

Supporting Information

Effect of Alkyl Chain Length of C₇₀-PCBX Acceptors on the Device Performance of P3HT:C₇₀-PCBX Polymer Solar Cells

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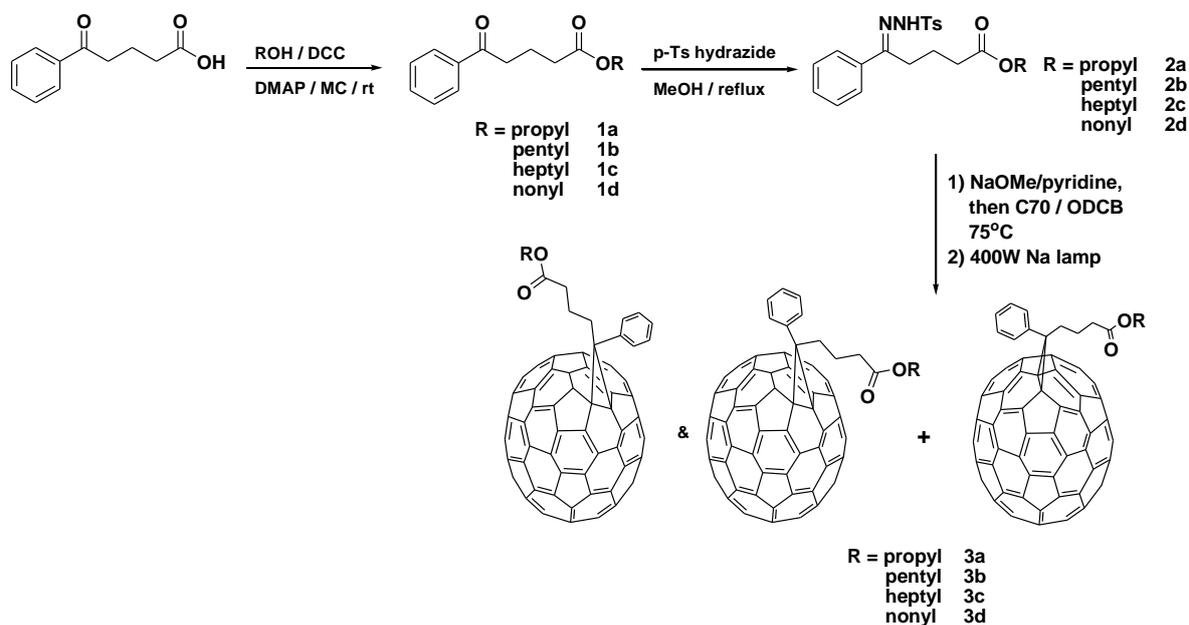
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Materials and Characterization

All reagents and solvents were obtained commercially from Aldrich and used without further purification unless otherwise noted. [70]PCBM and [70]-Fullerene were purchased from Nano-C[®].

¹H NMR and ¹³C NMR spectra were obtained with a Bruker DPX-300 instrument as indicated, at 298K using TMS as an internal standard. MALDI-TOF data was acquired on a Voyager-DE STR instrument in Reflector Mode with a laser intensity of 2000. 200 shots were averaged to give the resulting spectra.

Synthesis of C70-PCBX (Phenyl-C71-butyric acid alkyl ester)



General procedure for the synthesis of alkyl 5-oxo-5-phenylpentanoate (**1a-1d**)

Propyl 5-oxo-5-phenylpentanoate (**1a**)

To a solution of 4-benzoylbutyric acid (5.0 g, 26.0 mmol) in dry CH_2Cl_2 (80 mL), DCC (5.9 g, 23.4 mmol) was added. After stirring for 1 h, 1-propanol (2.3 mL, 31.2 mmol) and DMAP (0.32 g, 2.6 mmol) were added. The reaction mixture was stirred at RT for 6 h and then quenched with 1M HCl; the mixture was then extracted into dichloromethane, washed with brine, and dried.

The crude product was chromatographed on silica by using 20% ethyl acetate in hexane as an eluent

A yellow oil was obtained. Yield: 5.5 g (91 %).

^1H NMR (CDCl_3 , 300 MHz); δ (ppm): 7.95-7.52 (m, 5H), 4.07-4.05 (m, 2H), 3.06-3.01 (m, 2H), 2.45-2.40 (m, 2H), 2.09-2.03 (m, 2H), 1.62-1.55 (m, 2H), 0.96-0.91 (m, 3H)

Pentyl 5-oxo-5-phenylpentanoate (**1b**)

Yield: 6.0 g (89 %).

¹H NMR (CDCl₃, 300 MHz); δ (ppm): 8.00-7.93 (m, 5H), 4.10-4.06 (m, 2H), 3.18-3.03 (m, 2H), 2.44-2.39 (m, 2H), 2.11-2.01 (m, 2H), 1.63-1.54 (m, 2H), 1.31-1.27 (m, 4H), 0.91-0.86 (m, 3H)

Heptyl 5-oxo-5-phenylpentanoate (**1c**)

Yield: 6.6 g (88 %).

