

Supporting Information

Strategic Side-Chain Engineering Approach for Optimizing Thermoelectric Properties of Isoindigo- Based Conjugated Polymers

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I. Synthesis of alkyl-iodine chains.

1. 7-(iodomethyl)pentadecane

Into a solution of 2-hexyl-1-decanol (3.636 g, 15 mmol), imidazole (820 mg, 12 mmol) and triphenylphosphine (3.161 g, 12 mmol) in dry DCM (24 mL), iodine (2.929 g, 11.5 mmol) was added under ice bath. The mixture was stirred at room temperature for overnight with the ice bath warmed to room temperature naturally, then quenched by the solution of Na₂SO₃ (5.3 g, 42 mmol) in 200 mL water. The organic phase was concentrated by rotary evaporation, and the residue was dissolved with Hexane, washed by water (2 x 150mL) and brine (150 mL), then passed through a shorter silica gel column. The hexane solution was evaporated to afford the title product as colorless oil (4.357g, 82%). ¹H NMR (CDCl₃, 600 MHz, ppm): δ 3.25 (d, 2H), 1.36-1.17 (m, 24H), 0.87-0.85 (t, 6H).

2. 9-(iodomethyl)nonadecane

9-(iodomethyl)nonadecane was synthesized using 2-octyl-1-dodecanol with the same procedure used for 7-(iodomethyl)pentadecane. The resulting monomer was obtained in 5.57g (91 %). ¹H NMR (CDCl₃, 600 MHz, ppm): δ 3.25 (d, 2H), 1.36-1.20 (m, 32H), 0.88-0.86 (t, 6H).

3. 11-(iodomethyl)tricosane

11-(iodomethyl)tricosane was synthesized using 2-decyl-1-tetradecanol with the same procedure used for 7-(iodomethyl)pentadecane. The resulting monomer was obtained in 6.619g (95%). ¹H NMR (CDCl₃, 600 MHz, ppm): δ 3.25 (d, 2H), 1.29-1.21 (m, 40H), 0.88-0.85(t, 6H).

4. 13-(iodomethyl)heptacosane

13-(iodomethyl)heptacosane was synthesized using 2-dodecyl-1-hexadecanol with the same procedure used for 7-(iodomethyl)pentadecane. The resulting monomer was obtained in 7.18g (92%). ¹H NMR (CDCl₃, 600 MHz, ppm): δ 3.25 (d, 2H), 1.31-1.20 (m, 48H), 0.88-0.85(t, 6H).

II. Synthesis of alkylated 6,6'-dibromoisindigo derivatives (IID-R)

1. 6,6'-dibromo-N,N'-(2-hexyldecyl)-isoindigo (IID68)

To a solution of 6,6'-dibromoisindigo (210 mg, 0.5 mmol), potassium carbonate (357 mg, 2.58 mmol) in 15 mL dimethylformamide (DMF), 7-(iodomethyl)pentadecane (704 mg, 2 mmol) was

added under nitrogen. The mixture was stirred overnight at 100 °C. After cooling to room temperature, the reaction was quenched by pouring into water and extracted by using dichloromethane (100 mL). The organic layer was washed with water (2 x 100 mL) and brine (100 mL), dried over magnesium sulfate, and solvent was removed under reduced pressure. The crude product was purified by silica gel chromatography with Hexane/DCM as an eluent, and final product (IID68) was obtained as a deep-red solid (315 mg, 72.5 %). ¹H NMR (CDCl₃, 600 MHz, ppm) δ: 9.05 (d, J = 8.6 Hz, 2H), 7.15 (d, J = 8.6 Hz, 2H), 6.89 (d, 2H), 3.60 (d, 4H), 1.87-1.83 (m, 2H), 1.36-1.14 (m, 48H), 0.86-0.84 (m, 12H). ¹³C NMR (CDCl₃, 600 MHz, ppm): δ 168.30, 146.33, 132.71, 131.17, 126.82, 125.26, 120.46, 111.72, 44.85, 36.23, 32.01, 31.65, 30.12, 29.79, 29.43, 26.48, 22.81, 14.22.

