Supporting Information

Influence of the Isomeric Composition of the Acceptor on the Performance of Organic Bulk Heterojunction P3HT:bis-PCBM Solar Cells

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S1 Experimental

S1.1 Device fabrication

P3HT and the fullerene derivatives were dissolved in a 1:1.2 weight ratio in chloroform and the solution was stirred overnight. The photoactive layers were spin-cast under nitrogen atmosphere on clean glass substrates pre-patterned with indium tin oxide and a 60 nm thick film of poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonic acid) (VP AI4083, H.C. Starck). The as-cast layers were annealed subsequently at 135 °C for 15 minutes. The devices were finished by thermal evaporation of a LiF(1 nm)/Al(100 nm) cathode. Electrical measurements were conducted in an N_2 controlled atmosphere in dark and under illumination of a Steuernagel SolarConstant 1200 metal halide lamp, which was set to 1 Sun intensity using a silicon reference cell and correcting for spectral mismatch.

Hole-only devices were fabricated in a similar way as the solar cells, where only the top electrode is different. In order to prevent electron injection in the fullerene phase, a high work function Pd(20 nm)/Au(80 nm) top electrode was used instead of LiF/Al, obtaining a glass/ITO/PEDOT:PSS/P3HT:fullerene/Pd/Au structure. The hole mobility was obtained by fitting the steady-state *J*-*V* characteristics with the space-charge-limited current formula.

S1.2 Device Characterization

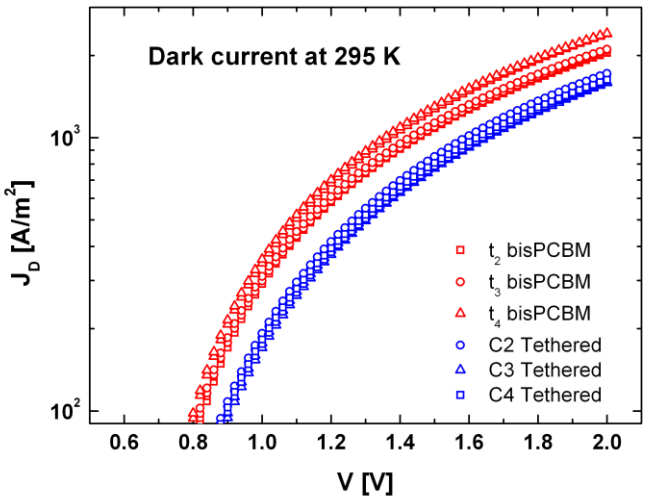

Fig. S1 Dark currents at 295 K for the P3HT-based solar cells with the tethered adducts and their transesterified tbis-PCBM counterparts.

S1.3 Materials

All reagents and solvents were used as received or purified using standard procedures. [60]-Fullerene (99.5 %) was purchased from Bucky USA and used without further purification. Flash chromatography was performed using silica gel (Kieselgel Merck Type 9385 (230-400 mesh)). ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Unity Plus (500MHz), on a Varian AMX-400 (400 MHz), or on a Varian VXR-200 (200 MHz) instrument as indicated, at 298 K using TMS as an internal standard, *J* values are given in Hertz. IR measurements were performed on a Nicolet Nexus FT-IR instrument. High Resolution Mass Spectroscopy (HRMS) was performed on a JEOL JMS 600 spectrometer. HPLC analyses were performed on a Hewlett Packard HPLC Chemstation 3D (HP 1100 Series) using an analytical Cosmosil Buckyprep column (4.6 x 250 mm) or a Econosphere silica column (3 x 100 mm). Elemental analysis was performed by the Micro Analytical Department of this laboratory.

S1.4 Synthesis

The preparation of C2-bis(keto ester), the corresponding C2-bis(tosylhydrazone), the addition thereof to C_{60}, and the subsequent transesterification to $t_2$bis-PCBM have been described elsewhere[1].

C3-bis(keto ester). 10.0 g 4-benzoylbutyric acid (52 mmol) was dissolved in 100 mL dry toluene along with 1.8 mL 1,3-propanediol (0.5 equiv.) and three drops of concentrated sulfuric acid in a Dean-Stark setup. The resulting mixture was heated to reflux temperature under N_2 atmosphere and stirred at this temperature overnight. The resulting yellow solution was cooled to room temperature and solvent was removed *in vacuo*. The residue was dissolved in ethyl acetate, the solution was washed 10% Na_2CO_3 (2 x 50 mL) to remove starting compounds and side products. The organic layer was washed water (2 x 50 mL) and then with brine (50 mL), dried over Na_2SO_4 and stripped of solvent *in vacuo*, yielding a yellow oil. The oil was absorbed on SiO_2 and purified using column chromatography (SiO_2, heptane/ethyl acetate 1:1). After crystallization from diethyl ether, 8.3 g of pure product was obtained as white crystals.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93-7.89 (m; 4H), 7.53 – 7.47 (m; 2H), 7.43-7.37 (m; 4H), 4.12 (t, J = 6.3; 4H), 3.00 (t, J = 7.1; 4H), 2.44 (t, J = 7.2; 4H), 2.02 (p, J = 7.1; 4H), 1.92 (p, J = 6.2; 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.40, 173.23, 136.90, 133.18, 128.70, 128.51, 128.11, 77.55, 77.23, 76.91, 61.08, 37.50, 33.36, 28.09, 19.40, and 19.27.

C4-bis(keto ester) 10.0 g benzoylbutyric acid (52 mmol) was dissolved in 100 mL dry toluene in a Dean-Stark setup along with 2.3 mL 1,4-butanediol (0.5 equiv) and three drops of concentrated sulfuric acid. The solution was heated to reflux temperature and stirred during 48 hours. The resulting yellow solution was cooled to room temperature and solvent was removed *in vacuo*. The residue was dissolved in ethyl acetate and the solution was washed 10% Na_2CO_3 (2 x 50 mL) to remove starting compounds and side products. The organic layer was washed with water (2 x 50 mL) and then with brine (50 mL), dried on Na_2SO_4, and stripped of solvent *in vacuo* yielding a yellow oil. The oil was absorbed on SiO_2 and further purified through column chromatography (SiO_2, heptane/ethyl acetate 1:1). Crystallization from dry diethyl ether yielded 7.1 g of the pure keto ester as white powder (16 mmol, 62%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.91 (m; 4H), 7.56 – 7.50 (m; 3H), 7.46 – 7.39 (m; 5H), 4.07 (m; 4H), 3.08-2.99 (m; 4H), 2.47 (t, *J* = 7.1; 2H), 2.41 (t, *J* = 7.2; 4H), 2.13 – 2.03 (m; 4H), 1.66 (m; 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.58, 199.48, 178.74, 173.45, 136.96, 136.93, 133.29, 133.27, 128.77, 128.19, 77.55, 77.23, 76.91, 64.06, 37.61, 37.49, 33.50, 33.17, 25.47, 19.53, and 19.20.

