Supporting Information for:

Highly Efficient Light Harvesting Organofullerenes.

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Normalized UV-vis absorption (solid line) and fluorescence (dashed line) (excitation wavelength 510 nm) of **12** in dichloromethane.

Fluorescence spectra (excitation wavelength 510 nm) of the fullerene-perylene dyad **10**.

Excitation spectrum of **10** (solid line) taken at 710 nm and UV-vis spectrum (dotted line) in dichloromethane.

Synthetic procedures.

4-Aminobenzophenone-*p*-tosylhydrazone (**2**).

To a solution of 4-amionobenzophenone (**1**) (1g, 5 mmol) and *p*-tosylhydrazide (930 mg, 5 mmol) in 20 ml of absolute ethanol, three drops of hydrochloric acid are added under argon atmosphere. After stirring for three days at room temperature, the yellow precipitate is collected, washed thoroughly with diethylether and dried to yield 1.55 g (85%) of **2** as a yellow solid.

M.p. (diethylether): 199-201°C.

¹H-NMR (CDCl₃, 200 MHz) δ= 7.81-7.63 (m, 2H), 7.43-7.40 (m, 3H), 7.24-7.15 (m, 4H), 7.02-6.98 (m, 1H), 6.84 (d, *J*= 8.60 Hz, 1H) 6.68 (d, *J*= 8.60 Hz, 1H) 6.48 (d, *J*= 8.78 Hz, 1H), 3.65 (bs, 2H), 2.34 (s, 3H).

¹³C-NMR (CDCl₃, 50 MHz) δ= 155.15, 148.19, 144.20, 137.36, 135.81, 131.79, 130.07, 129.80, 129.31, 128.44, 128.27, 128.10, 127.30, 118.6, 115.58, 114.60, 21.78.

FTIR (KBr, cm⁻¹) ν= 3402, 3327, 3176, 2923, 1628, 1608, 1560, 1319, 1153, 551.

MS (EI, %I) 365 (M⁺, 10), 210 (100), 180 (45), 152 (11) 91 (16).

1-(4'-Aminophenyl)-1-phenyl[6,6]methanofullerene (**3**).

To a solution of **2** (73 mg, 0.17 mmol) in 4 ml of dry pyridine, sodium methoxyde (10 mg, 0.18 mmol) is added under argon atmosphere. After stirring at room temperature for 15 minutes, a solution of [60]fullerene (100 mg, 0.13 mmol) in 13 ml of *o*-DCB is

added at once and the mixture is then heated at 180°C for 18 h. After cooling to room temperature, the solvent is stripped away in a rotary evaporator and the remaining solid is then purified by column chromatography (silica gel, hexane 2/ toluene 8) to yield 30 mg (26%) of **3** as a black solid.

¹H-NMR (CDCl₃/CS₂, 300 MHz) δ= 8.28 (d, *J*= 8.64 Hz, 2H), 8.04 (d, *J*= 8.64 Hz, 2H), 7.75-7.70 (m, 2H), 7.64-7.57 (m, 1H), 6.94 (d, *J*= 8.64 Hz, 2H), 3.99 (s, 2H).

¹³C-NMR (CDCl₃/CS₂, 75 MHz) δ= 149.08, 149.05, 147.03, 146.11, 145.90, 145.89, 145.84, 145.43, 145.41, 145.30, 145.07, 141.05, 144.58, 143.72, 143.66, 142.95, 142.91, 142.88, 142.85, 141.61, 140.23, 139.18, 138.96, 132.71, 131.47, 129.82, 129.12, 128.85, 128.69, 115.60, 79.96, 58.73.

FTIR (KBr, cm⁻¹) ν= 3454, 3371, 3032, 2922, 2850, 1618, 1514, 1425, 1283, 1173, 526.

MS (ESI) 910 (M⁺).

4,4'-(Trifluoroacetamido)benzophenone (5).

