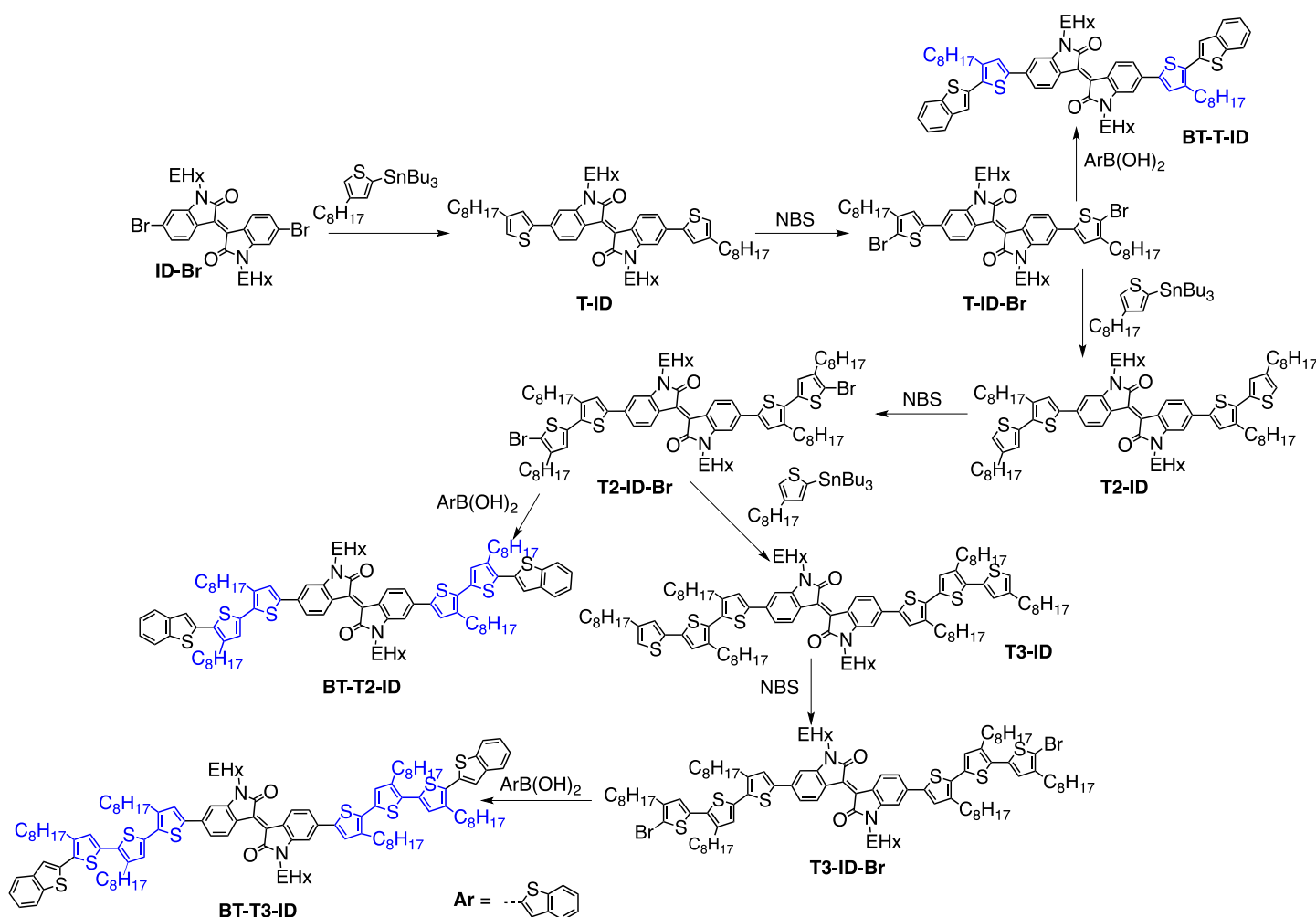


Isoindigo-Containing Molecular Semiconductors: Effect of Backbone Extension on Molecular Organization and Organic Solar Cell Performance

Yi Ren,^{†,‡} Anna K. Hailey,[†] Anna M. Hiszpanski,[†] Yueh-Lin Loo^{†,‡*}

[†] Department of Chemical and Biological Engineering, Princeton University, Princeton, NJ 08544, USA;

[‡] Princeton Center for Complex Materials, Princeton University, Princeton, NJ 08544, USA.



Scheme S1. Synthesis of isoindigo-based small molecules having extended conjugation lengths.

Synthesis of **T-ID**, **T2-ID**, and **T3-ID**:

In a 1-necked 250 mL Schlenk flask, **ID-Br** or **T-ID-Br**, or **T2-ID-Br** (1.0 mole equ.) was mixed with tributyl(4-octylthiophen-2-yl)stannane (2.2 mole equ.), tris(dibenzylideneacetone)dipalladium(0) (0.05 mole equ.) and tri(*o*-tolyl)phosphine (0.2 mole equ.) in anhydrous THF (40 mL). The resulting mixture was degassed for 10 min, then refluxed under argon overnight. The reaction mixture was allowed to cool to room temperature, after which it was poured into 10 mL of water. The organic layer was extracted with chloroform. The crude product was purified by flash chromatography using dichloromethane and hexanes as eluent (from 1:9 to 4:6 by volume).

T-ID: ^1H NMR (CD_2Cl_2 , 300 MHz, δ): 9.15 (d, $J = 8.5$ Hz, 2H), 7.30 (d, $J = 1.4$ Hz, 2H), 7.27 (dd, $J = 8.4$ Hz, $J = 1.7$ Hz, 2H), 7.0-6.97 (m, 4H), 3.80 – 3.59 (m, 4H), 2.64 (t, $J = 7.7$ Hz, 4H), 1.95-1.80 (m, 2H), 1.67 (m, 4H), 1.49 – 1.21 (m, 40H), 1.03 – 0.81 (m, 18H) ppm.

T2-ID: ^1H NMR (CD_2Cl_2 , 300 MHz, δ): 9.15 (d, $J = 8.5$ Hz, 2H), 7.30 (s, 1H), 7.26 (dd, $J = 8.5$ Hz, $J = 1.7$ Hz, 2H), 7.05 (d, $J = 1.5$ Hz, 2H), 7.00 – 6.94 (m, 4H), 3.84 – 3.58 (m, 4H), 2.78 (t, $J = 7.8$ Hz, 4H), 2.63 (t, $J = 7.7$ Hz, 4H), 1.93 – 1.85 (m, 2H), 1.74 – 1.63 (m, 8H), 1.48 – 1.26 (m, 52H), 1.03 – 0.79 (m, 24H) ppm.

T3-ID: ^1H NMR (CDCl_3 , 300 MHz, δ): 9.12 (d, $J = 8.5$ Hz, 2H), 7.26 – 7.23 (m, 2H), 7.22 (s, 2H), 6.99 (s, 2H), 6.96 (d, $J = 1.4$ Hz, 2H), 6.94 – 6.87 (m, 4H), 3.79 – 3.58 (m, 4H), 2.81 – 2.71 (m, 8H), 2.60 (t, $J = 7.7$ Hz, 4H), 1.91 – 1.82 (m, 2H), 1.66 – 1.20 (m, 10H), 1.49 – 1.17 (m, 89H), 1.02 – 0.77 (m, 30H) ppm.

Synthesis of **T-ID-Br**, **T2-ID-Br**, and **T3-ID-Br**:

In a 1-necked 250 mL Schlenk flask, N-bromosuccinimide (NBS) (2.1 mole equ.) was added to a solution of **T-ID** or **T2-ID** or **T3-ID** (1.0 mole equ.) in anhydrous THF (40 mL). The resulting mixture was degassed for 10 min, then stirred under argon overnight. The reaction mixture was quenched with 10 mL of water. The organic layer was extracted with chloroform. The crude product was purified by flash chromatography using dichloromethane and hexanes as eluent (from 1:9 to 4:6 by volume).

T-ID-Br: ^1H NMR (CDCl_3 , 300 MHz, δ): 9.12 (d, $J = 8.4$ Hz, 2H), 7.17 (dd, $J = 8.4$ Hz, $J = 1.7$ Hz, 2H), 7.07 (s, 2H), 6.85 (d, $J = 1.7$ Hz, 2H), 3.76 – 3.60 (m, 4H), 2.61 – 2.51 (m, 4H), 1.89 – 1.79 (m, 2H), 1.66 – 1.56 (m, 4H), 1.39 – 1.23 (m, 40H), 0.98 – 0.81 (m, 18H) ppm.

T2-ID-Br: ^1H NMR (CDCl_3 , 300 MHz, δ): 9.08 (d, $J = 8.4$ Hz, 2H), 7.34 – 7.16 (m, 2H), 6.85 (d, $J = 1.7$ Hz, 2H), 6.80 (s, 2H), 3.73 – 3.55 (m, 4H), 2.66 (t, $J = 7.8$ Hz, 4H), 2.50 (t, $J = 7.7$ Hz, 4H), 1.84 – 1.74 (m, 2H), 1.65 – 1.52 (m, 8H), 1.41 – 1.18 (m, 52H), 0.91 – 0.80 (m, 24H) ppm.

