Supplementary Information

Powering reductive charge shift reactions - linking fullerenes of different electron acceptor strength to secure an energy gradient

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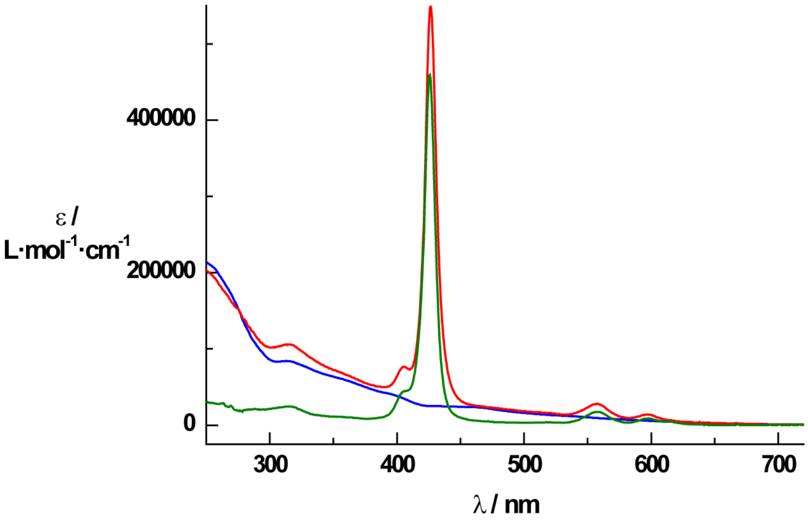


Figure S1. UV-vis spectra of compounds **1** (red), **2** (blue) and **3** (green) recorded in THF at $1 \cdot 10^{-6}$M.

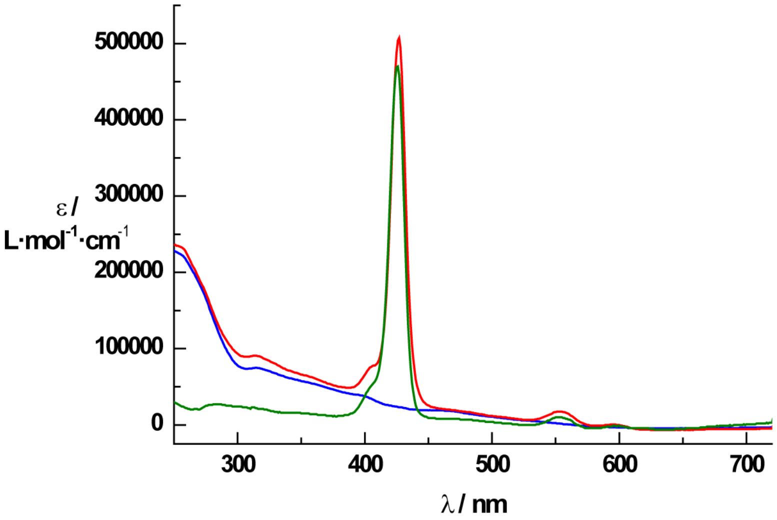


Figure S2. UV-vis spectra of compounds **1** (red), **2** (blue) and **3** (green) recorded in $CHCl_3$ at $1 \cdot 10^{-6}$M.

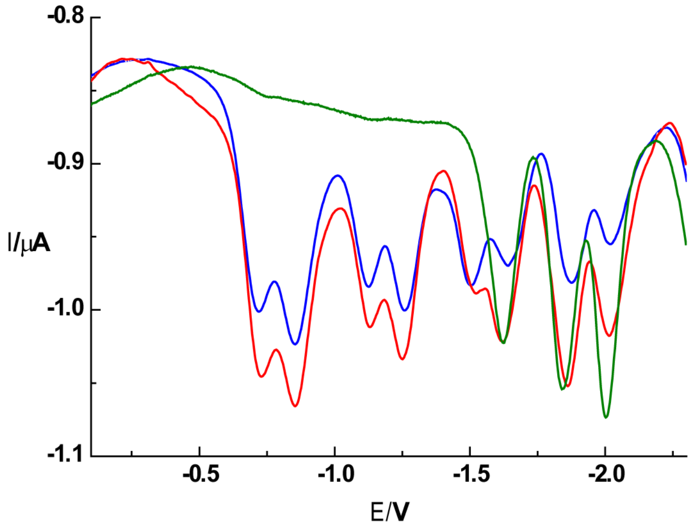
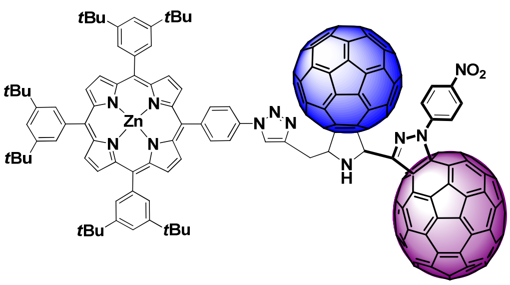


Figure S3. OSWV voltammograms of **1** (red), **2** (blue) and **3** (green). V vs Ag/AgNO$_3$; GCE as the working electrode; 0.1 M TBAP; *o*-DCB/MeCN (4:1); scan rate 100 mV/s.

Compound 1



Zn-azidoporphyrin[1] **3** (63 mg, 0.06 mmol, 1.5 equiv.) and **2** (72 mg, 0.04 mmol, 1 equiv.) were dissolved in $CHCl_3$, then copper (II) sulfate pentahydrate (0.7 mg, 0.004 mmol, 0.1 equiv.), sodium ascorbate (1.6 mg, 0.008 mmol, 0.2 equiv.) and copper (0) (0.3 mg, 0.004 mmol, 0.1 equiv.) were added in distilled H_2O. The mixture was stirred at room temperature during 48 h, under argon atmosphere. The solution was washed with water. Then the solvent was evaporated, and the solid was purified by column chromatography on silica gel (eluent: $CHCl_3$) to give **1** as a purple solid mixture of six possible isomers (46 mg, 40 %). UV-Vis ($CHCl_3$): λ_{max}= 595 nm (ε= 666 $L\cdot mol^{-1}\cdot cm^{-1}$), λ_{max}= 552 nm (ε= 17300 $L\cdot mol^{-1}\cdot cm^{-1}$), λ_{max}= 465 nm (ε= 20000 $L\cdot mol^{-1}\cdot cm^{-1}$) λ_{max}= 427 nm (ε= 507300 $L\cdot mol^{-1}\cdot cm^{-1}$), λ_{max}= 360 nm (ε= 61300 $L\cdot mol^{-1}\cdot cm^{-1}$) λ_{max}= 315 nm (ε= 90600 $L\cdot mol^{-1}\cdot cm^{-1}$), λ_{max}= 253 nm (ε= 234600 $L\cdot mol^{-1}\cdot cm^{-1}$). FT-IR (KBr): 2955, 2923, 2860, 1736, 1592, 1330, 834 y 530 cm^{-1}. MS (MALDI+): m/z calculated for $C_{210}H_{85}N_{11}O_2Zn$ 2858.6 [M], 2137.6 [M-C_{60}], found 2859.7 [M+1], 2138.6 [M+1-C_{60}].

