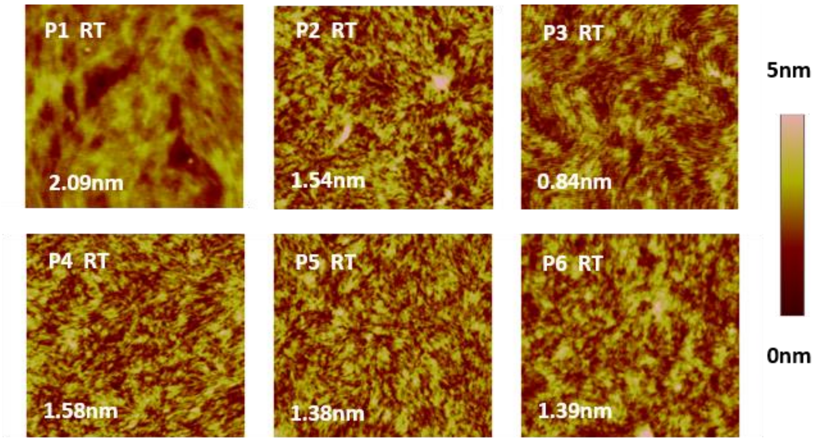


Figure S3. AFM topography images (2 µm × 2 µm) of P1-P6 films without annealing.

Table S2. The device performance of P1-P6.

Polymer	T (°C)	p ($cm^2v^{-1}s^{-1}$)		$V_{th\ ave}$ (V)	I_{on}/I_{off}	n ($cm^2v^{-1}s^{-1}$)		$V_{th\ ave}$ (V)	$I_{on/Ioff}$
		μ_{max}	μ_{ave}			μ_{max}	μ_{ave}		
P1	**RT**	**NA**	**NA**	**NA**	**NA**	**NA**	**NA**	**NA**	**NA**
	200	**1.0×10^{-2}**	**7.8×10^{-3}**	**-4**	**10^{2}-10^{3}**	**NA**	**NA**	**NA**	**NA**
P2	**RT**	**6.1×10^{-2}**	**3.5×10^{-2}**	**-38**	**10^{2}-10^{3}**	**0.13**	**0.11**	**60**	**10^{2}-10^{3}**
	200	**0.37**	**0.32**	**-15**	**10^{2}-10^{3}**	**7.1×10^{-2}**	**5.5×10^{-2}**	**73**	**10^{2}-10^{3}**
	260	**0.29**	**0.27**	**-8**	**10^{2}-10^{3}**	**8.3×10^{-2}**	**8.0×10^{-2}**	**61**	**10^{2}-10^{3}**
	290	**0.67**	**0.49**	**-6**	**10^{2}-10^{3}**	**4.5×10^{-2}**	**3.7×10^{-2}**	**64**	**10^{2}-10^{3}**
P3	**RT**	**5.9×10^{-3}**	**5.0×10^{-3}**	**-11**	**10-10^{2}**	**NA**	**NA**	**NA**	**NA**
	200	**1.8×10^{-2}**	**1.4×10^{-2}**	**-11**	**10-10^{2}**	**NA**	**NA**	**NA**	**NA**
P4	**RT**	**1.33**	**0.81**	**-23**	**10^{2}-10^{3}**	**0.31**	**0.29**	**66**	**10^{2}-10^{3}**
	200	**1.05**	**0.84**	**-22**	**10^{2}-10^{3}**	**0.39**	**0.30**	**61**	**10^{2}-10^{3}**
	260	**0.70**	**0.56**	**-30**	**10^{2}-10^{3}**	**0.94**	**0.75**	**74**	**10^{2}-10^{3}**
	290	**0.70**	**0.57**	**-12**	**10^{2}-10^{3}**	**0.58**	**0.47**	**58**	**10^{2}-10^{3}**
P5	**RT**	**0.97**	**0.86**	**-28**	**10^{2}-10^{3}**	**0.61**	**0.54**	**62**	**10^{2}-10^{3}**
	200	**1.19**	**1.01**	**-26**	**10^{2}-10^{3}**	**0.88**	**0.72**	**61**	**10^{2}-10^{3}**
	260	**1.66**	**1.39**	**-22**	**10^{2}-10^{3}**	**0.61**	**0.50**	**68**	**10^{2}-10^{3}**
	290	**0.96**	**0.78**	**-15**	**10^{2}-10^{3}**	**0.62**	**0.56**	**57**	**10^{2}-10^{3}**
P6	**RT**	**0.93**	**0.76**	**-36**	**10^{3}-10^{4}**	**0.86**	**0.80**	**61**	**10^{3}-10^{4}**
	200	**1.54**	**1.31**	**-31**	**10^{3}-10^{4}**	**1.37**	**1.31**	**55**	**10^{3}-10^{4}**
	260	**1.68**	**1.48**	**-35**	**10^{3}-10^{4}**	**1.33**	**1.19**	**54**	**10^{3}-10^{4}**
	290	**1.19**	**0.92**	**-34**	**10^{3}-10^{4}**	**0.69**	**0.58**	**62**	**10^{3}-10^{4}**

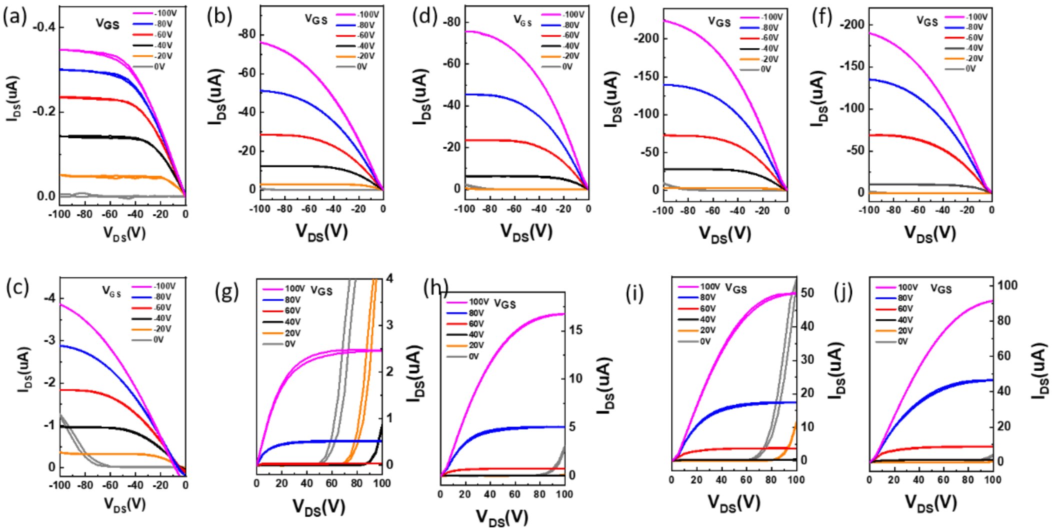


Figure S4. Representative output (a) curves of P1, (b, g) of P2, (c) of P3, (d, h) of P4, (e, i) of P5, and (g, j) of P6 annealed at 200 °C.

Experimental Section

The naphthalene bis-isatin **1**, 6-bromo-indolin-2-one **2**, BIID1-2, 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (BT) and P1-P6 were synthesized according to previously-reported methods.[30-35] Tris(dibenzylideneacetone)dipalladium ($Pd_2(dba)_3$), tri(o-tolyl)phosphine ($P(o\text{-}tol)_3$), 5,5'-bis(trimethylstannyl)-3,3-difluoro-2,2'-bithiophene (2FBT) and other chemicals were purchased from Sigma-Aldrich, Alfa Aesar, and Sinopharm Chemical Reagent Co. Ltd., China and used as received.

Measurements and Characterization

Nuclear magnetic resonance (NMR) spectra were recorded using an Agilent VNMRS600 spectrometer. Molecular weights were characterized by gel permeation chromatography (GPC) using a Waters Series 1525 binary HPLC pump and 1,2,4-trichlorobenzene as the eluent and polystyrene as the standard. Elemental analysis was carried out using a vario EL cube instrument. Polymer films were cast onto quartz glass from a chloroform solution to measure the absorption spectra using an Agilent Cary 5000 model spectrophotometer. Electrochemical cyclic voltammetry (CV) was conducted under nitrogen using a CHI 660D electrochemical analyzer in anhydrous acetonitrile solution containing 0.1 M tetra-n-butylammounium hexafluorophosphate with a scan rate of 0.1 V/s. A platinum (Pt) electrode was used as both the working and auxiliary electrode, and the Ag/Ag^+ electrode was used as the reference electrode. Ultraviolet photoelectron spectroscopy (UPS) was examined using a Thermo ESCALAB 250Xi with a UV excitation source of He I ($h\nu$ = 21.2 eV). Grazing-incidence-X-ray diffraction (GIXD) measurements were performed using 3C beamlines at the Pohang Accelerator Laboratory (PAL) in Korea. The fabrication of GIXD samples was identical for all devices (in the Device Fabrication section). Atomic force microscopy (AFM) images were obtained using a SPA300HV instrument.