¹H NMR (CDCl₃, 300 MHz); δ (ppm): 8.01-7.26 (m, 5H), 4.10-4.05 (m, 2H), 3.18-3.03 (m, 2H), 2.46-2.41 (m, 2H), 2.12-2.03 (m, 2H), 1.64-1.57 (m, 2H), 1.30-1.27 (m, 8H), 0.90-0.85 (m, 3H)

Nonyl 5-oxo-5-phenylpentanoate (**1d**)

Yield: 7.0 g (85 %).

¹H NMR (CDCl₃, 300 MHz); δ (ppm): 7.98-7.43 (m, 5H), 4.09-4.05 (m, 2H), 3.08-3.03 (m, 2H), 2.46-2.41 (m, 2H), 2.12-2.03 (m, 2H), 1.63-1.58 (m, 2H), 1.30-1.26 (m, 12H), 0.90-0.85 (m, 3H)

General procedure for the synthesis of alkyl 5-phenyl-5-(2-tosylhydrazono)pentanoate (**2a-2d**)

Propyl 5-phenyl-5-(2-tosylhydrazono)pentanoate (**2a**)

To a solution of Propyl 5-oxo-5-phenylpentanoate (**1a**) (3.8 g, 16.4 mmol) in MeOH (15 mL) was added p-toluenesulfonyl hydrazide (3.6 g, 19.7 mmol). The resulting mixture was refluxed for 6 h. After cooling to RT no crystallization took place. Mixture was concentrated in vacuo. During concentration crystallization started. The mixture was left in the refrigerator (~4°C) overnight. The obtained crystals were filtered off yielding a white powder which was washed with cold MeOH and dried in vacuo.

Yield: 5.4 g (82 %)

¹H NMR (CDCl₃, 300 MHz); δ (ppm): 9.29 (s, 1H), 7.98-7.26 (m, 9H), 4.18-4.14 (m, 2H), 2.66-2.61 (m, 2H), 2.44-2.40 (m, 3H), 2.33-2.29 (m, 2H), 2.01-1.79 (m, 2H), 1.50-1.20 (m, 2H), 0.99-0.91 (m, 3H)

Pentyl 5-phenyl-5-(2-tosylhydrazono)pentanoate (**2b**)

Yield: 5.6 g (80 %)

¹H NMR (CDCl₃, 300 MHz); δ (ppm): 9.29 (s, 1H), 7.95-7.26 (m, 9H), 4.17-4.22 (m, 2H), 2.66-2.61 (m, 2H), 2.44-2.40 (m, 3H), 2.32-2.28 (m, 2H), 2.01-1.79 (m, 2H), 1.55-1.27 (m, 6H), 0.95-0.89 (m, 3H)

Heptyl 5-phenyl-5-(2-tosylhydrazono)pentanoate (**2c**)

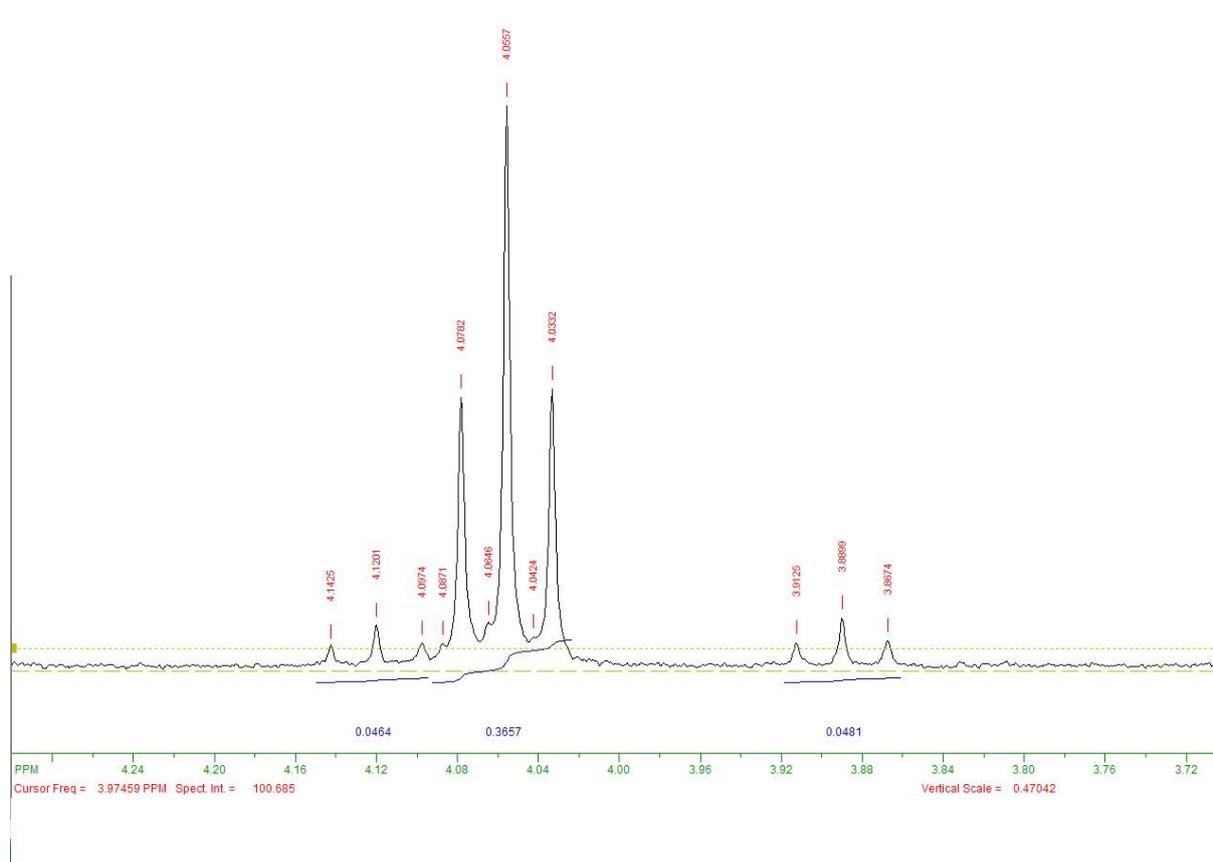
Yield: 5.9 g (79 %)