T3-ID-Br: ^1H NMR (CDCl_3 , 300 MHz, δ): 9.13 (d, $J = 8.4$ Hz, 2H), 7.26 (d, $J = 1.8$ Hz, 2H), 7.22 (s, 2H), 6.98 (s, 2H), 6.81 (s, 2H), 2.78 (t, $J = 7.9$ Hz, 4H), 2.70 (t, $J = 7.9$ Hz, 4H), 2.55 (t, $J = 7.9$ Hz, 4H), 1.93 – 1.82 (m, 2H), 1.71- 1.59 (m, 3H), 1.44 – 1.21 (m, 89H), 0.97 – 0.80 (m, 30H) ppm.

Synthesis of **BT-T-ID**, **BT-T2-ID**, and **BT-T3-ID**

The synthesis procedures of these three final products are very similar. In a 1-necked 250 mL Schlenk flask, the respective dibromo precursor (**T-ID-Br**, **T2-ID-Br**, and **T3-ID-Br**) (1.0 mole equ.) was mixed with benzothiophen-2-boronic acid (2.2 mole equ.), tris(dibenzylideneacetone)dipalladium(0) (0.05 mole equ.), tri-tert-butylphosphonium tetrafluoroborate (0.25 mole equ.), and potassium phosphate (9.0 mole equ.) in a mixture of THF and water (4:1 v/v). The resulting mixture was degassed for 10 min, then refluxed under argon overnight. The reaction mixture was allowed to cool to room temperature, after which it was poured into 10 mL of water. The organic layer was extracted with chloroform. The crude product was purified by flash chromatography using dichloromethane and hexanes as eluent (from 1:9 to 4:6 by volume).

BT-T-ID was obtained as a dark blue solid. ^1H NMR (CDCl_3 , 500 MHz, δ): 9.14 (d, $J = 8.0$ Hz, 2H), 7.81 (d, $J = 8.0$ Hz, 2H), 7.77 (d, $J = 7.0$ Hz, 2H), 7.38 (s, 2H), 7.36 – 7.27 (m, 6H), 6.95 (d, $J = 1.0$ Hz, 2H), 3.78 – 3.65 (m, 4H), 2.85 (t, $J = 8.0$ Hz, 4H), 1.90 – 1.85 (m, 2H), 1.74 – 1.68 (m, 4H), 1.44 – 1.23 (m, 36H), 0.97 – 0.90 (m, 12H), 0.86 – 0.90 (t, $J = 6.5$ Hz, 6H) ppm. ^{13}C NMR (CDCl_3 , 125 MHz, δ): 168.9, 145.9, 142.7, 142.3, 140.1, 140.1, 137.5, 136.3, 132.11, 131.8, 130.4, 127.6, 124.9, 124.7, 123.7, 122.5, 122.2, 121.4, 119.2, 104.9, 44.3, 38.0, 32.1, 31.0, 30.9, 29.8, 29.6, 29.5, 29.2, 24.5, 23.3, 22.9, 24.5, 23.3, 22.9, 14.4, 14.3, 11.1 ppm. HRMS: $m/z = 1139.37$ ([M], Calcd. 1139.73). Elemental analysis calcd (%) for $\text{C}_{72}\text{H}_{86}\text{N}_2\text{O}_2\text{S}_4$: C 75.88, H 7.61, N 2.46; found: C 74.97, H 7.71, N 2.54. Elemental analysis provided low than expected carbon content, likely due to the presence of water in the sample

BT-T2-ID was obtained as a dark blue solid. ^1H NMR (CDCl_3 , 500 MHz, δ): 9.15 (d, $J = 8.0$ Hz, 2H), 7.82 (d, $J = 8.0$ Hz, 2H), 7.78 (d, $J = 7.5$ Hz, 2H), 7.39 – 7.27 (m, 10H), 7.06 (s, 2H), 6.96 (d, $J = 1.0$ Hz, 2H), 3.81 – 3.66 (m, 4H), 2.88 – 2.72 (m, 8H), 1.92 – 1.87 (m, 2H), 1.76 – 1.69 (m, 8H), 1.46 – 1.25 (m, 56H), 0.99 – 0.933 (m, 12H), 0.89 – 0.87 (m, 12H) ppm. ^{13}C NMR (CDCl_3 , 125 MHz, δ): 168.9, 145.8, 141.7, 140.2, 140.0, 137.5, 136.2, 135.1, 132.0, 131.8, 131.0, 130.3, 129.1, 127.6, 124.8, 124.6, 123.7, 122.3, 122.2, 121.3, 119.1, 104.8, 38.0, 32.1, 31.0, 30.9, 30.8, 29.9, 29.9, 29.8, 29.7, 29.7, 29.5, 29.5, 29.2, 24.5, 23.3, 22.9, 14.4, 14.3, 11.1 ppm. HRMS: $m/z = 1528.60$ ([M], Calcd. 1528.40). Elemental analysis calcd (%) for $\text{C}_{96}\text{H}_{122}\text{N}_2\text{O}_2\text{S}_6$: C 75.44, H 8.05, N 1.83; found: C 74.73, H 8.25, N 1.93. Elemental analysis provided low than expected carbon content, likely due to the presence of water in the sample

BT-T3-ID was obtained as a dark blue solid. ^1H NMR (CDCl_3 , 500 MHz, δ): 9.13 (d, $J = 8.5$ Hz, 2H), 7.80 (d, $J = 8.0$ Hz, 2H), 7.76 (d, $J = 8.0$ Hz, 2H), 7.37 – 7.25 (m, 10H), 7.01 (s, 2H), 7.00 (s, 2H), 6.94 (s, 2H), 3.79 – 3.65 (m, 4H), 2.85 – 2.78 (m, 12H), 1.90 – 1.86 (m, 2H), 1.73 – 1.67 (m, 12H), 1.42 – 1.23 (m, 76H), 0.97 – 0.91 (m, 12H), 0.87 – 0.84 (m, 18H) ppm. ^{13}C NMR (CDCl_3 , 125 MHz, δ): 168.9, 159.9, 141.5, 141.3, 141.1, 140.4, 140.1, 140.0, 137.6, 136.3, 135.0, 134.1, 132.0, 130.9, 130.7, 130.3, 129.1, 128.9, 127.7, 124.8, 124.5, 123.6, 122.2, 121.3, 119.1, 38.0, 32.1, 32.1, 31.0, 30.9, 30.8, 29.9, 29.8, 29.8, 29.7, 29.5, 29.5, 29.2, 24.5, 23.3, 22.9, 22.9, 14.4, 14.4, 11.1 ppm. HRMS: $m/z = 1916.80$ ($[\text{M}]$, Calcd. 1917.07). Elemental analysis calcd (%) for $\text{C}_{120}\text{H}_{158}\text{N}_2\text{O}_2\text{S}_8$: C 75.18, H 8.31, N 1.46; found: C 74.46, H 8.36, N 1.59. Elemental analysis provided low than expected carbon content, likely due to the presence of water in the sample