Fabrication and Performance of the Organic Field-Effect Transistors (OFETs)

Bottom-gate/top-contact (BG/TC) OFET devices were fabricated on a gate of n-doped Si with a 300-nm thick SiO_2 dielectric layer. First, 5 mg mL^{-1} polymer/chloroform solution was heated at 48 °C for 4 h and then spin-coated onto perfluoropolymer (CYTOP)-treated Si/SiO_2 at 4000 rpm for 40 s in a glove box to obtain a film with a thickness of about 80 nm. Polymer films were annealed in a glove box at four temperatures: R.T., 200 °C, 260 °C, and 290 °C. Au source-drain electrodes were prepared by thermal evaporation. The OFET device had a channel length (L) of 100 μm and a channel width (W) of 1000 μm. Devices were first characterized under vacuum conditions and then measured under ambient air conditions using a Keithley 4200 semiconductor parametric analyzer. Mobility (μ) was obtained using the following equation in the saturation regime: $I_d = (W/ 2L)\, C_i\mu\, (V_g - V_{th})^2$, where I_d is the drain current, C_i is the capacitance of the gate dielectric, V_g is the gate-source voltage, and V_{th} is the threshold voltage.

Synthetic Procedures

Synthesis of [3E,8E]-3,8-bis(6-bromo-7-aza-1-(2-decyltetradecyl)-2-oxoindolin-3-ylidene)- 1,6-decyltetradecyl-6,8-dihydroindolo[7,6-g]indole-2,7(1H,3H)-dione **(BAID1)**. In a round-bottom flask was added **1a** (252 mg, 0.458 mmol), **2b** (200 mg, 0.213 mmol), TsOH·H_2O (19.40 mg, 0.102mmol), P_2O_5 (21.2 mg, 0.149mmol), and acetic acid (12.00 mL). The mixture was evacuated and backfilled with nitrogen thrice and then stirred at 130 °C for 24 h. After the mixture was cooled to room temperature, water (20.0 mL) was added. The mixture was extracted with CH_2Cl_2. The organic extracts were washed with brine and dried with $MgSO_4$. After the solvent had been removed, the residue was purified by column chromatography on silica gel using petroleum ether (PE) : dichloromethane (DCM) (5:3, v/v) to afford **BAID1** as a dark brown solid in a yield of 75% (320 mg). ^{1}H NMR ($CDCl_3$, 600 MHz, ppm): δ 9.15 (d, J = 8.2 Hz, 2H), 9.09 (d, J = 9.3 Hz, 2H), 7.83 (d, J = 9.2 Hz, 2H), 7.12 (d, J = 8.2 Hz, 2H), 4.21 (d, J = 7.4 Hz, 4H), 3.79 (d, J = 7.3 Hz, 4H), 2.04 (d, J = 41.8 Hz, 4H), 1.23 (m, 178H), 0.86 (m, 24H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 169.9, 167.6, 158.0, 143.9, 143.3, 138.1, 133.2, 130.5, 124.7, 123.4, 121.5, 119.9, 117.6, 115.0, 47.4, 43.9, 37.2, 36.2, 32.0, 29.7, 29.6, 29.4, 27.1, 26.2, 26.1, 22.7, 14.1.

Synthesis of [3E,8E]-3,8-bis(6-bromo-7-aza-1-(2-decyltetradecyl)-2-oxoindolin-3-ylidene)-1,6-didodecyl-6,8-dihydroindolo[7,6-g]indole-2,7(1H,3H)-dione **(BAID2)**. **BAID2** was synthesized in a same procedure from **1b** and **2b**. Yield: 75% (415 mg). ^{1}H NMR ($CDCl_3$, 600 MHz, ppm): δ 9.19 (d, J = 8.2 Hz, 2H), 9.10 (d, J = 9.4 Hz, 4H), 7.82 (d, J = 7.3 Hz, 2H), 7.15 (d, J = 8.2 Hz, 2H), 4.26 (t, J = 15.3 Hz, 4H), 3.79 (d, J = 7.2 Hz, 4H), 1.95 (m, 6H), 1.25 (m, 119H), 0.86 (m, 19H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 169.9, 167.6, 158.0, 143.9, 143.3, 138.1, 133.2, 130.5, 124.7, 123.4, 121.5, 119.98, 117.6, 115.0, 47.4, 43.9, 37.2, 36.2, 32.0, 31.5, 31.0, 30.1, 29.7, 29.6, 26.2, 26.1, 22.7, 14.1.

Synthesis of [3E,8E]-3,8-bis(6-bromo-7-aza-1-(4-decyltetradecyl)-2-oxoindolin-3-ylidene)- 1,6-didodecyl-6,8-dihydroindolo[7,6-g]indole-2,7(1H,3H)-dione **(BAID3)**. **BAID3** was synthesized in a same procedure from **1b** and **2c**. Yield: 39% (214 mg). ^{1}H NMR ($CDCl_3$, 600 MHz, ppm): δ 9.19 (d, J = 8.2 Hz, 2H), 9.11 (d, J = 9.4 Hz, 2H), 7.79 (d, J = 9.4 Hz, 2H), 7.14 (d, J = 8.3 Hz, 2H), 4.25 (t, J = 15.3 Hz, 4H), 3.88 (t, J = 14.9 Hz, 4H), 1.83 (m, 4H), 1.76 (m, 4H), 1.25 (m, 125H), 0.86 (m, 18H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 169.5, 167.3, 157.5, 143.8, 143.4, 138.3, 133.2, 130.3, 125.0, 123.1, 121.6, 119.7, 117.0, 115.1, 43.6, 40.0, 37.1, 33.6, 32.0, 30.9, 30.2, 29.7, 29.6, 29.4, 27.0, 26.7, 24.8, 22.7, 14.1.

Polymerization for **P1 (PBIID1-BT)**. [3E,8E]-3,8-bis(6-bromo-1-(2-decyltetradecyl) -2-oxoindolin-3-ylidene)-1,6-decyltetradecyl-6,8-dihydroindolo[7,6-g]indole-2,7(1H,3H)-dione

(BIID1) (0.14 g, 0.07 mmol), 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (BT) (0.037 g, 0.07 mmol), and anhydrous chlorobenzene (10 mL) were added to a 100 mL Schlenck tube. After the tube was charged with nitrogen through a freeze-pump-thaw cycle for three times, $Pd_2(dba)_3$ (2.7 mg) and $P(o\text{-}tol)_3$ (3.6 mg) were added quickly in one portion. The mixture was stirred at 130 °C for 72 h. After being cool to room temperature, the reaction mixture was poured into 80 mL methanol and was stirred for another 2 h. The precipitation was collected by filtration and purified by Soxhlet extraction using methanol, n-hexane, acetone and dichloromethane for the removal of low-molecular-weight. Finally, the remaining solid was extracted with hot chloroform. After removal of the solvent under reduced pressure, a black solid was collected (0.13 g, 80%). GPC: Mn = 34.8 kDa, PDI = 1.82. Anal. Calcd: C, 80.22, H, 10.67, N, 2.77, S, 3.17. Found: C, 80.43, H, 10.94, N, 2.54, S, 3.508.

Polymerization for **P2** **(PBIID2-BT)**. A mixture of [3E,8E]-3,8-bis(6-bromo-1-(2-decyltetradecyl) -2-oxoindolin-3-ylidene)- 1,6-didodecyl -6,8-dihydroindolo[7,6-g]indole-2,7(1H,3H)-dione **(BIID2)** (0.10 g, 0.06 mmol), BT (0.031 g, 0.06 mmol), $Pd_2(dba)_3$ (2.3 mg), and $P(o\text{-}tol)_3$ (3.0 mg) were taken in chlorobenzene (10 mL) to synthesize PBIID2-BT according to the procedure of **PBIID1-BT**. A black solid was collected (0.09 g, 85%). GPC: Mn = 33.1 kDa, PDI = 2.29. Anal. Calcd: C, 79.14, H, 9.93, N, 3.33, S, 3.81. Found: C, 79.60, H, 9.63, N, 3.25, S, 3.84.