¹H NMR (CDCl₃, 300 MHz); δ (ppm): 9.29 (s, 1H), 7.98-7.26 (m, 9H), 4.22-4.17 (m, 2H), 2.66-2.61 (m, 2H), 2.46-2.40 (m, 3H), 2.32-2.28 (m, 2H), 2.02-1.79 (m, 2H), 1.57-1.25 (m, 10H), 0.92-0.85 (m, 3H)

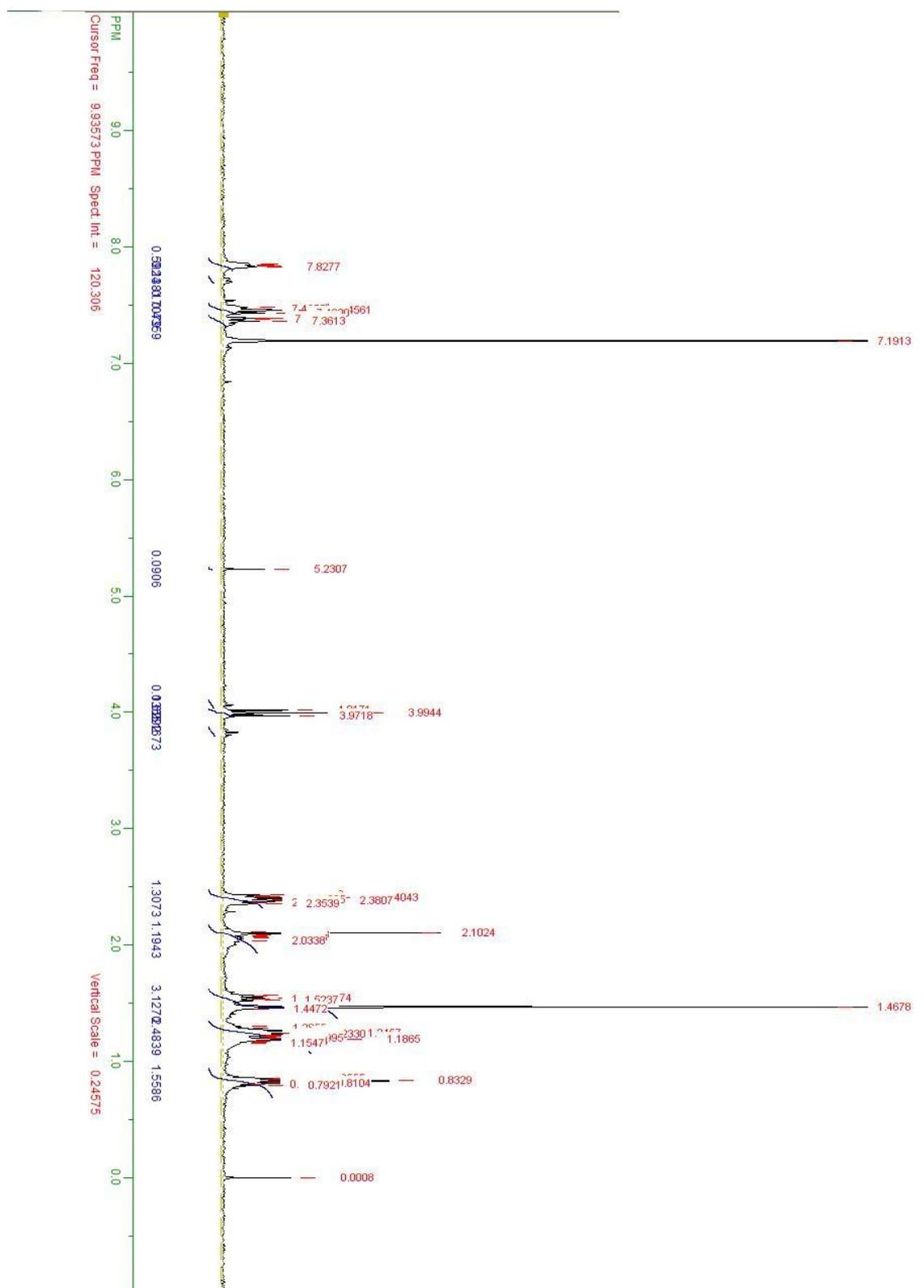
Nonyl 5-phenyl-5-(2-tosylhydrazono)pentanoate (**2d**)