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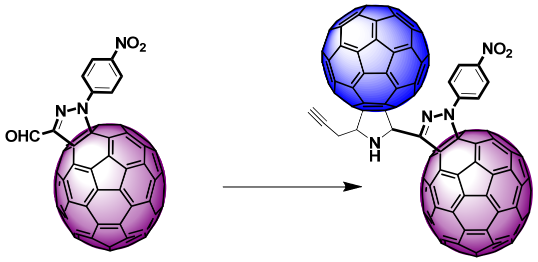
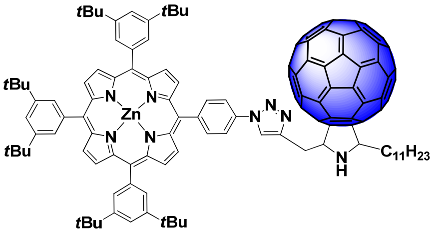
[1] a) Fazio, M. A.; Lee, O. P.; Schuster, D. I. *Org. Lett*. **2008**, *10*, 4979; b) Blanco, M.J.; Chambron, J-C.; Heitz, V.; Sauvage, J-P. *Org. Lett*. **2000**, *2*, 3051.

Compound 2



To a solution of C_{60} (500 mg, 0.69 mmol, 5 equiv.) in chlorobenzene, *DL*-propargylglycine (15.7 mg, 0.14 mmol, 1 equiv.) and compound **4**[2] were added (143.2 mg, 0.14 mmol, 1 equiv.). The solution was refluxed for 18 h. Then the solvent was evaporated, and the solid was purified by column chromatography on silica gel (eluent: CS_2, then CS_2:Toluene 8:2) to afford a brown solid **2** as mixture of six possible isomers (140 mg, 57 %). UV-Vis ($CHCl_3$): λ_{max}= 398 nm (ε= 37500 L·mol^{-1}·cm^{-1}), λ_{max}= 315 nm (ε= 75000 L·mol^{-1}·cm^{-1}), λ_{max}= 253 nm(ε= 226500 L·mol^{-1}·cm^{-1}). FT-IR (KBr): 3289, 2920, 2852, 1737, 1586, 1316, 839 y 527 cm^{-1}. MS (MALDI -): m/z calculated for $C_{142}H_{10}N_4O_2$: 1803.084 [M], found 1803.007 [M].

Compound 5



Zn-azidoporphyrin **3** (49 mg, 0.04 mmol, 1.5 equiv.) and **6** (30 mg, 0.03 mmol, 1 equiv.) were dissolved in $CHCl_3$, then copper (II) sulfate pentahydrate (0.5 mg, 0.003 mmol, 0.1 equiv.), sodium ascorbate (1.2 mg, 0.006 mmol, 0.2 equiv.), copper (0) (0.2 mg, 0.003 mmol, 0.1 equiv.) were added in distilled H_2O. The mixture was stirred during 7 h at room temperature under argon atmosphere. The solution was washed with water. Then the solvent was evaporated, and the solid was purified by column chromatography on silica gel (eluent: $CHCl_3$) to give **5** as a purple solid mixture of two possible isomers (50 mg, 81 %). UV-Vis ($CHCl_3$): λ_{max}= 552 nm (ε= 10000 L·mol^{-1}·cm^{-}

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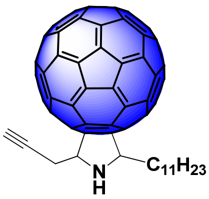
[2] a) Delgado, J. L.; Cardinali, F.; Espíldora, E.; Torres, M. R.; Langa, F.; N. Martín *Org. Lett.* **2008**, *10*, 3705; b) Delgado, J. L.; Oswald, F.; Cardinali, F.; Langa, F.; N. Martín, *J. Org. Chem.* **2008**, *73*, 3184.c) Delgado, J. L.; Espíldora, E.; Liedtke, M.; Sperlich, A.; Rauh, D.; Baumann, A.; Deibel, C.; Dyakonov, V.; Martín, N. *Chem.– Eur. J.*, **2009**, *15*, 13474.

^{1}), λ_{max}= 426 nm (ε= 432000 L·mol^{-1}·cm^{-1}), λ_{max}= 310 nm (ε= 47000 L·mol^{-1}·cm^{-1}), λ_{max}= 258 nm (ε= 112000 L·mol^{-1}·cm^{-1}). FT-IR (KBr): 2957, 2925, 2857, 1591 y 527 cm^{-1}. MS (MALDI +): m/z calculated for $C_{144}H_{104}N_8Zn$ 2009.771 [M], 1288.768 [M-C_{60}], 1260.761 [M-C_{60}-N_2], found 2010.821 [M+1], 1289.777 [M+1-C_{60}], 1261.779 [M+1-C_{60}-N_2].

