Supporting Information

Light harvesting tetrafullerene nanoarray for organic solar cells

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Experimental Section

General. All solvents were dried and distilled according to standard procedures. Reagents were used as purchased. Compound **1** was obtained by previously reported procedures.[S1] All air-sensitive reactions were carried out under an argon atmosphere. Flash chromatography was performed using silica gel (Merck, kiesegel 60, 230-240 mesh o Scharlau 60, 230-240 mesh). Analytical thin layer chromatography (TLC) was performed using aluminum coated Merck Kieselgel 60 F254 plates. Melting points were determined on a Gallenkamp apparatus. NMR spectra were recorded on Bruker AC-200

(^{1}H: 200 MHz; ^{13}C: 50 MHz), Bruker Avance 300 (^{1}H: 300 MHz; ^{13}C: 75 MHz) or Bruker AMX-500 spectrometers at 298 K using partially deuterated solvents as internal standards. Coupling constants (J) are denoted in Hz and chemical shifts (δ) in ppm. Multiplicities are denoted as follows: s = singlet, d = doublet, m = multiplet, br = broad. FT-IR spectra were recorded on a Nicolet-Magna-IR 5550 spectrometer. UV-Vis spectra were recorded in a Varian Cary 50 spectrophotometer by using $CHCl_3$ as solvent. Mass spectra by electrospray ionization (ESI) were recorded on a HP1100MSD spectrometer. Cyclic voltammetry was performed using an Autolab PGStat 30 equipment. These measurements were made in a low-volume BAS cell. A glassy carbon working electrode (BAS MF-2012) was used after being polished with alumina (0.3 μ) for 1 min, and platinum wire was used as counter electrode. A Ag/Ag^+ electrode was used as a reference. Tetrabutylammonium perchlorate (0.1 M) was used as the supporting electrolyte and o-dichlorobencene/acetonitrile (4:1) as solvent. The samples were purged with argon prior to measurement. The scan rate was 100 mV/s.

PV devices were prepared as follows: ITO covered glass substrates (140 nm) were cleaned by soap solution (rubbing and sonication), rinsing with demineralized water, sonication in isopropanol and UV-ozone treatment (PR100 photoreactor; UVP). Poly(ethylenedioxythiophene): poly(styrene sulfonate) (PEDOT:PSS) was spincoated from an aqueous suspension (Bayer AG). Subsequently the photoactive layer was spincoated from chlorobenzene (20 mg/mL). Finally, the back electrode of LiF (1 nm) and aluminum (100 nm) was deposited by vacuum evaporation through a shadow mask at 5×10^{-6} mbar. The active area of the reported cells was 0.1 cm^2. *I/V* characterization was

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[S1] C. Atienza, B. Insuasty, C. Seoane, N. Martín, J. Ramey, G.M.A. Rahmand and D.M. Guldi, *J. Mater. Chem.*, 2005, **15**, 124.

performed in a protective N_2 environment with a computer controlled Keithley 2400 source meter, using a tungsten halogen lamp (ca. 75 mW/cm^2) as a light source.