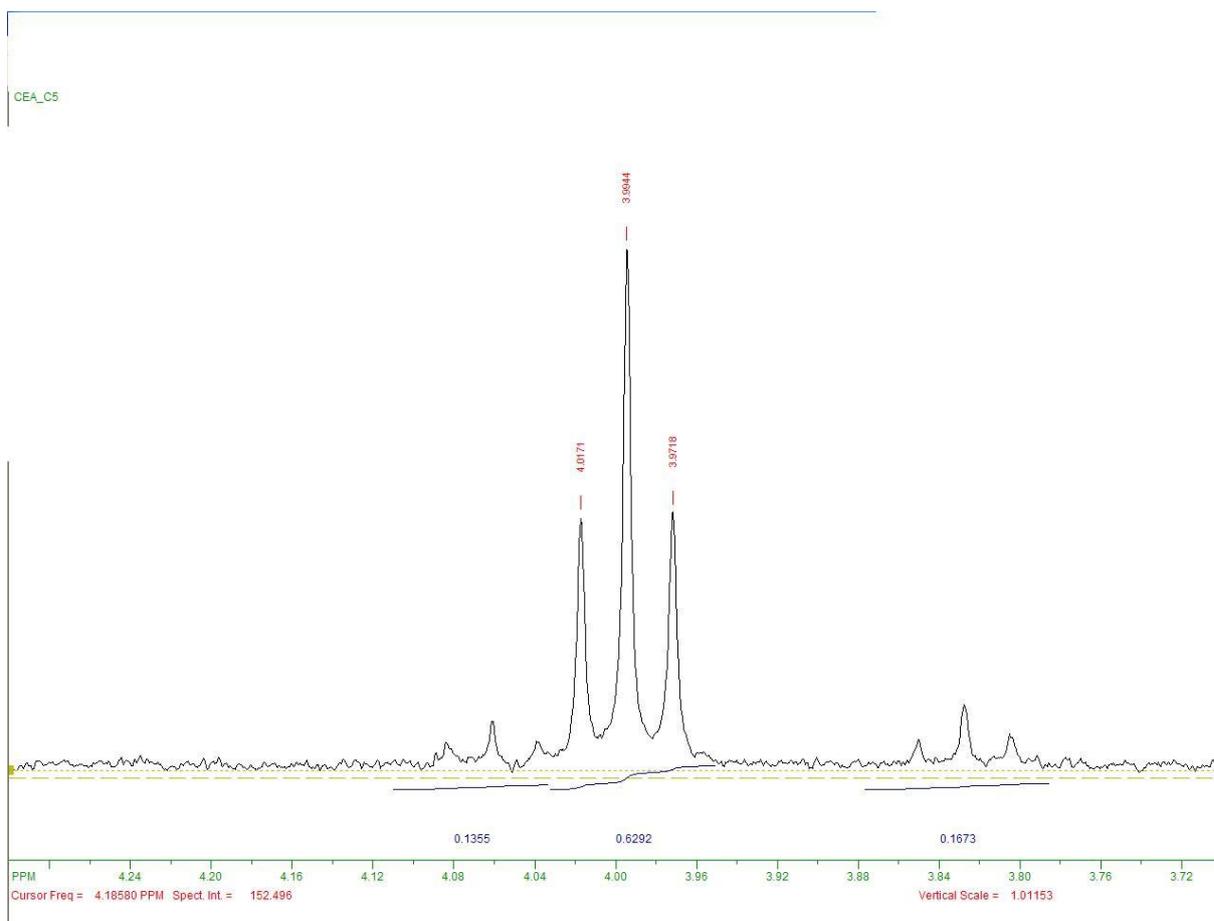
Yield: 6.1 g (77 %)

^1H NMR (CDCl_3 , 300 MHz); δ (ppm): 9.29 (s, 1H), 7.98-7.26 (m, 9H), 4.22-4.17 (m, 2H),
2.66-2.60 (m, 2H), 2.51-2.40 (m, 3H), 2.32-2.25 (m, 2H), 1.81-1.62 (m, 2H), 1.33-1.33 (m,
14H), 0.91-0.86 (m, 3H)

