ELECTRONIC SUPPLEMENTRAY INFORMATION

Photoinduced Charge Separation in Oligophenylenevinylene-Based Hamilton-type Receptor Supramolecularly Associating Two C_{60}-Barbiturate Guests

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Contents

Experimental Section

1,4-Bis(dodecyloxy)benzene (4). NaH (1.8 g, 0.045 mol) was added in portions to a cold solution of hydroquinone (2 gr, 0.018 mol) in dry DMF (20 mL) under N_2 atmosphere. After the reaction mixture reached room temperature, 1-bromododecane (11.2 g, 0.045 mol) diluted in 20 mL dry DMF was added. The mixture was stirred at 80 ^oC overnight, brought to r.t. and water was added. The white precipitate was filtered off and recrystallized from cold methanol, to furnish compound **4** as light pink-white solid (7.8 g, 97% yield).
^1H NMR (300 MHz, ppm) $CDCl_3$: 6.81, (s, 4H), 3.89 (t, J = 6.6 Hz, 4H), 1.75 (qui, J = 6.6 Hz, 4H), 1.30-1.26 (m, 36H), 0.88 (t, J = 6.6 Hz, 6H); ^{13}C NMR (75 MHz, ppm) $CDCl_3$: 153.18, 115.38, 68.67, 31.92, 29.66-29.35, 26.06, 22.69, 14.12.

2,5-Bis(bromomethyl)-1,4-bis(dodecyloxy)benzene (5). To a suspension of **4** (2 g, 4.48 mmol) and paraformaldehyde (0.296 g, 9.86 mmol) in acetic acid (15 mL), HBr (2.2 mL, 33 wt % in acetic acid) was added. The mixture was heated to 70 °C and stirred for 2 h. After cooling down to room temperature, the reaction mixture was poured into distilled water (150 mL). The precipitates were filtered and dissolved in hot chloroform. Finally, re-precipitation of the resulting solution in cold methanol gave **5** (1.9 g, 67% yield) as a white solid.
^1H NMR (300 MHz, ppm) $CDCl_3$: 6.84, (s, 2H), 4.52 (s, 4H), 3.98 (t, J = 6.4 Hz, 4H) 1.79 (m, 4H), 1.49-1.19 (m, 36H), 0.87 (t, J = 6.6 Hz, 6H); ^{13}C NMR (75 MHz, ppm) $CDCl_3$: 150.59, 127.42, 114.54, 68.93, 31.92, 29.67, 29.64, 29.60, 29.35, 29.30, 28.82, 26.06, 22.70, 14.15.

2,5-bis(dodecyloxy)-1,4-phenylene)bis(methylene) tetraethyl bis(phosphite) (6). A suspension of **5** (0.632 g, 1.0 mmol) and triphenylphosphine (0.550 g, 2.1 mmol) in toluene was heated at reflux for 3 h. The reaction mixture was then cooled down to room temperature and a white solid precipitated. The product **6**, collected after filtration, was used in the next step without further purification.

2,5-Bis(dodecyloxy)benzene-1,4-dialdehyde (7). To a suspension of **5** (1 g, 1.58 mmol) in 40 mL DMSO, $NaHCO_3$ (2 g, 23.71 mmol) was added and the reaction mixture was heated up to 115 ^oC. When the reaction mixture turned from colorless to pale yellow and TLC showed that **5** was completely consumed (after 1h), the mixture was left to cool down, and poured into 500 mL of distilled water. The aqueous phase was extracted by dichloromethane and after removal of solvent, column chromatography (silica, dichloromethane/petroleum ether 3/7) gave pure **7** (0.351g, 30%) as a yellow solid.
^1H NMR (300 MHz, ppm) CDCl3: 10.51 (s, 2H), 7.42 (s, 2H), 4.08 (t, J = 6.4 Hz, 4H), 2.06 (s, 4H), 1.81 (m, 4H), 1.56–1.16 (m, 36H), 0.87 (t, J = 6.6 Hz, 6H); ^{13}C NMR (75 MHz, ppm) $CDCl_3$: 189.46, 155.18, 129.19, 111.53, 69.18, 31.90, 29.63, 29.61, 29.56, 29.53, 29.33, 29.30, 29.02, 25.99, 22.68, 14.12.

2,5-Bis(dodecyloxy)-1,4-bis[(2,5-didodecoxy-4-formyl)phenylenevinylene] benzene (8). Compound **6** (0.231 g, 0.2 mmol) along with dialdehyde **7** (0.2 g, 0.4 mmol) was dissolved under N_2 in dry dichloromethane (20 mL) and potassium *tert*-butoxide (0.056 g, 0.5mmol) was added in portions under vigorous stirring at 0 ^0C. The base should be added at such a rate that the transient red color produced instantly upon the addition of base should not persist. The resulting solution was allowed to stir for 1 h after the completion of base addition at 0 ^oC. Then, the mixture was allowed to reach room temperature and washed with distilled water. After the removal of the sol-

vent, the residue contained both E- and Z-isomers. A solution of this isomeric mixture and iodine (catalytic amount) in toluene (20 mL) was stirred at room temperature overnight. The dark purple solution was then diluted with dichloromethane and washed repeatedly with aqueous $Na_2S_2O_3$ (0.3 M, 3 × 20 mL) and water (3 × 20 mL). After evaporation of the solvents, the crude product was purified by column chromatography (petroleum ether / dichloromethane 1/1), to afford 1.07 g of **8** as a yellow solid (0.123 g, 43% yield).
^{1}H NMR (300 MHz, ppm) $CDCl_3$: 10.45 (s, 2H), 7.60 (d, *J* = 16.6 Hz, 2H), 7.50 (d, *J* = 16.6 Hz, 2H), 7.33 (s, 2H), 7.20 (s, 2H), 7.15 (s, 2H), 4.13 – 4.02 (m, 12H), 1.85 (m, 12H) 1.59 – 0.95 (m, 108H), 0.90 – 0.85 (m, 18H); ^{13}C NMR (75 MHz, ppm) $CDCl_3$: 189.07, 156.05, 151.31, 150.68, 134.48, 127.59, 127.06, 123.80, 123.58, 123.27, 110.78, 110.24, 109.71, 84.74, 84.44, 77.41, 76.98, 76.56, 69.29, 31.90, 29.71, 29.66, 29.51, 29.41, 29.35, 26.29, 26.16, 22.67, 14.09.