Polymerization for **P3 (PBAID1-BT)**. A mixture of **BAID1** (0.14 g, 0.07 mmol), BT (0.034 g, 0.07 mmol), $Pd_2(dba)_3$ (2.6 mg), and $P(o\text{-}tol)_3$ (3.4 mg) were taken in chlorobenzene (10 mL) to synthesize **PBAID1-BT** according to the procedure of **PBIID1-BT**. A black solid was collected (0.13 g, 90%). GPC: Mn = 39.5 kDa, PDI = 2.36. Anal. Calcd: C, 77.26, H, 9.87, N, 3.92, S, 3.84. Found: C, 76.96, H, 9.22, N, 3.98, S, 3.84.

Polymerization for **P4 (PBAID2-BT)**. A mixture of **BAID2** (0.10 g, 0.06 mmol), BT (0.030 g, 0.06 mmol), $Pd_2(dba)_3$ (2.3 mg), and $P(o\text{-}tol)_3$ (3.0 mg) were taken in chlorobenzene (10 mL) to synthesize **PBAID2-BT** according to the procedure of **PBIID1-BT**. A black solid was collected (0.087 g, 87%). GPC: Mn = 56.8 kDa, PDI = 2.45. Anal. Calcd: C, 78.95, H, 10.56, N, 4.15, S, 3.17. Found: C, 78.52, H, 10.59, N, 4.08, S, 3.30.

Polymerization for **P5 (PBAID3-BT)**. A mixture of **BAID3** (0.12 g, 0.07 mmol), BT (0.035 g, 0.07 mmol), $Pd_2(dba)_3$ (2.6 mg), and $P(o\text{-}tol)_3$ (3.5 mg) were taken in chlorobenzene (10 mL) to synthesize **PBAID3-BT** according to the procedure of **PBIID1-BT**. A black solid was collected (0.117 g, 97%). GPC: Mn = 52.3 kDa, PDI = 2.70. Anal. Calcd: C, 77.62, H, 9.80, N, 4.98, S, 3.80. Found: C, 77.78, H, 9.95, N, 4.91, S, 3.90.

Polymerization for **P6 (PBAID3-2FBT)**. A mixture of **BAID3** (0.12 g, 0.07 mmol), 2FBT (0.038 g, 0.07 mmol), $Pd_2(dba)_3$ (2.6 mg), and $P(o\text{-}tol)_3$ (3.5 mg) were taken in chlorobenzene (10 mL) to synthesize **PBAID3-2FBT** according to the procedure of **PBIID1-BT**. A black solid was collected (0.12 g, 98%). GPC: Mn = 40.06 kDa, PDI = 2.41. Anal. Calcd: C, 76.00, H, 9.48, N, 4.88, S, 3.72. Found: C, 76.31, H, 9.67, N, 3.78, S, 3.94.

NMR

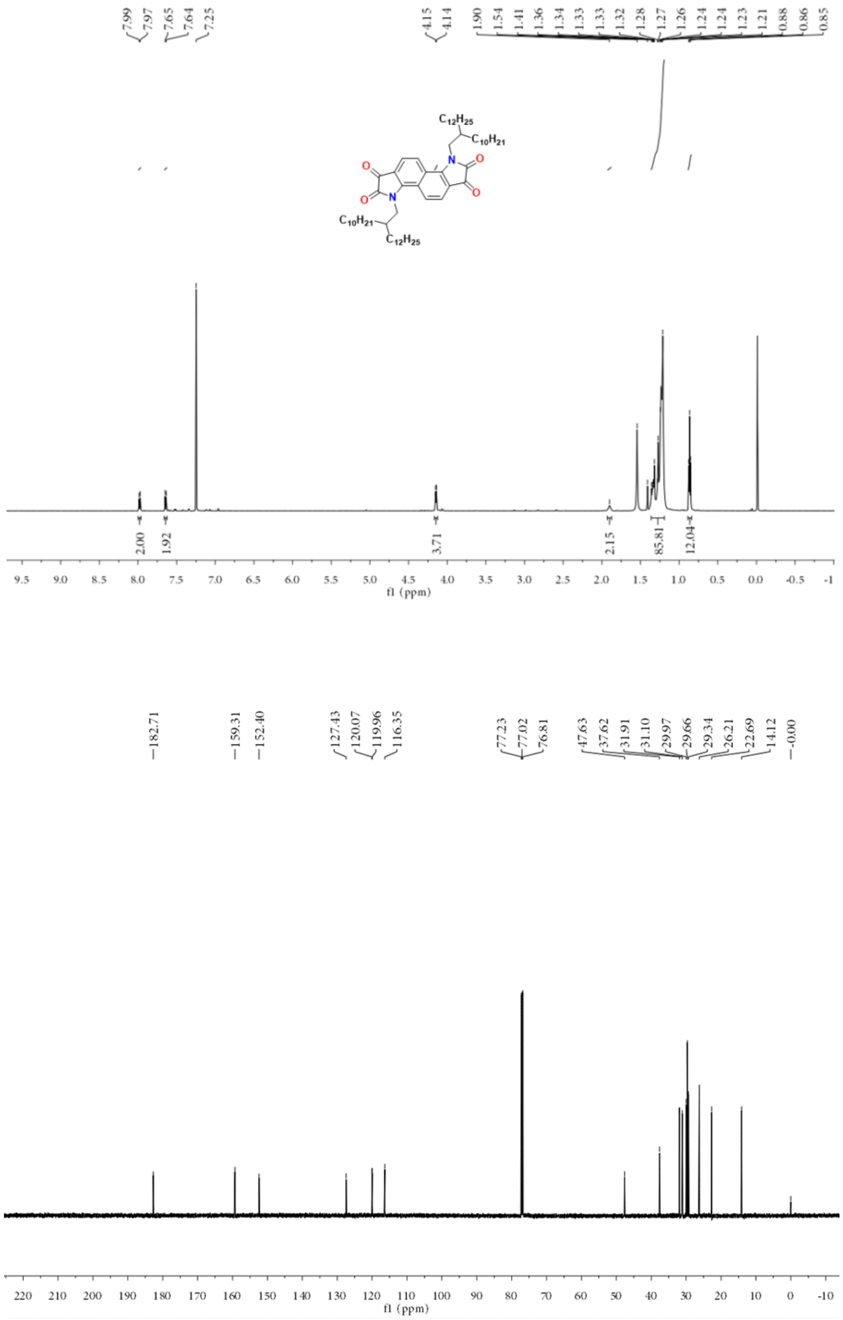


Figure S5. ^{1}H NMR (top) and ^{13}C NMR (bottom) spectra of (N-(2-decyltetradecyl))-napthalene bisisatin.

