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Supporting Information for

Diels-Alder Adducts of C_{60} and Esters of 3-(1-Indenyl) Propionic Acid: Alternatives for [60]PCBM in Polymer:Fullerene Solar Cells

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General information.

Synthesis of the fullerene derivatives [60]IPE, [60]IPB, and [60]IPH.

Fabrication of Solar cells.

General information

All chemicals for synthesis were commercially available and used as received. The 3-(1-indenyl) propionic acid alkyl esters were synthesized using a procedure reported in literature.[1] Fullerene C_{60} was >99.5% by HPLC and used without further purification. NMR measurements were performed on an Agilent Technologies 400/54 400 MHz NMR apparatus at 25 °C. Values are reported in ppm, using the signal of $CHCl_3$ as reference (at 7.26 ppm for ^1H and at 77.0 ppm for ^{13}C measurements). Multiplicities are denoted as follows: s = singlet, d = doublet, t = triplet, qr = quartet, m = multiplet. *J* values are reported in Hz. The NMR spectra of the fullerene derivatives are depicted in Figure S1 – S6.

IR measurements were performed on a Nicolet Nexus FT-IR instrument using an ATR reflection set-up. Relative intensities are noted as follows: w = weak, m = medium, s = strong.

HPLC analyses were performed on an Agilent HP1100 series instrument, using an analytical Cosmosil Buckyprep column (4.6 x 250 mm) and a detection wavelength of 360 nm, with toluene as the eluent. MS spectra of the fullerene derivatives were obtained using an Agilent 6120 Quadrupole LC/MS attached to the HPLC system. UV-Vis spectra of the fullerene derivatives were obtained on the same system, using the UV-Vis diode-array detector.

Cyclic Voltammetry (CV) measurements were performed under N_2 in a home-made electrochemical cell. Experimental conditions were as follows: Bu_4NPF_6 as supporting electrolyte (0.1M) and ODCB/acetonitrile (4:1 v/v) as solvent. The scan rate was 10 mV/s. The fullerene compound was dissolved at 0.7–1 mg/mL. A Pt working electrode was used, and a Pt wire was used as counter electrode. The reference was an Ag/AgCl electrode. Ferrocene (Fc/Fc^+) was used as internal reference (0.05–0.08 mg/mL). The experimental error for the system is 0.005–0.010 V, as determined from repeated measurements on [60]PCBM.

Synthesis of [60]IPE

A mixture of 10.8 grams of C_{60} (>99.5% purity; 15 mmol) and 6.48 g of 3-(1-indenyl) propionic acid ethyl ester (30 mmol) in 1.5 L of o-dichlorobenzene (ODCB) was heated to reflux under N_2 atmosphere for 40 h. The reaction mixture was cooled down and the volume was partially reduced in vacuo. Column chromatography (silica gel; xylenes) gave the crude product, and 7.4 grams of unreacted C_{60}. The crude product was further purified on a second silica gel column to remove various side-products and a small amount of residual C_{60}. The fractions containing the desired product were combined and concentrated in vacuo. The product was then redissolved in chloroform, precipitated in methanol, washed repeatedly with methanol and pentane, and dried at 60 °C. This gave 3.6 g (3.8 mmol; 25%) of [60]IPE as a brown solid.

^1H NMR (400 MHz, $CDCl_3$): δ 7.63–7.60 (m, 1H); 7.51–7.43 (m, 3H); 4.93 (s, 1H); 4.22 (qr, *J* = 7.0 Hz, 2H); 3.63 (d, *J* = 10.2 Hz, 1H); 3.40–3.32 (m, 1H); 3.15–3.07 (m, 1H); 2.99–2.91 (m, 1H); 2.83–2.74 (m, 1H); 2.81 (d, *J* = 9.8 Hz, 1H); 1.32 (t, *J* = 7.0 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ 173.37; 156.72; 155.03; 154.84; 153.79; 147.18; 146.64; 146.28; 146.18; 146.13; 146.10; 146.05; 145.92; 145.72; 145.63; 145.39; 145.36; 145.34; 145.24; 145.15; 145.11; 145.07; 144.90; 144.60; 144.58; 144.33; 144.30; 143.05; 142.75; 142.65; 142.63; 142.48; 142.14; 142.12; 142.05; 142.03; 142.01; 141.97; 141.87; 141.72; 141.71; 141.69; 140.14; 139.67; 139.39; 137.63; 137.31; 137.25; 137.18; 127.43; 127.30; 124.29; 122.91; 78.71; 77.12; 64.80; 60.77; 56.69; 48.17; 31.51; 25.72; 14.29 ppm

LC-MS (relative intensity): M+ = 936 (100); M+1 = 937 (68); M+2 = 938 (24). The molecular formula of [60]IPE is $C_{74}H_{16}O_2$.

IR (neat; in cm^{-1}): 2970 (w); 2866; 1732 (s); 1462 (m); 1180 (s); 750 (s).

Synthesis of [60]IPB

[60]IPB was synthesized as described for IPE, using 3-(1-indenyl) propionic acid butyl ester as the starting material instead of the ethyl ester. For the reaction, 14.4 grams (20 mmol) of C_{60} was used. After column chromatography, 8.4 grams of unreacted C_{60} and 5.9 grams of [60]IPB (6.0 mmol; 30% yield) were obtained.

^1H NMR (400 MHz, $CDCl_3$): δ 7.63–7.60 (m, 1H); 7.51–7.42 (m, 3H); 4.93 (s, 1H); 4.17 (t, *J* = 6.7 Hz, 2H); 3.63 (d, *J* = 10.0 Hz, 1H); 3.40–3.32 (m, 1H); 3.16–3.08 (m, 1H); 3.00–2.91 (m, 1H); 2.83–2.74 (m, 1H); 2.81 (d, *J* = 10 Hz, 1H); 1.70–1.63 (m, 2H); 1.47–1.37 (m, 2H); 0.96 (t, *J* = 7.0 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ 173.46; 156.72; 155.02; 154.82; 153.78; 147.17; 146.63; 146.27; 146.17; 146.12; 146.09; 146.04; 145.92; 145.72; 145.62; 145.38; 145.35; 145.33; 145.21; 145.15; 145.12; 145.10; 145.06; 144.90; 144.59; 144.57; 144.32; 144.29; 143.04; 142.74; 142.65; 142.63; 142.47; 142.15; 142.12; 142.03; 142.00; 141.94; 141.86; 141.70; 141.68; 140.13; 139.67; 139.38; 137.61; 137.29; 137.24; 137.16; 127.43; 127.29; 127.29; 122.89; 78.70; 77.10; 64.77; 64.71; 56.68; 48.15; 31.48; 30.65; 25.74; 19.19; 13.77 ppm.

LC-MS (relative intensity): M+ = 964 (100); M+1 = 965 (70); M+2 = 938 (29). The molecular formula of [60]IPB is $C_{76}H_{20}O_2$.

IR (neat; in cm^{-1}): 2952 (w); 2925 (w); 2866; 1732 (s); 1462 (m); 1179 (s); 750 (s).