2. 6,6'-dibromo-N,N'-(2-octyldodecyl)-isoindigo (IID810)

Synthesis of IID810 was proceeded using 9-(iodomethyl)nonadecane following the same procedure used for IID68. IID810 was obtained as a red solid (412 mg, 84%). ¹H NMR (CDCl₃, 600 MHz, ppm) δ: 9.06 (d, J = 8.6 Hz, 2H), 7.15 (d, J₁ = 8.6 Hz, J₂ = 1.5 Hz, 2H), 6.89 (d, J = 1.5 Hz, 2H), 3.61 (d, 4H), 1.87 (m, 2H), 1.36-1.16 (m, 64H), 0.87-0.84 (m, 12H). ¹³C NMR (CDCl₃, 600 MHz, ppm): δ 168.27, 146.36, 132.73, 131.17, 126.81, 125.25, 120.54, 111.70, 44.84, 36.22, 32.05, 31.63, 30.11, 29.76, 29.43, 26.50, 22.80, 14.17.

3. 6,6'-dibromo-N,N'-(2-decyltetradecyl)-isoindigo (IID1012)

Synthesis of IID1012 was proceeded using 11-(iodomethyl)tricosane following the same procedure used for IID68. IID1012 was obtained as a red solid (437 mg, 80%). ¹H NMR (CDCl₃, 600 MHz, ppm) δ: 9.07 (d, J = 8.6 Hz, 2H), 7.16 (d, J = 8.6 Hz, 2H), 6.90 (d, 2H), 3.61 (d, 4H), 1.87 (m, 2H), 1.41-1.23 (m, 80H), 0.88-0.85 (m, 12H). ¹³C NMR (CDCl₃, 600 MHz, ppm): δ 168.23, 146.32, 132.74, 131.05, 126.76, 125.14, 120.51, 111.72, 44.78, 36.16, 32.01, 31.57, 30.06, 29.72, 29.4, 26.43, 22.77, 14.20.

4. 6,6'-dibromo-N,N'-(2-dodecylhexadecyl)-isoindigo (IID1214)

Synthesis of IID1214 was proceeded using 13-(iodomethyl)heptacosane following the same procedure used for IID68. IID1214 was obtained as a red solid (518mg, 86%). ¹H NMR (CDCl₃,

600 MHz, ppm) δ : 9.06 (d, J = 8.6 Hz, 2H), 7.16 (d, J = 8.6 Hz, 2H), 6.89 (d, 2H), 3.61 (d, 4H), 1.98-1.85 (m, 2H), 1.34-1.14 (m, 96 H), 0.87-0.85 (t, 12H).

^{13}C NMR (CDCl_3 , 600 MHz, ppm): δ 168.21, 146.38, 132.79, 131.18, 126.82, 125.27, 120.55, 111.72, 44.85, 36.23, 32.09, 31.65, 30.13, 29.78, 29.52, 26.50, 22.85, 14.28.

III. Procedures for Stille Polymerization and Polymer Purification

In a 50 mL two neck round flask, 2,5-bis(trimethylstannyl)thienothiophene (96 mg, 0.2 mmol), IID-R (R = 68, 810, 1012, and 1214) (173mg, 0.2mmol), tris(dibenzylideneacetone)dipalladium(0) ($\text{Pd}_2(\text{dba})_3$) (6mg) and tri(*o*-tolyl)phosphine ($\text{P}(\text{o-Tol})_3$) (10mg) were dissolved in anhydrous toluene (6 mL). The mixture was stirred at 100 °C under nitrogen for 24hr and poured into acetone after cooled down to room temperature. The polymer was collected by filtration, purified by Soxhlet extraction with acetone and diethyl ether in sequence for 24hr and then dissolved in chloroform. The chloroform fraction was concentrated and poured into acetone. Finally, the polymer was collected by filtration through 0.45 μm Teflon filter and dried under vacuum. (PIID68-TT: M_n = 43.04 kDa, PDI = 9.47, PIID810-TT: M_n = 60.66 kDa, PDI = 7.68, PIID1012-TT: M_n = 36.92 kDa, PDI = 4.79, PIID1214-TT: M_n = 27.22 kDa, PDI = 3.44, Figure S5).