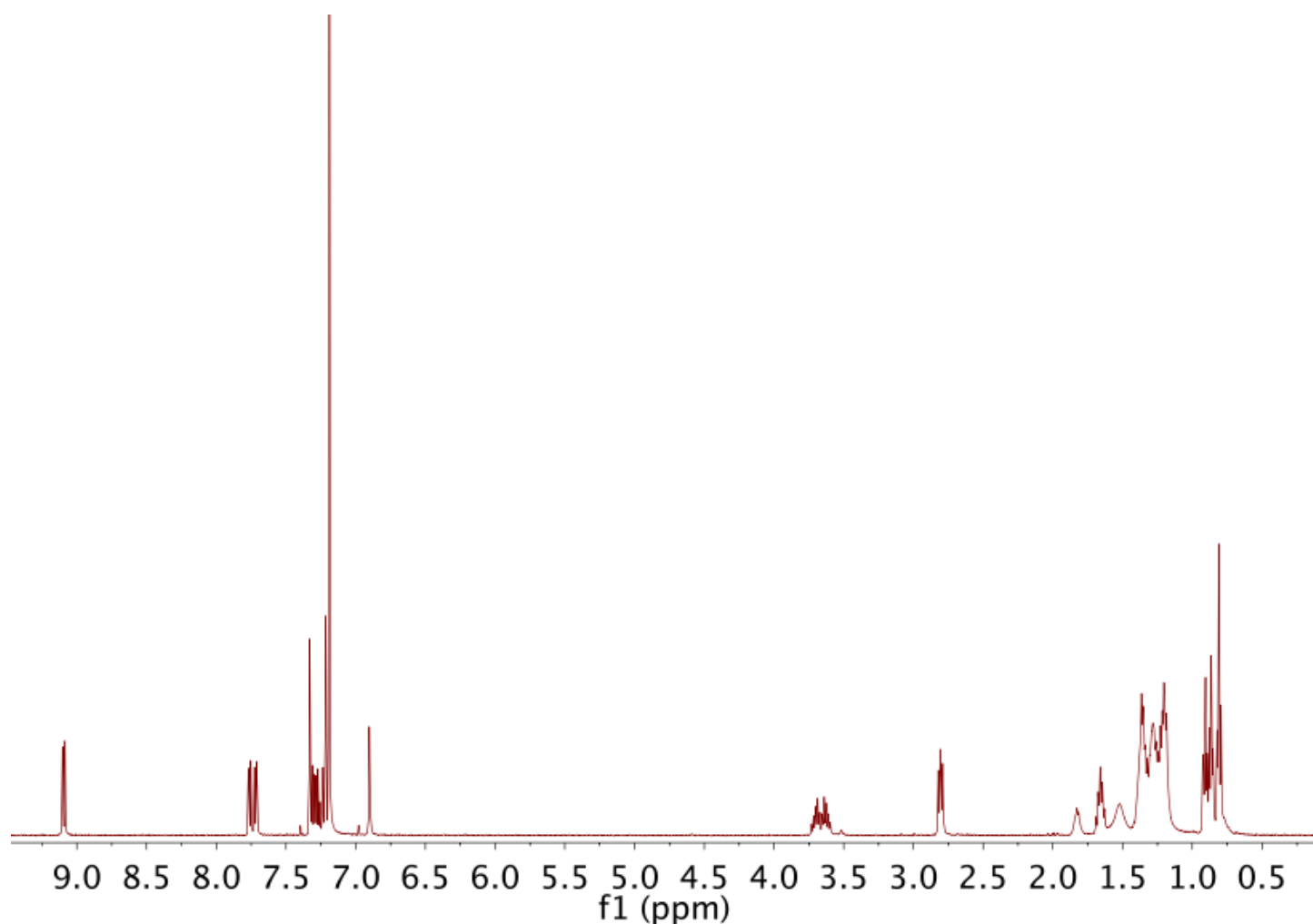


Figure S1. ^1H NMR spectrum of **BT-T-ID** in CDCl_3 .

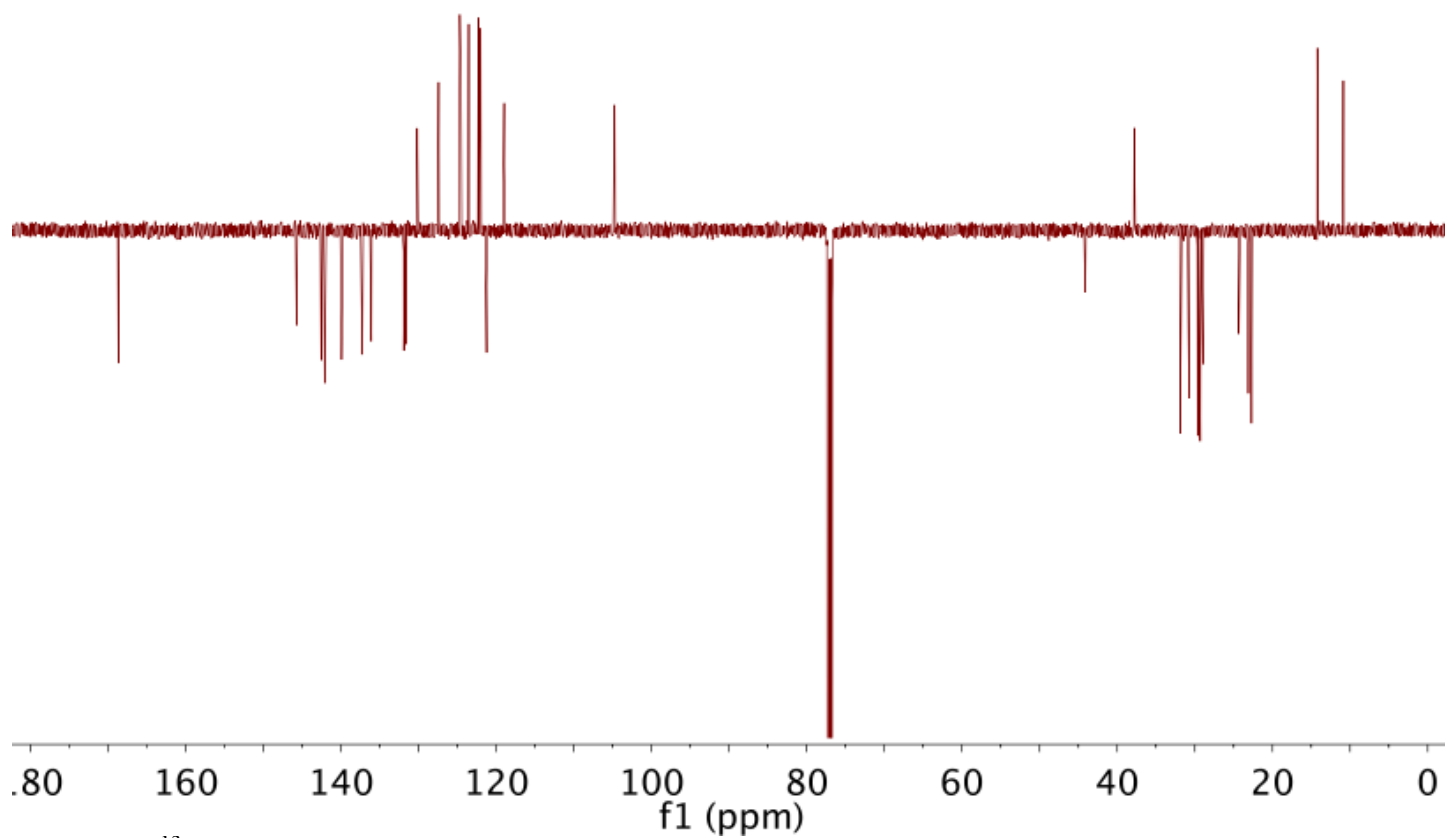


Figure S2. ^{13}C NMR spectrum of **BT-T-ID** in CDCl_3 .

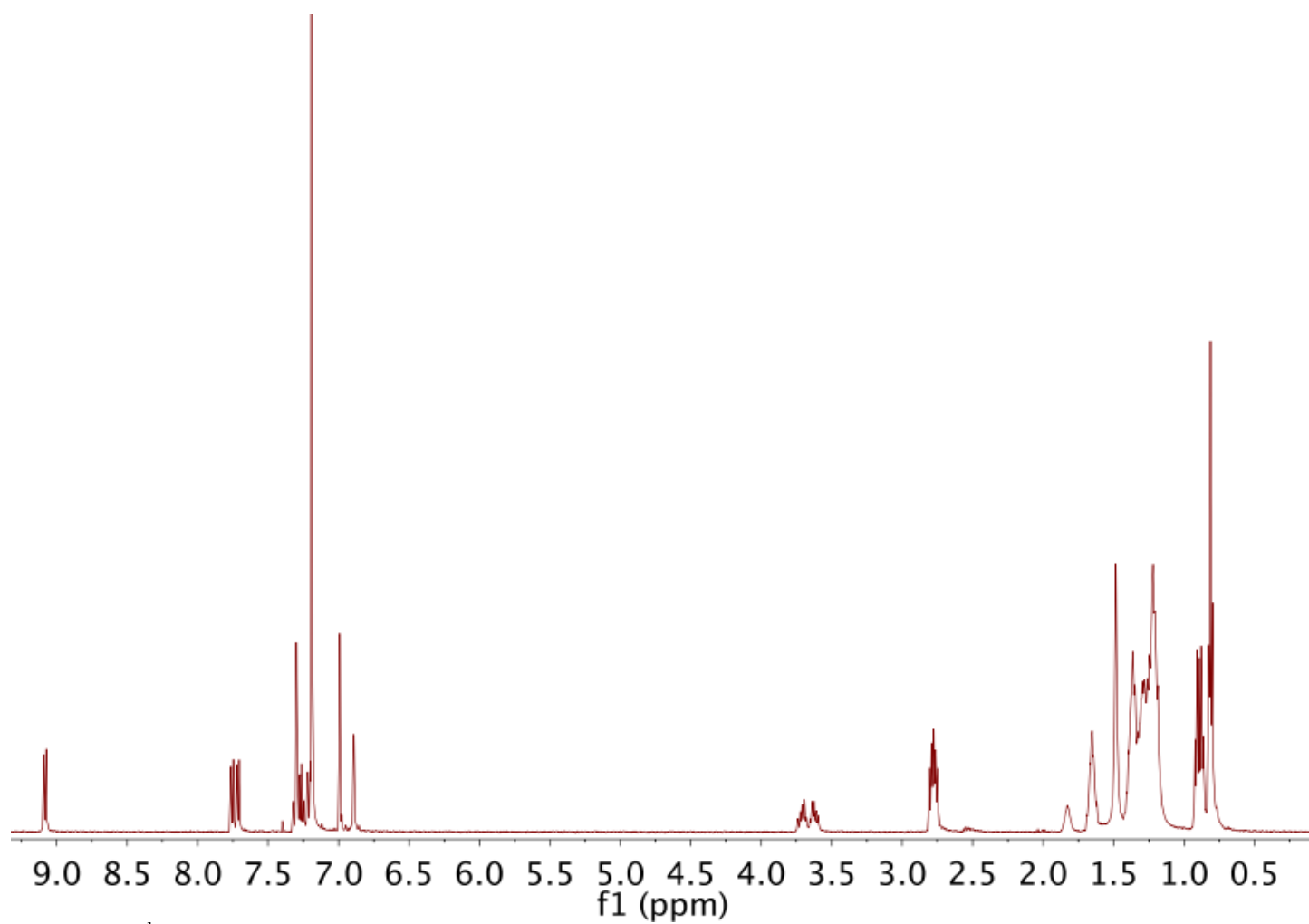


Figure S3. ^1H NMR spectrum of **BT-T2-ID** in CDCl_3 .