Synthesis of [60]IPH

A mixture of 3.1 g of [60]IPE, 10 mL of 1-hexanol and 60 mg of dibutyltin oxide in 75 mL of ODCB was heated at 80 °C under N_2 for 40 h. HPLC analysis showed almost full conversion. The reaction mixture was concentrated in vacuo and the crude product was redissolved in a small amount of ODCB. The product was then purified by repetitive column chromatography (silica gel; toluene/cyclohexane 1:1 (v/v)). After two columns, the fractions containing pure product (by HPLC analysis) were combined and concentrated in vacuo. The product was redissolved in a small amount of chloroform and then precipitated and washed as described for [60]IPE. Drying at 60 °C gave 3.5 g of [60]IPH as a brown powder.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63–7.60 (m, 1H); 7.51–7.42 (m, 3H); 4.93 (s, 1H); 4.16 (t, *J* = 6.5 Hz, 2H); 3.63 (d, *J* = 10.2 Hz, 1H); 3.40–3.32 (m, 1H); 3.15–3.07 (m, 1H); 3.00–2.91 (m, 1H); 2.83–2.74 (m, 1H); 2.81 (d, *J* = 10.2 Hz, 1H); 1.70–1.63 (m, 2H); 1.47–1.25 (m, 6H); 0.89 (t, *J* = 7.0 Hz, 3H) ppm.

13C NMR (100 MHz, $CDCl_3$): δ 173.33; 156.68; 154.97; 154.76; 153.75; 147.11; 146.57; 146.21; 146.11; 146.08; 146.04; 145.99; 145.86; 145.68; 145.60; 145.35; 145.31; 145.27; 145.16; 145.09; 145.06; 145.02; 144.85; 144.55; 144.53; 144.27; 144.23; 143.00; 142.68; 142.60; 142.57; 142.42; 142.11; 142.09; 142.07; 142.01; 141.97; 141.95; 141.91; 141.82; 141.66; 141.63; 140.09; 139.64; 139.62; 139.35; 137.56; 137.27; 137.19; 137.14; 127.41; 127.25; 124.26; 122.84; 78.67; 77.07; 64.94; 64.76; 56.65; 48.15; 31.48; 31.39; 28.56; 25.71; 25.61; 22.53; 14.04 ppm

LC-MS (relative intensity): M+ = 992 (100); M+1 = 993 (76); M+2 = 994 (33). The molecular formula of [60]IPH is $C_{78}H_{24}O_2$.

IR (neat; in cm^{-1}): 2947 (w); 2920 (w); 2851; 1731 (s); 1462 (m); 1170 (s); 750 (s).

Melting points of all three fullerene derivatives, as determined by flash differential scanning calorimetry under N_2 atmosphere, are around 275 °C. The observed melting was irreversible, which could either be because the material did not resolidify properly (all three compounds are fine, amorphous brown powders), or because of subsequent decomposition above the melting point.

Additional NMR Spectra

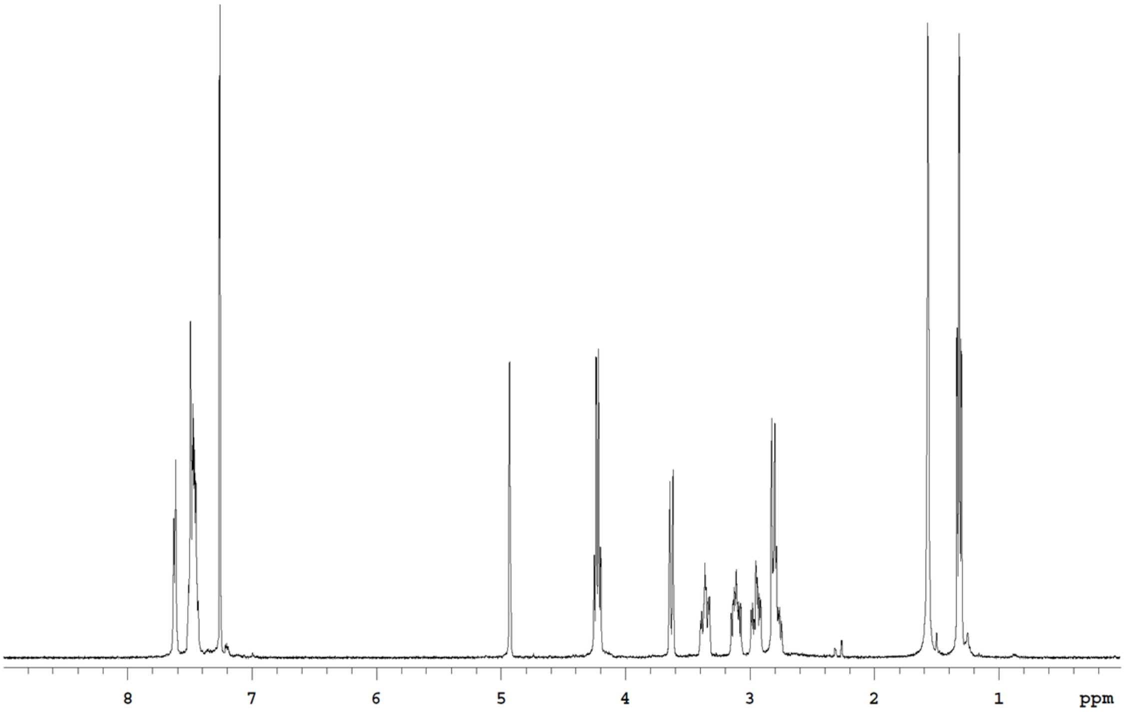

Figure S1. ^{1}H NMR spectrum of [60]IPE.