1,4-bis(2-(4-(2,2-dibromovinyl)phenyl)ethynyl)-2,5-dihexyloxybenzene (2). Bisaldehyde **1** (130 mg, 0.97 mmol) was added to a solution of CBr_4 (322.53 mg, 0.97 mmol) and PPh_3 (510.10 mg, 1.94 mmol) in CH_2Cl_2 (10 mL). After stirring at room temperature for 1 h, the solution was extracted with CH_2Cl_2 and washed with H_2O and brine. Compound **2** was purified by column chromatography by using a mixture hexane/CH_2Cl_2 (2/1) as eluent. 97% yield. Mp: 109-110 ºC; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 7.57-7.51 (m, 8H), 7.49 (s, 2H), 7.02 (s, 2H), 4.06-4.02 (m, 4H), 1.91-1.81 (m, 4H), 1.60-1.53 (m, 4H), 1.51-1.32 (m, 8H), 0.93-0.88 (m, 6H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ: 154.09, 136.64, 135.35, 131.94, 128.74, 124.04, 117.21, 114.31, 95.11, 90.72, 87.81, 70.0, 32.01, 29.71, 26.16, 23.07, 14.48; DEPT 135 ($CDCl_3$, 75 MHz) δ: 136.64 (CH), 131.94 (CH), 128.74 (CH), 117.21 (CH), 87.81 (CH_2), 70.0 (CH_2), 32.01 (CH_2), 29.71 (CH_2), 26.16 (CH_2), 23.07 (CH_2), 14.48 (CH_3); FTIR (KBr) ν: 810, 8323, 1218, 1282, 1680, 2320, 2570, 3041, 3042 cm^{-1}; UV-vis λ_{max} ($CHCl_3$): 385, 326 nm; MS m/z (ESI). (%I): 841 (M, 50), 840 (M+, 45), 609 (19), 531 (33), 301 (32), 223 (58). Anal. Cald. for $C_{38}H_{38}Br_4O_2$: %C: 53.93, %H: 4.53. Found: %C: 53.40, %H: 4.50.

1,4-bis[[1,4-bis[4-(4-formylphenyl)-2-(4-formylphenyl)ethynyl]but-1-en-3-ynyl]-(phenyl)ethynyl]]-2,5-dihexyloxybenzene (4) To a solution of compounds **2** (130 mg, 0.153 mmol) and **3** (321 mg, 2.46 mmol) in a mixture Et_3N:CH_3OH (1:4) (50 mL), $Pd(PPh_3)_2Cl_2$ (15.44 mg, 0.02 mmol) y CuI (4.18 mg, 0.02 mmol) were added. The resulting mixture was bubbled with argon for 5 min. After that, the resulting mixture was heated up to 50 ºC for 5h and the solvent was removed under vacuum. Compound **4** was purified by column chromatography by using a mixture hexane:CH_2Cl_2 (2:1) as eluent. 72% yield. Mp > 200 ºC; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 10.04 (br, 4H), 7.93-7.86 (m, 12H), 7.33-7.68 (m, 12H), 7.60 (s, 2H), 7.03 (s, 2H), 4.16-4.03 (m, 4H), 1.87-1.84 (m, 4H), 1.57-1.37 (m, 4H), 1.28-1.24 (m, 8H), 0.91-0.86 (m, 6H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ: 191.99, 191.71, 191.64, 191.55, 154.16, 144.91, 136.63, 136.33, 136.07, 135.39, 133.49, 133.39, 132.60, 132.57, 132.41, 132.04, 130.05, 129.95, 129.55, 129.27, 128.99, 127.89, 125.28, 117.24, 114.40, 103.25, 94.73, 92.92, 90.51, 88.77, 82.51, 76.99, 70.01, 32.31, 31.98, 30.08, 29.69, 26.14, 23.03, 14.43; FTIR (KBr) ν: 835, 1284, 1301, 1380, 1415, 1512, 1560, 1600, 1697, 1749, 2208, 2341, 2358, 2854, 2923 cm^{-1}; UV-vis. λ_{max} ($CHCl_3$): 428, 363, 339 nm. MS m/z (ESI). (%I): 1042 (M, 12), 1041 (M+, 40), 863 (21), 719 (100).