3-bromopropyl methyl malonate (10). Diisopropylethylamine (920 mg, 7.123 mmol) was added to a solution of 3-bromopropanol (900 mg, 6.475 mmol) in dry CH_2Cl_2 (30 mL) and the mixture was cooled at 0 ºC. After 30 min, methyl malonyl chloride dissolved in dry CH_2Cl_2 (10 mL) was added dropwise. The reaction mixture was stirred at 0 ºC for 1.5 h and at room temperature overnight, under nitrogen atmosphere. The progress of the reaction was monitored by TLC (ethyl acetate/petroleum ether 1/4). Finally, water was added to the reaction mixture and then extracted with CH_2Cl_2. The organic phase was dried over Na_2SO_4, filtered, and the solvent was evaporated to dryness *in vacuo*. The residue was further purified via column chromatography (silica gel, ethyl acetate/petroleum ether 1/5) to give **10** as a yellowish oil (1g, 65%).
^{1}H NMR (300 MHz, ppm) $CDCl_3$: 4.30 (t, *J*= 6.4 Hz, 2H), 3.75 (s, 3H), 3.46(t, *J* = 6.4 Hz, 2H), 3.40 (s, 2H), 2.20 (m, 2H); ^{13}C NMR (75MHz, ppm) $CDCl_3$: 166.86, 166.29, 63.16, 52.58, 41.42, 31.42, 29.03.

Fullerene derivative (11). 1,8-Diazabicycloundec-7-ene (144 mg, 0.940 mmol) was added dropwise to a suspension containing C_{60} (680 mg 0.940 mmol), CBr_4 (314 mg 0.940 mmol), and malonic ester **10** (150 mg, 0.628 mmol) in dry toluene (400 mL) under N_2 atmosphere. The reaction mixture was stirred at room temperature overnight and the progress of the reaction was monitored by TLC (toluene). The product was isolated by flash chromatography (silica gel, toluene) and dried *in vacuo* to give **11** (303 mg, 50 %).
^{1}H NMR (300 MHz, ppm) $CDCl_3$: 4.65 (t, *J* = 6.4 Hz, 2H), 4.10 (s, 3H), 3.57 (t, *J* = 6.4 Hz, 2H), 2.40 (m, 2H); ^{13}C NMR (75MHz, ppm) $CDCl_3$: 163.63, 163.00, 145.14, 145.06, 145.04, 144.94, 144.83, 144.76, 144.70, 144.55, 144.54, 144.54, 144.53, 144.48, 144.45, 143.75, 143.73, 142.95, 142.89, 142.83, 142.06, 141.74, 141.71, 140.89, 140.85, 139.19, 138.65, 71.16, 64.64, 53.82, 31.35, 28.87. MS (ESI): $[M]^+$=957.