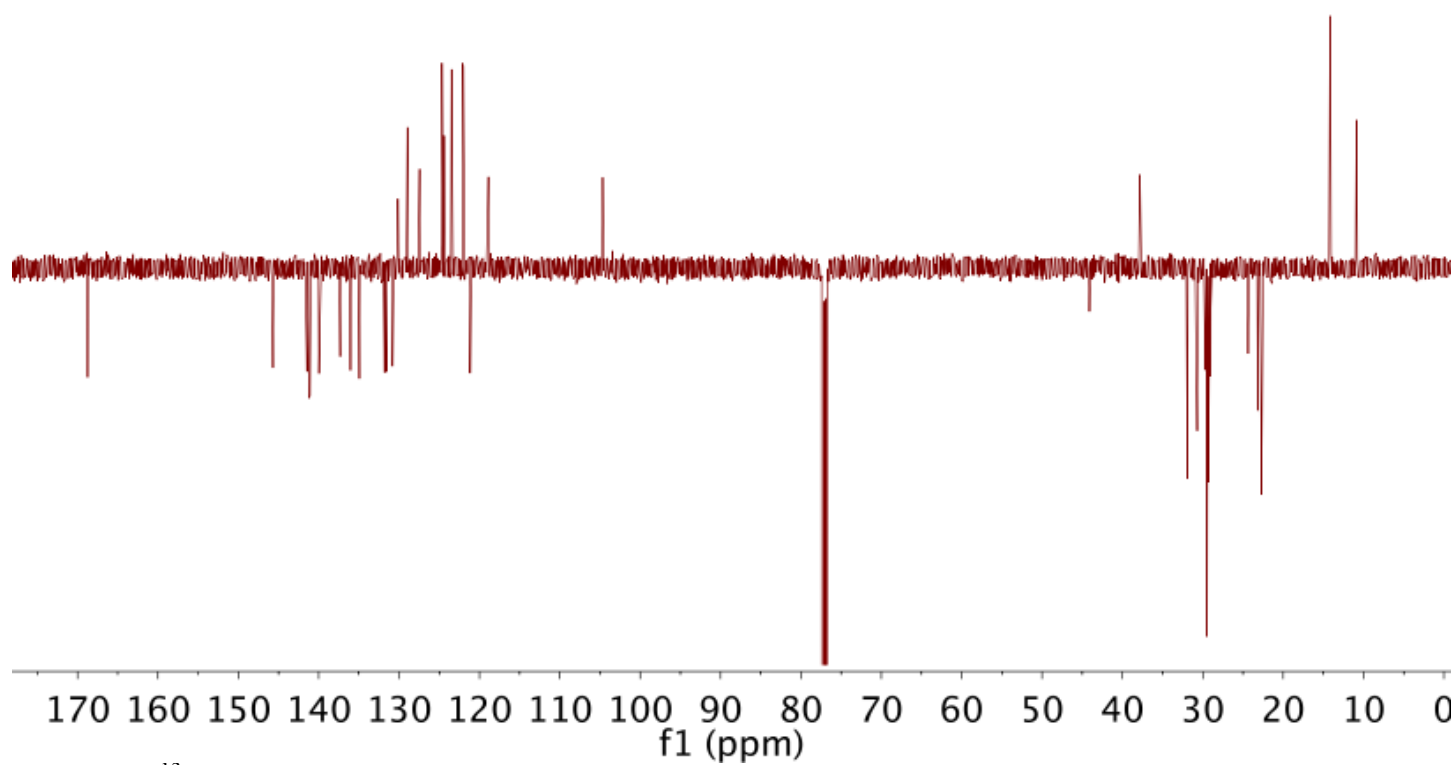


Figure S4. ^{13}C NMR spectrum of **BT-T2-ID** in CDCl_3 .

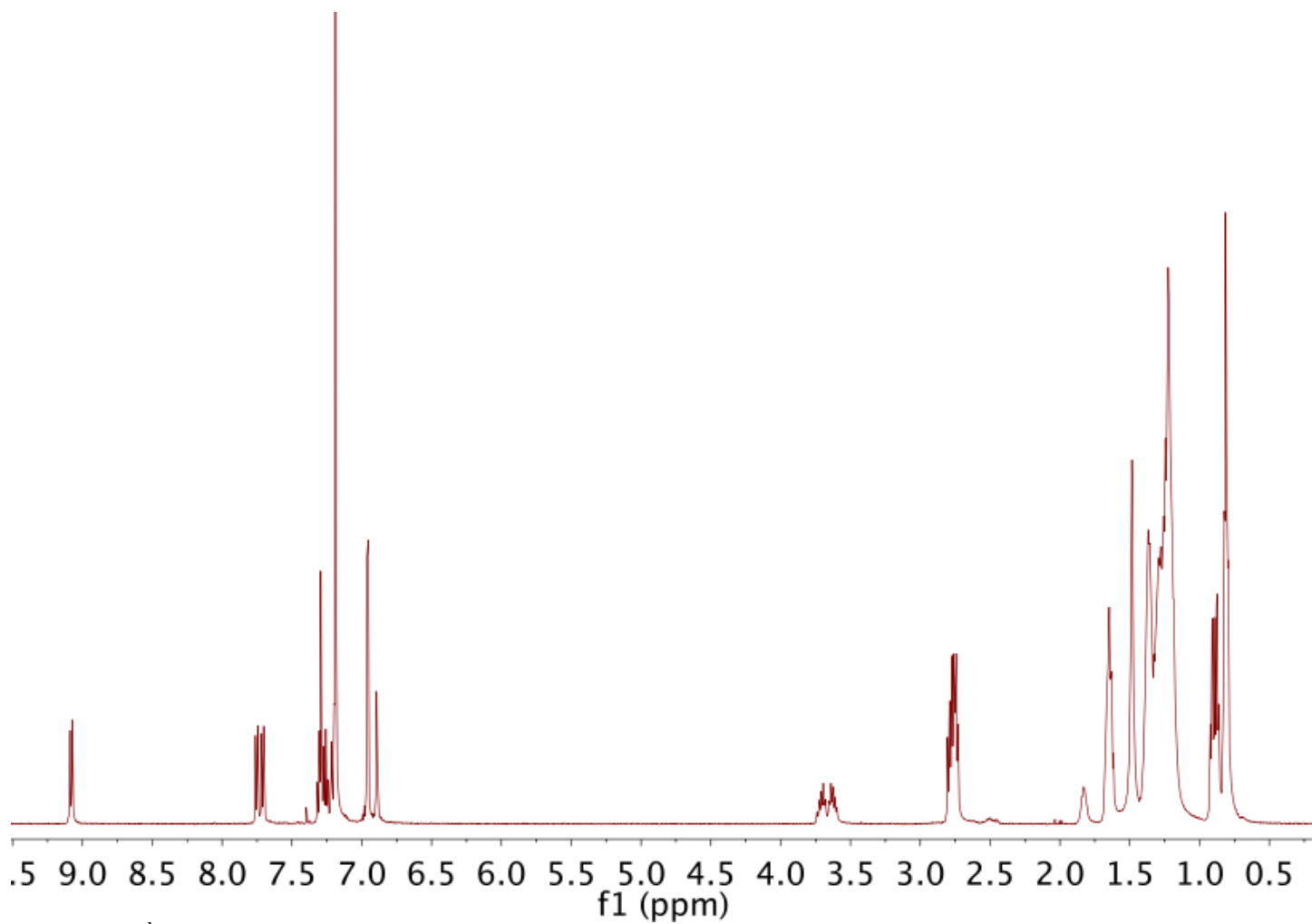


Figure S5. ^1H NMR spectrum of **BT-T3-ID** in CDCl_3 .