Compound 6



To a solution of C_{60} (586 mg, 0.81 mmol, 3 equiv.) in chlorobenzene, *DL*-propargylglycine (92 mg, 0.81 mmol, 3 equiv.) and dodecanal were added (0.06 ml, 0.27 mmol, 1 equiv.). The solution was refluxed for 4 h. Then the solvent was evaporated, and the solid was purified by column chromatography on silica gel (eluent: CS_2, then CS_2:Toluene 8:2). to afford a brown solid **6** as mixture of two possible isomers (210 mg, 80 %). ^{1}H-RMN ($CDCl_3/CS_2$, 300 MHz) δ 5.15-5.10, 4.92-4.85, 4.73-4.68, 3.53-3.14, 2.69-2.43, 2.35-2.24, 2.04-1.79, 1.57-1.28, 0.90-0.85 ppm. ^{13}C-RMN ($CDCl_3/CS_2$, 75 MHz) δ 156.0, 154.8, 154.5, 152.4, 147.5, 147.5, 147.0, 147.0, 146.9, 146.8, 146.7, 146.7, 146.6,146.6, 146.6, 146.5, 146.5, 146.4, 146.4, 146.3, 146.3, 146.1, 146.0, 146.0, 145.9, 145.8, 145.8, 145.7, 147.7, 145.6, 145.6, 144.9, 144.9, 144.8, 144.7, 143.6, 143.6, 143.5, 143.1, 143.0, 143.0, 142.8, 142.8, 142.6, 142.6, 142.5, 142.3, 142.3, 142.2, 142.2, 140.6, 140.5, 140.2, 140.1, 137.4, 136.8, 136.0, 135.8, 81.6, 72.5, 72.5, 70.5, 70.1, 68.8, 34.9, 32.3, 30.4, 30.1, 30.0, 29.7, 28.9, 28.5, 24.8, 23.1, 22.9, 14.5 ppm. UV-Vis ($CHCl_3$): λ_{max}= 312 nm (ε= 31700 L·mol^{-1}·cm^{-1}), λ_{max}= 257 nm (ε= 102000 L·mol^{-1}·cm^{-1}). FT-IR (KBr): 3301, 2920, 2848 y 527 cm^{-1}. MS (MALDI +): m/z calculated for $C_{76}H_{29}N$ 955.230 [M], found 956.189 [M+1].

NMR

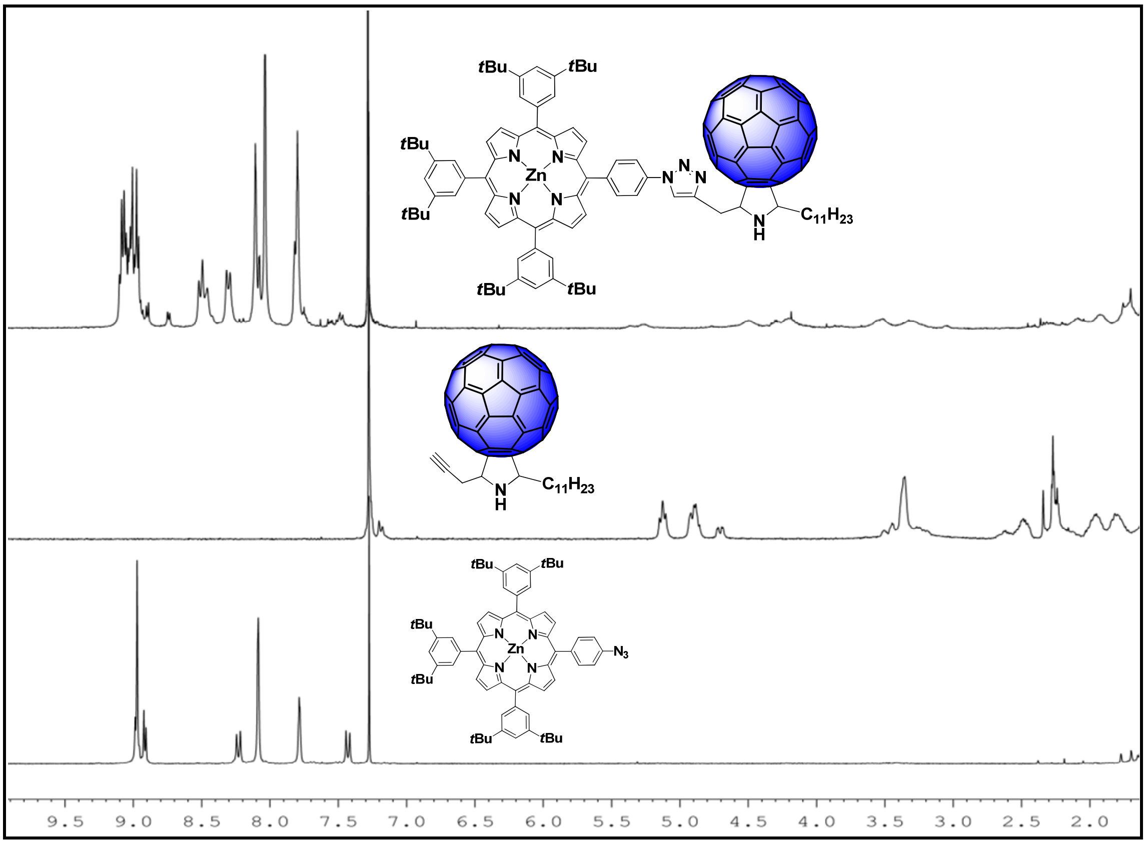


Figure S4: ^{1}H-NMR (CDCl$_3$/CS$_2$, 300 MHz) of **3**, **5** and **6**.