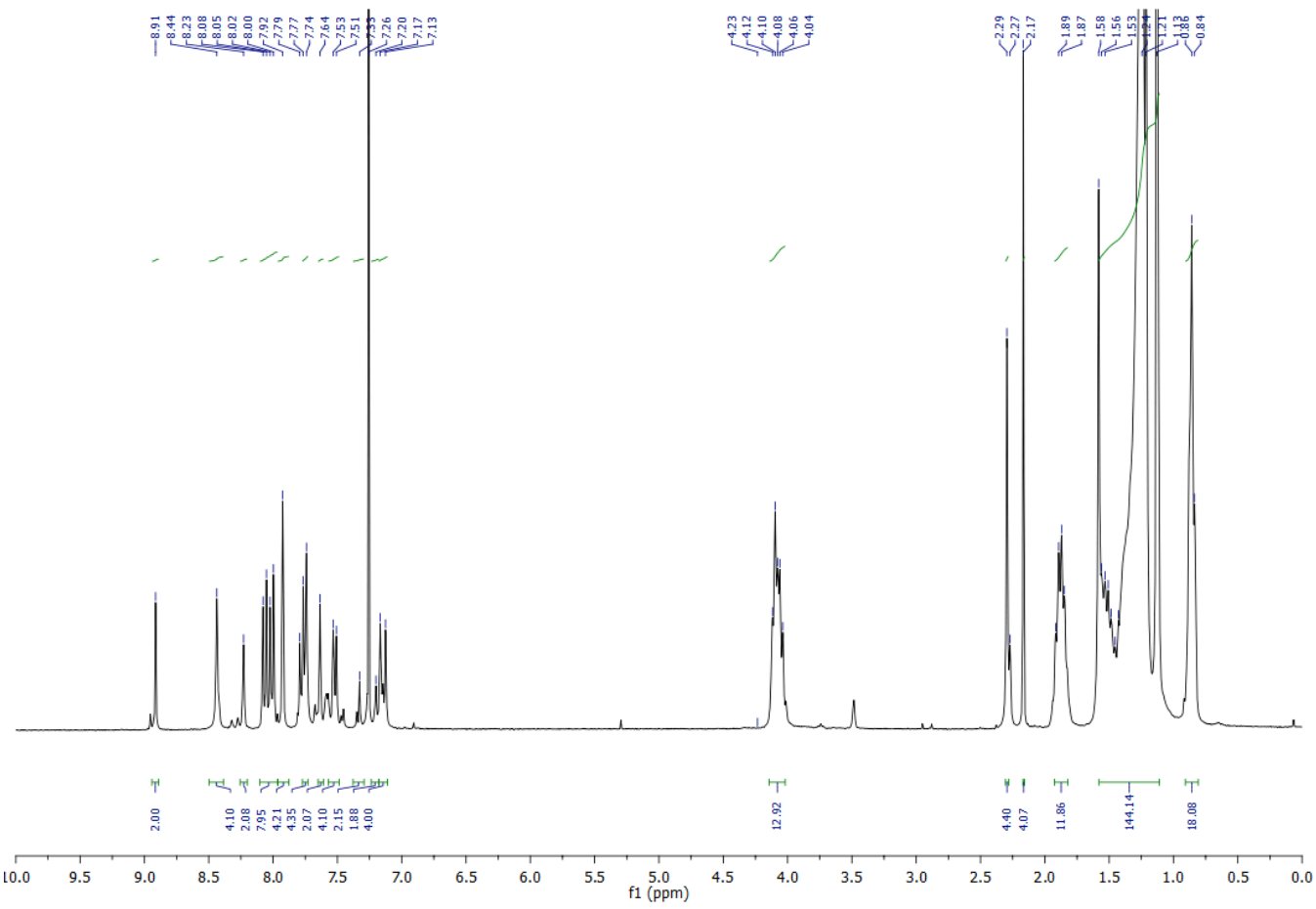

Figure S1. ^{1}H NMR spectrum of Hamilton-type OPV-based host **1**, in $CDCl_3$.

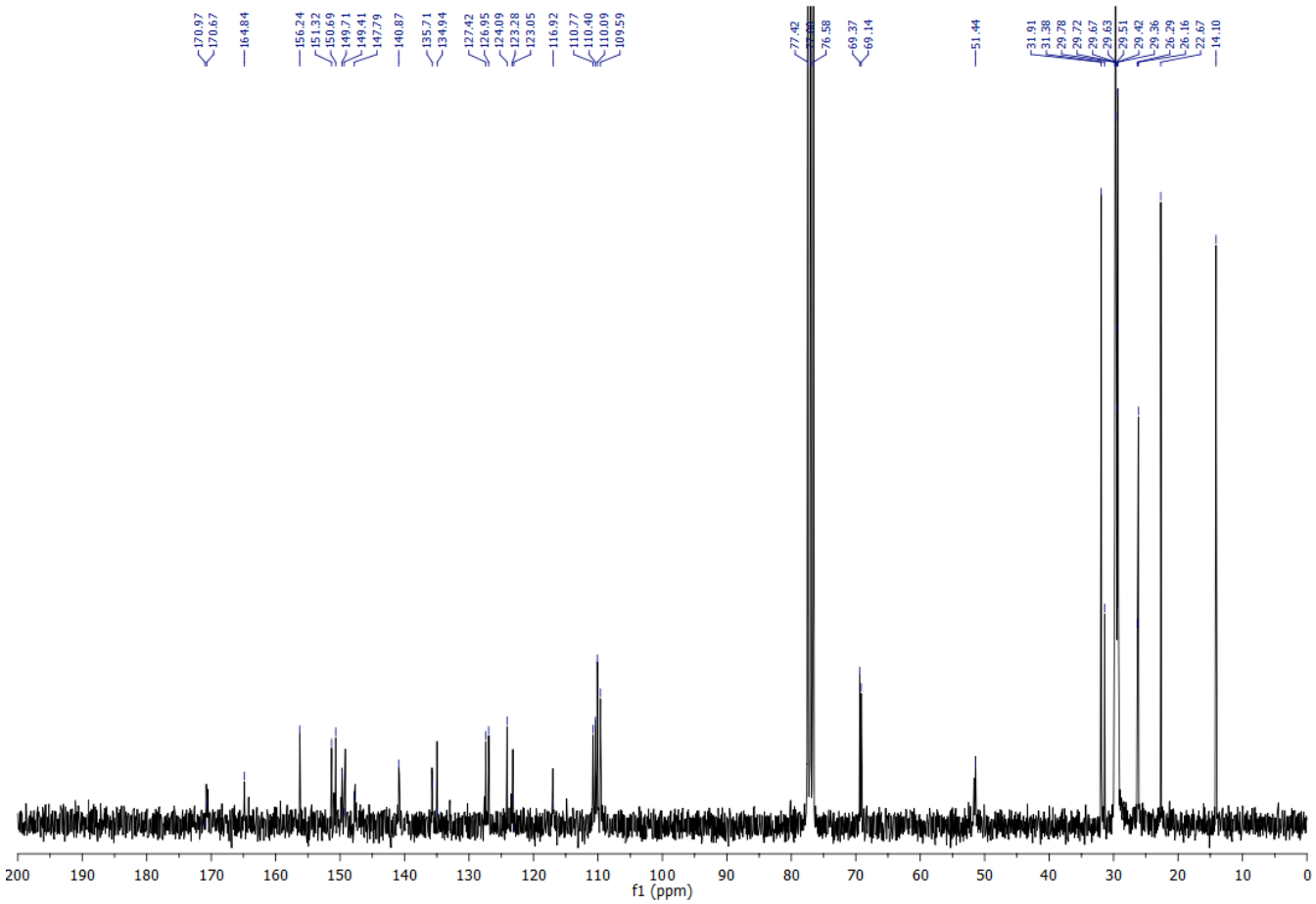

Figure S2. ^{13}C NMR spectrum of Hamilton-type OPV-based host **1**, in $CDCl_3$.