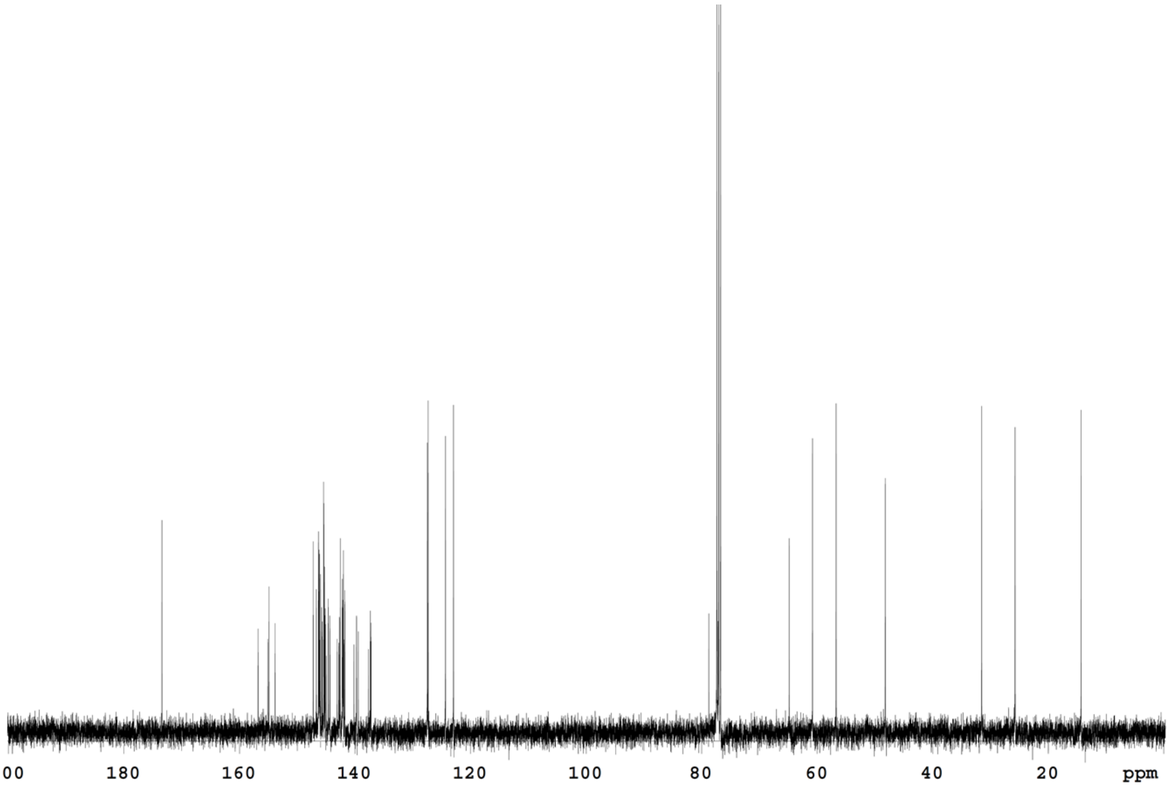

Figure S2. ^{13}C NMR spectrum of [60]IPE

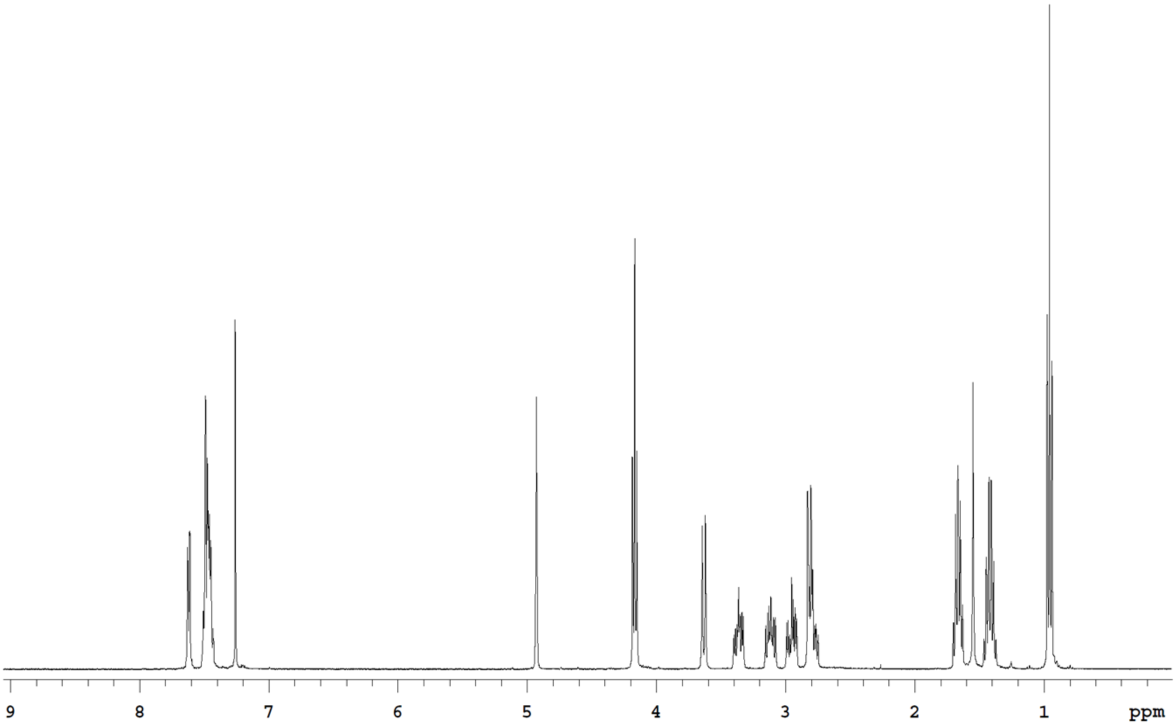

Figure S3. ^{1}H NMR spectrum of [60]IPB.

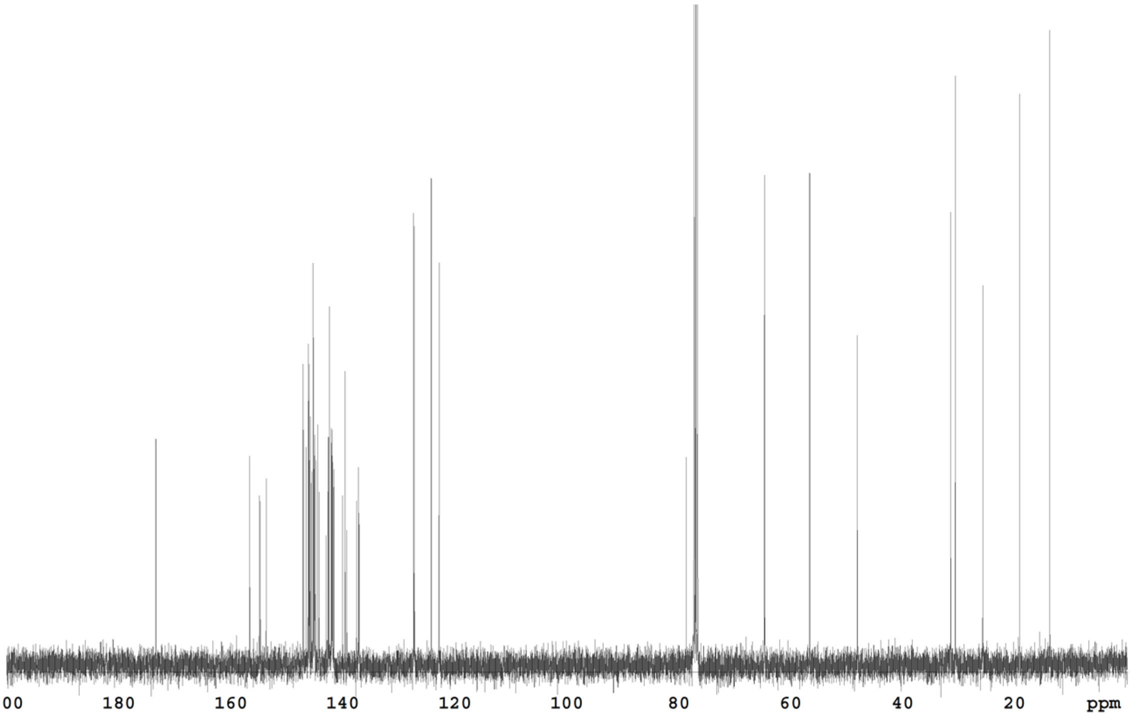

Figure S4. ^{13}C NMR spectrum of [60]IPB.