Compound 5. To a solution of C_{60} (317.46 mg, 0.44 mmol) in chlorobencene (85 mL) was added N-octylglycine (123.42 mg, 0.66 mmol) and compound **4** (115 mg, 0.110 mmol). The resulting mixture was refluxed under argon atmosphere for 6 h. The reaction was cooled to room temperature and then the solvent was evaporated. The product was purified by column chromatography by using a mixture cyclohexane:CS_2 (2:1) as eluent. Subsequently, the solvent was evaporated to dryness and the solid residue was transferred into a centrifuge tube, washed several times with cyclohexane, ether and methanol and then dried under vacuum. 42 % yield. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 7.78-7.77 (br, 4H), 7.53-7.51 (br, 12H), 7.44-7.42 (m, 4H), 7.29 (br, 2H), 7.20-7.16 (m, 4H), 6.99 (s, 2H), 5.12 (d, J = 9.48 Hz, 4H), 5.07 (s, 4H), 4.15 (d, J = 9.33 Hz, 4H), 4.07-4.03 (m, 4H), 3.27-3.18 (m, 4H), 2.62-2.53 (m, 4H), 2.3-1.96 (m, 12H), 1.86-1.75 (m, 12H), 1.72-1.57 (m, 50H), 1.50-1.47 (m, 18H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ: 156.75, 154.53, 153.69, 153.38, 148.0, 147.24, 147.08, 147.05, 147.01, 146.95, 146.92, 146.84, 146.69, 146.62, 146.45, 146.36, 146.18, 146.05, 145.98, 145.90, 145.44, 145.40, 145.13, 143.85, 143.47, 143.39, 143.34, 142.98, 142.89, 142.83, 142.77, 142.63, 142.45, 142.33, 141.03, 140.79, 140.39, 139.37, 137.66, 137.25, 136.64, 136.41, 133.63, 131.29, 130.15, 129.12, 128.31, 122.99, 83.11, 82.90, 78.42, 77.15, 76.78, 69.50, 67.65, 54.27, 33.24, 31.41, 31.01, 30.72, 29.69, 28.81, 28.37, 24.25; FTIR (KBr) ν: 527, 735, 885, 1630, 1665, 2180, 2390 cm^{-1}; UV-vis. λ_{max} ($CHCl_3$): 430, 405, 329, 258 nm. MS m/z (ESI). (%I): 4429, 3425, 1949, 720.

Table S-1. Redox potentials of compounds **4, 5** and C_{60}

Potential	**Compound**		
	C_{60}	**4**	**5**
E^1_{ox}	—	1.04	1.12
E^2_{ox}	—	1.39	1.39
E^3_{ox}	—	—	1.49
E^1_{red}	-0.76	—	-0.88
E^2_{red}	-1.18	—	-1.27
E^3_{red}	—	-1.70	-1.50
E^4_{red}	-1.65	—	-1.81
E^5_{red}	-2.13	—	-2.26

Experimental Conditions: V vs Ag/Ag^+; 100 mV/s as scan rate; ODCB/MeCN (4/1) as solvent; Bu_4NClO_4 (0.1 M) as supporting electrolite; GCE as working electrode.