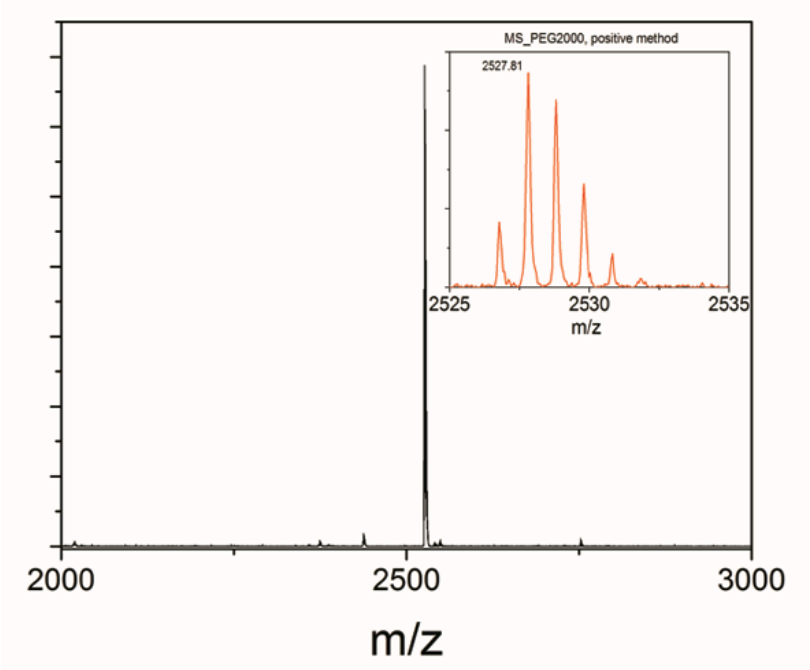

Figure S3. MALDI-TOF mass spectrum analysis of Hamilton-type OPV-based host **1** using dithranol as matrix. Inset: MALDI-TOF spectrum (positive method) of exact mass using PEG 2000 as calibration standard.

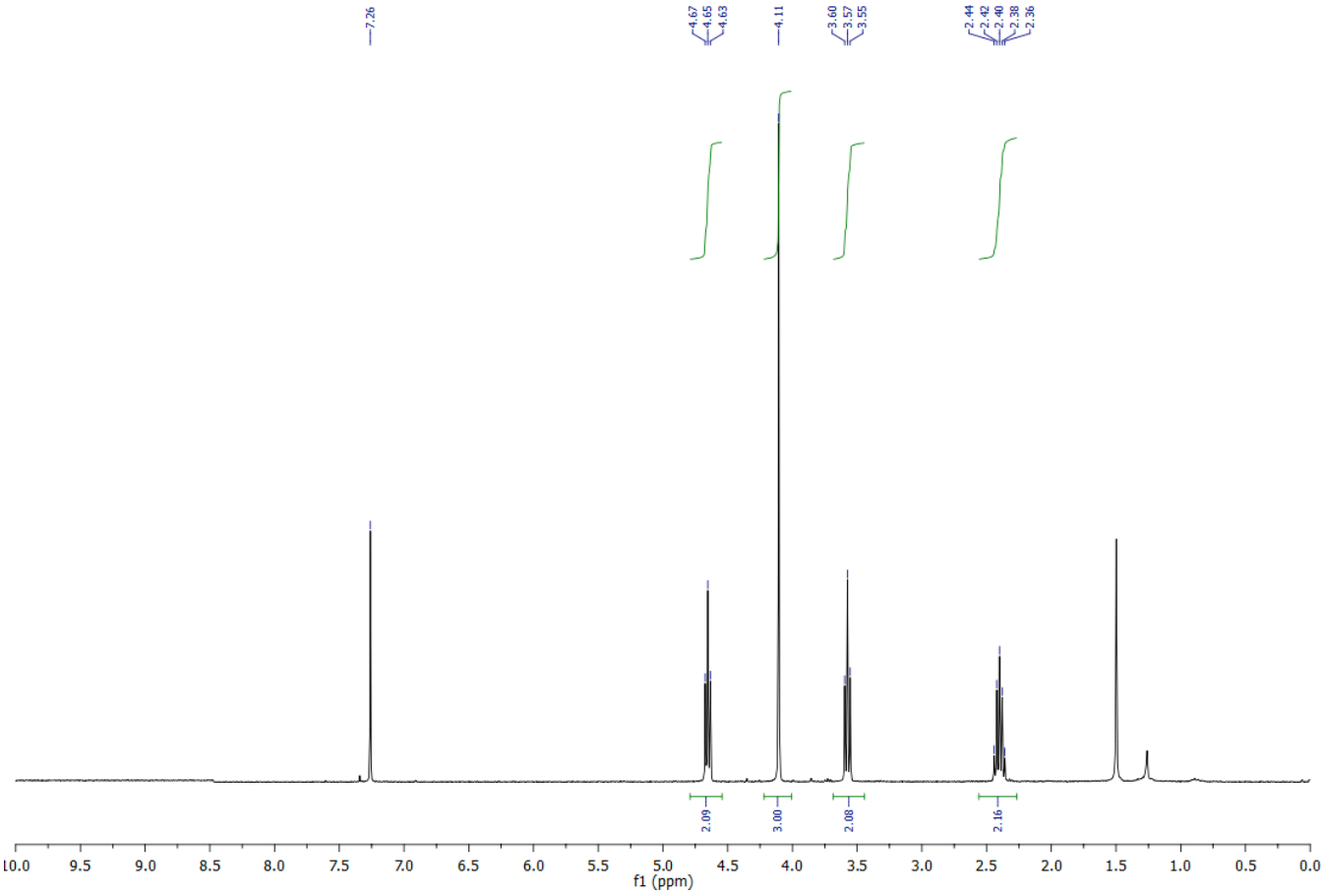

Figure S4. ^{1}H NMR spectrum of fullerene derivative **11**, in $CDCl_3$.