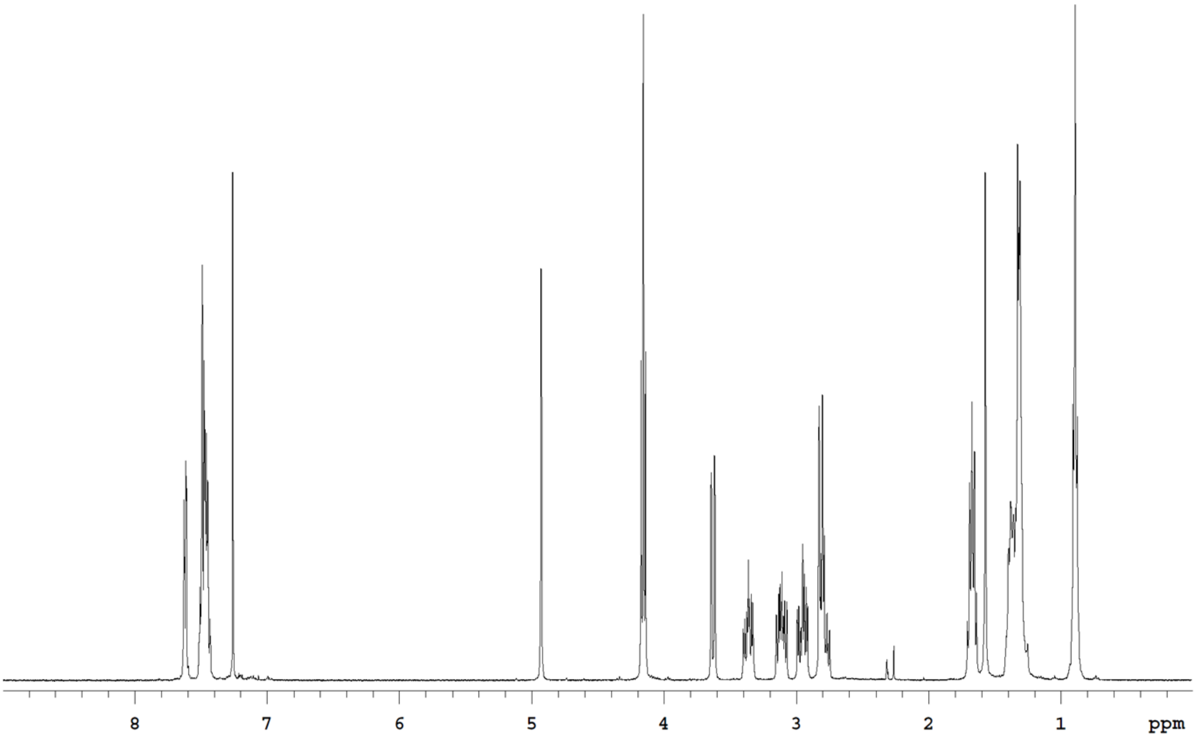

Figure S5. ^{1}H NMR spectrum of [60]IPH.

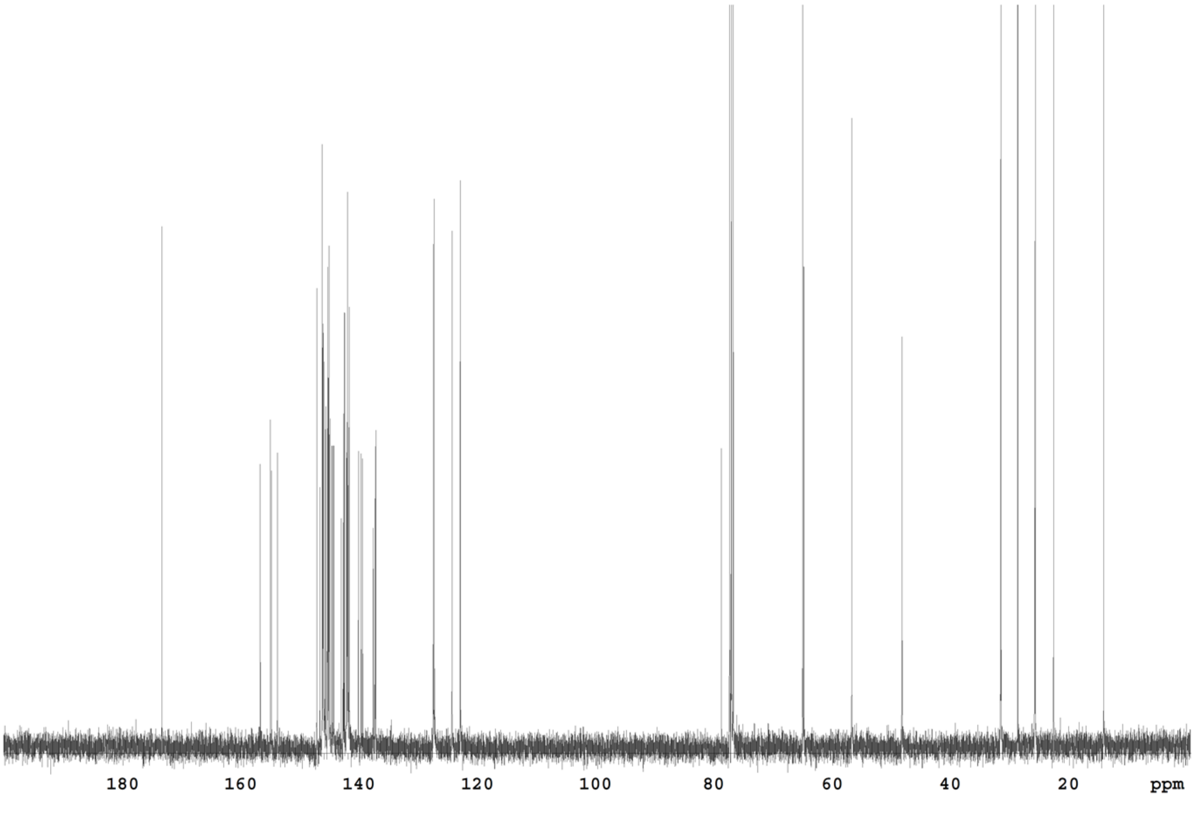

Figure S6. ^{13}C NMR spectrum of [60]IPH.