C3-bis(tosyl hydrazone). 8.8 g C3-keto ester (20.7 mmol) was dissolved in 100 mL toluene under N_2 atmosphere in a Dean-Stark setup. 7.7 g tosylhydrazide (41.4 mmol, 2 equiv.) was added and the reaction mixture was stirred overnight at reflux temperature. The resulting yellow solution was cooled to room temperature and placed in an ice/water bath overnight while stirring. The solids were filtered off, washed with diethyl ether, and dried in a vacuum oven. The pure product was obtained as white powder (14.9 g, 19.6 mmol; 95%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.24 (s; 2H), 7.90 (d, *J* = 8.3; 4H), 7.70 – 7.59 (m; 4H), 7.38 – 7.31 (m; 6H), 7.30 – 7.22 (m; 4H), 4.33 (t, *J* = 6.1; 4H), 2.71 – 2.59 (m; 4H), 2.46 – 2.30 (m; 10H), 2.15 – 2.00 (m; 2H), 1.81 – 1.61 (m; 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.60, 154.17, 143.92, 136.31, 136.08, 129.67, 129.62, 128.57, 128.07, 126.39, 61.61, 32.51, 27.94, 26.06, 21.72, and 21.12.

C4-bis(tosyl hydrazone). 4.5 g C4-keto ester (10.2 mmol) was dissolved in 100 mL toluene under N_2 atmosphere in a Dean-Stark setup. 3.8 g tosylhydrazide (20.4 mmol, 2 equiv.) was added and the reaction mixture was stirred overnight at reflux temperature. The solution turned from colorless to orange overnight. It was cooled to room temperature and placed in an ice/water bath overnight. The solids that were formed were filtered off, washed three times with cold diethyl ether and dried in a vacuum oven. The pure product was obtained as white powder (6.5 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.25 (s; 2H), 7.93-9.87 (m; 4H), 7.66 – 7.62 (m; 4H), 7.35– 7.30 (m; 6H), 7.30 – 7.25 (m; 4H), 4.27-4.21 (m; 4H), 2.67 – 2.61 (m; 4H), 2.44 – 2.33 (m; 10H), 1.80-1.75 (m; 2H), 1.75 – 1.64 (m; 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.70, 154.07, 143.94, 136.35, 136.16, 129.69, 128.61, 128.12, 126.41, 64.98, 32.55, 26.12, 25.42, 21.77, and 21.16.

C2-Tethered C_{60} bisadduct. C2-bis(tosylhydrazone) (0.5g, 0.69 mmol) was dissolved in 50 mL pyridine in a flame-dried 2 L flask under inert atmosphere. 0.22 mL 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was added (1.47 mmol, 2.1 equiv.) and the resulting mixture was stirred for 30 minutes. A solution of 0.5 g C_{60} (0.69 mmol) in 1 L ODCB was added. The resulting solution was heated with aid of a heat-gun in 15 minutes to 82 ^{o}C and then overnight illumination with a 150 W sodium lamp was started.

The mixture was concentrated *in vacuo* and purified by column chromatography (SiO_2, toluene). After removal of the eluent *in vacuo* a dark solid remained. The solid was precipitated from ODCB in pentane and subsequently centrifuged. The remaining red pellet was washed twice with pentane and dried in a vacuum oven at 40 ^{o}C overnight. This yielded 183 mg red brown solid (0.17 mmol, 25%). ^{13}C NMR (126 MHz, CS_2 with D_2O inlet) δ 169.15, 169.07, 168.90, 168.81, 168.75, 168.72, 168.66, 168.42, 168.33, 149.32, 148.30, 148.23, 147.86, 147.67, 147.05, 146.84, 146.62, 146.01, 145.49, 145.15, 145.06, 145.02, 144.97, 144.91, 144.74, 144.62, 144.59, 144.30, 144.26, 144.15, 144.02, 143.98, 143.80, 143.77, 143.74, 143.70, 143.66, 143.60, 143.52, 143.48, 143.41, 143.34, 143.27, 143.16, 143.12, 143.05, 143.01, 142.96, 142.90, 142.82, 142.79, 142.63, 142.56, 142.49, 142.42, 142.39, 142.31, 142.25, 142.22, 142.15, 142.07, 142.01, 141.96, 141.93, 141.85, 141.77, 141.61, 141.57, 141.53, 141.45, 141.36, 141.34, 141.30, 141.22, 141.16, 141.08, 141.02, 140.96, 140.87, 140.84, 140.77, 140.65, 140.40, 140.36, 140.27, 140.07, 139.99, 139.83, 139.76, 139.66, 139.59, 139.56, 139.41, 139.34, 139.29, 139.23, 139.21, 139.00, 138.90, 138.79, 138.75, 138.65, 138.62, 138.54, 138.42, 138.21, 138.13, 137.90, 137.20, 137.14, 136.56, 136.44, 136.30, 135.44, 135.36, 135.24, 135.15, 135.07, 134.96, 134.85, 134.56, 134.48, 134.35, 134.26, 133.94, 133.85, 133.76, 133.72, 133.40, 133.30, 133.16, 132.94, 132.75, 132.12, 131.21, 130.84, 130.75, 130.29, 129.86, 129.77, 129.65, 129.31, 129.14, 128.86, 128.43, 128.23, 128.10, 126.77, 126.71, 126.30, 126.20, 126.05, 125.94, 125.92, 125.87, 125.83, 125.44, 125.28, 124.58, 123.19, 78.57, 77.86, 77.65, 77.02, 76.71, 75.48, 75.28, 75.12, 75.02, 74.86, 74.80, 74.11, 73.96, 73.42, 72.66, 71.97, 60.87, 60.64, 60.47, 60.10, 60.03, 59.80, 59.54, 59.33, 59.27, 51.12, 47.54, 47.04, 46.94, 46.62, 45.45, 45.36, 44.98, 42.98, 32.60, 32.22, 32.08, 31.81, 31.61, 31.15, 30.95, 30.83, 30.77, 30.60, 30.43, 30.30, 30.19, 30.03, 29.86, 28.81, 28.68, 28.38, 27.99, 27.69, 23.24, 21.28, 21.21, 20.72, 20.23, 19.81, 19.76, 19.60, 19.50, 18.96, 18.61, and 12.54, *m/z* (ESI) 1098 (M^- requires 1098).