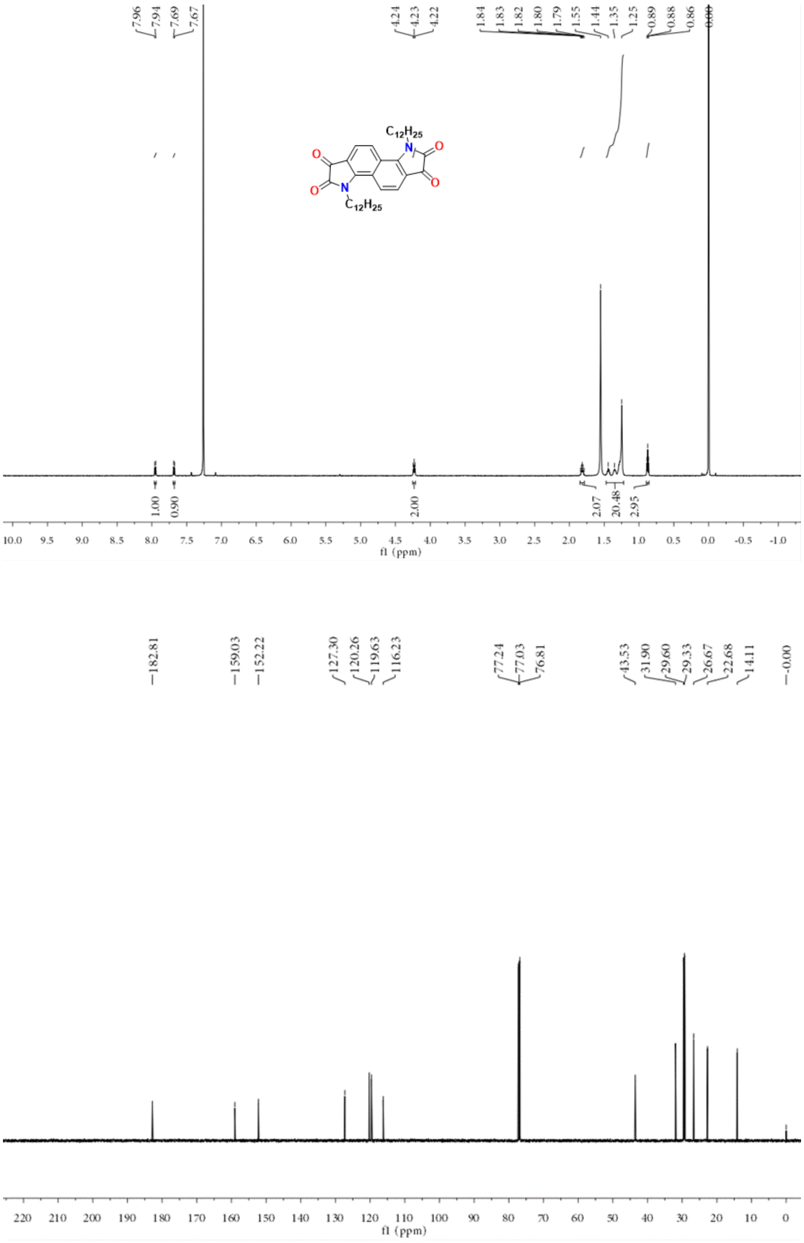


Figure S6. ^{1}H NMR (top) and ^{13}C NMR (bottom) spectra of (N-(1-dodecyl))-napthalene bisisatin.