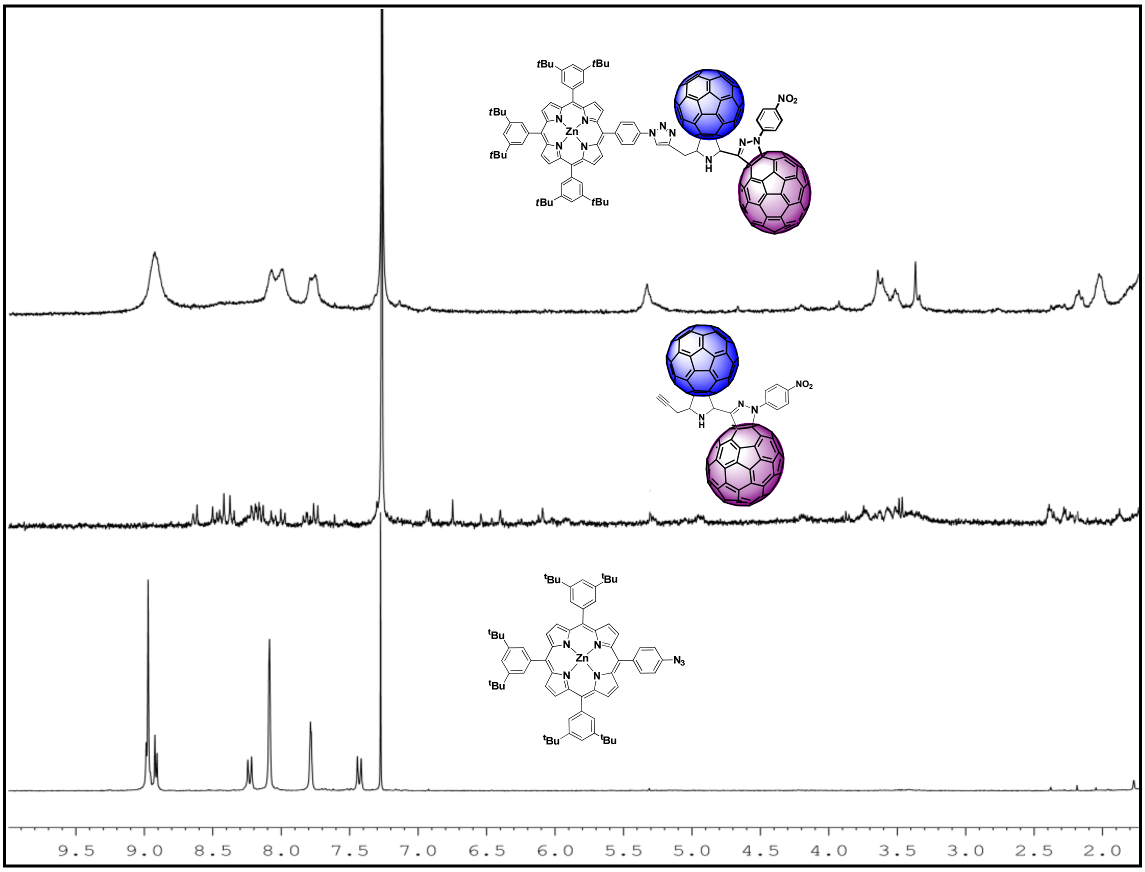


Figure S5: ^{1}H-NMR ($CDCl_3/CS_2$, 300 MHz) of **1**, **2** and **3**.

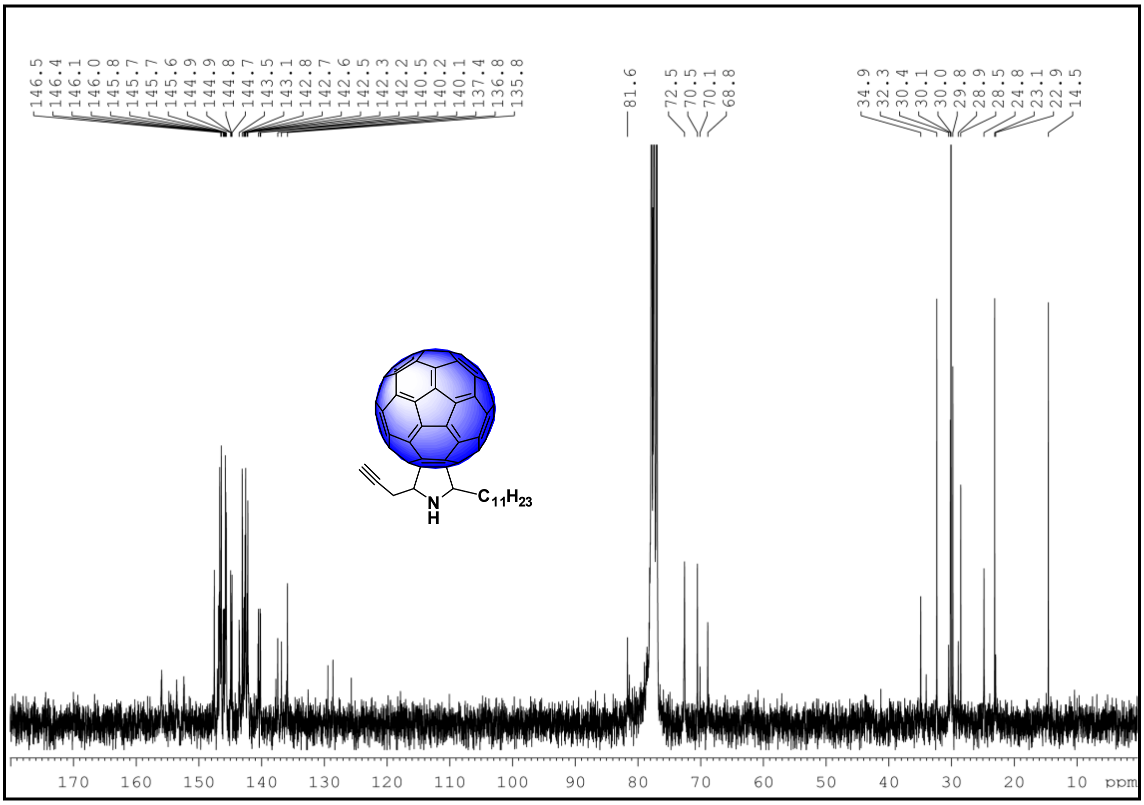


Figure S6: ^{13}C-NMR ($CDCl_3/CS_2$, 75 MHz) of **6**.

HPLC

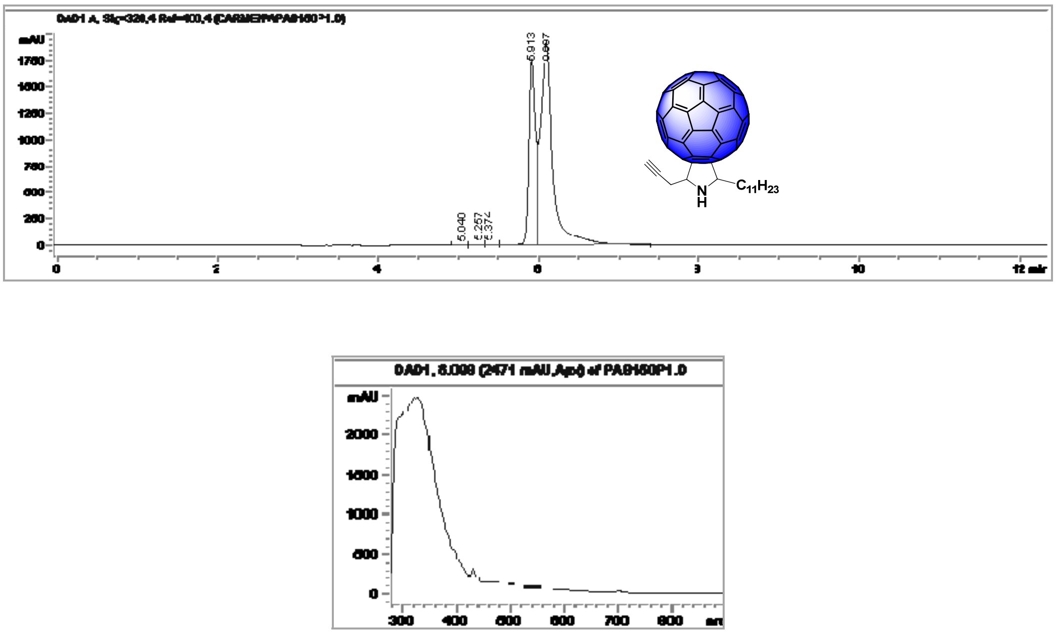


Figure S7. HPLC of compound **6**, peaks at 5.8-6.9 min (two possible isomers of **6**) Toluene 0.7 ml/min (top). UV-Vis of the peaks at 5.8-6.9 min (bottom).