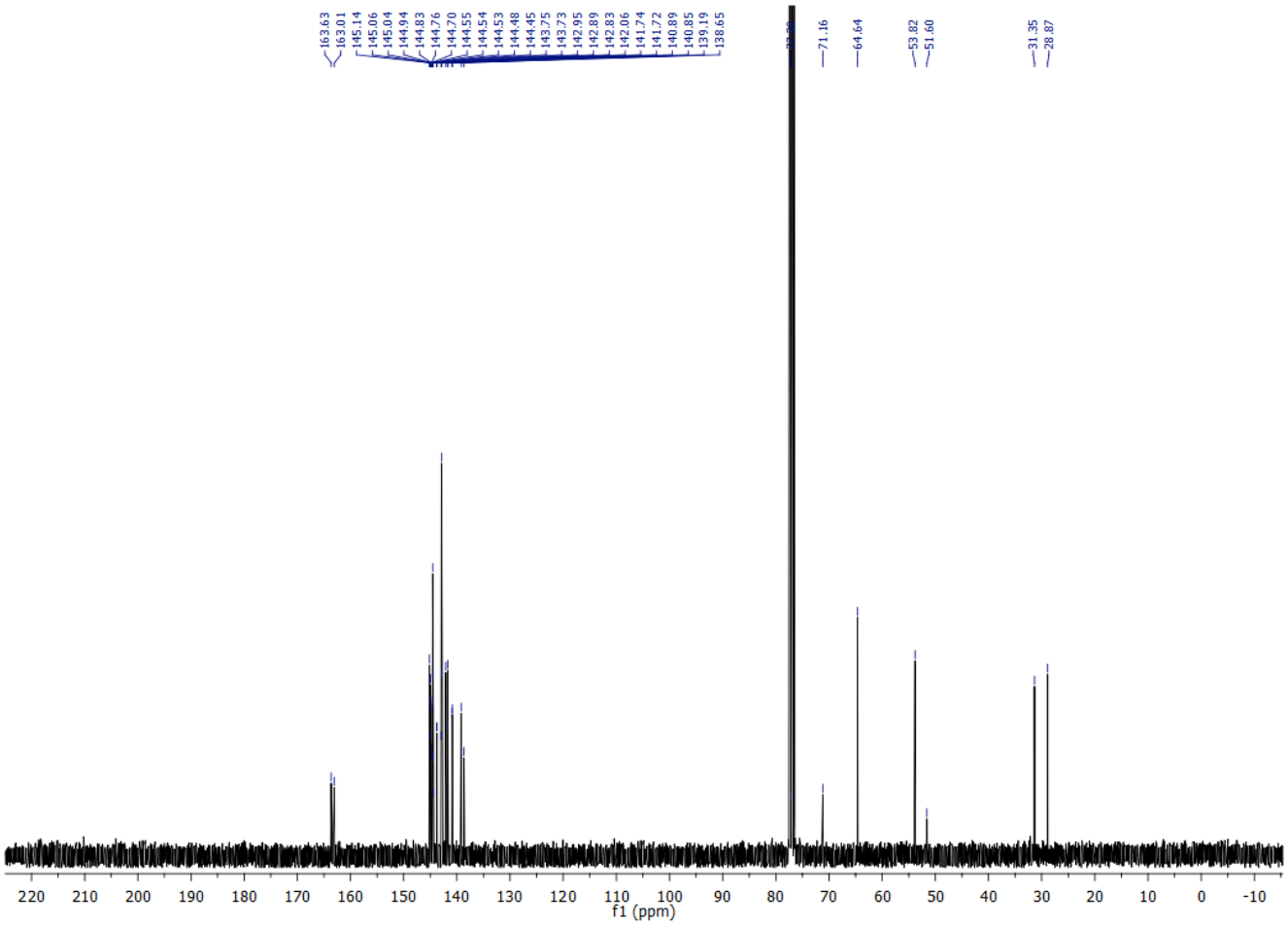

Figure S5. ^{13}C NMR spectrum of fullerene derivative **11**, in $CDCl_3$.

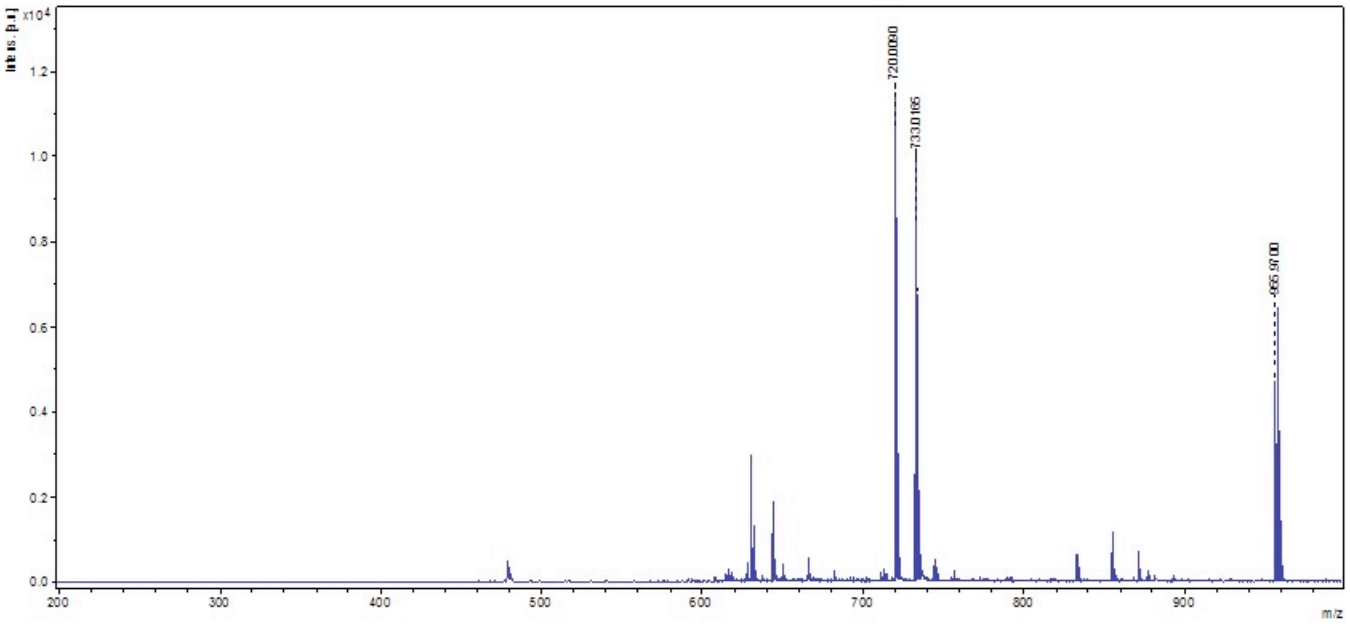

Figure S6. MALDI-TOF mass spectrum of fullerene derivative **11**, using dithranol as matrix.