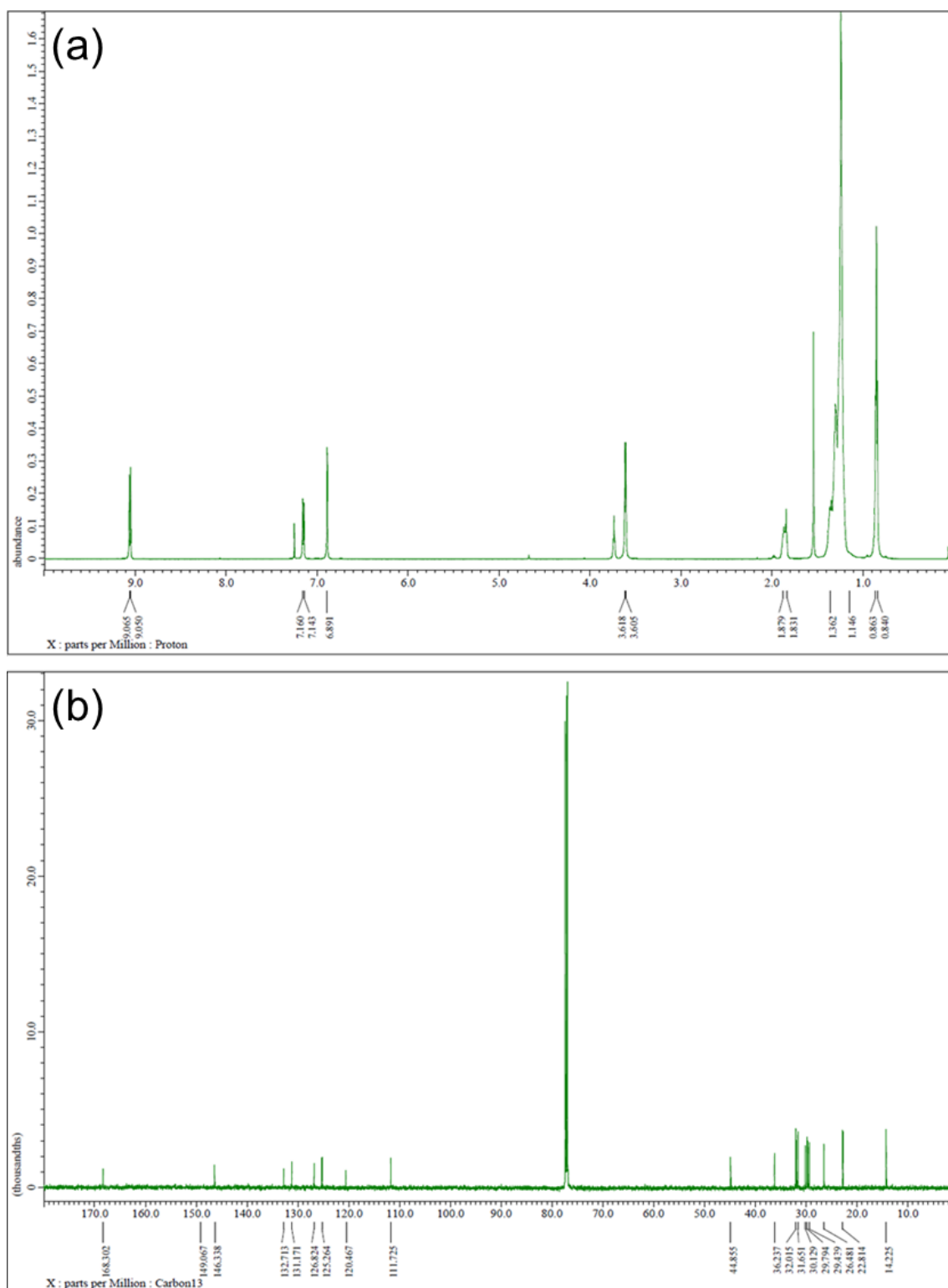


Figure S1. (a) ^1H NMR and (b) ^{13}C NMR spectra of IID68.