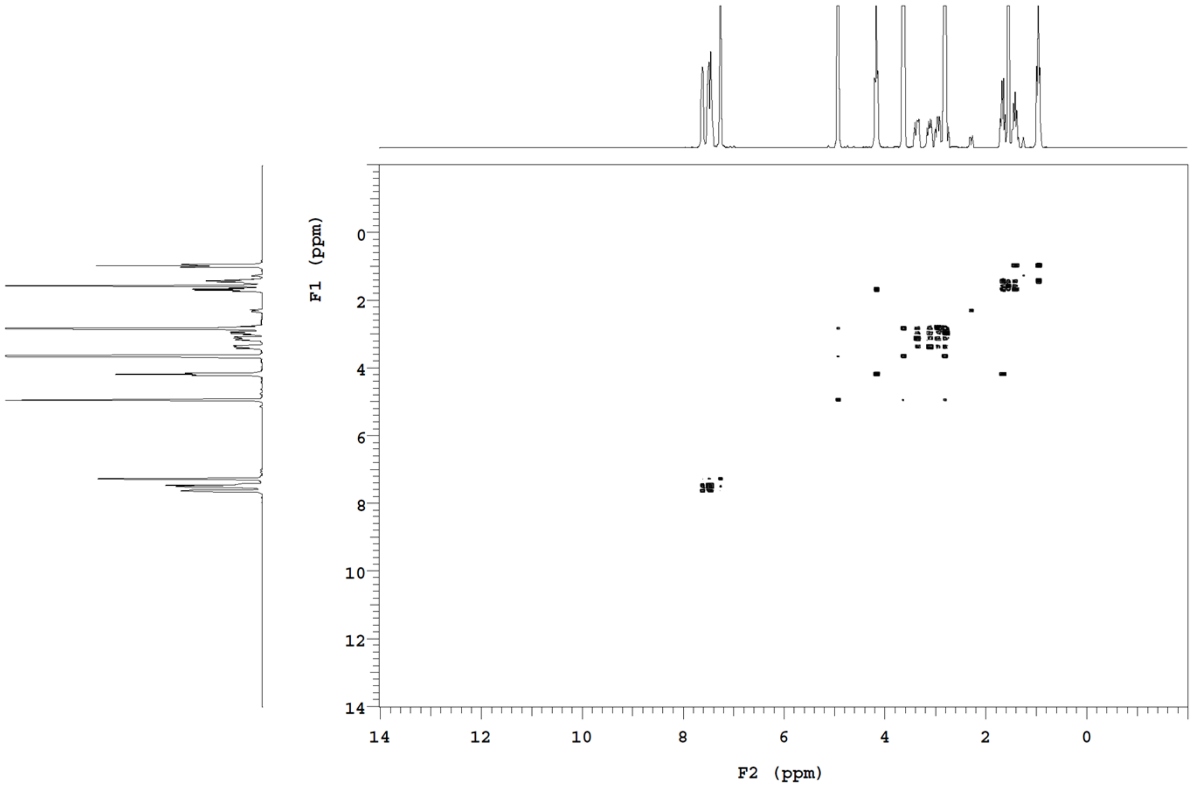

Figure S7. ^{1}H-^{1}H COSY spectrum of [60]IPB.

Electrochemical properties

The cyclic voltammogram of [60]IPE is shown here as an example. For further details see the experimental section. The first, second and third reduction are clearly all reversible. The signal at approximately +0.5 V is that of ferrocene, which is used as the internal reference.

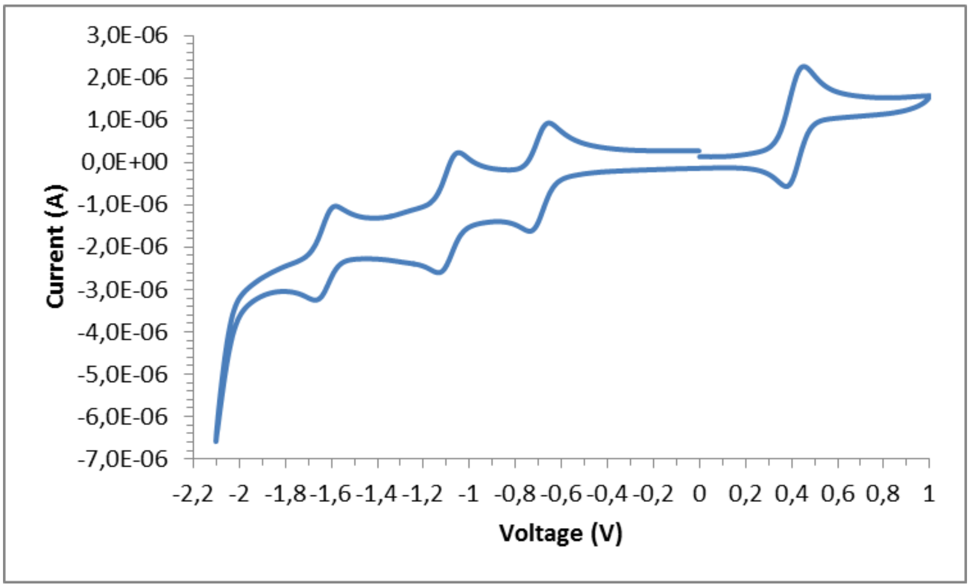

Figure S8. Cyclic voltammogram of [60]IPE.

Table S1. Cyclic voltammetry data of C_{60}, [60]PCBM, and [60]IPE, in ODCB:acetonitrile (4:1 (v/v)) with Bu_4NPF_6 as supporting electrolyte. The first reduction potentials ($E_{1/2}$) are listed relative to ferrocene (Fc/Fc^+) and to C_{60}.

Compound	**E ½ vs. Fc/Fc+**	**E ½ vs. C_{60}**
C_{60}	–0.99 V	0.00 V
[60]PCBM	–1.08 V	–0.09 V
[60]IPE	–1.11 V	–0.12 V