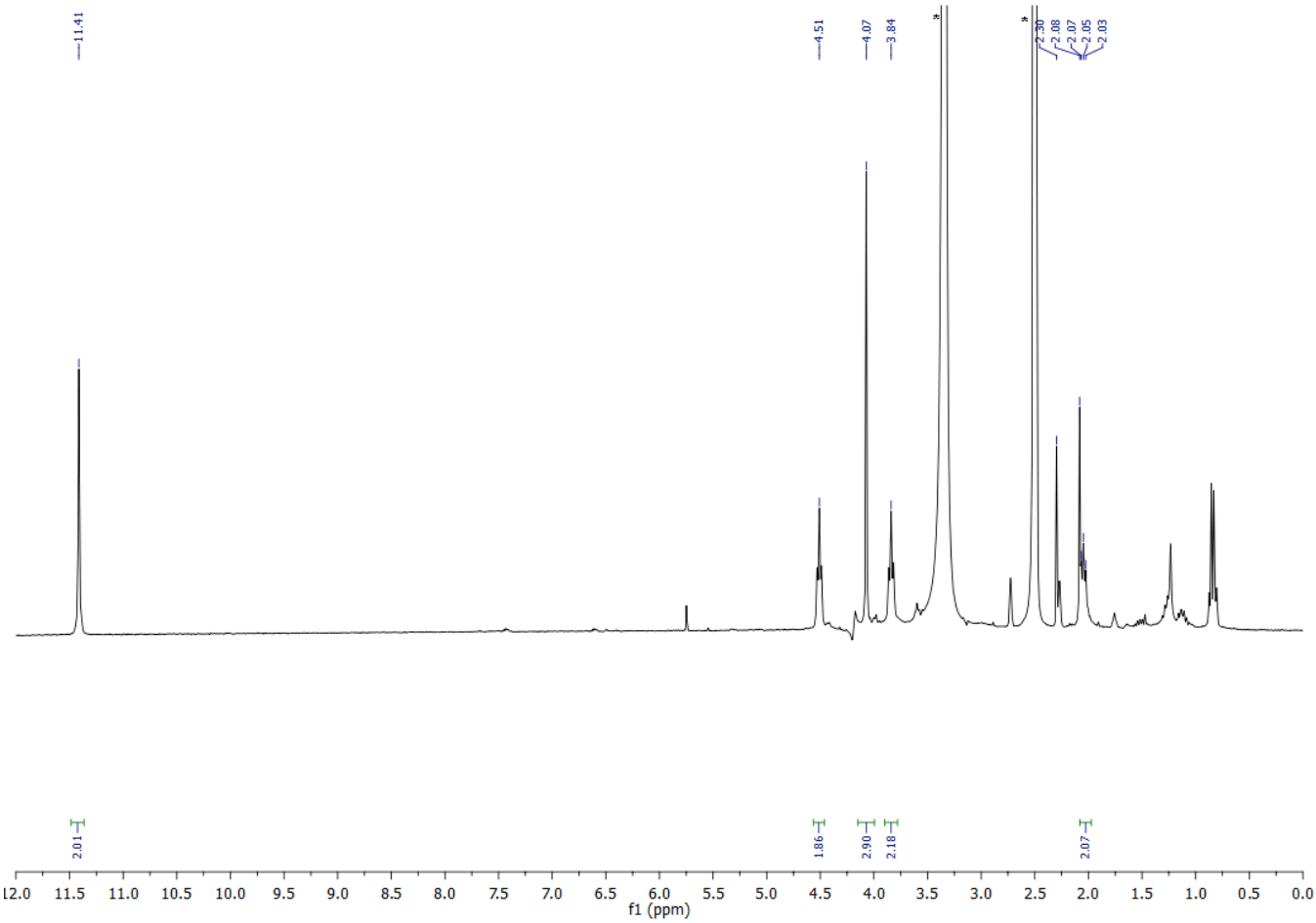

Figure S7. ^{1}H NMR spectrum of C_{60}-barbiturate guest **2**, in DMSO-d6.