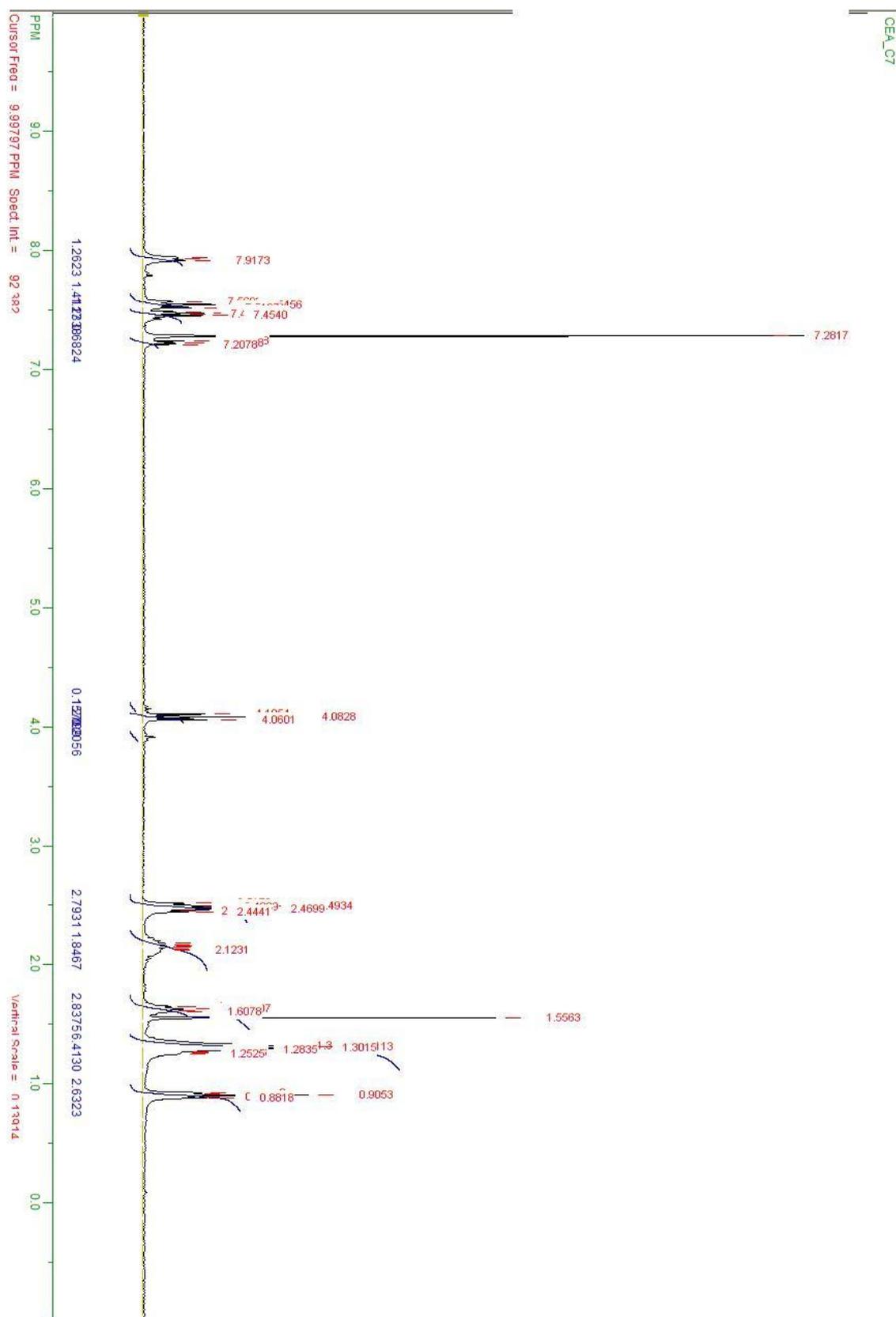


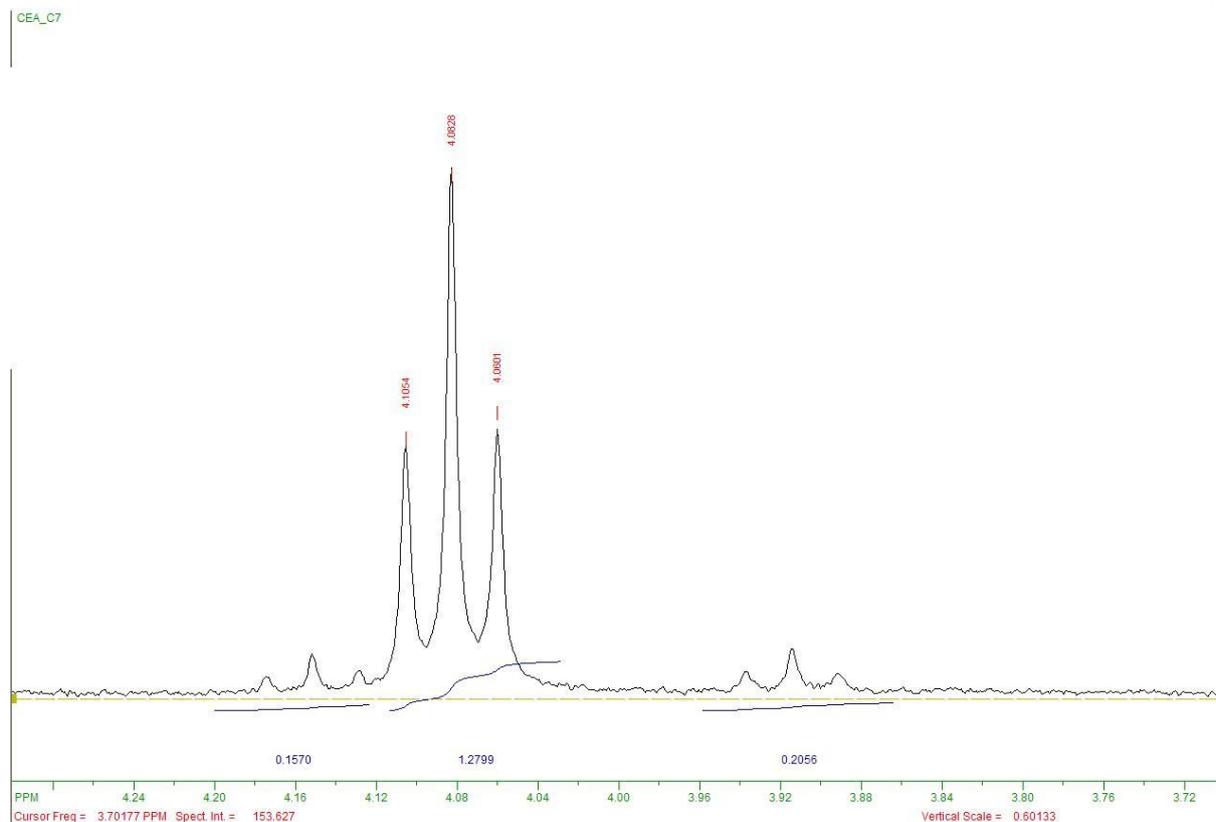
(b) $^1\text{H-NMR}$ of [6,6]-Phenyl C_{71} -butyric acid pentyl ester (**3b**)