UV-Vis spectroscopy

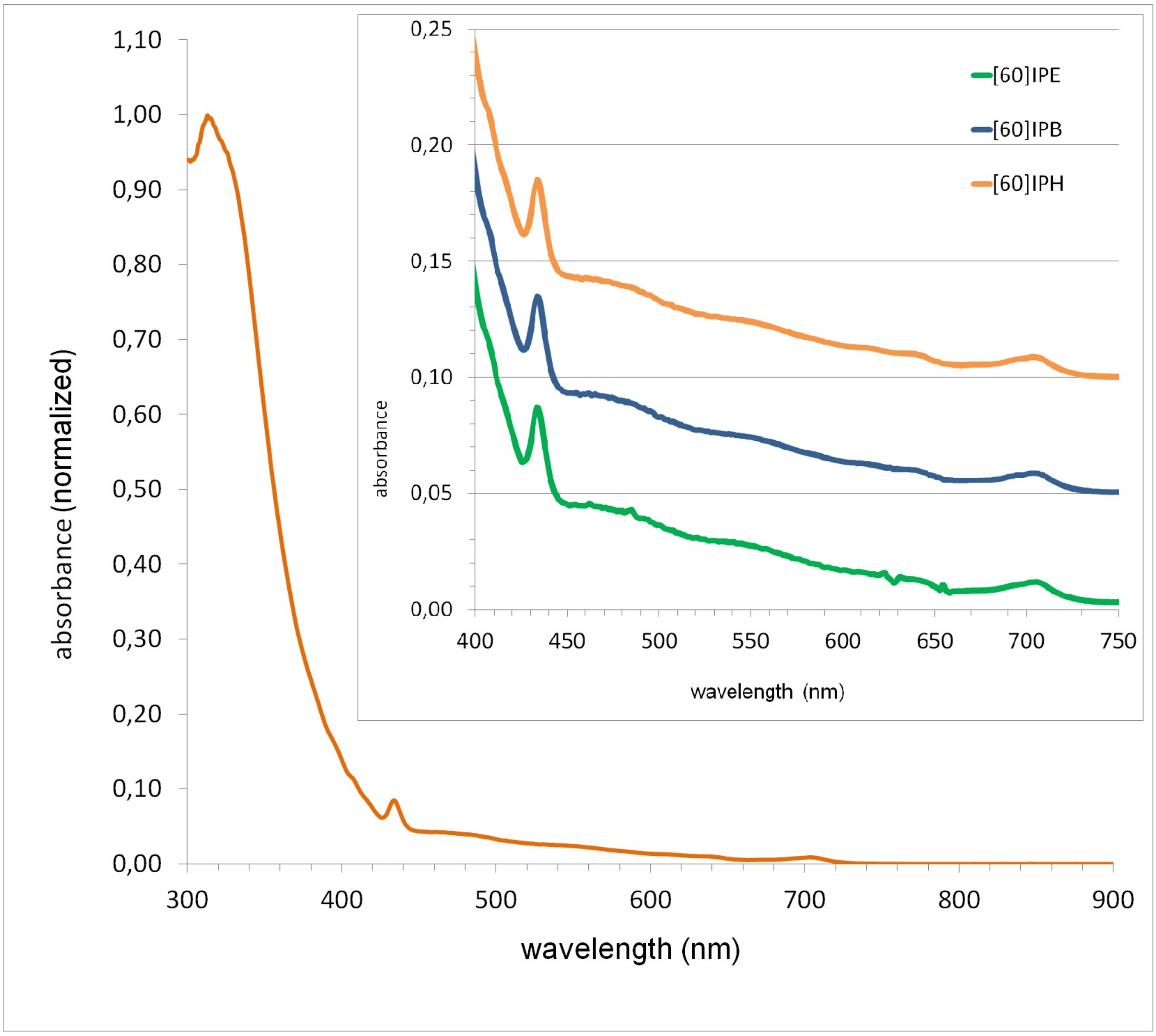

Figure S9. Normalized UV-Vis spectrum of [60]IPH, obtained from HPLC analysis. All three compounds gave identical spectra within experimental error. The inset shows enlargements of the 400–750 nm region for [60]IPE, [60]IPB, and [60]IPH. These spectra were normalized relative to the maximum absorption at 314 nm, and the curves were subsequently offset by 0.05 (for [60]IPB) and 0.10 (for [60]IPH), to show the strong similarity of the absorbance of the three fullerene derivatives.

Fabrication of Organic Solar Cells

Indium tin oxide (ITO) glass substrates (20Ω/sq) were cleaned *via* ultrasonication in acetone and isopropanol then dried with a stream of nitrogen. The substrates were coated with a layer of poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS PVP Al 4083; HC Stark) that was filtered through a 0.45 micron polyvinylidene fluoride (PVDF) filter and spin coated at 4000 rpm for 40 seconds then annealed at 165 °C for 10 minutes producing a ~ 35 nm film. The active layers were spin-coated on top of the PEDOT:PSS layer from P3HT:fullerene (1:0.7) chlorobenzene (CB) solutions (2.0 wt% solid content). The active layer solutions spin coated in two steps: 1000 rpm for 45 seconds followed by 2000 rpm for 7 seconds. The devices were then annealed at 160 °C for 7 minutes. Top contacts of a bilayer of 10 nm calcium followed by 85 nm aluminum were deposited through a shadow mask in high vacuum (>10^{-6} Torr). Each substrate contains 8 cells with an active area of 0.05 cm^2. The current-voltage characteristics were measured using a Xenon lamp (Newport) with a Keithley 2400 SMU measured in a nitrogen environment under 100 mW/cm^2 illumination equipped with an AM 1.5G filter.

Additional J-V Measurements

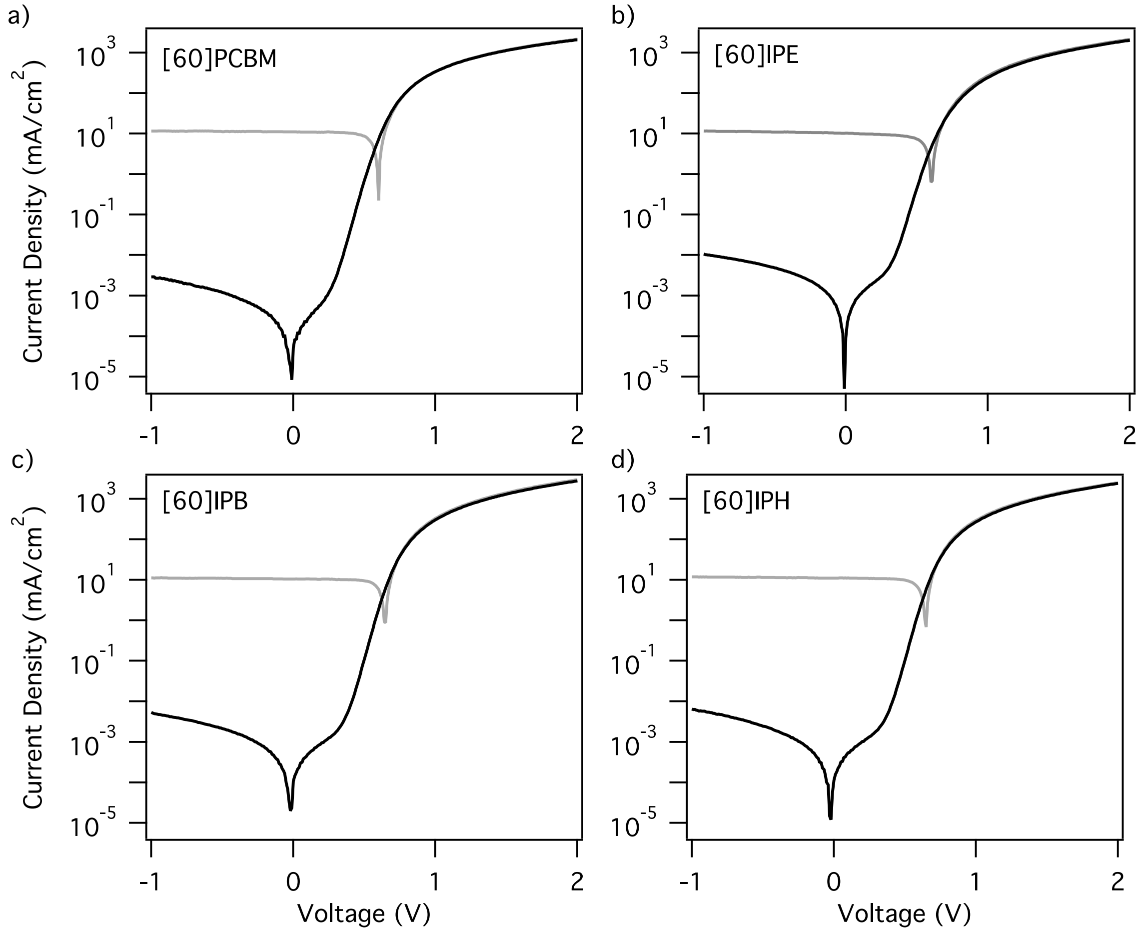

Figure S10. Current–voltage characteristics obtained under AM 1.5G illumination (grey) and dark conditions (black) for devices prepared with a P3HT:fullerene blend (1:0.7 weight ratio). Note that the solar cells were fabricated using the same fabrication conditions and active layer thicknesses.