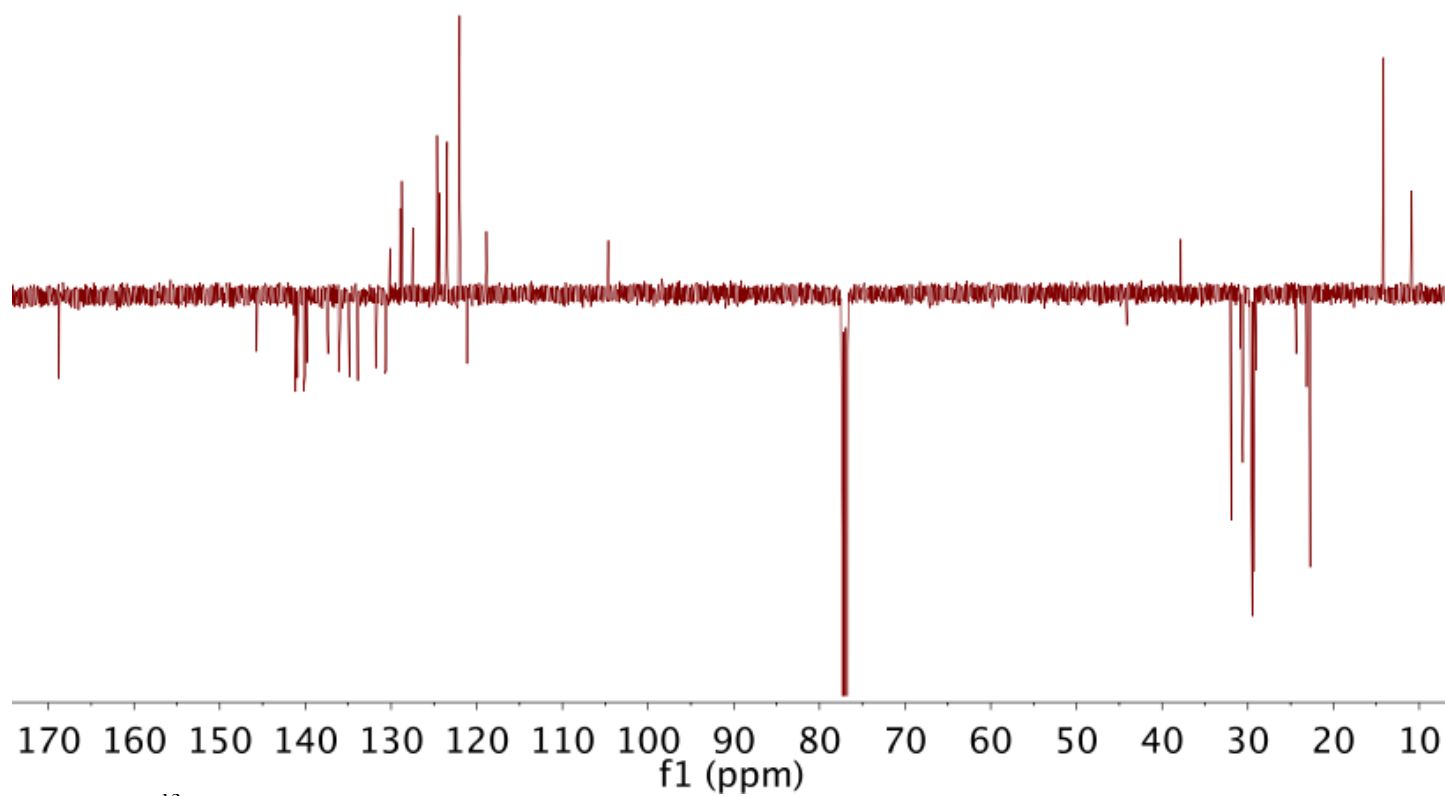


Figure S6. ^{13}C NMR spectrum of **BT-T3-ID** in CDCl_3 .

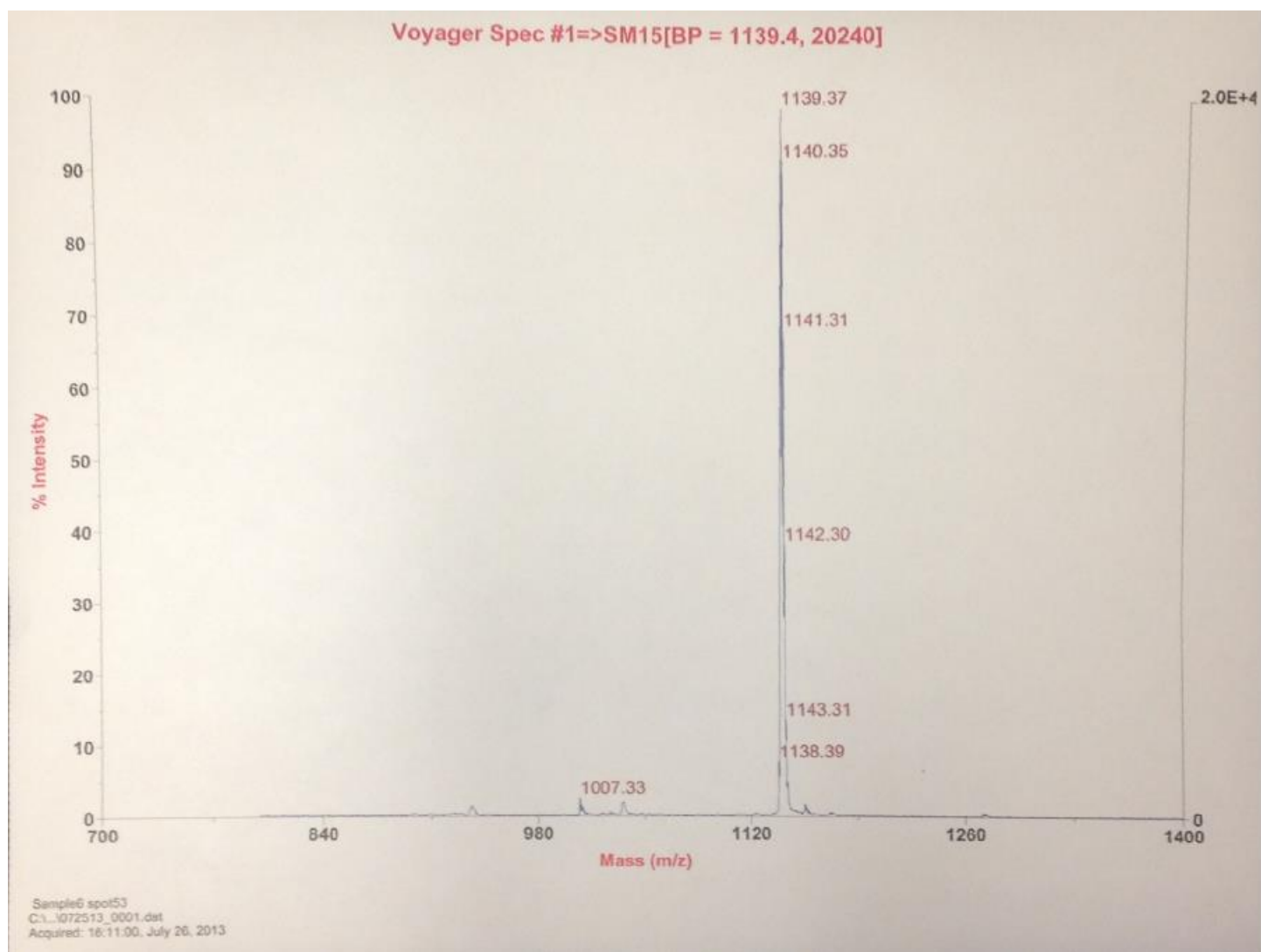


Figure S7. HRMS spectrum of BT-T-ID.