A solution of **4** (848 mg, 4 mmol) in 15 ml of dry THF, 12 ml of trifluoroacetic anhydride and a few drops of dry pyridine are refluxed for 4h under argon atmosphere. After cooling to room temperature, the reaction is quenched by cautiously adding methanol and water and extracted with dichloromethane. The organic phase is dried over magnesium sulphate and the solvent is then evaporated under reduced pressure. Purification of the residue by column chromatography (silica gel, hexane 7/ethyl acetate 3) yields 1.58 g (98%) of **5** as a white solid.

M.p. (hexane/ethyl acetate): 229-231°C.

¹H-NMR (MeOD, 200 MHz) δ= 6.21 (m, 8H).

¹³C-NMR (MeOD, 50 MHz) δ= 194.49, 140.50, 134.29, 130.78, 120.07.

FTIR (KBr, cm⁻¹) ν= 3284, 2927, 2850, 1708, 1643, 1604, 1541, 1311, 1248, 1184, 1159.

MS (EI, %I) 404 (M⁺, 43), 216 (100).

4,4'-(Trifluoroacetamido)benzophenone-*p*-tosylhydrazone (6).

Under argon atmosphere, a solution of **5** (808 mg, 2 mmol) and *p*-tosylhydrazide (364 mg, 2 mmol) in 60 ml of toluene and 8 ml of ethanol is refluxed for 24 h. After cooling to room temperature, the precipitate is collected by filtration, washed with hexane and dried to yield 1.07 g (93%) of **6** as an off-white solid.

M.p. (hexane): 214-216°C.

¹H-NMR (MeOD, 200 MHz) δ= 6.52 (m, 5H), 6.24 (d, *J*= 8.78 Hz, 2H), 6.08-5.89 (m, 5H), 1.08 (s, 3H).

¹³C-NMR (MeOD, 50 MHz) δ= 153.43, 144.08, 140.25, 137.67, 135.82, 134.49, 130.73, 129.50, 129.46, 129.15, 128.34, 128.04, 127.72, 125.52, 124.96, 121.25, 120.16, 120.04, 20.08.

FTIR (KBr, cm⁻¹) ν= 3320, 3175, 2924, 1734, 1701, 1604, 1541, 1413, 1320, 1246, 1203, 1163.

MS (EI, %I) 417 (M⁺-Tos, 6), 404 (10), 390 (65), 291 (29), 216 (100), 132 (52), 91 (62).

4,4'-Aminobenzophenone-*p*-tosylhydrazone (7).

A solution of **6** (1.3 g, 2.2 mmol) in 60 ml of methanol is treated with 40 ml of an aqueous solution of potassium carbonate (20%) and stirred for 24 hours at room temperature. The mixture is extracted with dichloromethane, the organic phase dried over anhydrous magnesium sulfate and the solvent evaporated under reduced pressure. The residue is then purified by column chromatography (silica gel, dichloromethane 9/ methanol 1) to yield 720 mg (84%) of **7** as a yellowish solid.

M.p. (dichloromethane/methanol): 215-217°C.

¹H-NMR (MeOD, 200 MHz) δ = 6.34 (d, J = 8.25 Hz, 2H), 6.06 (d, J = 8.25 Hz, 2H), 5.91 (d, J = 8.34 Hz, 2H), 5.53 (d, J = 8.34 Hz, 2H), 5.37 (d, J = 8.51 Hz, 2H), 5.16 (d, J = 8.51 Hz, 2H), 1.05 (s, 3H).

¹³C-NMR (MeOD, 50 MHz) δ = 132.98, 130.64, 129.90, 129.84, 128.50, 115.04, 114.36, 113.46, 19.76.

FTIR (KBr, cm⁻¹) ν = 3460, 3375, 3219, 3033, 2922, 1624, 1604, 1512, 1375, 1313, 1159, 553.