C3-Tethered C_{60} bisadduct. 1.1 g C3-bis(tosylhydrazone) was dissolved in 30 mL dry pyridine in a flame-dried 2 L three-necked flask under N_2 atmosphere. 0.45 mL DBU was added and the solution was stirred for 20 min at room temperature. A solution of 1.0 g C_{60} (1.4 mmol) in 1 L ODCB was prepared. The C_{60} solution was degassed three times and added to the pyridine solution. The resulting mixture was degassed a second time (three vacuum/N_2 purges) and the solution was heated to 85 ^{o}C, after which illumination with a 150 W Sodium lamp was started. The reaction mixture was stirred overnight at 85 ^{o}C under illumination. The solvent was removed *in vacuo* and the residue was extracted with toluene. The soluble fraction was submitted to column chromatography (SiO_2, toluene/ethyl acetate 95:5). The C3 tethered bisadduct fraction was collected, precipitated with methanol, washed twice with methanol, once with pentane, and dried overnight in a vacuum oven at 40 ^{o}C. The pure product was obtained as red powder (168 mg, 0.15 mmol; 11%).

^{13}C NMR (126 MHz, CS_2 with D_2O inlet) δ 172.08, 172.08, 172.00, 172.00, 171.92, 171.74, 171.47, 171.47, 171.31, 171.31, 171.22, 171.22, 171.16, 171.05, 171.05, 170.94, 170.94, 170.86, 170.73, 170.73, 170.68, 170.43, 170.25, 170.25, 151.79, 151.35, 150.62, 150.20, 149.62, 149.54, 149.15, 148.41, 147.97, 147.52, 147.48, 147.43, 147.39, 147.18, 147.15, 147.13, 147.09, 146.79, 146.63, 146.56, 146.40, 146.36, 146.27, 146.20, 146.12, 146.08, 146.02, 145.98, 145.94, 145.88, 145.79, 145.71, 145.50, 145.43, 145.41, 145.34, 145.26, 145.24, 145.19, 145.04, 145.00, 144.97, 144.93, 144.85, 144.75, 144.71, 144.64, 144.57, 144.52, 144.42, 144.36, 144.27, 144.21, 144.11, 144.00, 143.97, 143.93, 143.89, 143.80, 143.75, 143.63, 143.58, 143.56, 143.50, 143.46, 143.40, 143.34, 143.30, 143.09, 143.05, 142.88, 142.78, 142.68, 142.60, 142.46, 142.40, 141.97, 141.86, 141.72, 141.63, 141.40, 141.27, 141.22, 141.18, 141.02, 140.96, 140.92, 140.78, 140.43, 140.36, 140.08, 139.88, 139.66, 138.99, 138.83, 138.46, 138.34, 138.17, 137.96, 137.86, 137.79, 137.70, 137.61, 137.54, 137.40, 137.29, 137.27, 137.02, 136.78, 136.57, 136.49, 136.26, 135.96, 135.62, 135.53, 135.13, 134.70, 133.73, 133.17, 132.81, 132.28, 132.18, 132.14, 131.78, 131.57, 131.42, 131.28, 130.86, 130.63, 130.26, 129.16, 128.60, 128.46, 128.35, 128.26, 128.22, 128.17, 128.09, 127.76, 127.67, 127.56, 125.59, 81.72, 80.73, 80.73, 80.11, 80.11, 80.06, 80.06, 79.85, 79.85, 79.34, 79.34, 79.32, 78.79, 78.03, 78.03, 77.74, 77.74, 77.55, 77.46, 76.29, 76.29, 75.99, 75.36, 75.36, 74.97, 63.68, 63.56, 62.96, 61.90, 61.84, 61.47, 61.17, 60.97, 60.91, 60.73, 60.37, 60.27, 60.19, 60.11, 59.74, 59.54, 59.32, 59.09, 53.38, 52.39, 52.05, 50.93, 50.70, 49.75, 49.45, 49.15, 48.12, 47.83, 47.76, 47.10, 46.50, 35.82, 35.34, 35.26, 35.00, 34.87, 34.72, 34.44, 34.20, 34.11, 33.82, 33.71, 33.53, 33.38, 33.26, 33.06,

32.94, 32.86, 32.75, 32.26, 31.58, 31.22, 30.37, 29.44, 29.27, 29.20, 29.04, 28.87, 28.80, 28.53, 27.51, 25.03, 24.17, 23.65, 23.49, 23.01, 22.55, 22.38, 22.27, 22.14, 21.98, 21.76, 21.25, 21.12, 21.04, 20.84, 20.80, 20.34, and 19.35.

C4-Tethered C_{60} bisadduct. 1.1 g C4-bis(tosylhydrazone) was dissolved in 30 mL dry pyridine in a flame-dried 2 L three-neck flask under N_2 atmosphere. 0.45 mL DBU was added and the solution was stirred for 20 min at room temperature. A solution of 1.0 g C_{60} (1.4 mmol) in 1L ODCB was prepared. The C_{60} solution was degassed three times and added to the pyridine solution. The resulting mixture was degassed a second time (three vacuum/N_2 purges) and the solution was heated to 85 ^{o}C, after which illumination with a 150W Sodium lamp was started. The reaction mixture was stirred overnight at 85 ^{o}C under illumination. The solvent was removed *in vacuo* and the residue was extracted with toluene. The soluble fraction was submitted to column chromatography (SiO_2, toluene/ethyl acetate 95:5). The C4-tethered bisadduct fraction was collected, precipitated with methanol, washed twice with methanol, once with pentane, and dried overnight in a vacuum oven at 40 ^{o}C. The pure product was obtained as red powder (345 mg, 0.3 mmol; 22%).

^{13}C NMR (126 MHz, CS_2 with D_2O inlet) δ 171.88, 171.83, 171.59, 171.56, 171.40, 171.36, 171.34, 171.31, 171.28, 171.08, 170.94, 170.74, 170.69, 170.61, 151.77, 151.47, 150.70, 150.23, 150.02, 149.73, 149.66, 149.59, 149.14, 149.00, 148.25, 148.15, 148.05, 147.89, 147.59, 147.53, 147.50, 147.43, 147.39, 147.37, 147.31, 147.22, 147.15, 147.13, 147.10, 147.04, 146.97, 146.92, 146.81, 146.76, 146.71, 146.61, 146.57, 146.54, 146.52, 146.39, 146.33, 146.28, 146.26, 146.20, 146.18, 146.13, 146.09, 146.07, 146.05, 146.00, 145.98, 145.94, 145.91, 145.89, 145.82, 145.76, 145.69, 145.62, 145.59, 145.54, 145.52, 145.43, 145.39, 145.36, 145.33, 145.26, 145.23, 145.19, 145.14, 145.05, 145.01, 144.97, 144.95, 144.93, 144.92, 144.86, 144.83, 144.75, 144.73, 144.72, 144.63, 144.58, 144.55, 144.53, 144.51, 144.46, 144.43, 144.39, 144.38, 144.36, 144.33, 144.29, 144.24, 144.21, 144.02, 143.96, 143.94, 143.84, 143.82, 143.80, 143.74, 143.72, 143.65, 143.62, 143.55, 143.48, 143.46, 143.41, 143.40, 143.37, 143.30, 143.29, 143.21, 143.14, 143.13, 143.04, 142.97, 142.90, 142.86, 142.81, 142.75, 142.73, 142.70, 142.67, 142.63, 142.57, 142.44, 142.41, 142.30, 142.22, 142.13, 142.11, 141.96, 141.95, 141.87, 141.80, 141.76, 141.73, 141.68, 141.62, 141.60, 141.55, 141.40, 141.34, 141.28, 141.26, 141.22, 141.15, 141.08, 141.03, 140.98, 140.96, 140.92, 140.86, 140.84, 140.58, 140.48, 140.37, 140.31, 140.15, 140.05,