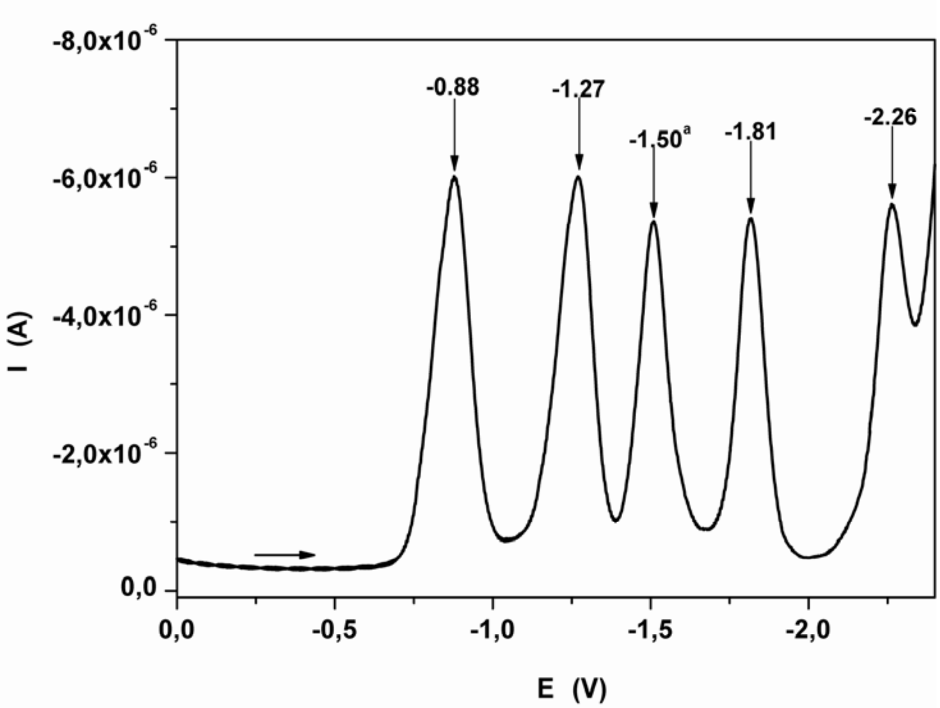

Fig S.-1 Differential pulse voltammetry of compound **5** ([a] Corresponding to the π-conjugated central oligomer).

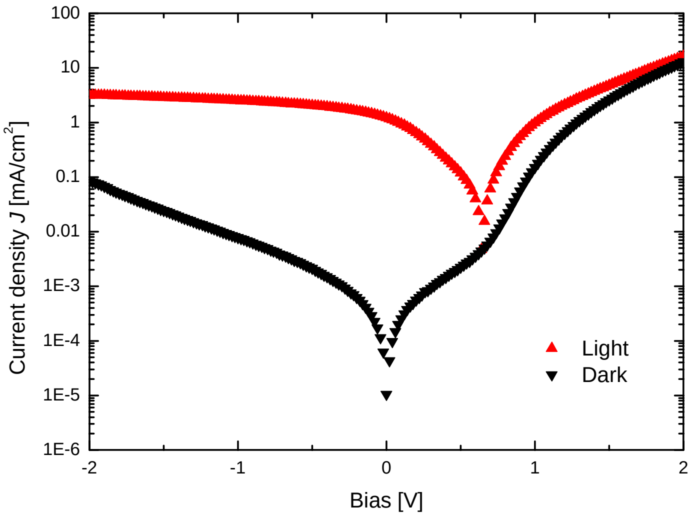

Figure S-2: Current-voltage characteristics of a **5**:P3HT (1:1 wt. ratio) blend sandwiched between ITO/PEDOT:PSS and LiF/Al electrodes. Device area 0.1 cm^2, illumination by tungsten-halogen lamp at 75 mW/cm^2.