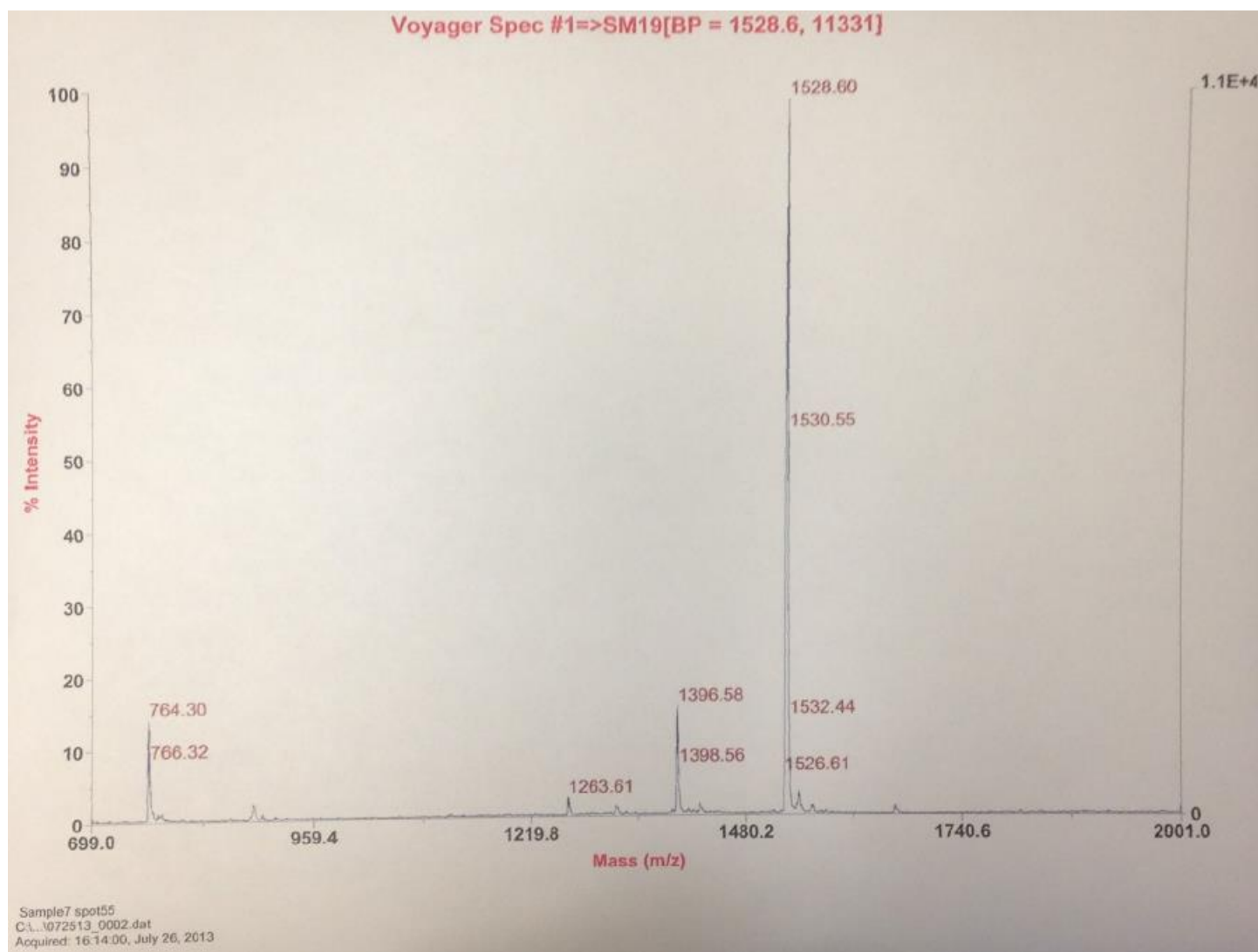


Figure S8. HRMS spectrum of **BT-T2-ID**.

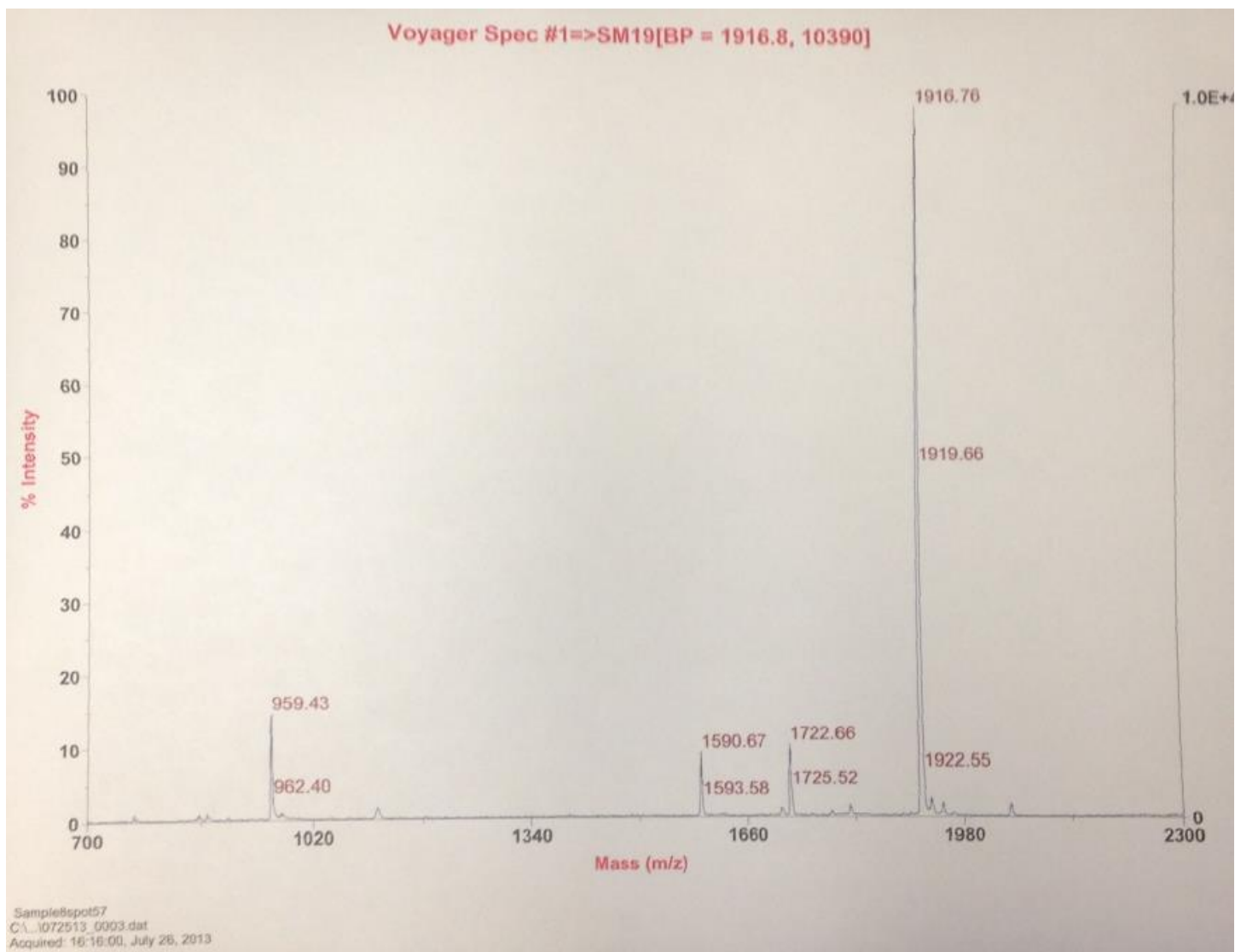


Figure S9. HRMS spectrum of BT-T3-ID.