Grazing-incidence X-Ray Diffraction. Thin films of P3HT:fullerene blends were fabricated with identical solutions to the solar cells on clean Si substrates. 2D GIXD experiments were performed at beamline D1 at the Cornell High Energy Synchrotron Source with a 2D detector (PILATUS3 200K from Dectris). The resulting patterns were carefully normalized for sample thickness, area, penetration depth, and illumination time, which enabled direct comparison of the diffraction patterns between samples (patterns presented in **Figure S11**). Films were typically exposed for 1 s at an incidence angle of 0.15°. The quasi-pole figures generated from the images at an angular resolution of 0.25° and width of 0.1 Å^{-1}.

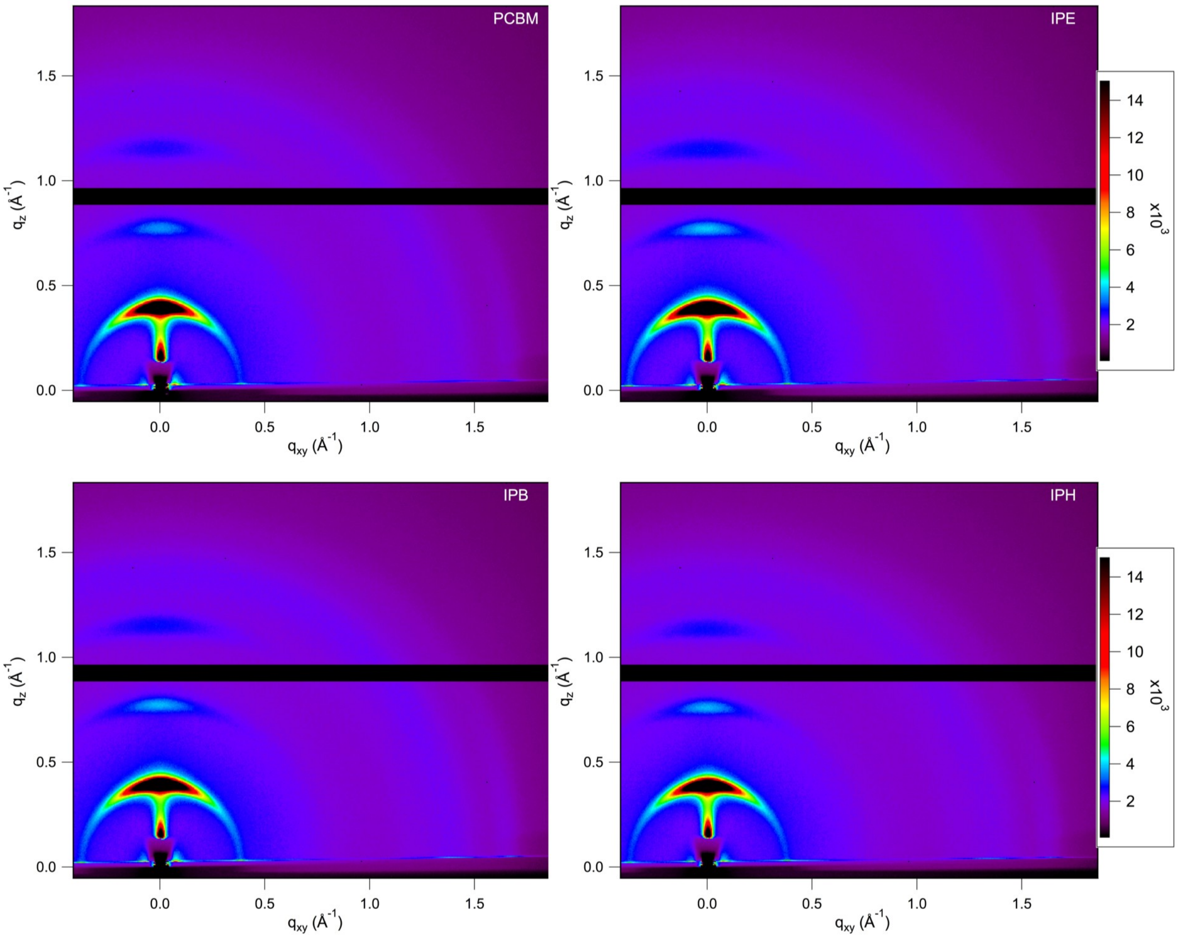

Figure S11. 2D GIXD patterns of thin films of the P3HT:fullerene blends (fullerene derivative annotated on image) used in this study. All films were measured after annealing at 160 ˚C for 7 min.

Flash Differential Scanning Calorimetry. A small mount of the same solar cell solutions (i.e. 2.5 µL) was drop cast on a clean Si wafer and then annealed at 160 ˚C for 7 min. A portion of this film was removed and placed on a microchip sensor. The resulting thermograms can be found in **Figure S12**, which were collected after heating to 350 ˚C (black), then quenching to either 140 ˚C, 150 ˚C, 155 ˚, 160 ˚C, or 165 ˚C at a rate of 5000 ˚C•s^{-1}, holding for 1 second, and then subsequently reheating to 350 ˚C at a rate of 500 ˚C•s^{-1}. The color of the traces corresponding to the crystallization temperature of 140 ˚C, 150 ˚C, 155 ˚C, 160 ˚C, or 165 ˚C is blue, maroon, red, orange, and yellow respectively. The melting temperature of P3HT was then extracted and plotted as a function of crystallization temperature. All measurements were performed under N$_2$ atmosphere.