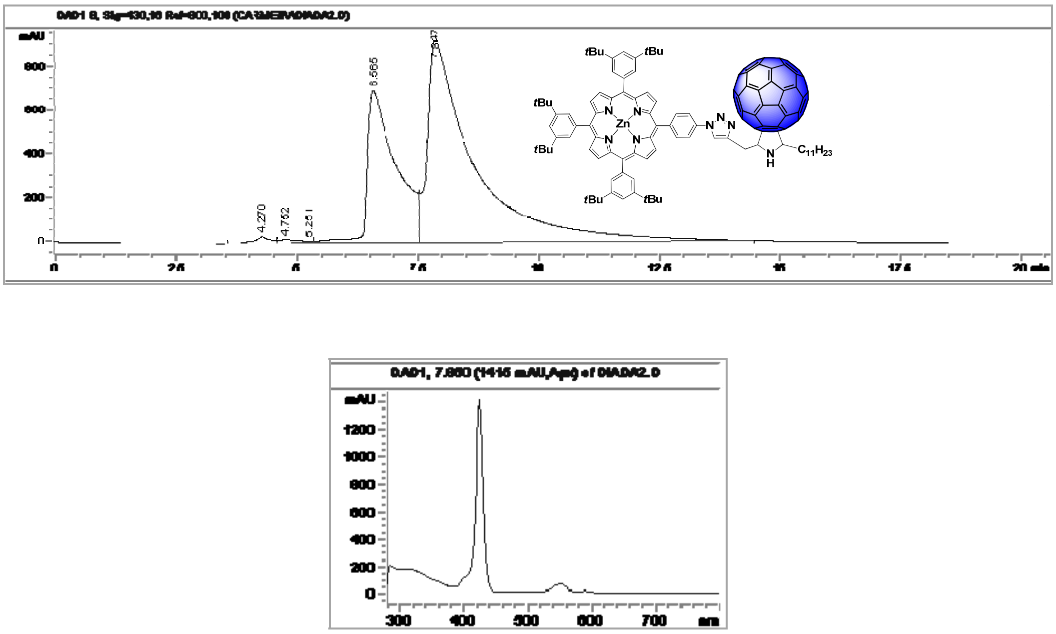


Figure S8. HPLC of compound **5**, peaks at 6.2-12.5 min (two possible isomers of **5**) Toluene 0.7 ml/min (top). UV-Vis of the peaks at 6.2-12.5 min (bottom).

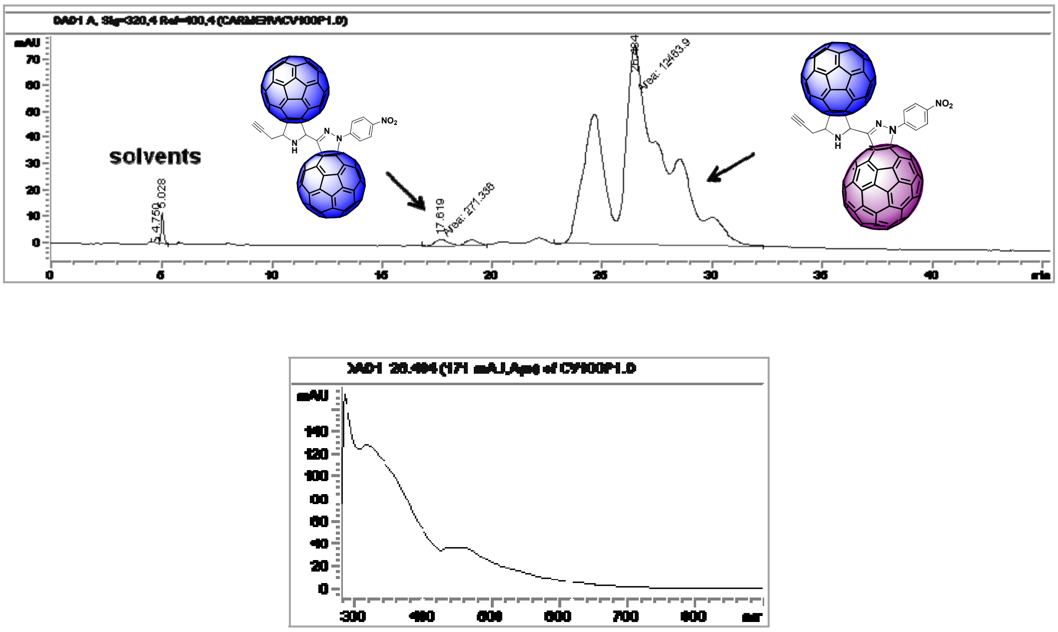


Figure S9. HPLC of compound **2**, peaks at 23.2-31.2 min (six possible isomers of **2**), peaks at 17.1-19.8 min (fullerene C_{60} dimers formed due to the C_{60} impurity on the C_{70} batch 97%). Toluene/Acetonitrile (99:1), 0.7 ml/min (top). UV-Vis of the peaks at 23.2-31.2 min (bottom).