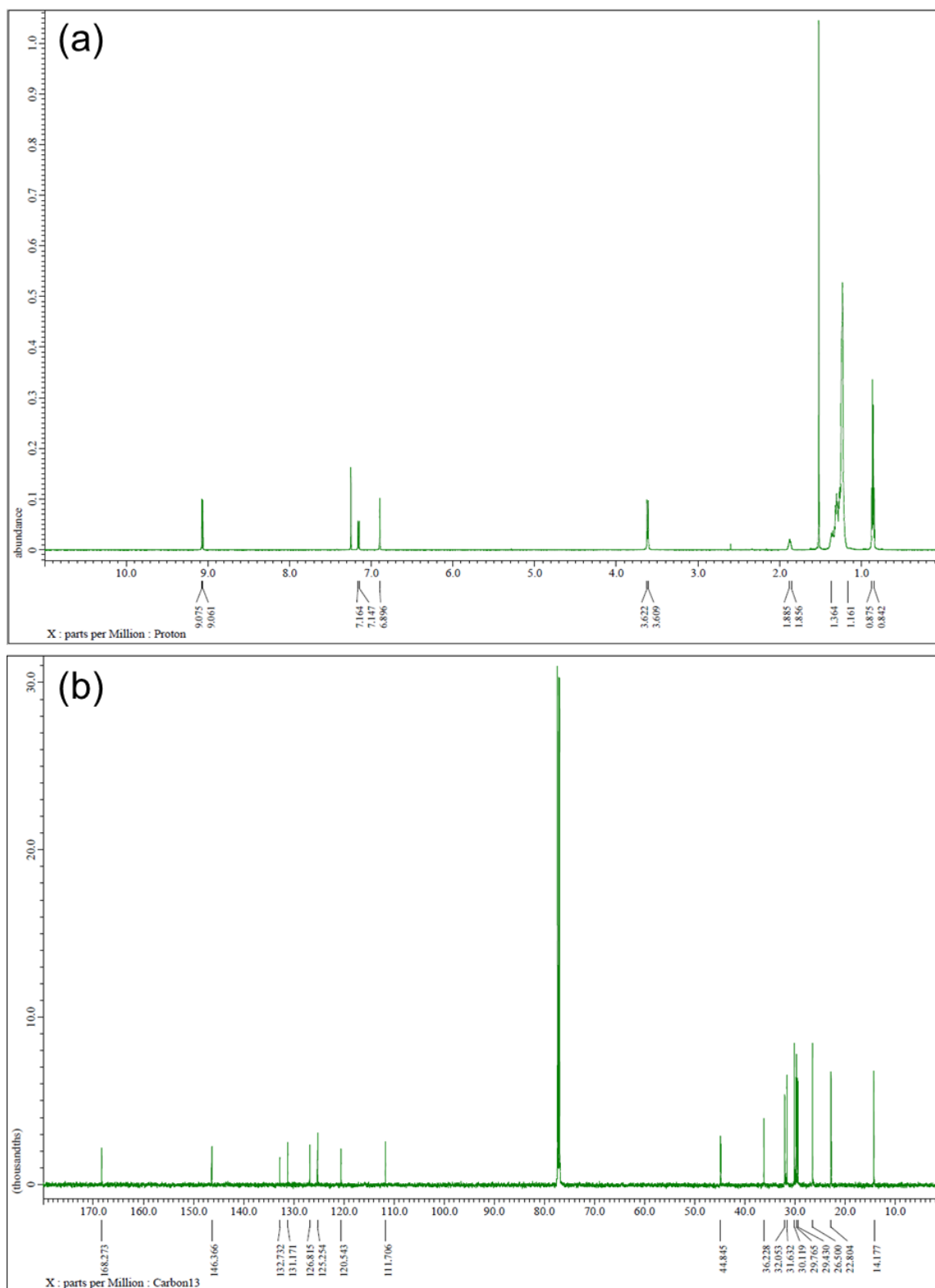


Figure S2. (a) ^1H NMR and (b) ^{13}C NMR spectra of IID810.