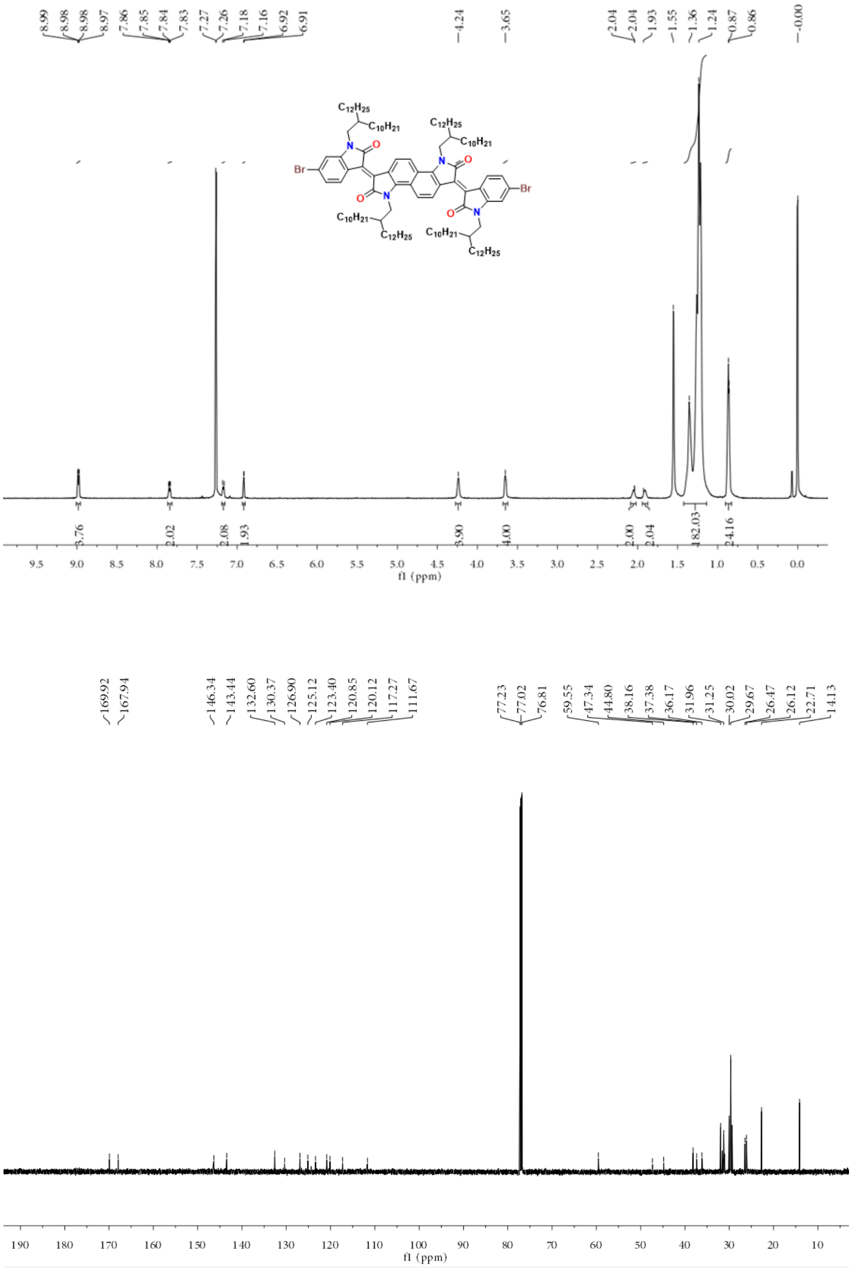


Figure S7. ^{1}H NMR (top) and ^{13}C NMR (bottom) spectra of **BIID1.**

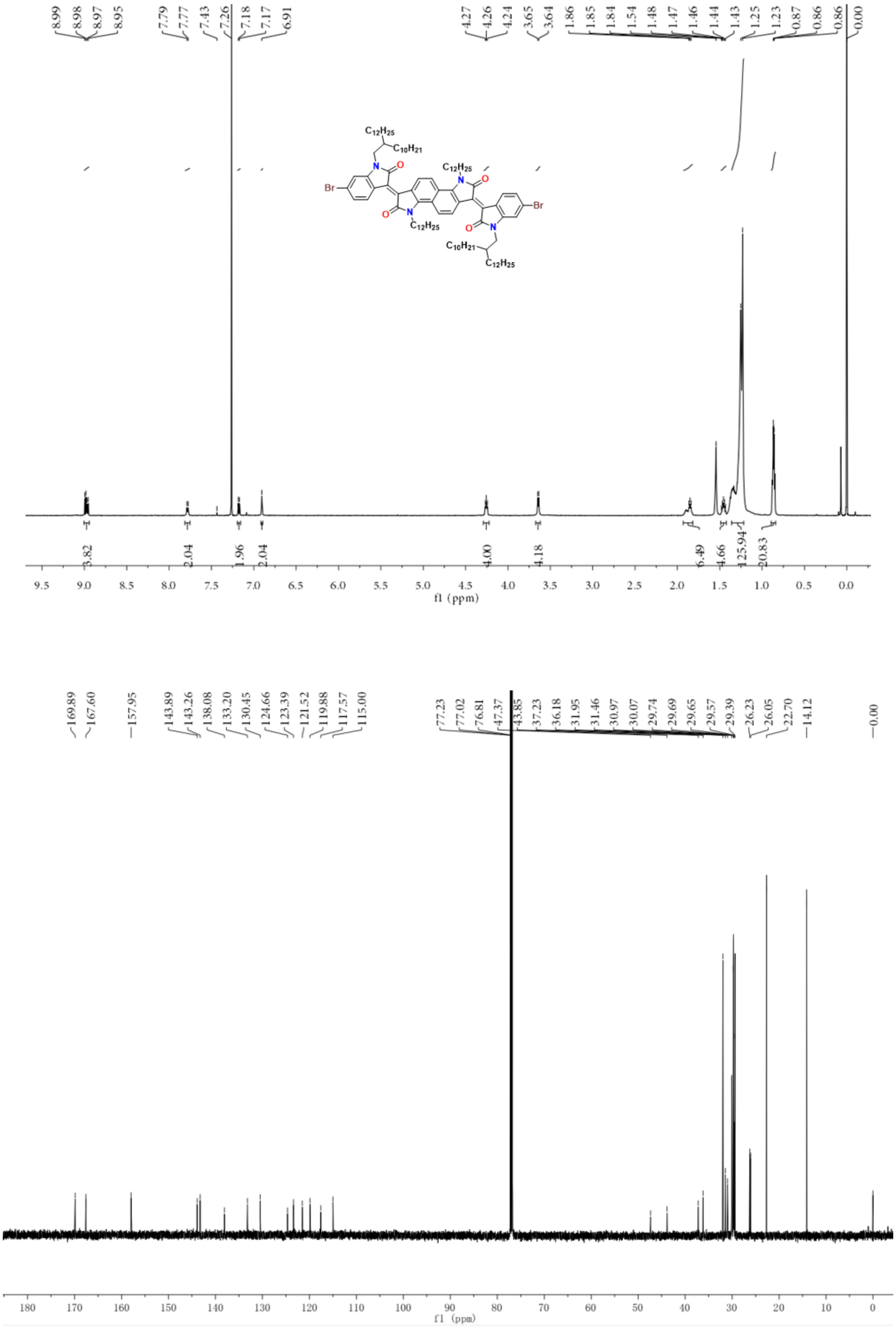


Figure S8. ^{1}H NMR (top) and ^{13}C NMR (bottom) spectra of **BIID2.**

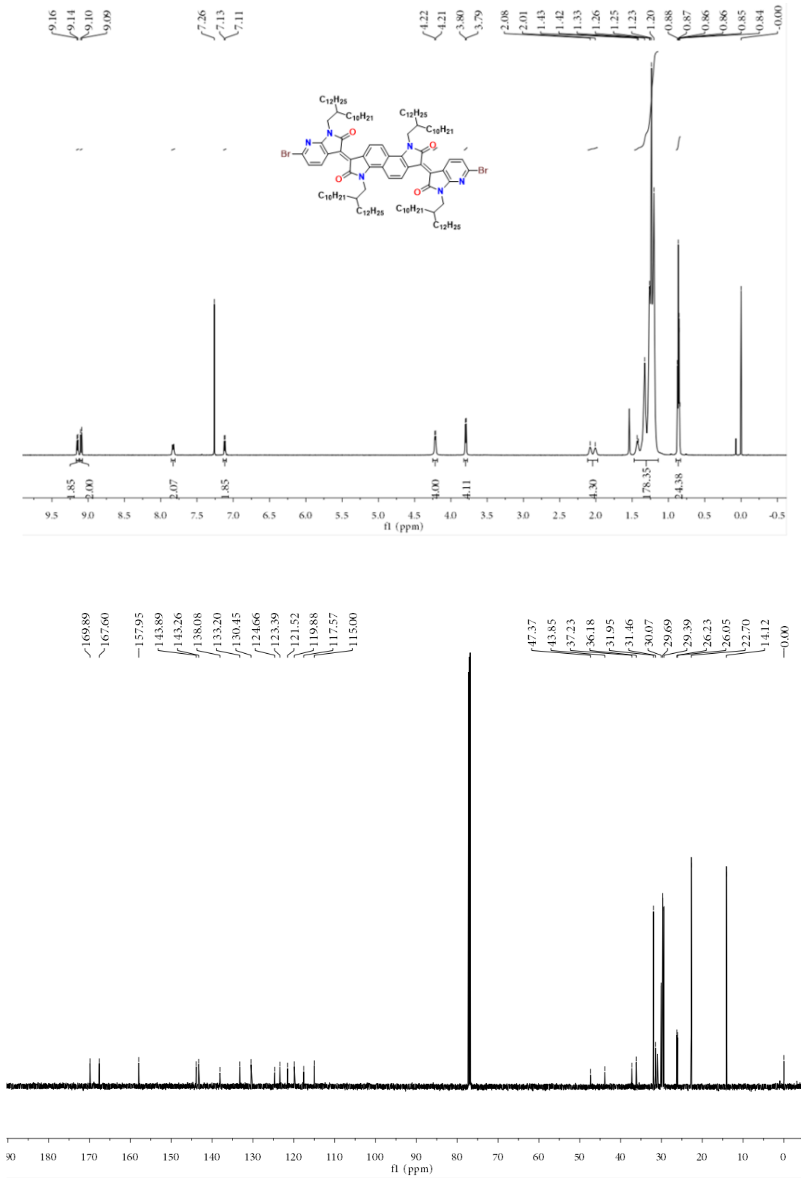