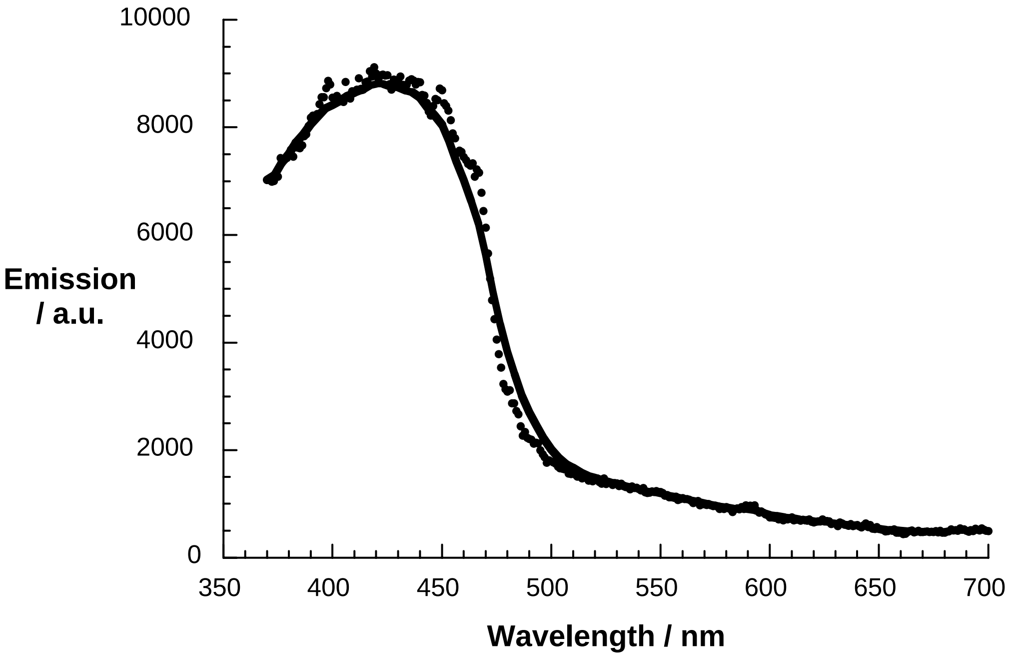

Figure S-3: Room temperature excitation spectrum of compound **5** recorded in toluene – emission wavelength is 720 nm.

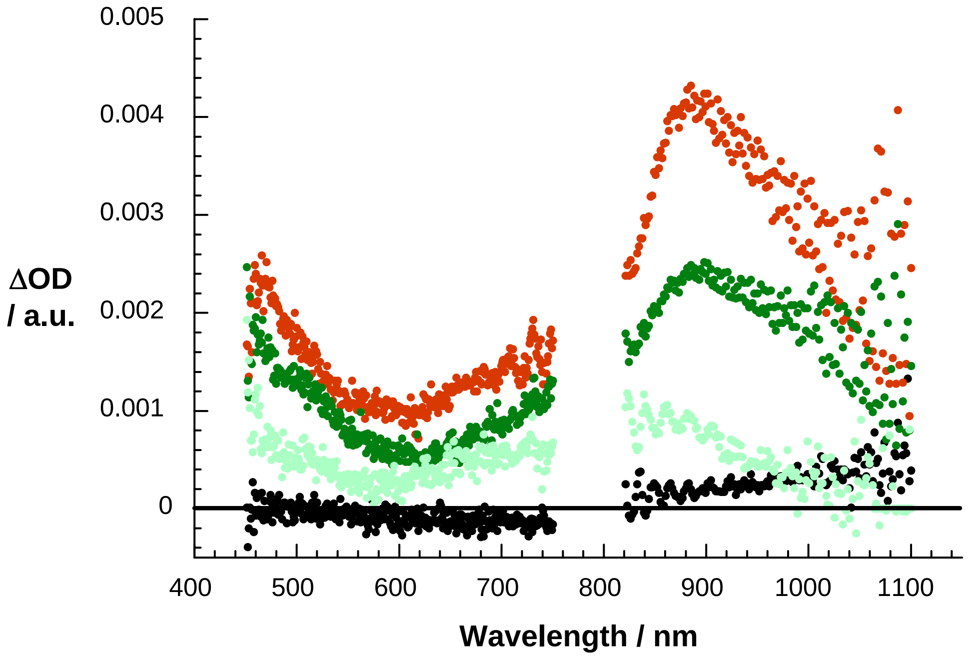

Figure S-4: Differential absorption spectra (visible, near-infrared) obtained upon femtosecond photolysis (387 nm) of **5** in nitrogen saturated toluene after 0 ps (black spectrum), 1 ps (red spectrum), 5 ps (dark green spectum), and 1500 ps (light green spectrum). The spectra correspond to the baseline, oliogmer singlet excited state, C_{60} singlet excited state and C_{60} triplet excited state features.