MS (EI, %I) 380 (M⁺, 2), 225 (47), 212 (54), 198 (100), 180 (34), 120 (72), 106 (37), 92 (58), 65 (53).

[6,6]-Bis-(4-aminophenyl)methanofullerene (8).

To a solution of **7** (68 mg, 0.18 mmol) in 4 ml of dry pyridine, sodium methoxyde (10 mg, 0.18 mmol) is added under argon atmosphere. After stirring at room temperature for 15 minutes, a solution of [60]fullerene (100 mg, 0.13 mmol) in 15 ml of *o*-DCB is added at once and the mixture is heated at 180°C for 18 h. After cooling to room temperature, the solvent is stripped away in a rotary evaporator and the remaining solid purified by column chromatography (silica gel, toluene 8/ ethyl acetate 2) to yield 33 mg (20%) of **8** as a black solid.

¹H-NMR (DMSO/CF₃COOD, 300 MHz) δ = 8.53 (d, J = 8.15 Hz, 2H), 7.73 (d, J = 8.15 Hz, 2H), 7.71-7.62 (m, 2H), 6.96-6.93 (d, J = 8.64 Hz, 2H), 3.97 (m, 4H).

¹³C-NMR (DMSO/CF₃COOD, 75 MHz) δ = 148.07, 145.61, 144.64, 144.58, 144.12, 144.11, 144.02, 143.74, 143.27, 142.43, 142.33, 141.56, 141.47, 140.07, 136.95, 132.33, 123.54, 123.04, 117.81, 112.08, 106.35, 78.66, 56.32.

FTIR (KBr, cm⁻¹) ν = 3456, 3373, 3025, 2922, 2850, 1734, 1618, 1514, 1283, 1172, 526.
MS (ESI) 916 (M⁺).

Fullerene-perylenebisimide derivative 10.

A mixture of N-(10-nonadecyl)-3,4,9,10-perylenetetracarboxylic acid 3,4-anhydride-9,10-imide (**9**, 197 mg, 0.3 mmol), **3** (90 mg, 0.1 mmol) and zinc acetate (38 mg, 0.21 mmol) in 40 ml of *o*-DCB and 10 ml of dry pyridine is refluxed under argon atmosphere for 90 h. After cooling to room temperature, the solvent is evaporated under reduced pressure and the residue is purified by repetitive column chromatography (silica gel, dichloromethane; and hexane 1/ dichloromethane 1) to yield **10** as a red powder (100 mg, 65%).

¹H-NMR (CDCl₃, 500 MHz) δ= 8.72 (d, *J*= 8.02 Hz, 2H), 8.70-8.60 (m, 6H), 8.36 (d, *J*= 8.36 Hz, 2H), 8.18 (d, *J*= 8.36 Hz, 2H), 7.55-7.44 (m, 3H), 7.23-7.19 (m, 2H), 5.21 (m, 1H), 2.27 (m, 4H), 1.89 (m, 4H), 1.58-1.23 (m, 24H), 0.86 (m, 6H).

¹³C-NMR (CDCl₃, 125 MHz) δ= 163.87, 148.52, 148.48, 145.73, 145.71, 145.58, 145.57, 145.49, 145.15, 145.13, 145.12, 145.11, 145.05, 145.04, 144.68, 144.67, 14.65, 144.64, 144.26, 144.25, 144.24, 144.22, 143.39, 143.38, 143.36, 143.36, 143.35, 143.33, 142.88, 142.64, 142.57, 142.56, 142.52, 141.31, 141.26, 139.85, 138.96, 138.77, 138.59, 138.59, 135.63, 135.62, 135.06, 134.56, 134.56, 134.55, 134.54, 132.99, 132.24, 132.21, 132.20, 131.62, 130.95, 130.21, 130.01, 129.92, 129.49, 129.29, 128.78, 128.11, 127.04, 126.88, 126.78, 123.76, 123.74, 123.56, 123.52, 123.50, 123.43, 115.00, 79.29, 58.11, 55.27, 55.18, 53.81, 43.23, 32.76, 32.34, 30.10, 29.91, 29.90, 29.89, 29.84, 29.82, 29.68, 27.37, 27.36, 23.06, 23.03, 23.02, 14.42, 14.40.