Figure S9. ^{1}H NMR (top) and ^{13}C NMR (bottom) spectra of **BAID1.**

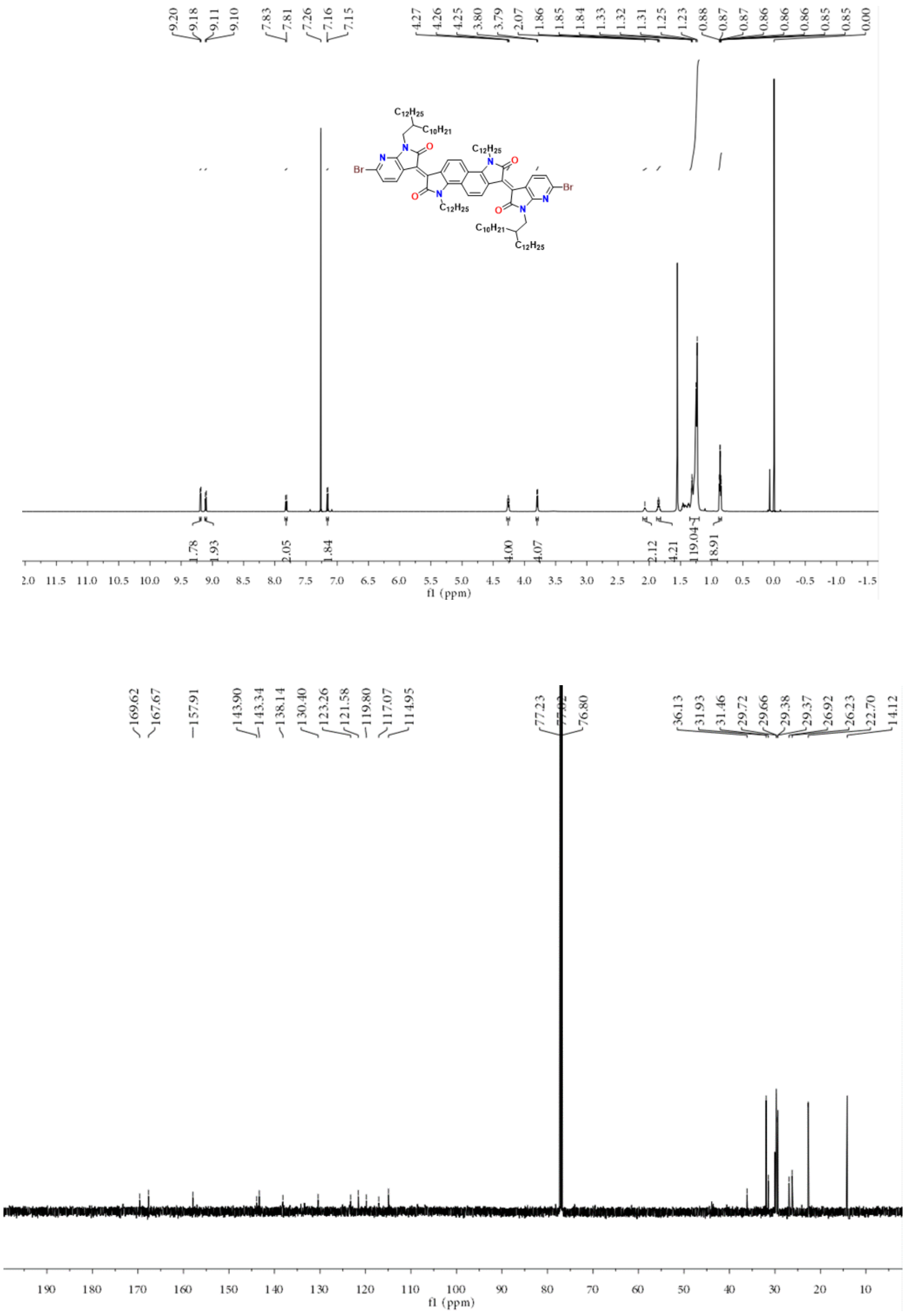


Figure S10. ^{1}H NMR (top) and ^{13}C NMR (bottom) spectra of **BAID2.**

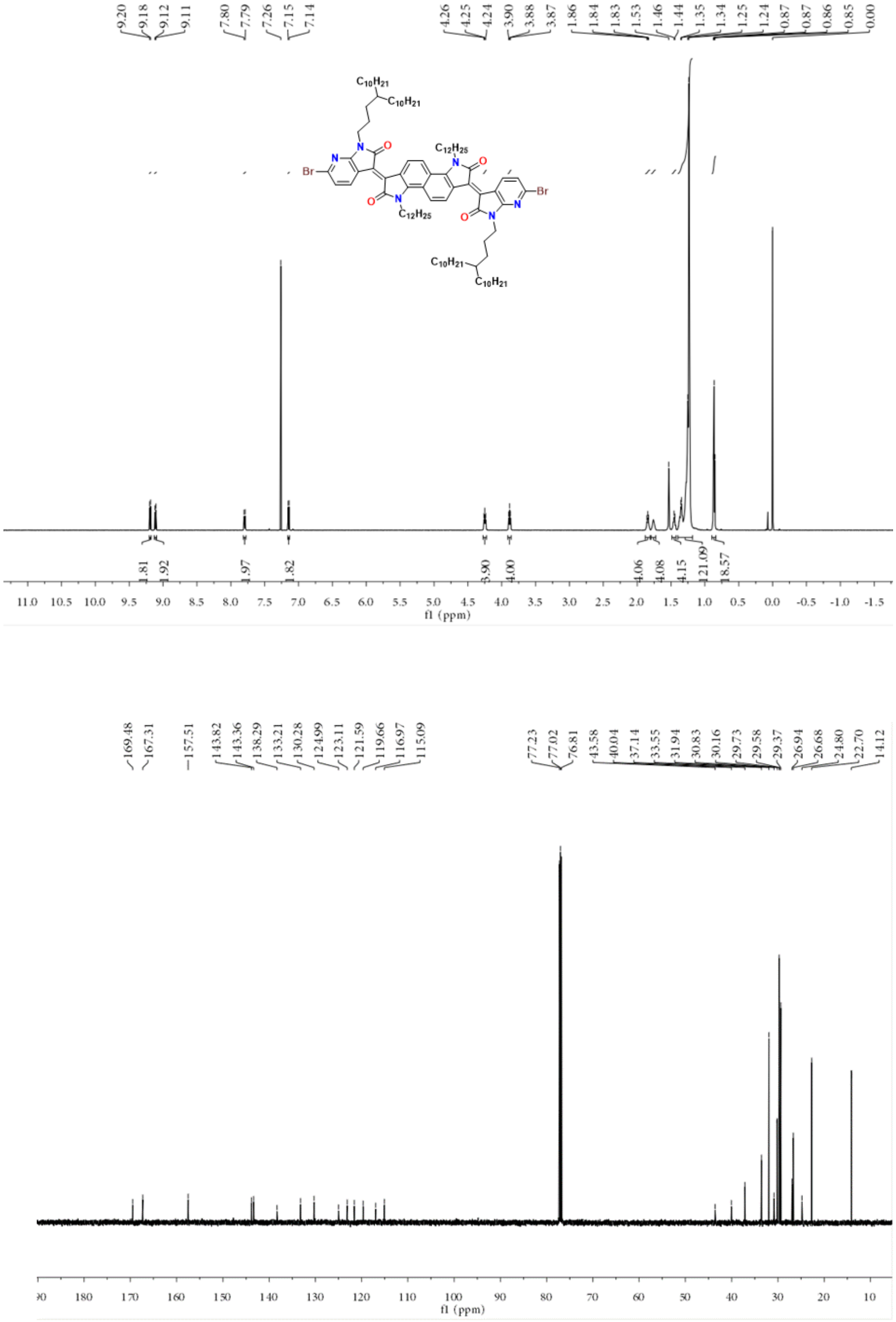
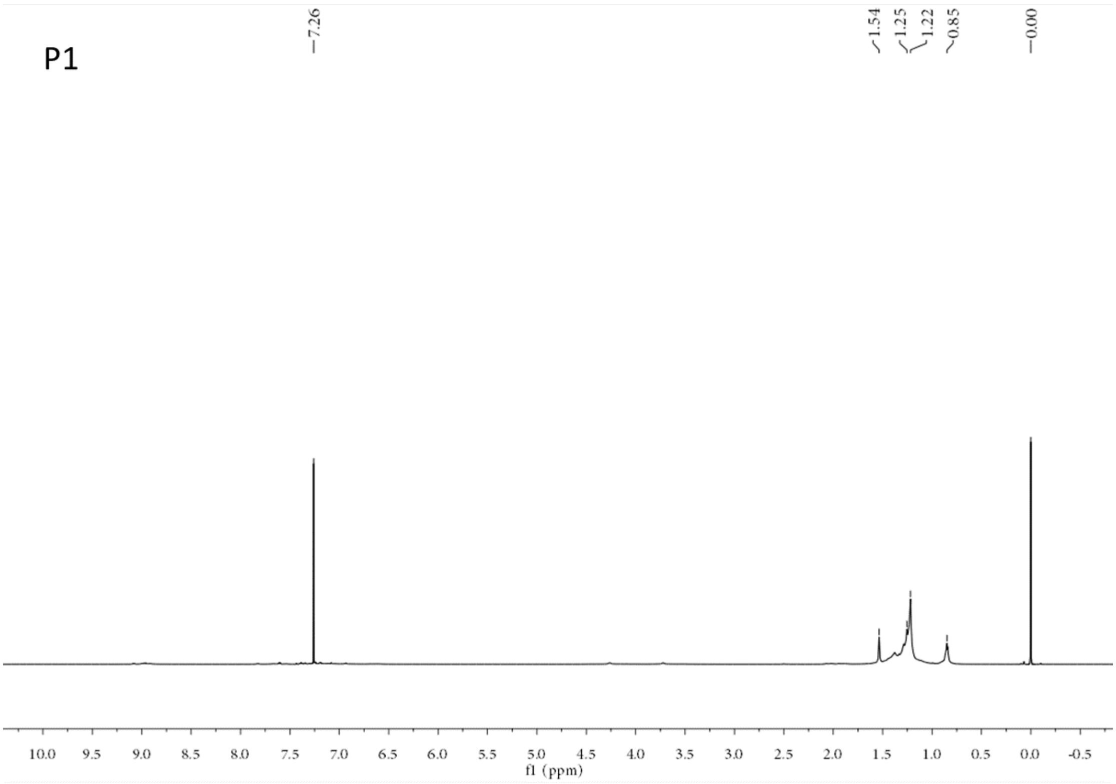