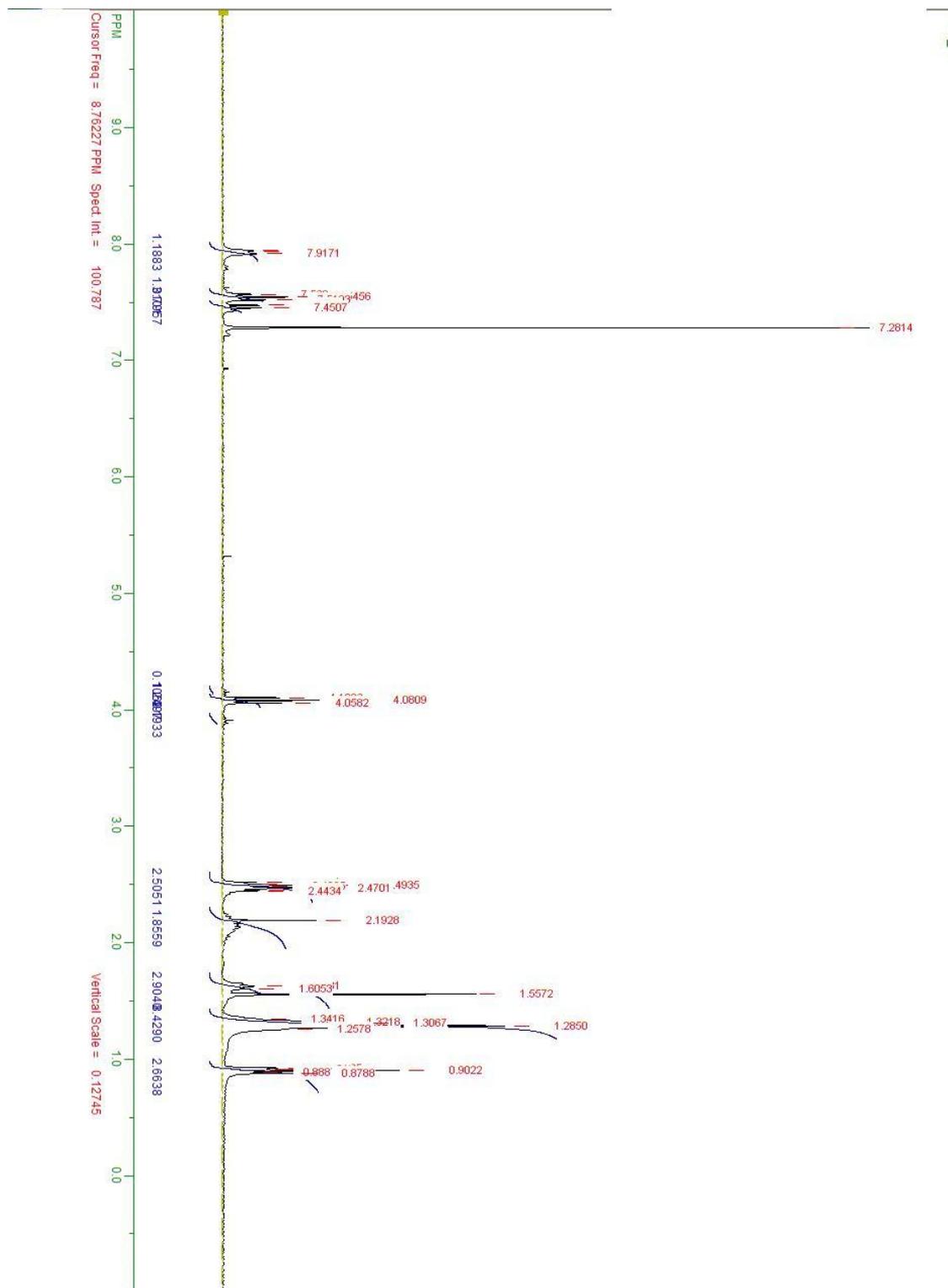


(c) $^1\text{H-NMR}$ of [6,6]-Phenyl C_{71} -butyric acid heptyl ester (**3c**)





(d) $^1\text{H-NMR}$ of [6,6]-Phenyl C_{71} -butyric acid nonyl ester (**3d**)