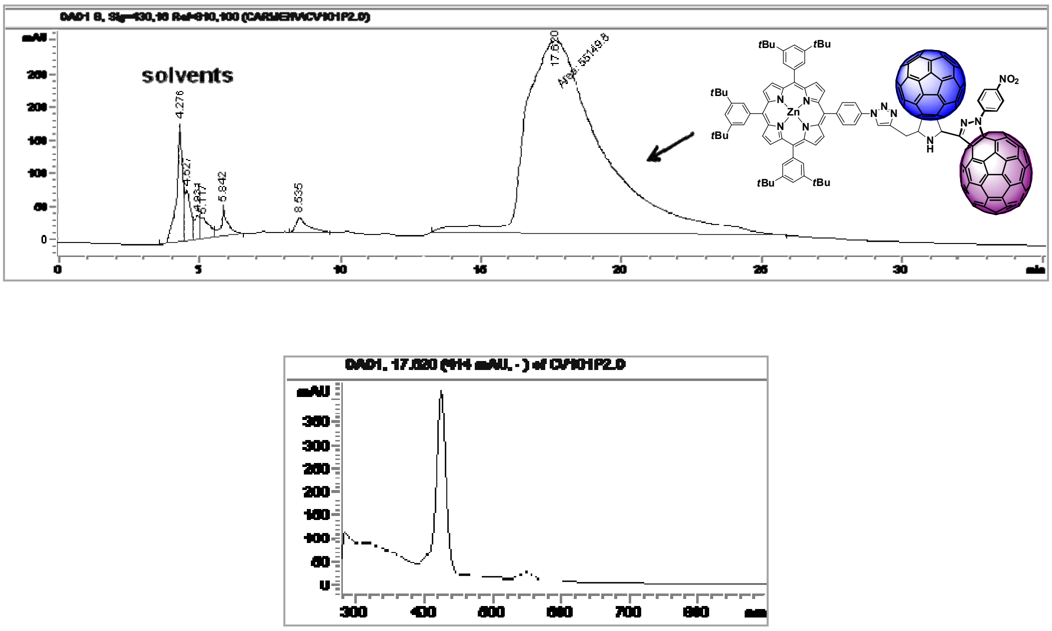


Figure S10. HPLC of compound **1**, peaks at 14.2-25.2 min (six possible isomers of **1**),. Toluene/Acetonitrile (99:1), 0.7 ml/min (top). UV-Vis of the peak at 14.2-25.2 min (bottom).

MASS SPECTROMMETRY

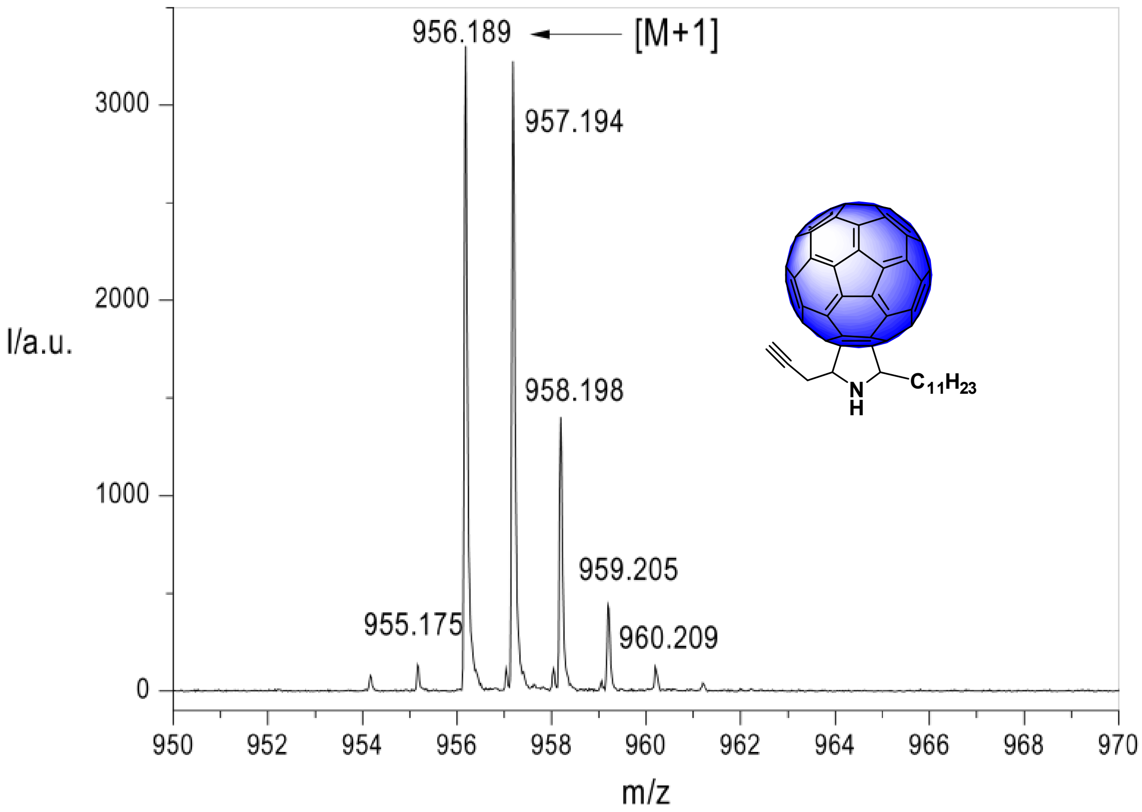


Figure S11. Mass spectrum of **6**.