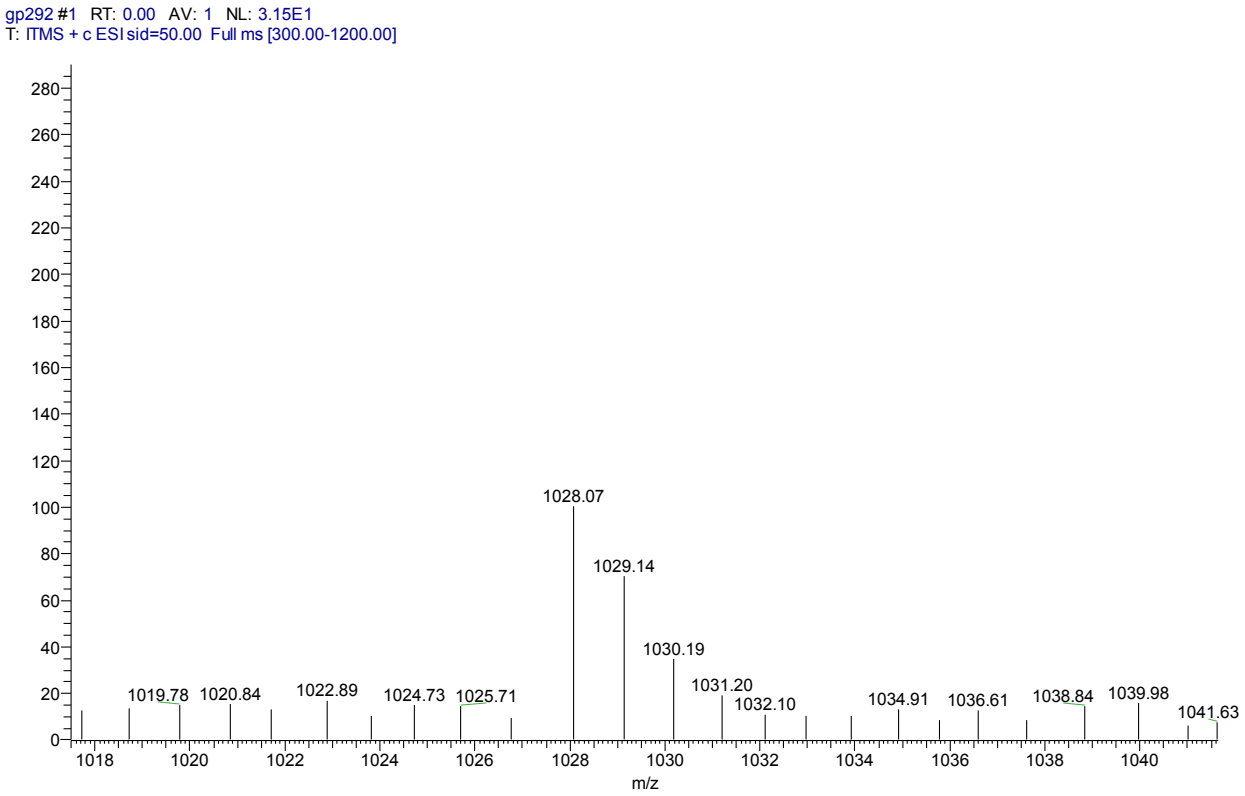

Figure S8. ESI Mass spectrum of C_{60}-barbiturate guest **2**.

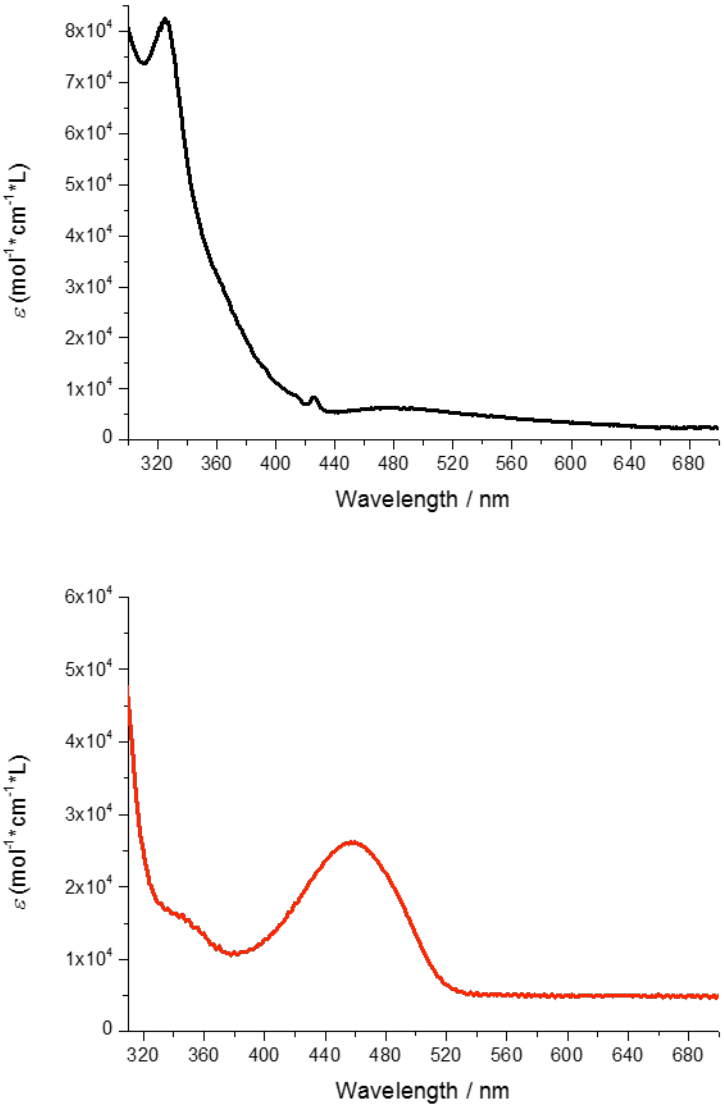

Figure S9. UV-Vis spectra of OPV-based host **1** (bottom spectrum) and C_{60}-barbiturate guest **2** (upper spectrum), obtained in THF.

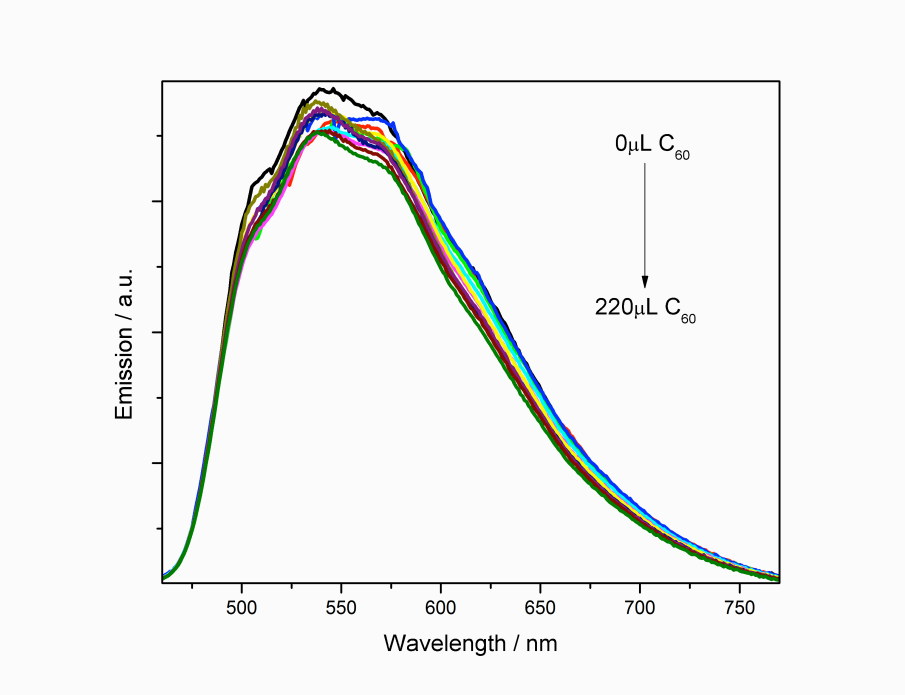

Figure S10. Photoluminescence spectra of Hamilton-type OPV-based host **1** monitored upon titration assays with pristine C_{60} (obtained in toluene, upon excitation at 440 nm).