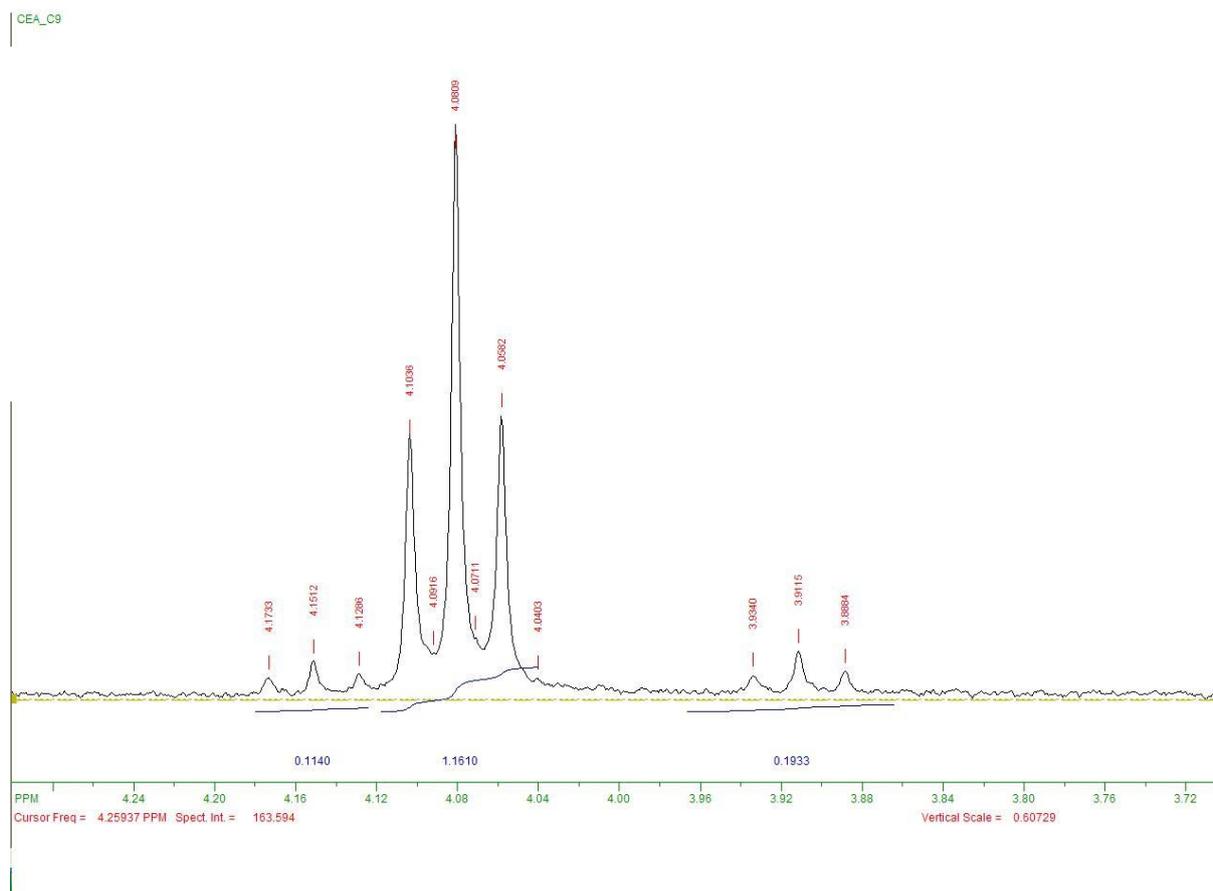


Figure S1. ^1H -NMR spectra of C_{70} -PCBX derivatives.

Solubility of C_{70} -PCBX

Saturated solutions of fullerene derivatives in chlorobenzene were prepared by stirring of excess solid material in solvent for at least 5 days. For this purpose, fullerene derivatives were added in small portions (~10 mg each) to 1.5-2 ml of pure solvent. From the date of observing undissolved solid, stirred another 5 days after adding further 10 mg. As-prepared saturated solutions were filtered through 0.45 μm PTFE syringe filter. Using the micro-pipet, 1 ml of filtered saturated solution were transported to the glass container. The solution were left in air to facilitate solvent evaporation until there were no weight difference for 24 hours. The mass of dissolved material was calculated by the difference between the weight of an empty container and the the same container with a solid residue after solvent evaporation.