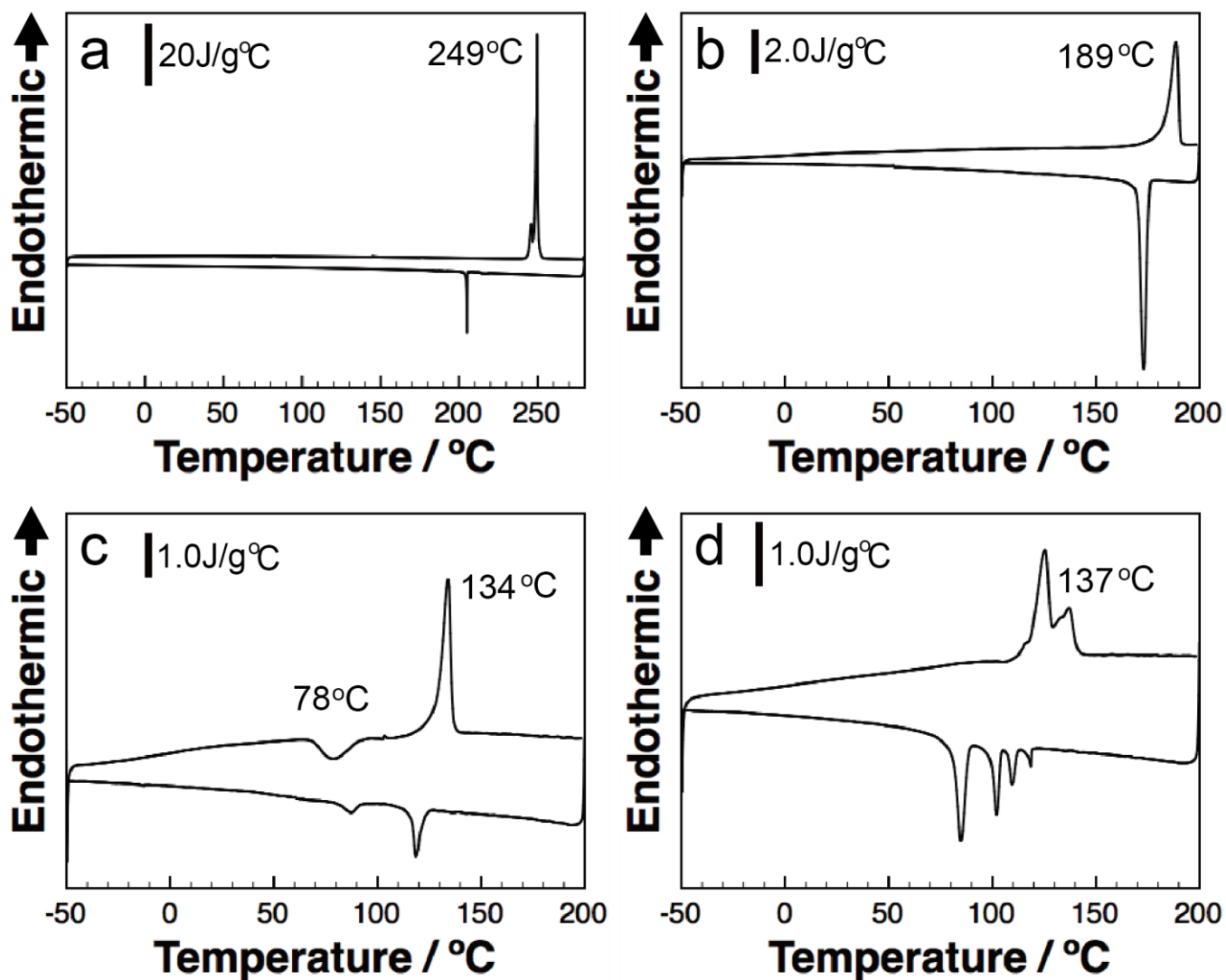


Figure S10. DSC traces of a) BT-ID b) BT-T-ID; c) BT-T2-ID; and d) BT-T3-ID at heating and cooling rates of 10 °C/min.

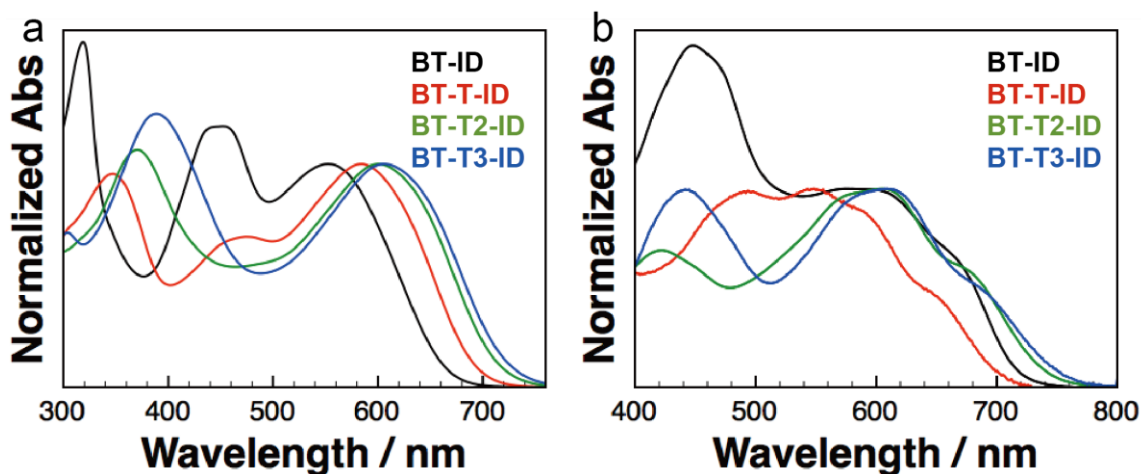


Figure S11. UV-vis absorption spectra of the isoindigo derivatives under study in (a) chloroform at concentrations $< 10^{-5}$ mol/L; and (b) in as-cast films. The spectra have been normalized at their respective low-energy λ_{max} for comparison.

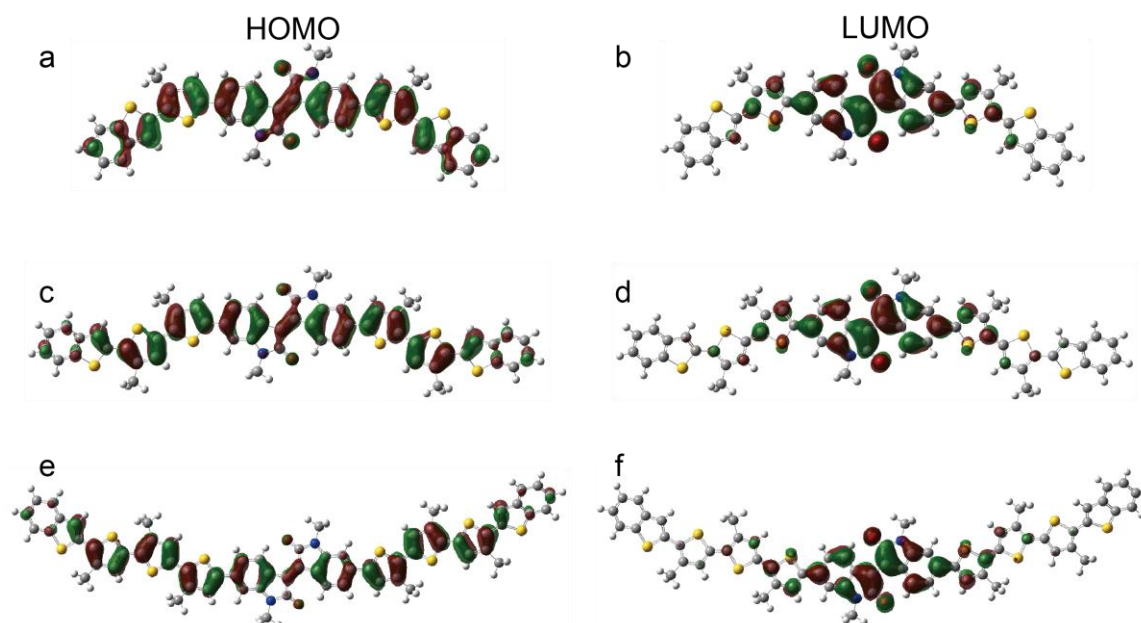


Figure S12. HOMO and LUMO orbitals of (a, b) **BT-T-ID'**; (c, d) **BT-T2-ID'**; (e, f) **BT-T3-ID'**. In order to reduce computation time, the ethylhexyl and octyl side chains were replaced with methyl substituents in these calculations. As such, these compounds are labeled **BT-T-ID'**, **BT-T2-ID'** and **BT-T3-ID'** with the apostrophe to signify this change in the alkyl chain substitution.

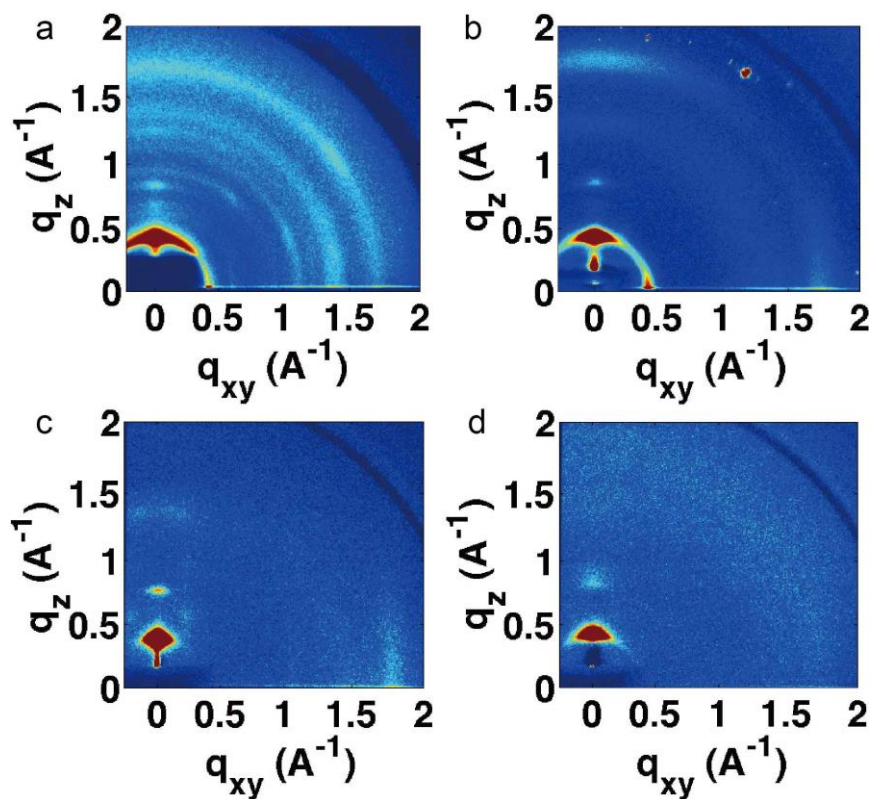


Figure S13. GIXD images of as-cast films of (a) **BT-ID**, (b) **BT-T-ID**, (c) **BT-T2-ID**, (d) **BT-T3-ID**.