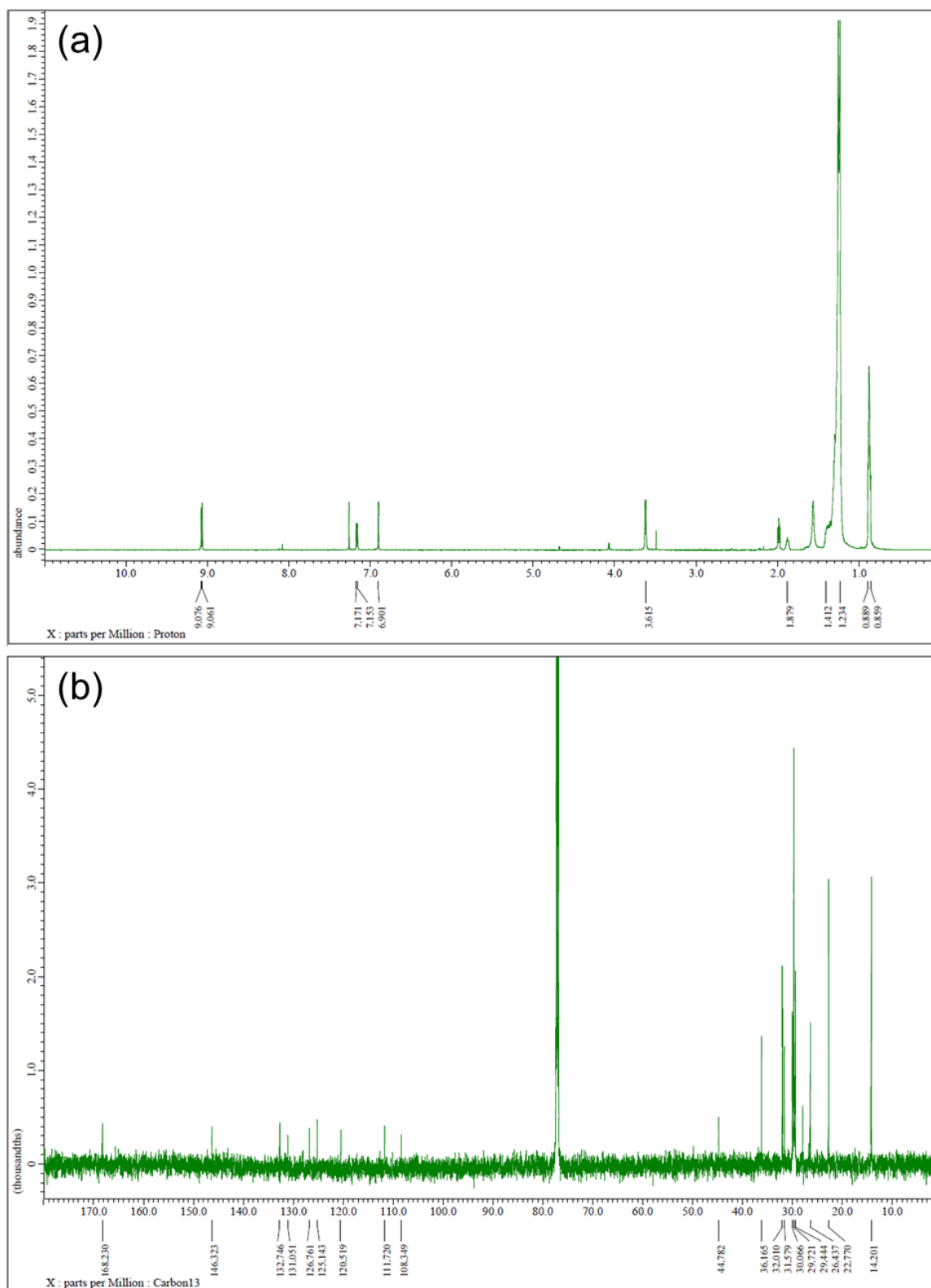


Figure S3. (a) ^1H NMR and (b) ^{13}C NMR spectra of IID1012.