Figure S11. ^{1}H NMR (top) and ^{13}C NMR (bottom) spectra of **BAID3.**

P1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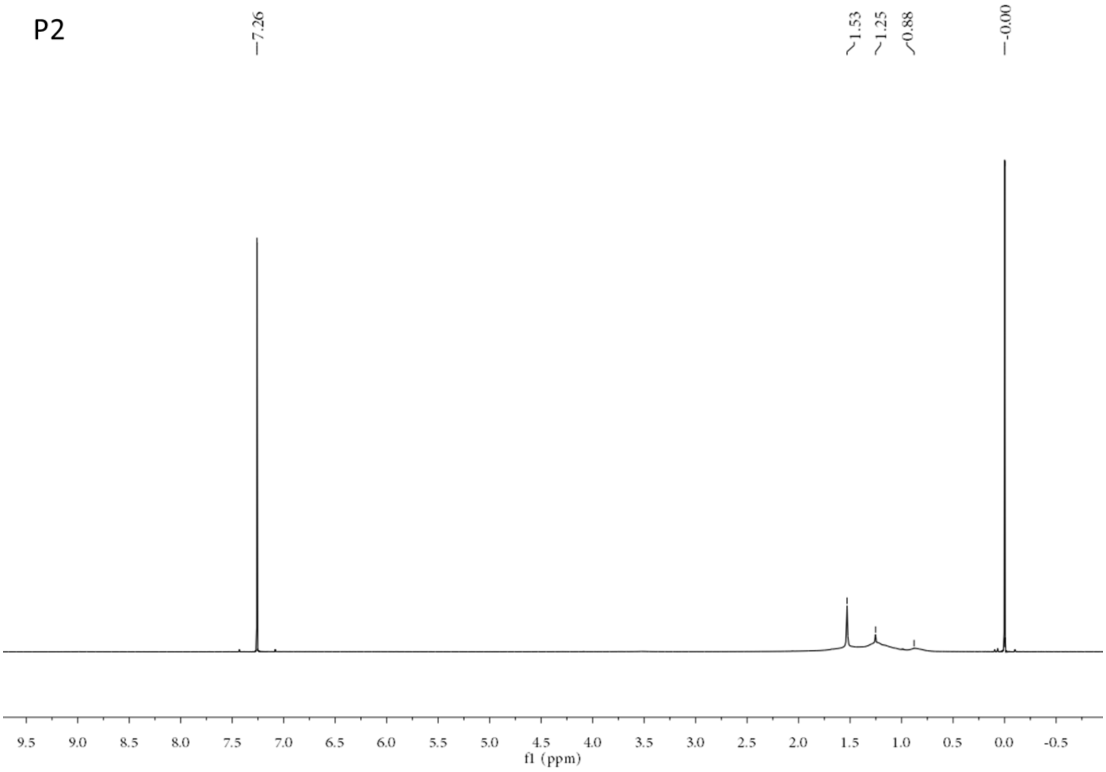
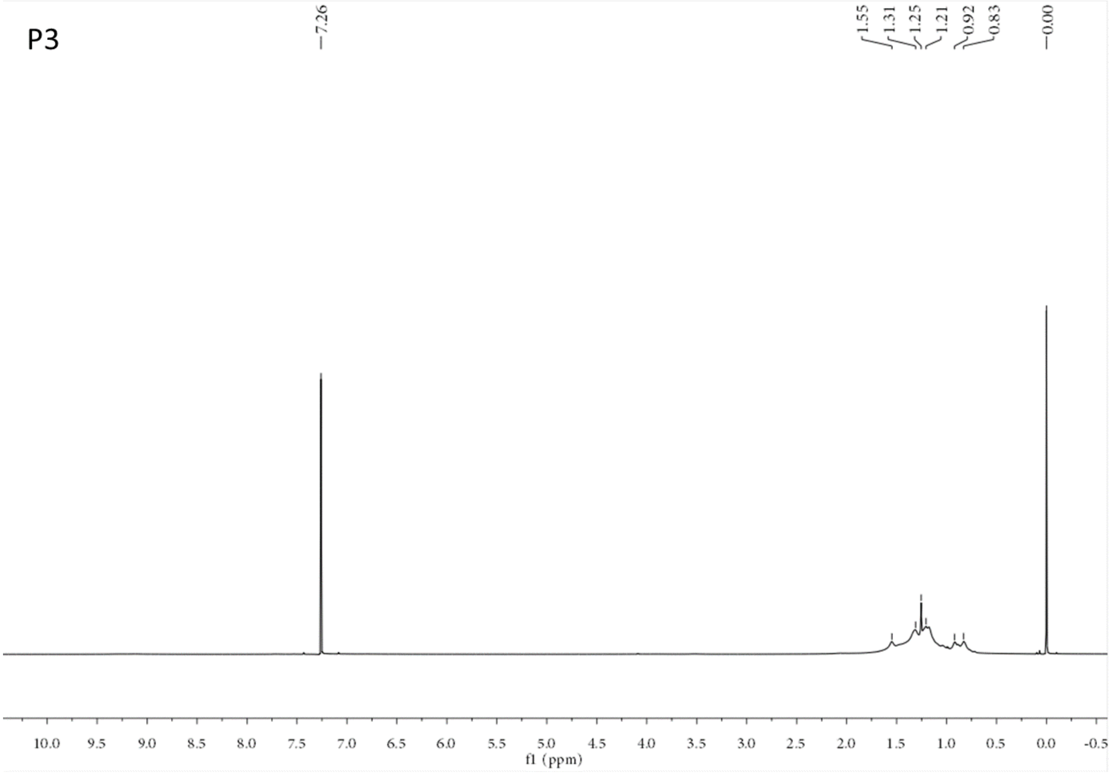
1.54
1.25
1.22
0.85
0.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

P2


7.26
1.53
1.25
0.88
0.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

P3



7.26
1.55
1.31
1.25
1.21
0.92
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0.00
10.0
9.5
9.0
8.5
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6.5
6.0
5.5
5.0
4.5
4.0
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3.0
2.5
2.0
1.5
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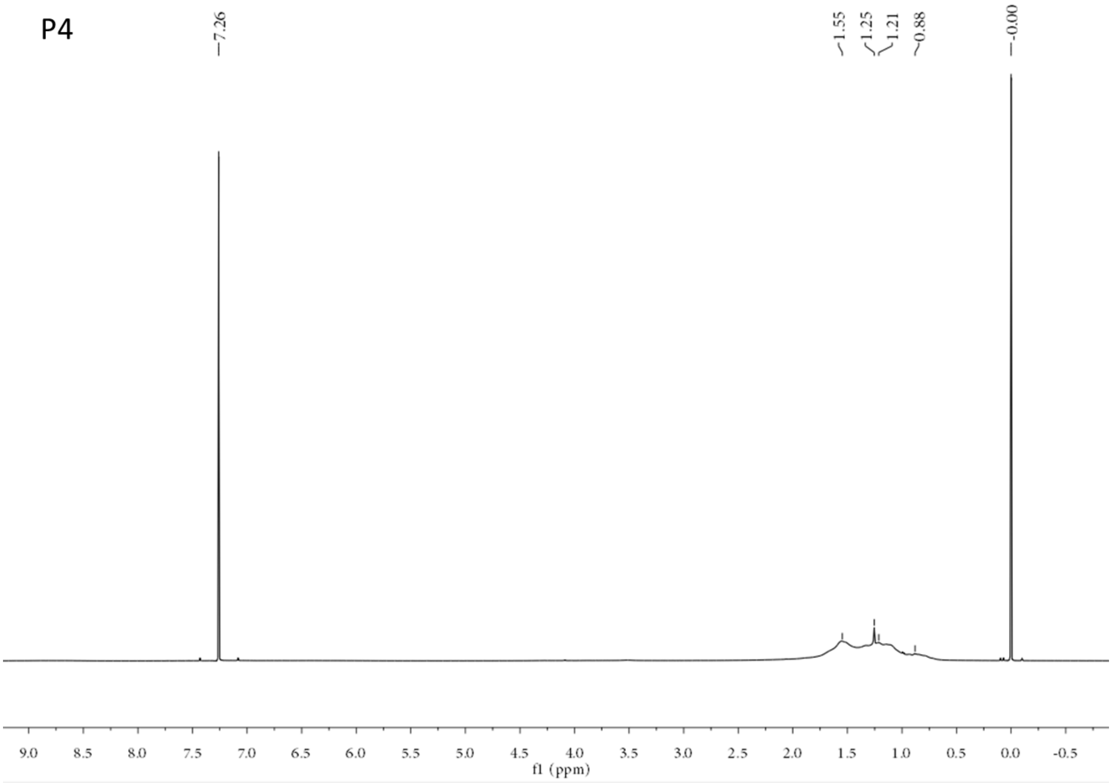
0.5
0.0
-0.5
f1 (ppm)

P4



7.26
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1.25
1.21
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8.0
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6.0
5.5
5.0
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1.0
0.5
0.0
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f1 (ppm)