140.00, 139.92, 139.69, 139.63, 139.56, 139.53, 139.39, 139.17, 139.02, 139.01, 138.84, 138.77, 138.71, 138.67, 138.60, 138.53, 138.45, 138.35, 138.26, 138.15, 138.08, 137.92, 137.84, 137.75, 137.66, 137.64, 137.62, 137.45, 137.41, 137.36, 137.35, 137.30, 137.23, 137.19, 137.14, 137.11, 137.00, 136.86, 136.81, 136.77, 136.71, 136.59, 136.57, 136.48, 136.39, 136.27, 135.97, 135.89, 135.75, 135.57, 135.49, 135.10, 134.75, 134.45, 134.12, 133.78, 133.63, 133.46, 133.28, 132.86, 132.24, 132.20, 131.97, 131.83, 131.72, 131.55, 131.25, 131.20, 130.89, 130.63, 130.40, 129.66, 129.17, 129.02, 128.70, 128.59, 128.47, 128.46, 128.34, 128.29, 128.27, 128.22, 128.21, 128.18, 128.10, 128.08, 127.79, 127.68, 127.63, 127.58, 125.59, 81.92, 80.83, 80.60, 80.46, 80.30, 79.66, 79.36, 79.05, 78.97, 78.26, 78.16, 78.03, 77.81, 77.31, 76.14, 75.95, 74.92, 74.55, 64.75, 64.72, 64.63, 64.41, 64.36, 64.22, 64.20, 64.15, 63.99, 63.90, 63.81, 63.76, 63.71, 63.61, 63.57, 63.52, 63.41, 61.15, 60.65, 60.48, 60.36, 60.03, 53.64, 52.12, 51.92, 51.20, 50.44, 49.55, 49.29, 49.23, 48.14, 47.94, 47.75, 47.58, 46.36, 35.40, 35.37, 35.15, 34.97, 34.88, 34.82, 34.67, 34.60, 34.38, 34.23, 34.20, 34.14, 34.00, 33.92, 33.87, 33.73, 33.67, 33.60, 33.56, 33.48, 33.40, 33.37, 33.32, 33.27, 33.23, 33.16, 33.05, 31.89, 31.65, 31.21, 27.60, 27.32, 27.27, 27.11, 26.91, 26.83, 26.75, 26.73, 26.54, 26.36, 26.20, 26.13, 25.83, 25.77, 25.68, 25.58, 25.52, 25.35, 24.70, 23.44, 23.21, 23.02, 22.95, 22.84, 22.79, 22.58, 22.51, 22.47, 22.24, 22.09, 21.98, 21.14, 20.86, 20.49, 20.32, 19.31.

General procedure for transesterification of tethered bisadducts. The tethered bisadduct was dissolved in 100 mL ODCB and 10 mL methanol and a catalytic amount of concentrated sulfuric acid. The mixture was stirred for 5 days. The reaction mixture was stripped of solvent *in vacuo*, the residue was dissolved in toluene and purified by column chromatography (SiO_2/toluene). Precipitation from ODCB in methanol and subsequent washing with methanol yielded the pure bis methyl esters as a red-brown solid.

t_2Bis-PCBM. ^{13}C NMR (126 MHz, D_2O) δ 171.84, 171.68, 171.60, 171.47, 171.42, 170.82, 151.92, 151.67, 150.66, 150.57, 150.36, 149.80, 149.74, 149.43, 149.15, 148.71, 148.22, 147.57, 147.53, 147.45, 147.41, 147.30, 147.26, 147.14, 147.09, 146.85, 146.79, 146.72, 146.68, 146.66, 146.59, 146.39, 146.25, 146.21, 146.15, 146.13, 146.10, 146.07, 146.05, 146.04, 146.00, 145.94, 145.91, 145.87, 145.84, 145.82, 145.76, 145.71, 145.68, 145.55, 145.53, 145.41, 145.37, 145.35, 145.33, 145.28, 145.22, 145.21, 145.17, 145.15, 145.04, 145.01, 144.97, 144.95, 144.86, 144.84, 144.77, 144.72, 144.68, 144.66, 144.65, 144.63,

144.60, 144.58, 144.55, 144.48, 144.45, 144.43, 144.39, 144.35, 144.31, 144.26, 144.23, 144.16, 144.08, 144.03, 144.00, 143.98, 143.91, 143.89, 143.86, 143.83, 143.76, 143.74, 143.71, 143.64, 143.55, 143.52, 143.44, 143.40, 143.39, 143.31, 143.18, 143.08, 142.81, 142.76, 142.71, 142.66, 142.61, 142.55, 142.39, 142.22, 142.17, 142.05, 142.01, 141.93, 141.79, 141.68, 141.66, 141.59, 141.42, 141.38, 141.31, 141.20, 141.10, 141.01, 140.98, 140.94, 140.86, 140.82, 140.41, 139.76, 139.64, 139.49, 139.18, 139.12, 138.95, 137.65, 137.63, 137.24, 137.18, 137.07, 136.94, 136.85, 136.80, 136.70, 136.64, 136.44, 136.17, 136.11, 135.93, 135.91, 135.81, 135.79, 135.58, 135.51, 135.12, 133.57, 133.16, 133.08, 132.16, 132.13, 132.09, 132.03, 131.83, 131.60, 131.35, 131.24, 130.63, 129.79, 128.64, 128.59, 128.55, 128.52, 128.46, 128.35, 128.31, 128.30, 128.29, 128.23, 128.20, 128.16, 128.14, 127.68, 80.60, 80.54, 80.24, 80.03, 79.07, 78.77, 78.46, 78.24, 78.12, 78.00, 77.86, 76.42, 75.25, 75.19, 74.49, 74.40, 61.95, 53.74, 51.20, 51.17, 51.15, 51.14, 51.12, 50.81, 49.46, 49.43, 49.33, 48.96, 48.86, 47.69, 47.46, 47.34, 34.63, 34.30, 34.16, 33.98, 33.78, 33.77, 33.71, 33.58, 33.49, 33.46, 33.44, 33.28, 32.77, 32.54, 30.35, 23.12, 23.02, 22.80, 22.68, 22.58, 22.43, 22.40, 22.36, 21.79, and 20.19. Mass: *m/z* (ESI) 1100 (M^- requires 1100).