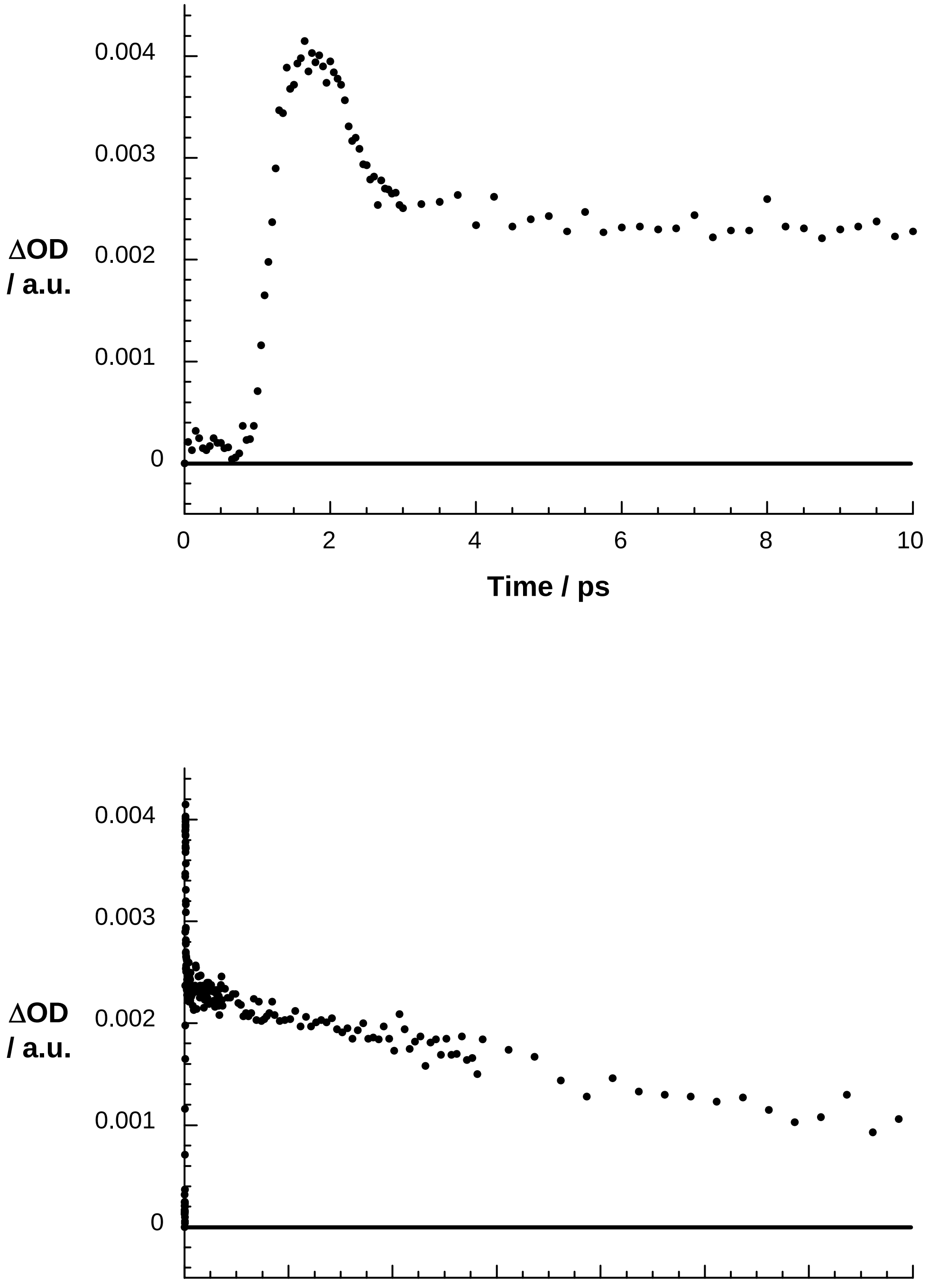

Figure S-5: Time-absorption profiles of the spectra shown in Figure S-4 at 900 nm.