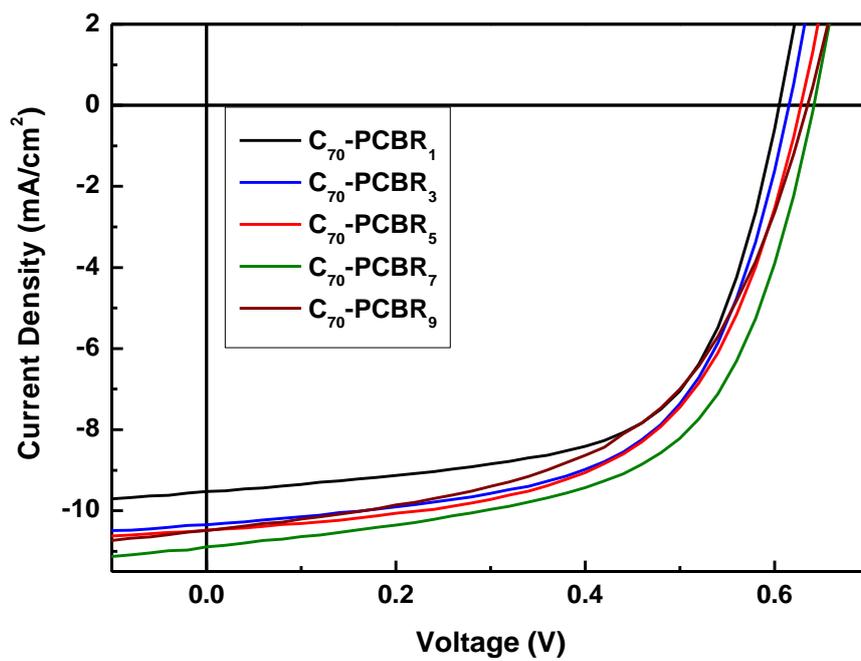


Figure S2. Representative I-V curves for P3HT/C₇₀-PCBX=1/0.9 blend solar cells

Table S1. Photovoltaic performance of different acceptors and donor/acceptor ratios.^a

P3HT/C ₇₀ - PCBX ratio	X	Jsc [mA/cm ²]	Voc [V]	FF	PCE [%]
1/0.7	R ₁	9.58	0.61	0.55	3.24
	R ₃	10.61	0.62	0.56	3.67
	R ₅	10.61	0.63	0.54	3.66
	R ₇	10.57	0.64	0.52	3.84
	R ₉	10.46	0.63	0.53	3.47
1/0.8	R ₁	9.36	0.61	0.57	3.29
	R ₃	10.18	0.62	0.55	3.47
	R ₅	10.64	0.64	0.56	3.82
	R ₇	10.66	0.65	0.58	3.98
	R ₉	10.50	0.63	0.55	3.64
1/0.9	R ₁	9.59	0.61	0.59	3.50
	R ₃	10.43	0.62	0.56	3.59
	R ₅	10.57	0.64	0.57	3.84
	R ₇	10.46	0.65	0.58	3.95
	R ₉	10.22	0.64	0.54	3.51
1/1.0	R ₁	9.51	0.61	0.61	3.54
	R ₃	10.19	0.62	0.56	3.56
	R ₅	10.25	0.63	0.55	3.57
	R ₇	10.29	0.65	0.58	3.86
	R ₉	10.08	0.63	0.53	3.38

^aEach Jsc, Voc, FF and PCE values represents the mean of over 24 devices from more than 6 different batches.

Computational calculation

The molecular structures of the 3-hexylthiophene repeating unit and of C₇₀-PCBX for the Blends calculation were pre-calculated with the density function theory (DFT) quantum mechanical molecular modeling program (DMol³, in 3 dimensions, in the Materials Studio software environment from Accelrys[®]) with symmetry restriction and the geometry optimized structures are shown in Figure S4.

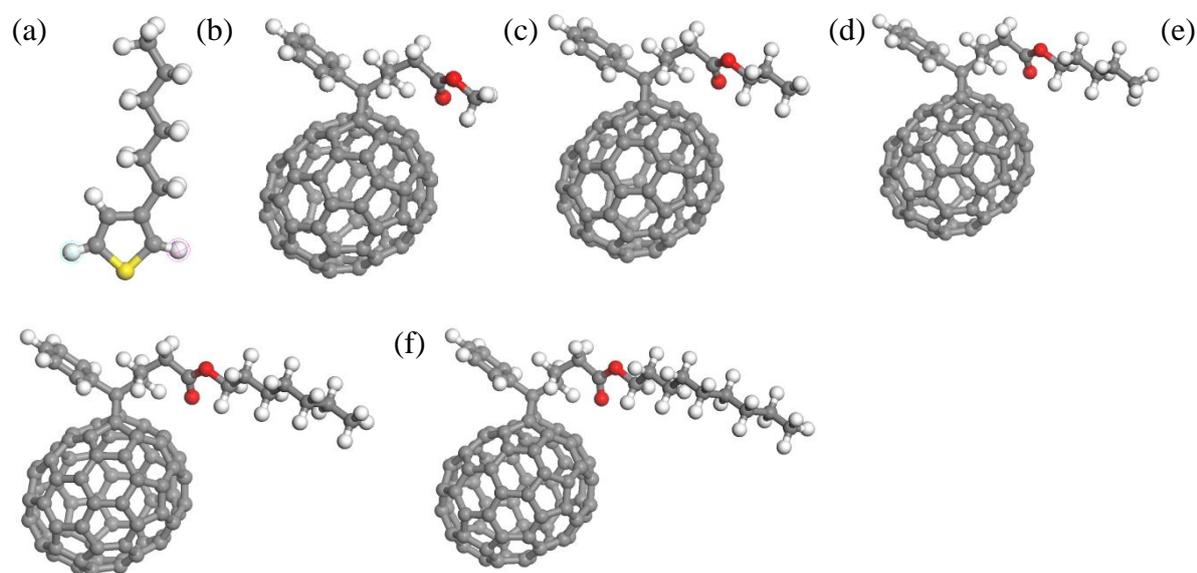


Figure S3. Geometry optimized structure of (a) a 3-hexylthiophene unit, (b) C₇₀-PCBR₁, (c) C₇₀-PCBR₃, (d) C₇₀-PCBR₅, (e) C₇₀-PCBR₇, and (f) C₇₀-PCBR₉.