t_3Bis-PCBM ^{13}C NMR (126 MHz, D_2O) δ 171.82, 171.71, 171.67, 171.58, 171.49, 171.45, 171.40, 171.34, 151.66, 150.65, 150.56, 150.36, 149.80, 149.73, 149.42, 149.14, 148.70, 148.35, 148.21, 148.16, 147.73, 147.57, 147.53, 147.50, 147.46, 147.41, 147.35, 147.30, 147.26, 147.14, 147.10, 147.07, 146.84, 146.79, 146.71, 146.66, 146.59, 146.50, 146.42, 146.39, 146.29, 146.21, 146.15, 146.13, 146.10, 146.08, 146.04, 146.00, 145.95, 145.91, 145.82, 145.75, 145.71, 145.69, 145.56, 145.41, 145.37, 145.33, 145.28, 145.22, 145.20, 145.17, 145.15, 145.04, 145.00, 144.97, 144.90, 144.86, 144.83, 144.80, 144.77, 144.72, 144.70, 144.69, 144.66, 144.65, 144.63, 144.60, 144.55, 144.47, 144.45, 144.39, 144.35, 144.31, 144.27, 144.23, 144.16, 144.03, 143.98, 143.91, 143.86, 143.80, 143.76, 143.71, 143.64, 143.55, 143.53, 143.49, 143.45, 143.40, 143.30, 143.23, 143.18, 143.08, 142.99, 142.96, 142.81, 142.75, 142.71, 142.66, 142.63, 142.58, 142.55, 142.48, 142.44, 142.39, 142.31, 142.26, 142.21, 142.17, 142.11, 142.04, 142.01, 141.97, 141.93, 141.79, 141.69, 141.66, 141.59, 141.42, 141.38, 141.31, 141.26, 141.20, 141.10, 141.01, 140.98, 140.94, 140.86, 140.82, 140.67, 140.54, 140.41, 140.25, 140.05, 139.90, 139.76, 139.66, 139.64, 139.49, 139.31, 139.18, 139.12, 138.95, 138.88, 138.73, 138.58, 138.54, 138.44, 138.34, 138.27, 138.21, 138.14, 138.04, 137.91, 137.81, 137.72, 137.69, 137.65, 137.62, 137.39, 137.25, 137.19, 137.16, 137.08, 137.04, 136.95, 136.91, 136.85, 136.80, 136.70, 136.65,

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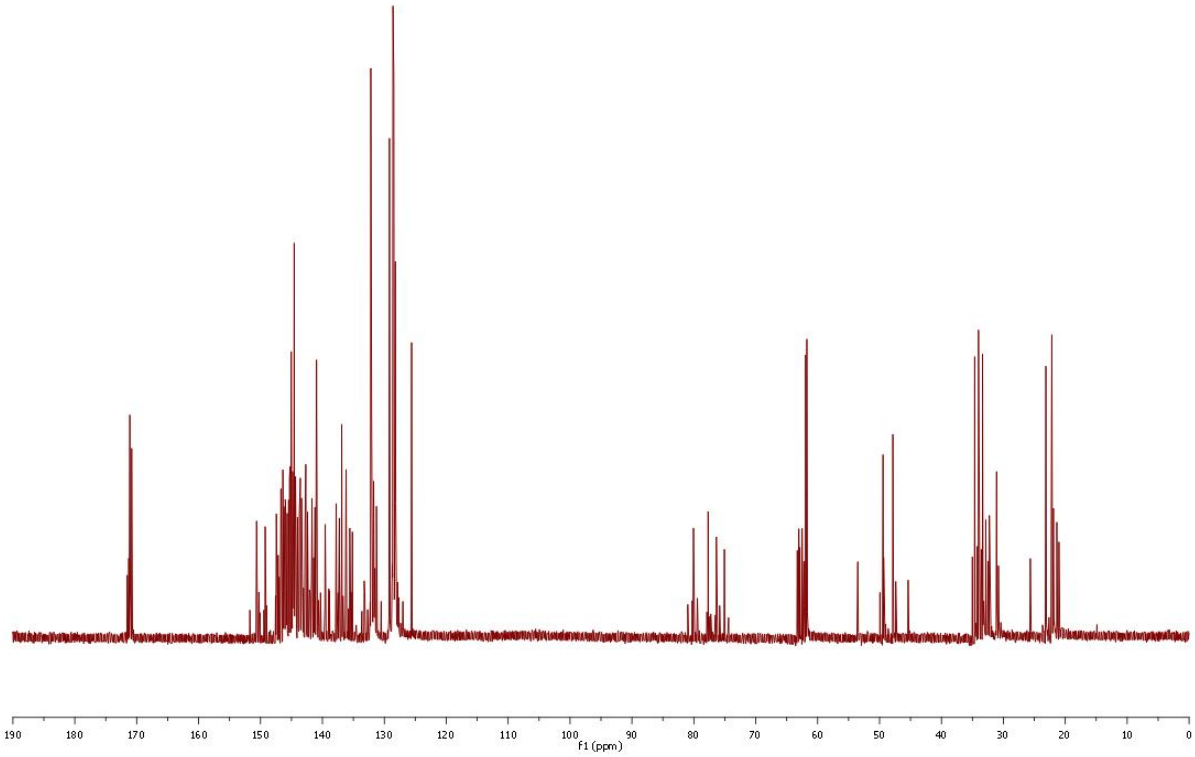
t_4Bis-PCBM. ^{13}C NMR (126 MHz, D_2O) δ 192.72, 192.70, 192.69, 192.69, 192.68, 192.67, 192.67, 192.66, 192.65, 192.65, 192.64, 192.64, 192.58, 192.53, 192.52, 192.51, 192.51, 192.50, 192.49, 192.49, 192.48, 192.47, 192.47, 192.46, 192.46, 192.45, 192.44, 192.43, 192.41, 171.83, 171.72, 171.68, 171.58, 171.50, 171.46, 171.41, 171.35, 151.91, 151.66, 150.65, 150.56, 150.36, 149.80, 149.73, 149.42, 149.14, 148.70, 148.34, 148.21, 148.16, 147.88, 147.57, 147.53, 147.50, 147.46, 147.41, 147.35, 147.30, 147.26, 147.17, 147.14, 147.10, 147.07, 146.84, 146.79, 146.71, 146.66, 146.59, 146.50, 146.48, 146.43, 146.39, 146.29, 146.25, 146.21, 146.16, 146.13, 146.10, 146.08, 146.03, 146.00, 145.95, 145.91, 145.84, 145.82, 145.75, 145.71, 145.68, 145.63, 145.61, 145.57, 145.41, 145.37, 145.33, 145.31, 145.29, 145.22, 145.20, 145.17, 145.15, 145.05, 145.00, 144.97, 144.96, 144.90, 144.86, 144.83, 144.80, 144.77, 144.72, 144.70, 144.69, 144.66, 144.65, 144.63, 144.60, 144.55, 144.47, 144.45, 144.41, 144.39, 144.35, 144.31, 144.27, 144.23, 144.16, 144.03, 144.00, 143.98, 143.91, 143.86, 143.80, 143.76, 143.71, 143.64, 143.59, 143.55, 143.53, 143.49, 143.45, 143.40, 143.30, 143.18, 143.15, 143.08, 142.99, 142.96, 142.81, 142.75, 142.71, 142.66, 142.64, 142.58, 142.55, 142.48, 142.39, 142.26, 142.21, 142.17, 142.11, 142.05, 142.01, 141.97, 141.93, 141.79, 141.71, 141.69, 141.66, 141.59, 141.42, 141.38, 141.31, 141.26, 141.22, 141.20, 141.10, 141.01, 140.98, 140.95, 140.86, 140.82, 140.67, 140.65, 140.54, 140.41, 140.25, 140.05, 139.90, 139.76, 139.66, 139.64, 139.49, 139.31, 139.18, 139.12, 138.95, 138.88, 138.73, 138.58, 138.53, 138.44, 138.28, 138.14, 138.03, 137.91, 137.81, 137.69, 137.65, 137.62, 137.39, 137.25, 137.22, 137.19, 137.16, 137.08, 137.04, 136.95, 136.91, 136.85, 136.80, 136.77, 136.72, 136.70, 136.65, 136.44, 136.18,