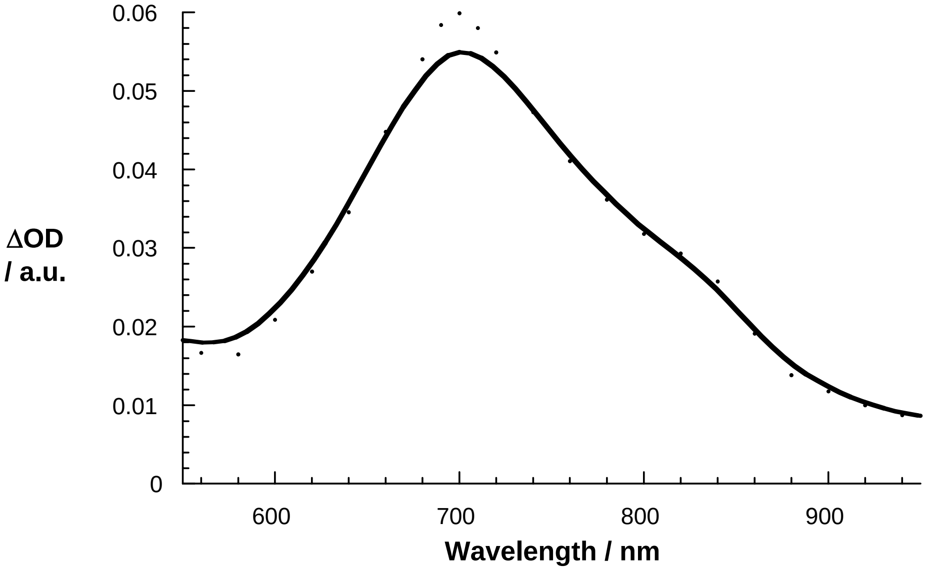

Figure S-6: Differential absorption spectrum (visible, near-infrared) obtained upon nanosecond flash photolysis (355 nm) of **5** in nitrogen saturated toluene. The spectrum corresponds to the C_{60} triplet excited state.

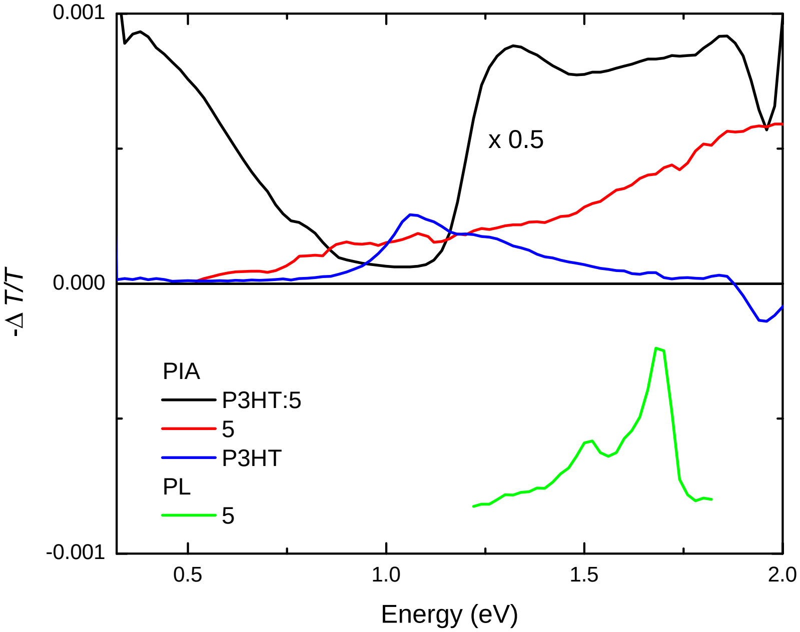

Figure S-7: Near-steady state photoinduced absorption (PIA) spectra of thin films of **5** (red line), P3HT (blue line), and a 1:1 blend of P3HT and **5** (black line, intensity reduced by a factor of 2), recorded at 80 K with modulated (275 Hz) excitation at 488 nm. The photoluminescence spectrum of **5** (green line) recorded under identical conditions is also shown (offset vertically for clarity).