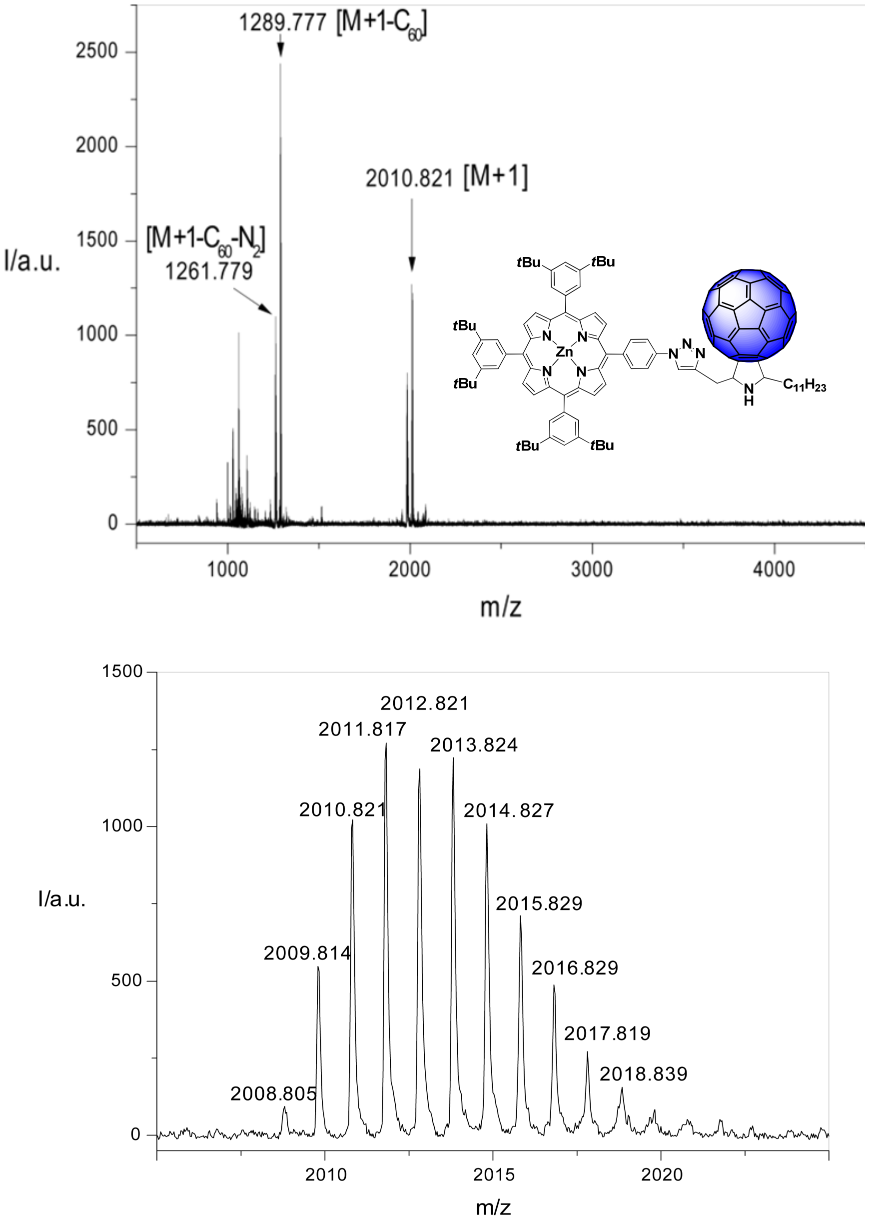


Figure S12. Mass spectra of **5**.

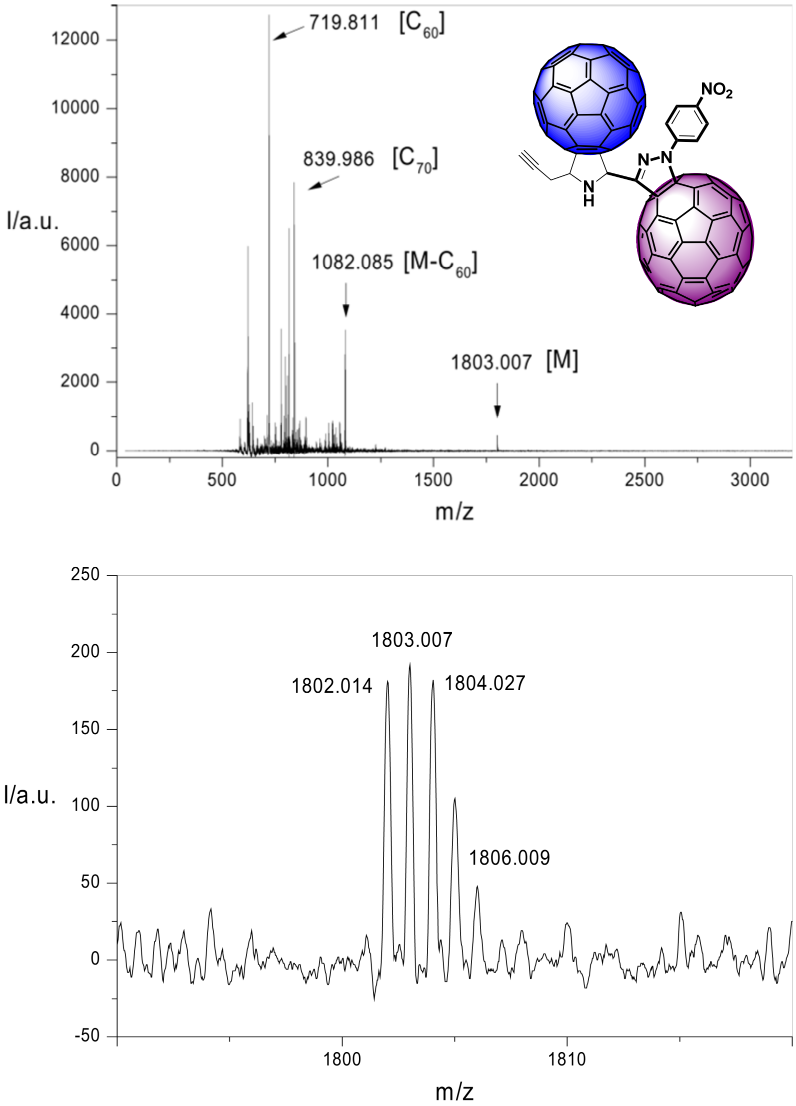


Figure S13. Mass spectra of **2**.