FTIR (KBr, cm⁻¹) ν= 2920, 2850, 1697, 1655, 1593, 1580, 1340, 1251, 810, 746, 526.

MS (ESI) 1541 (M⁺+H).

Fullerene-perylenebisimide derivative 11.

A mixture of N-(10-nonadecyl)-3,4,9,10-perylenetetracarboxylic acid 3,4-anhydride-9,10-imide (**9**, 216 mg, 0.33 mmol), **8** (100 mg, 0.11 mmol) and zinc acetate (40 mg, 0.22 mmol) in 70 ml of *o*-DCB and 10 ml of dry pyridine is refluxed under argon atmosphere for 90 h. After cooling to room temperature, the solvent is evaporated under reduced pressure and the residue is purified by repetitive column chromatography (silica gel, dichloromethane 8/ethyl acetate 2; dichloromethane 1/ethyl acetate 1; and dichloromethane 15/ acetone 0.15) to yield **11** as a red powder (131 mg, 60%).

¹H-NMR (CDCl₃, 500 MHz) δ= 8.67-8.64 (m, 10H), 8.47-8.40 (m, 10H), 7.67 (d, *J*= 8.18 Hz, 4H), 5.19 (m, 2H), 2.22 (m, 4H), 1.91 (m, 4H), 1.58 (bs, 12H), 1.33-1.22 (m, 44H), 0.86 (m, 12H).

¹³C-NMR (CDCl₃, 125 MHz) δ= 163.55, 148.33, 145.74, 145.47, 145.44, 145.09, 145.04, 144.94, 144.56, 144.13, 143.28, 143.18, 142.82, 142.38, 141.31, 141.18, 139.23, 138.81, 135.15, 134.16, 132.47, 131.89, 131.26, 129.72, 126.59, 126.42, 124.52, 123.79, 123.51, 123.30, 79.21, 57.61, 55.33, 32.78, 32.30, 30.00, 29.71, 27.51, 23.07, 15.68, 14.51.

FTIR (KBr, cm⁻¹) ν= 2920, 2850, 1697, 1654, 1558, 1541, 1340, 1252, 526.

MS (MALDI-TOF, dithranol) 2195 (M⁺+H).

Estimation of ΔG value for electron transfer. The value was determined by means of Weller's equation:

$$\Delta G_{cs} = e(E_{ox}(D) - E_{red}(A)) - E_{00} - \frac{e^2}{4\pi\epsilon_o\epsilon_s R_{cc}} - \frac{e^2}{8\pi\epsilon_0} \left(\frac{1}{r^+} + \frac{1}{r^-} \right) \left(\frac{1}{\epsilon_{ref}} - \frac{1}{\epsilon_s} \right) = -0.33 \text{ eV}$$

The following parameters were used in the calculations:

$$E_{\text{ox}} = 1.49 \text{ V}$$

$$E_{\text{red}} = -0.62 \text{ V}$$

$$E_{00} = 2.33 \text{ eV}$$

$$\epsilon_{\text{ref}} = 15.44$$

$$\epsilon_{\text{s}} = 9.1$$

$r^+ = 4.7 \text{ \AA}$ (The radius of the perylenebisimide cation was estimated from the density of N,N'-dimethylperylene-3,4:9,10-tetracarboxylic bisimide determined from the X-ray crystallographic data).¹

$$r^- = 4.4 \text{ \AA}$$

$R_{\text{cc}} = 14.2 \text{ \AA}$ (Determined from geometry of **10** and **11** optimised at the Molecular Mechanics level).

¹ Hádícke, E.; Graser, F. *Acta Cryst. C* **1986**, *42*, 189.