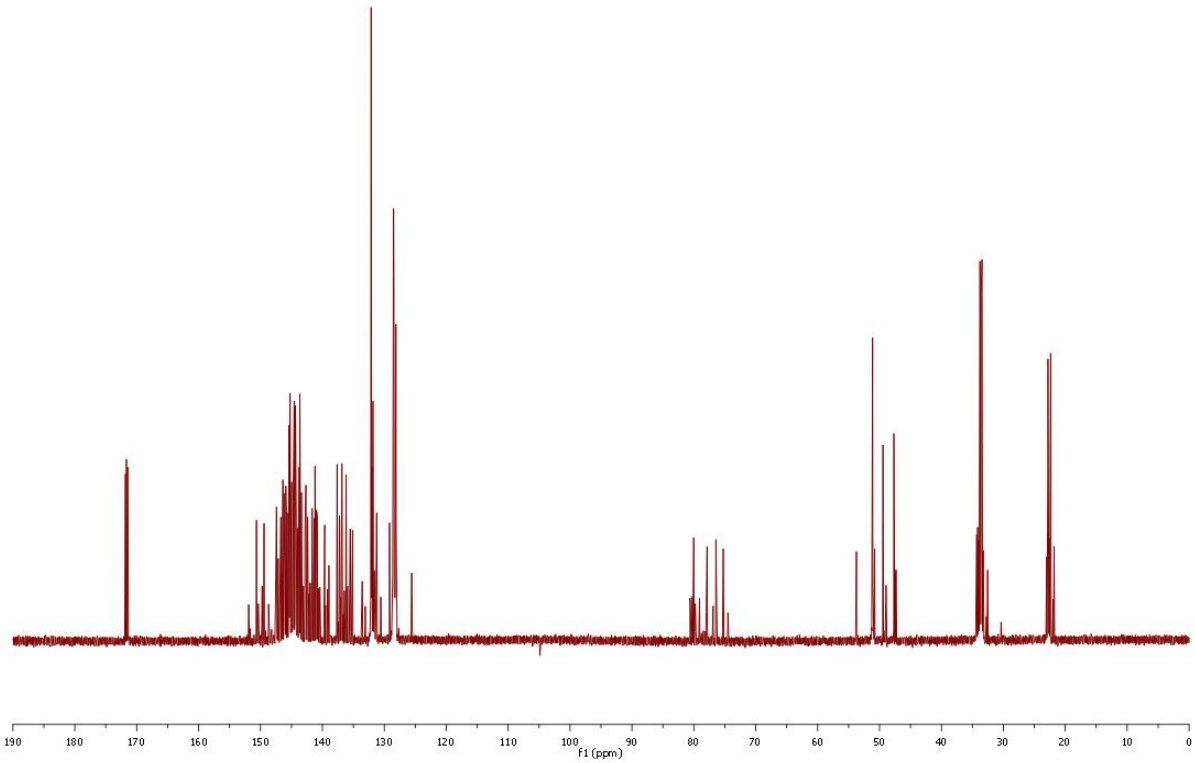
136.12, 135.93, 135.81, 135.79, 135.58, 135.51, 135.38, 135.12, 135.09, 134.43, 134.21, 133.81, 133.62, 133.57, 133.28, 132.54, 132.27, 132.16, 132.13, 132.09, 132.05, 132.03, 131.83, 131.62, 131.35, 131.24, 130.78, 130.63, 130.57, 129.16, 128.87, 128.64, 128.58, 128.54, 128.51, 128.45, 128.35, 128.29, 128.28, 128.23, 128.20, 128.13, 128.09, 127.79, 127.67, 127.58, 127.37, 82.49, 80.60, 80.54, 80.24, 80.05, 80.02, 79.83, 79.78, 79.07, 78.77, 78.45, 78.23, 78.11, 77.99, 77.86, 76.88, 76.43, 76.31, 75.25, 74.40, 61.09, 60.74, 60.54, 60.51, 60.14, 53.73, 52.26, 51.27, 51.19, 51.16, 51.15, 51.13, 51.11, 50.80, 49.45, 49.43, 49.32, 48.95, 48.85, 47.69, 47.46, 47.34, 35.53, 35.39, 35.04, 34.97, 34.30, 34.15, 33.98, 33.92, 33.89, 33.84, 33.78, 33.76, 33.71, 33.58, 33.49, 33.46, 33.44, 33.40, 33.34, 33.28, 33.23, 32.76, 32.54, 23.01, 22.93, 22.81, 22.80, 22.73, 22.68, 22.58, 22.44, 22.40, 22.36, 21.79, 20.28, 20.23, 20.16, 20.09, and 19.87.