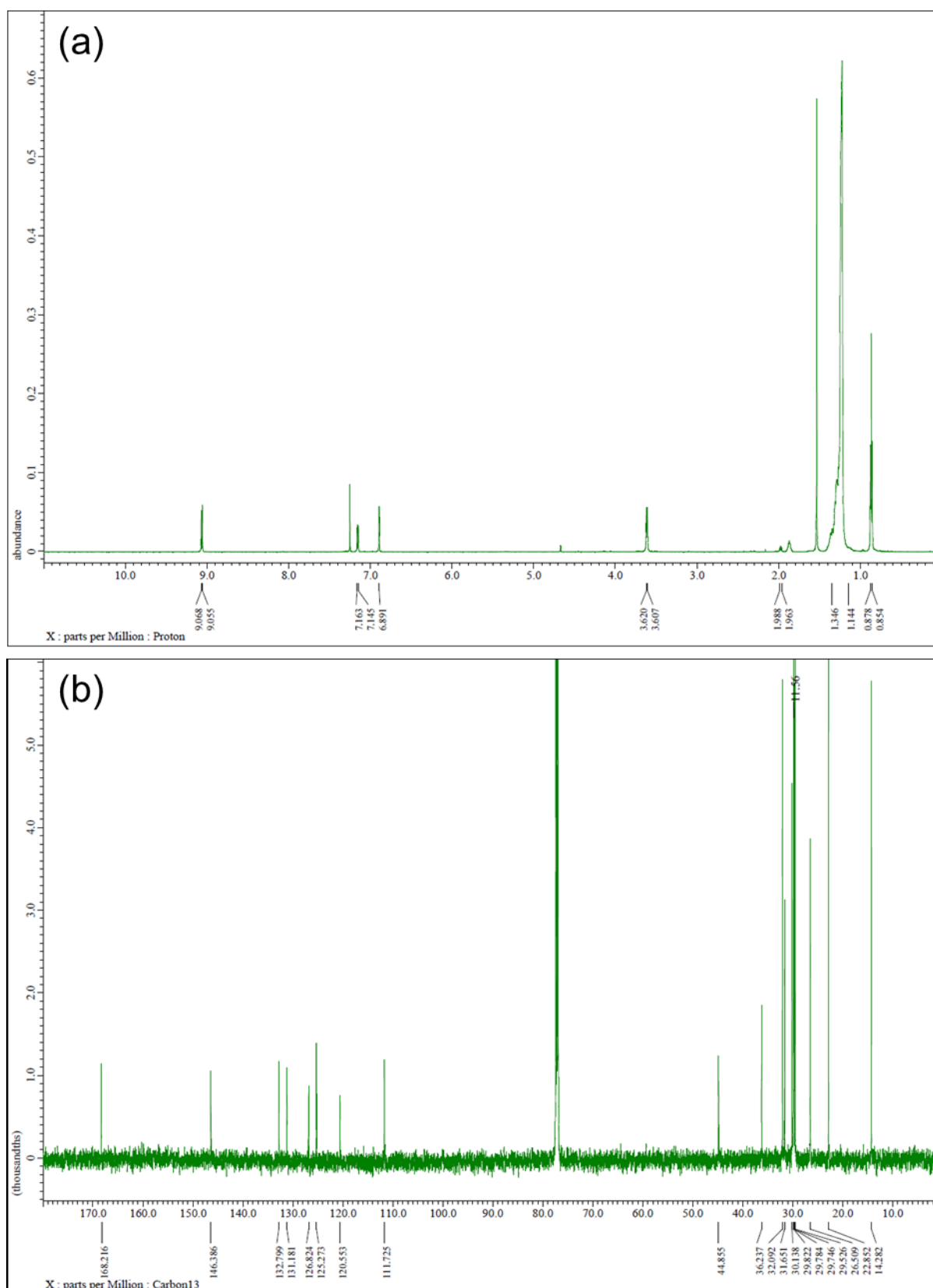


Figure S4. (a) ^1H NMR spectrum and (b) ^{13}C NMR spectrum of IID1214

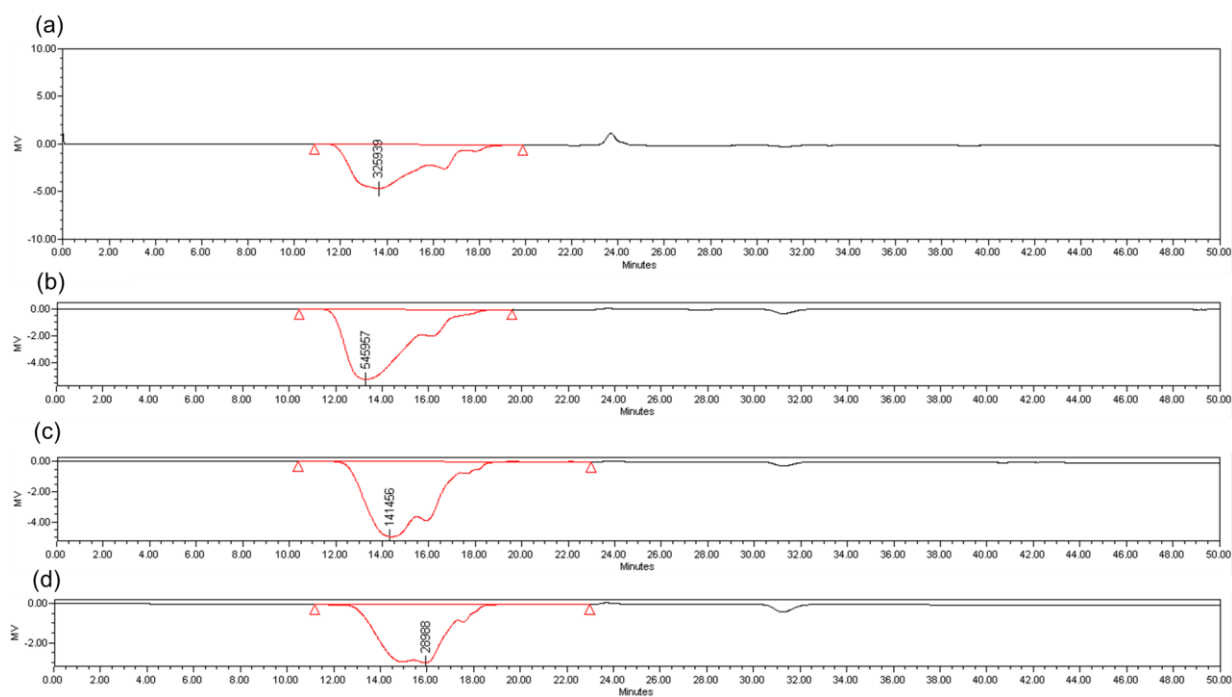


Figure S5. Molecular weight information of (a) PIID68-TT, (b) PIID810-TT, (c) PIID1012-TT, (d) PIID1214-TT obtained from gel permeation chromatography (GPC).