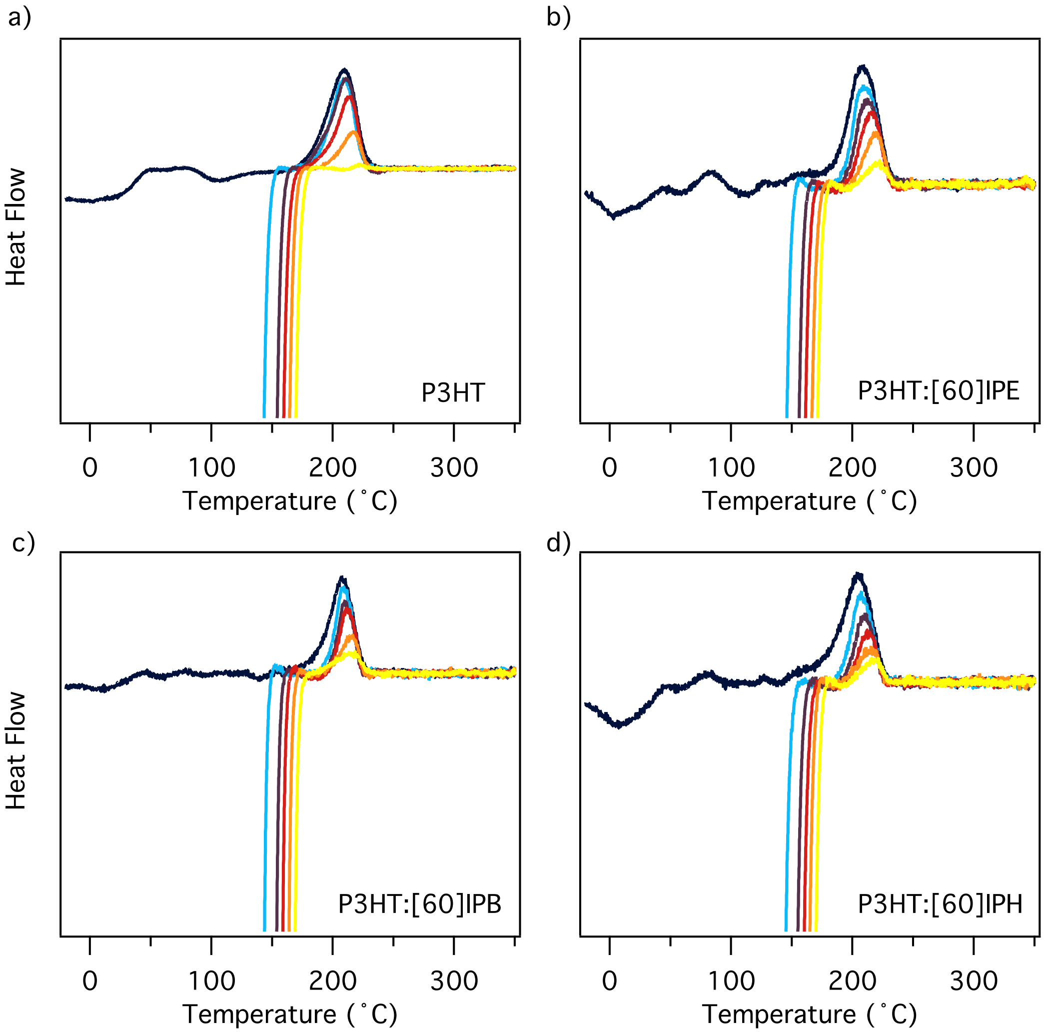

Figure S12. Flash differential scanning calorimetry thermograms of portions films of a) neat P3HT and P3HT blended with b) [60]IPE, c) [60]IPB, and d) [60]IPH. All films were measured after annealing at 160 ˚C for 7 min.

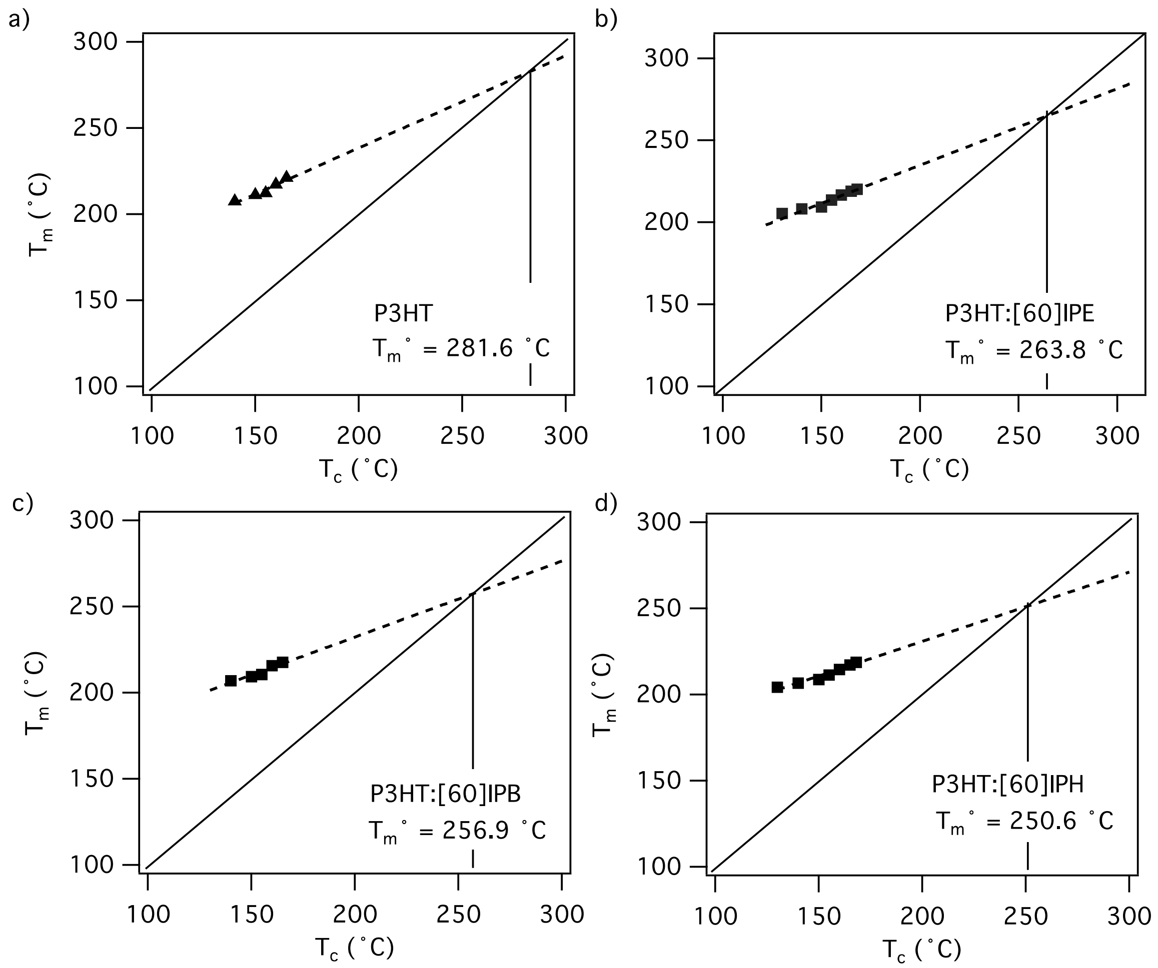

Figure S13. Melting point (T_m) plotted versus the crystallization temperature (T_c) for determining the equilibrium melting point of P3HT[2] a) without and with b) [60]IPE, c) [60]IPB, and d) [60]IPH. The data points were taken from the FDSC measurements (Figure S12).

References:

[1] R. R. Gentry, D. W. Peck, *Vol. US3641115*, **1972**.

[2] J. D. Hoffman, J. J. Weeks, *J Res Natl Bur Stand A* **1962**, *66*, 13-28.