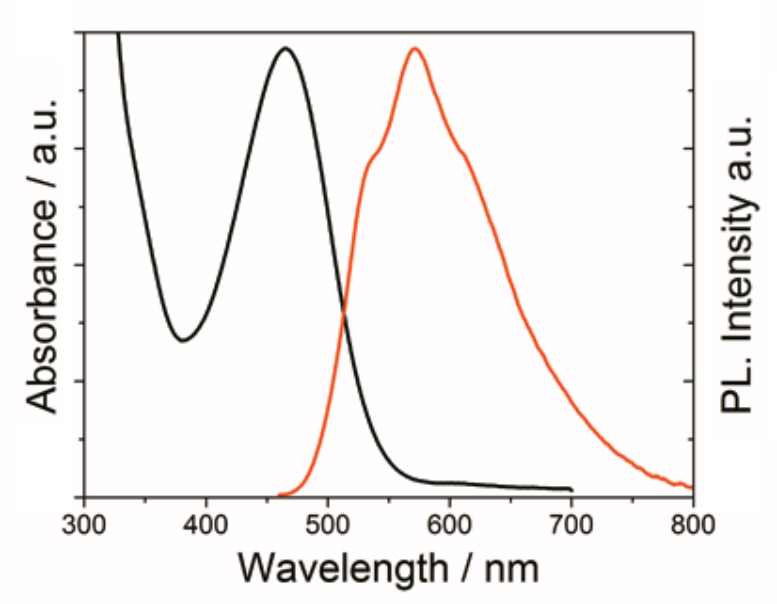

Figure S11. Absorption and fluorescence emission spectra of OPV-based Hamilton-type host **1**, obtained in toluene. The emission spectrum was obtained upon excitation at 440 nm.

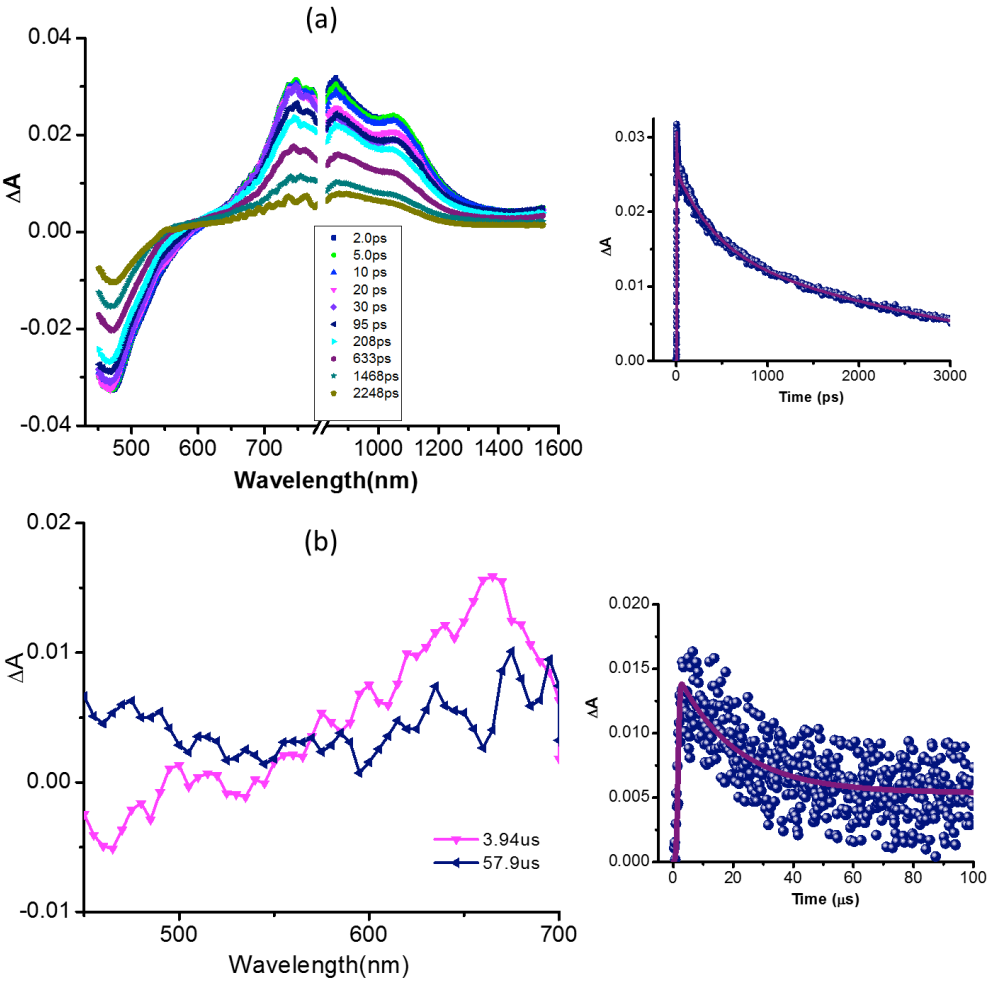

Figure S12. (a) Femtosecond transient spectra of Hamilton-type OPV-based host **1** in toluene at the indicated delay times at the excitation wavelength of 400 nm. The time profile of the 857 nm band is shown in the right hand side panel. (b) Nanosecond transient spectra of Hamilton-type OPV-based host **1** in toluene at the indicated delay times at the excitation wavelength of 420 nm. The time profile of the 665 nm band is shown in the right hand side panel.