S2 ^{13}C NMR spectra of the fullerene adducts

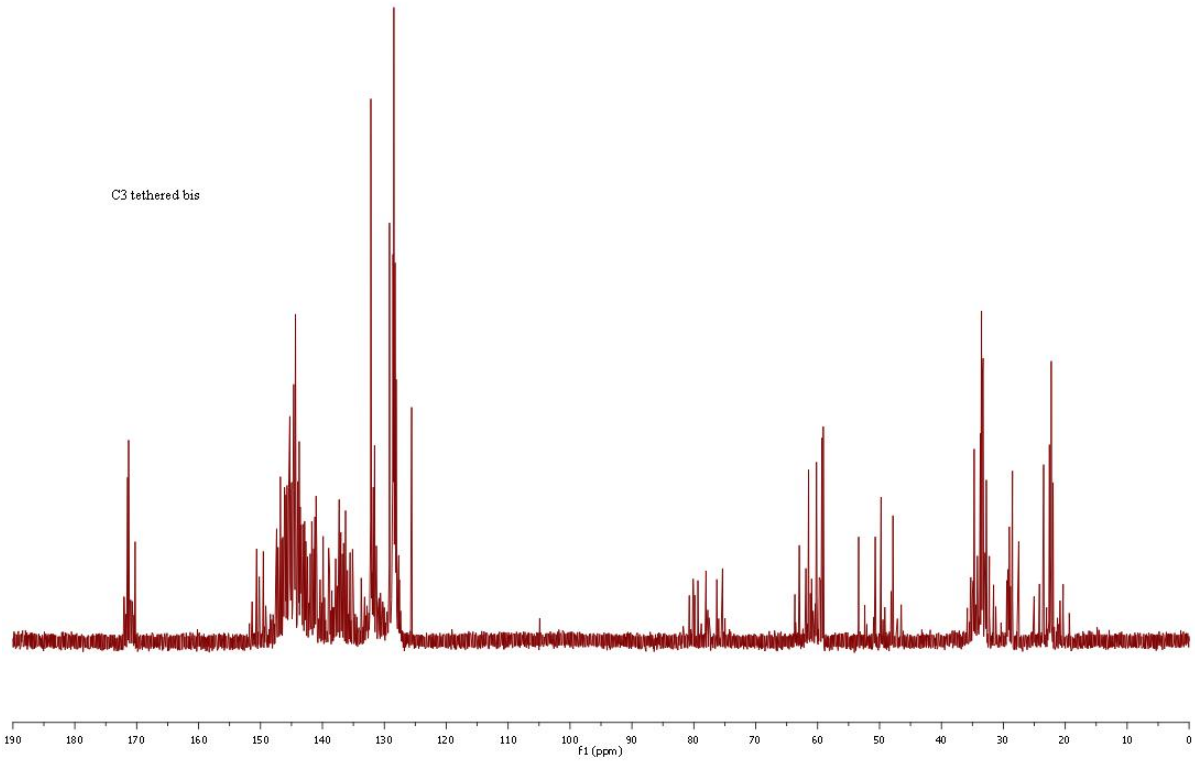
S2.1 C2-tethered bisadduct



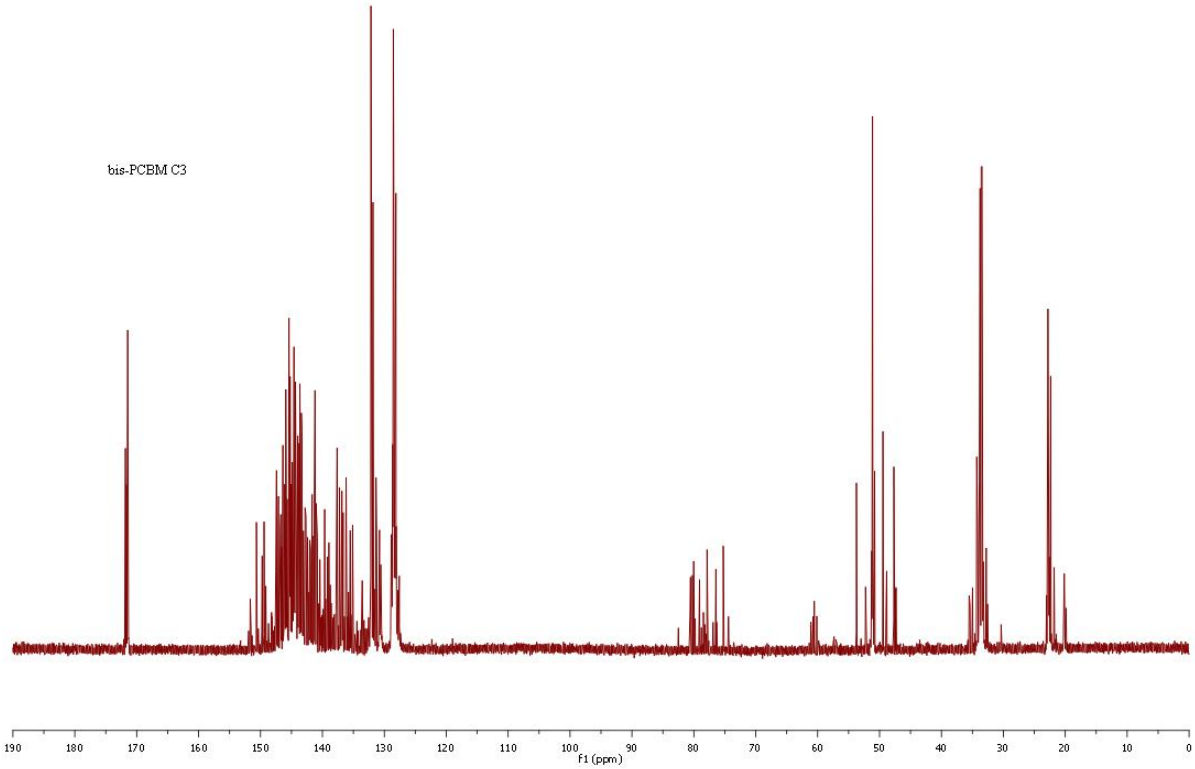
S2.2 t2bis-PCBM



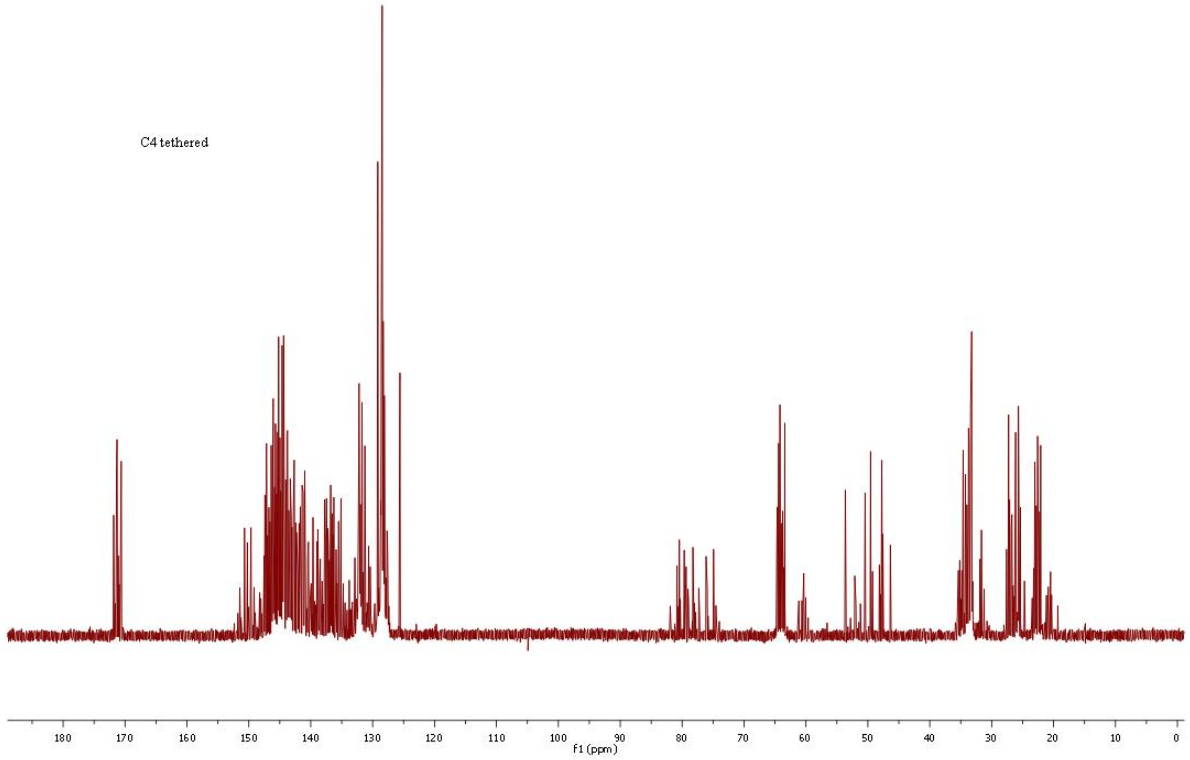
S2.3 C3-tethered bisadduct



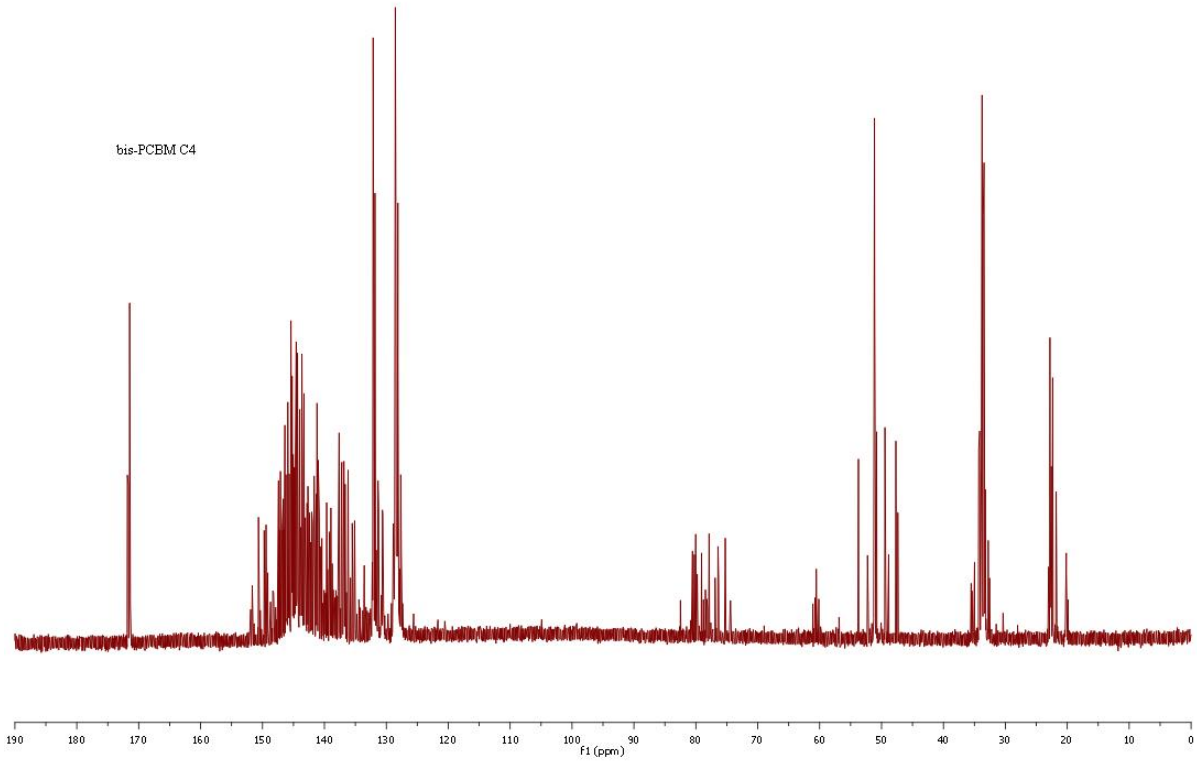
S2.4 t3bis-PCBM



S2.5 C4-tethered bisadduct



S2.6 t4bis-PCBM



S3 Molecular Modeling with PM3

Table S1: Calculated energies for lowest energy isomers of tethered bisadducts.

Isomer	Orientation	C2 tethered	C3 tethered	C4 tethered
Cis 1	endo-endo	28,927	32,359	33,855
Cis 1	endo-exo	24,429	27,460	28,502
Cis 1	exo-exo	18,301	23,077	19,486
Cis 1	exo-exo 2	19,456	21,306	18,450
Cis 2	endo-endo	0,886	1,924	3,434
Cis 2	endo-exo	0,374	0,005	0,592
Cis 2	exo-exo	1,224	4,702	5,302
Cis 2	exo-exo 2	11,838	11,062	11,512
Cis 3	endo-endo	37,954	25,146	25,291
Cis 3	endo-exo	4,214	3,560	0,633
Cis 3	exo-exo	8,852	7,938	4,497
E	ph endo	16,626	6,525	1,934
E	ph exo	0,000	0,000	1,385
Trans 4	endo-endo	38,332	23,233	11,725
Trans 4	endo-exo	14,909	9,252	6,786
Trans 4	exo-exo	1,328	4,357	0,000
Trans 3	endo-endo	10,064	5,194	3,439
Trans 3	endo-exo	9,192	5,255	3,937
Trans 3	exo-endo	38,312	23,819	11,764
Trans 3	exo-exo	16,620	12,851	7,990
Trans 2	endo-endo	Not possible	Not possible	110,667
Trans 2	endo-exo	83,069	55,075	46,942
Trans 2	exo-exo	29,967	15,644	12,195
Trans 2	Not possible	Not possible	52,346	33,040
Trans 1	endo-endo	Not possible	Not possible	Not possible
Trans 1	endo-exo	Not possible	76,502	121,993
Trans 1	exo-exo	147,985	112,956	55,377

S4 References

1 R.K.M. Bouwer and J.C. Hummelen, *Chem. Eur. J.* **2010**, 16, 11250