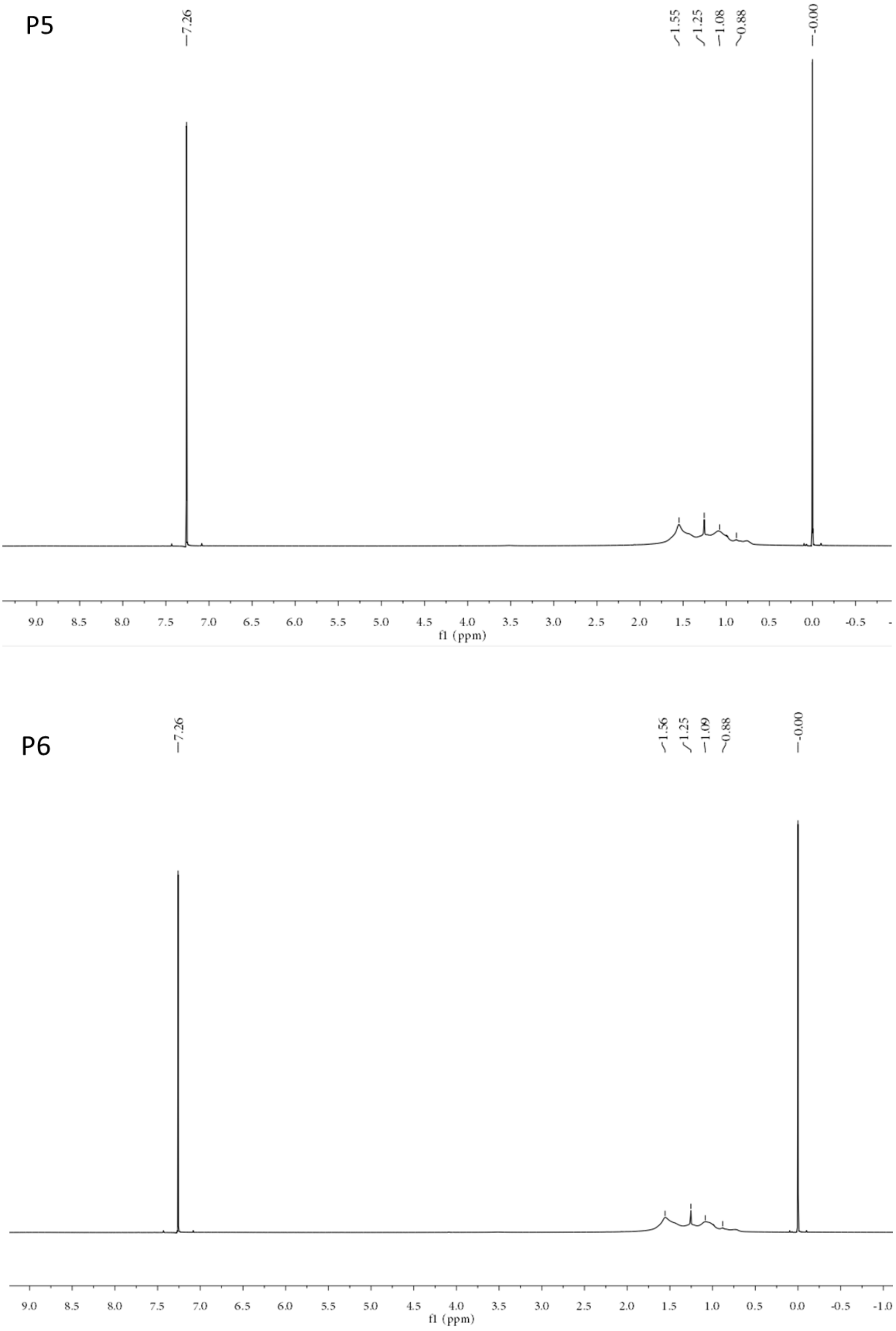

Figure S12. ^{1}H NMR spectra of **P1-P6.**

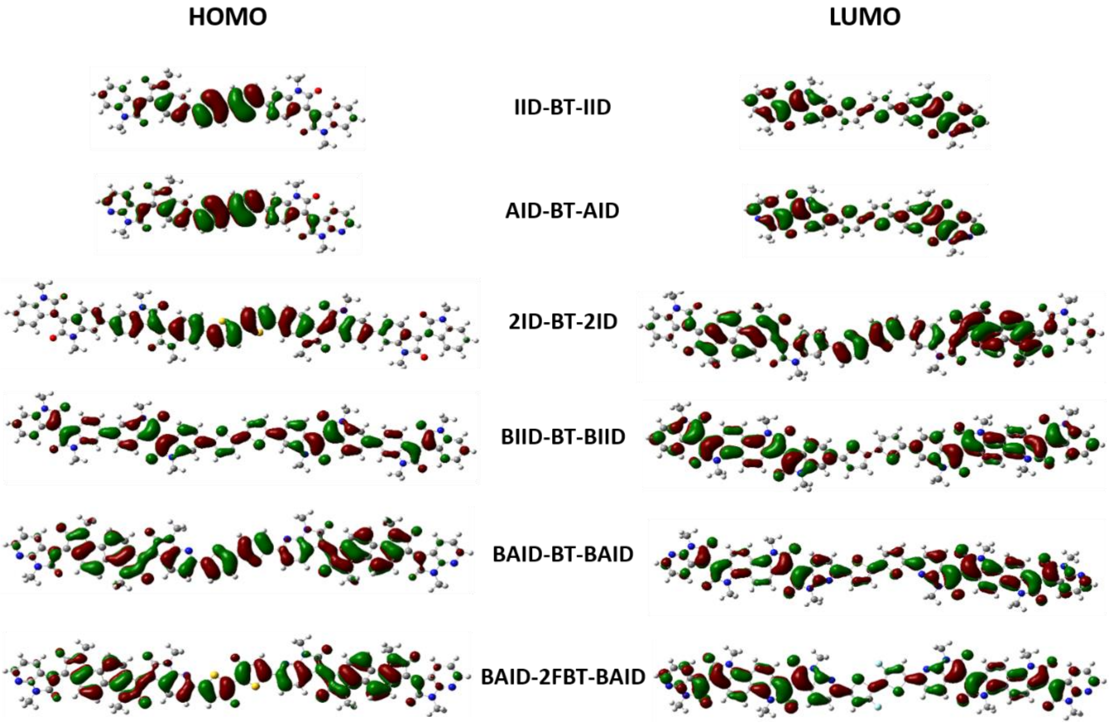

Figure S13. Frontier orbital distributions of methyl-substituted dimers obtained by DFT calculations.

Table S3. The device performance of P6 annealed at 200 °C after 173-day air storage in glassware.

Date	p (cm^{2}v^{-1}s^{-1})		n (cm^{2}v^{-1}s^{-1})		$\mu_{h\ ave}$ / $\mu_{e\ ave}$
	μ_{max}	μ_{ave}	μ_{max}	μ_{ave}	
2018.11.15	1.54	1.31	1.37	1.31	1/1
2019.05.06	0.43	0.39	0.28	0.23	1.70/1

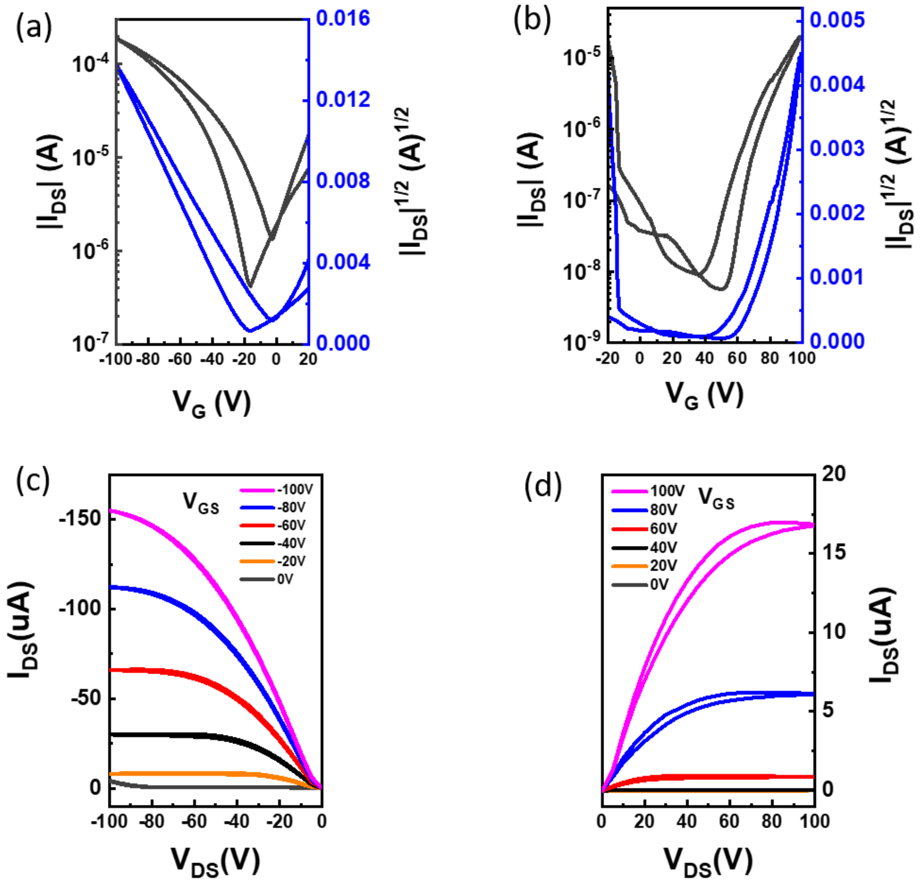

Figure S14. Representative transfer and output curves of P6 annealed at 200 °C (a-d) after 173-day air storage in glassware.