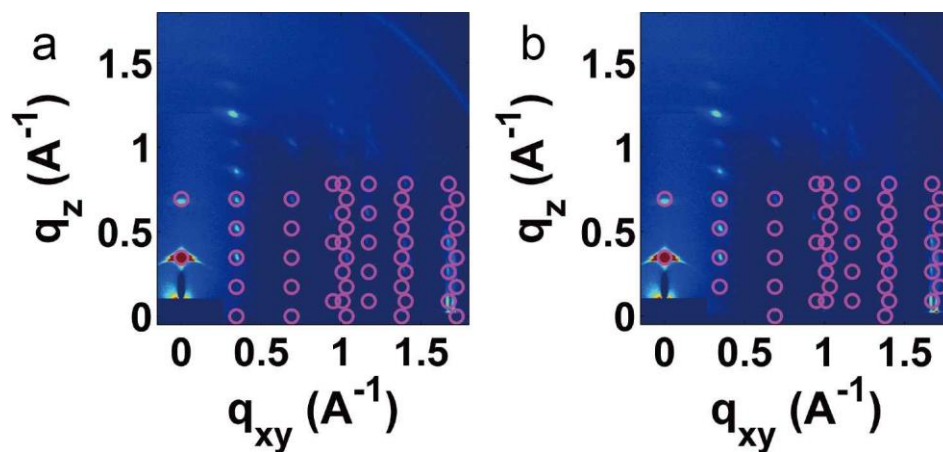


Figure S14. GIXD images of an annealed film of **BT-T2-ID** with reflections calculated using (a) the $P2/c$ space group and (b) the $P2_1/c$ space group, overlaid in magenta.

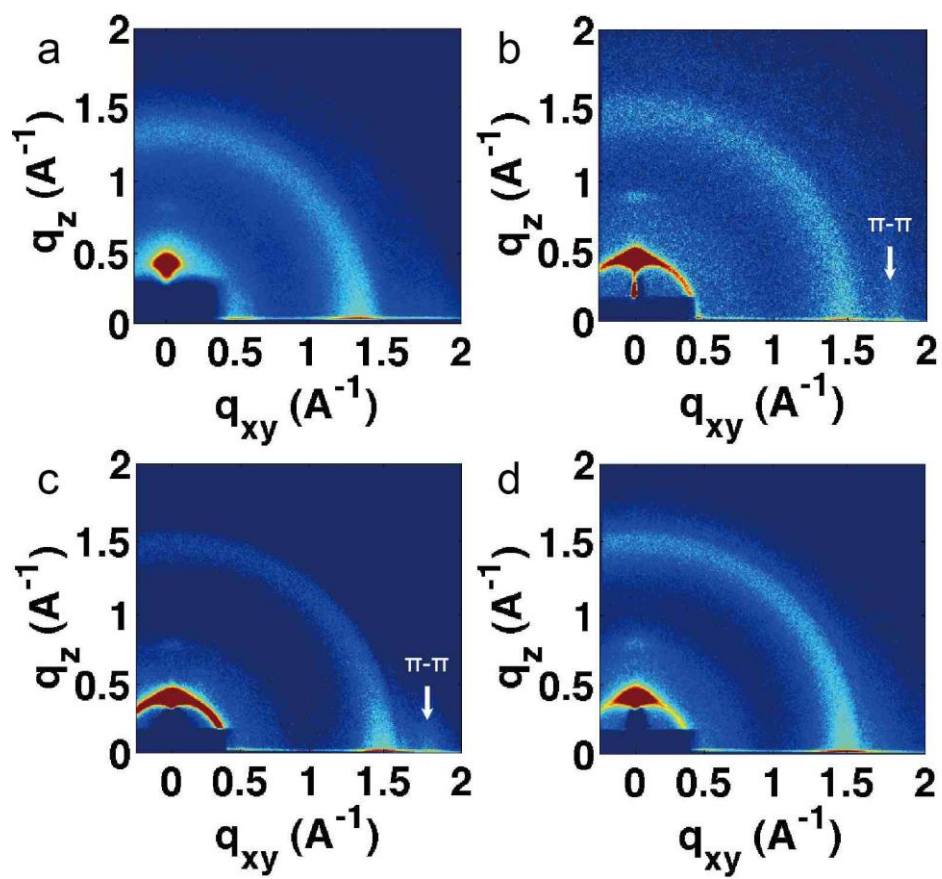


Figure S15. GIXD images of as-cast photoactive layers under the processing conditions employed to fabricate the optimized devices: (a) **BT-ID** and PC₇₁BM; (b) **BT-T-ID** and PC₆₁BM; (c) **BT-T2-ID** and PC₆₁BM; (d) **BT-T3-ID** and PC₆₁BM.

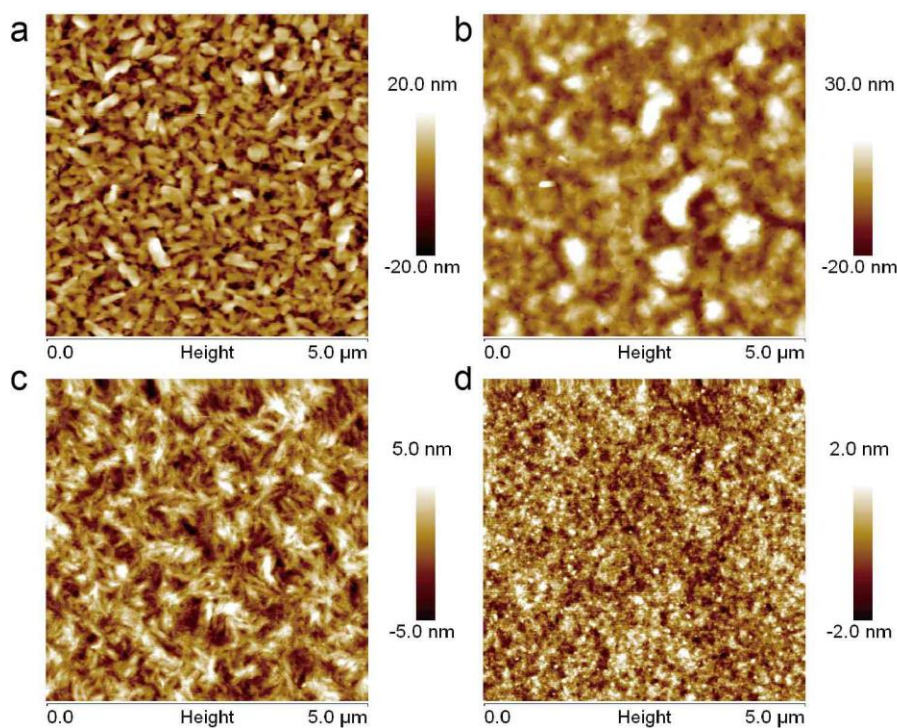


Figure S16. AFM images of annealed photoactive layers of (a) **BT-ID** and PC₇₁BM; (b) **BT-T-ID** and PC₆₁BM; (c) **BT-T2-ID** and PC₆₁BM; (d) **BT-T3-ID** and PC₆₁BM.

Table S1. Theoretical data of extended isoindigo derivatives.^a

Compound	HOMO [eV]	LUMO [eV]	$S_0 \Rightarrow S_1$	Transition Energy of $S_0 \Rightarrow S_1$ [nm]	f^b
BT-T-ID ^c	-5.09	-2.83	HOMO \Rightarrow LUMO	625.64 (1.98 eV)	1.42
BT-T2-ID ^c	-4.92	-2.83	HOMO \Rightarrow LUMO	678.27 (1.83 eV)	1.92
BT-T3-ID ^c	-4.80	-2.83	HOMO \Rightarrow LUMO	720.36 (1.72 eV)	2.12

^a TD-DFT calculated at theoretical level with TD-B3LYP/6-31G(d); ^b oscillator strength; ^c the apostrophe in the naming scheme signifies a change in the alkyl chain substitution; the ethylhexyl and octyl side chains were replaced with methyl substituents to reduce computation time during calculations.

Table S2. Diode mobilities of photoactive layers comprising the extended isoindigo derivatives.

Donor	Hole[10^{-6}] ^a cm ² /V·s as-cast blend	Hole[10^{-6}] ^a cm ² /V·s annealed blend	Electron[10^{-5}] ^b cm ² /V·s as-cast blend	Electron[10^{-5}] ^b cm ² /V·s annealed blend
BT-ID	0.10 ± 0.02	28 ± 3	1.0 ± 0.1	12 ± 2
BT-T-ID	2.6 ± 0.7	22 ± 2	6 ± 1	7 ± 1
BT-T2-ID	17 ± 1	67 ± 20	26 ± 4	73 ± 14
BT-T3-ID	7.8 ± 0.3	57 ± 11	21 ± 5	25 ± 13

^a based on hole-only diodes employing an architecture of ITO/PEDOT:PSS/organic layer/Au. ^b based on electron-only diodes employing an architecture of Al/organic layer/Al. Diode processing conditions are the same as those employed for fabricating the optimized OPV devices.