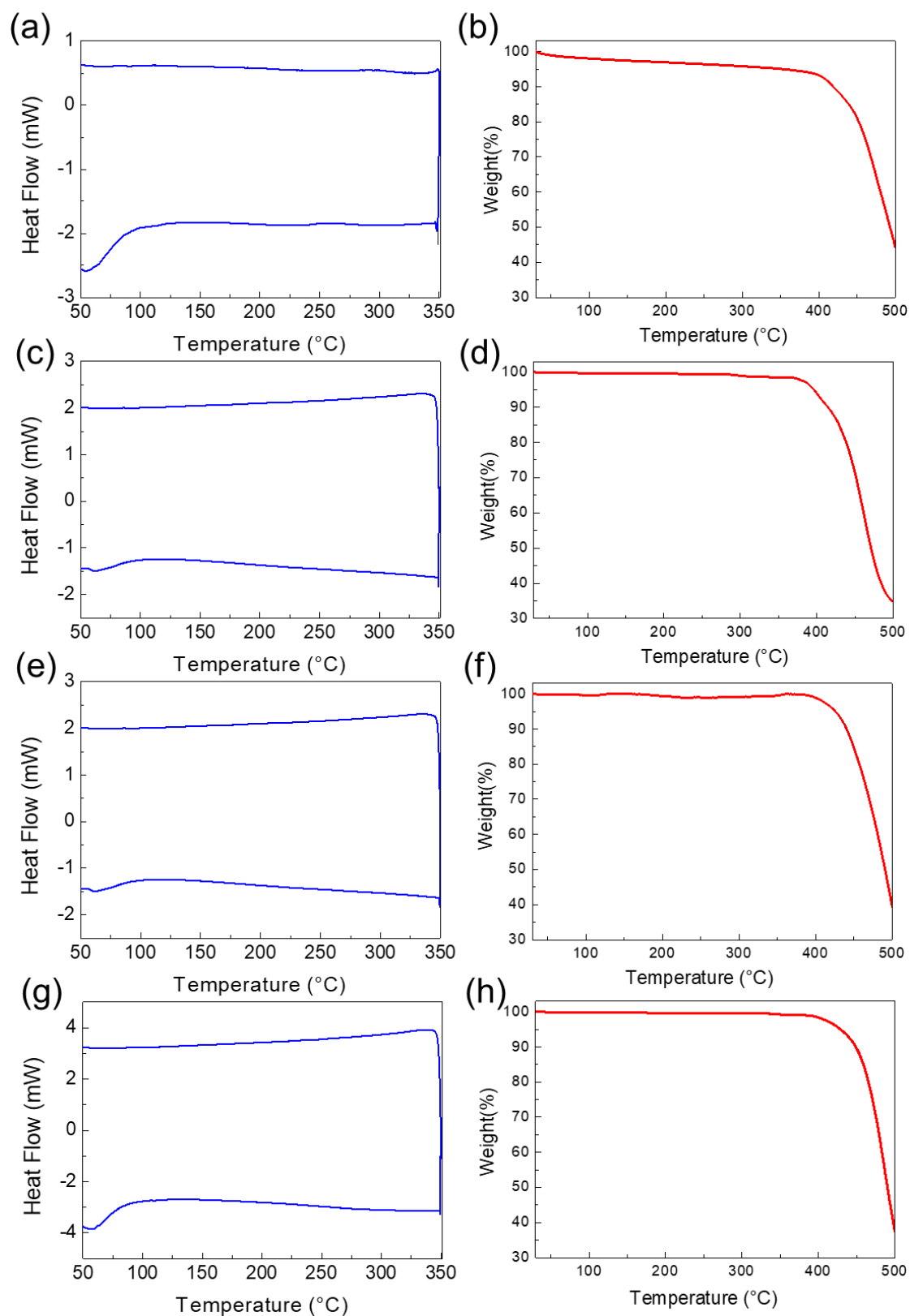


Figure S6. DSC (a, c, e, g) and TGA (b, d, f, h) spectra of PIID68-TT (a, b), PIID810-TT (c, d), PIID1012-TT (e, f), and PIID1214-TT (g, h).

Table S1. Summary of power factor values of reported doped donor-acceptor-type copolymers.

Polymer	Dopant	Power Factor [$\mu\text{W}/\text{mK}^2$]	Ref
PCQ	Gav	~12	S1
C8TBT	FeCl ₃	~2	S2
PBDTDTBTF -3	FeCl ₃	~0.6	S3
39PIC(c)T2	FeCl ₃	0.12	S4
PCDTBT	FeCl ₃	19	S5
F6BT	FeCl ₃	~1.6	S6
PCDTFBT	F ₄ TCNQ	31.5	S7
PIID810-TT	FeCl ₃	37.8	This work

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