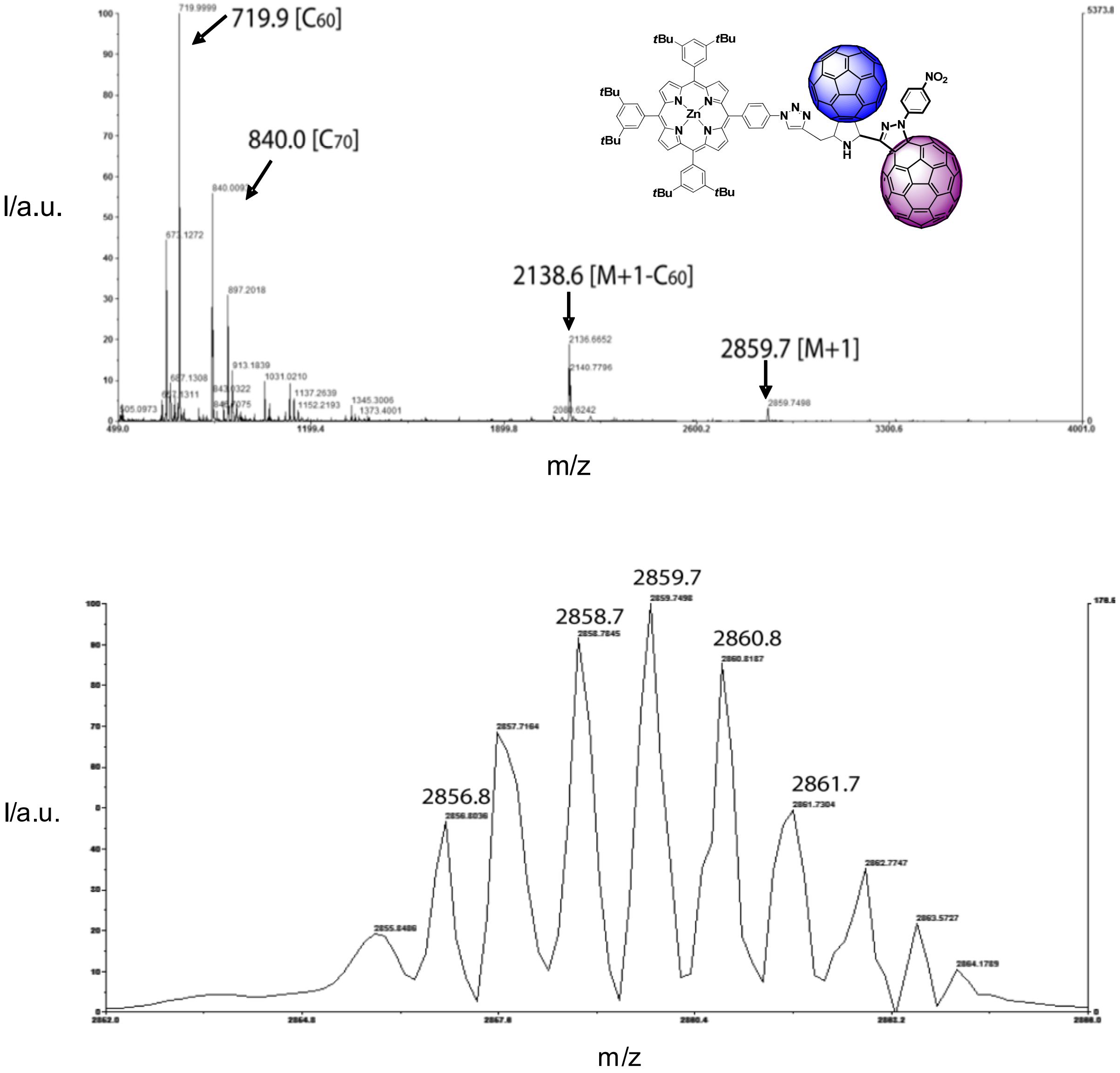


Figure S14. Mass spectra of **1**.

ELECTROCHEMISTRY

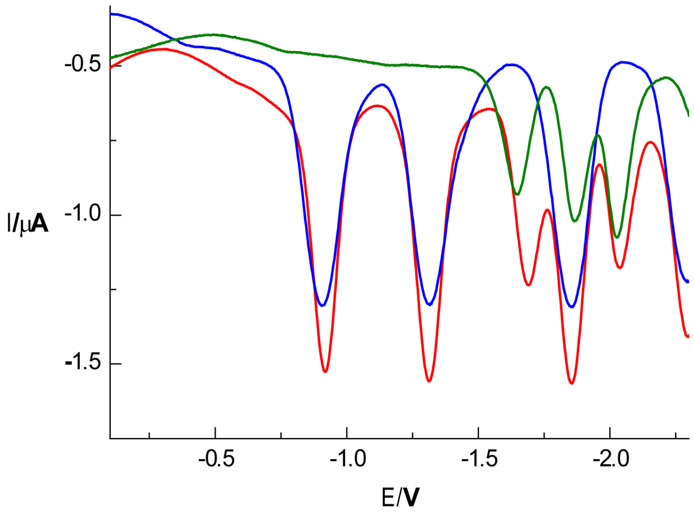


Figure S15. OSWV voltammograms of **3** (green), **5** (red) and **6** (blue). V vs Ag/$AgNO_3$; GCE as the working electrode; 0.1 M TBAP; *o*-DCB/MeCN (4:1); scan rate 100 mV/s.

Comp.	E^{1}*red*		E^{2}*red*		E^{3}*red*		E^{4}*red*	E^{5}*red*	E^{6}*red*		E^{7}*red*
1	-0.72	-0.85	-1.13	-1.25	-1.52	-1.62[a]	-	-	-1.86[b]	-2.01[c]	-
2	-0.72	-0.85	-1.13	-1.26	-1.50	-1.64	-	-	-1.87	-2.02	-
3	-	-	-	-	-	-	-1.62	-1.84	-	-	-2.00
5	-	-0.90	-	-1.31	-	-	-1.69	-	-	-1.86[d]	-2.03
6	-	-0.90	-	-1.31	-	-	-	-	-	-1.85	-

[a] Reduction wave of the azide unit superimposed to the third reduction wave of pirrolidino fragment.
[b] Reduction wave of the porphyrin unit superimposed to the fourth reduction wave of 2-pyrazolino fragment.
[c] Reduction wave of the porphyrin unit superimposed to the fourth reduction wave of pirrolidino fragment.
[d] Reduction wave of the porphyrin unit superimposed to the third reduction wave of pirrolidino fragment.

Table S1. Redox potentials (reduction) of **1**, **2**, **3**, **5** and **6**. V vs Ag/$AgNO_3$; GCE as the working electrode; 0.1 M TBAP; ODCB/MeCN (4:1); scan rate 100 mV/s.

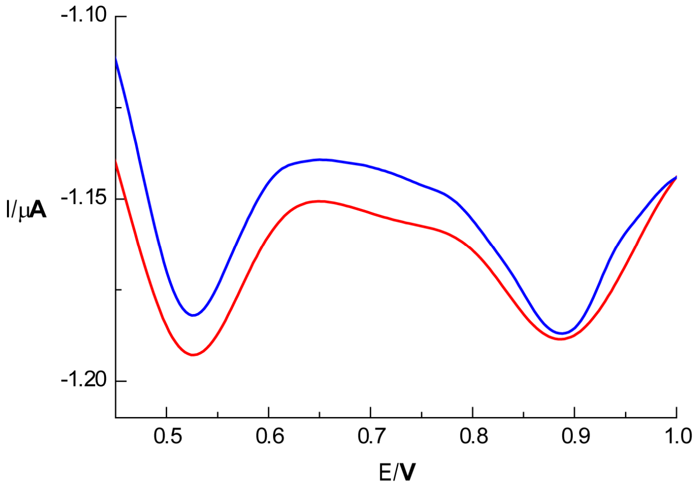


Figure S16. OSWV voltammograms of **1** (red) and **5** (blue). V vs Ag/AgNO$_3$; GCE as the working electrode; 0.1 M TBAP; *o*-DCB/MeCN (4:1); scan rate 100 mV/s.

Compound	E^1ox	E^2ox
1	+0.52	+0.89
2	-	-
3	+0.52	+0.90
5	+0.52	+0.89
6	-	-

Table S2. Redox potentials (oxidation) of **1**, **2**, **3**, **5** and **6**. V vs Ag/AgNO$_3$; GCE as the working electrode; 0.1 M TBAP; ODCB/MeCN (4:1); scan rate 100 mV/s.

UV-VIS

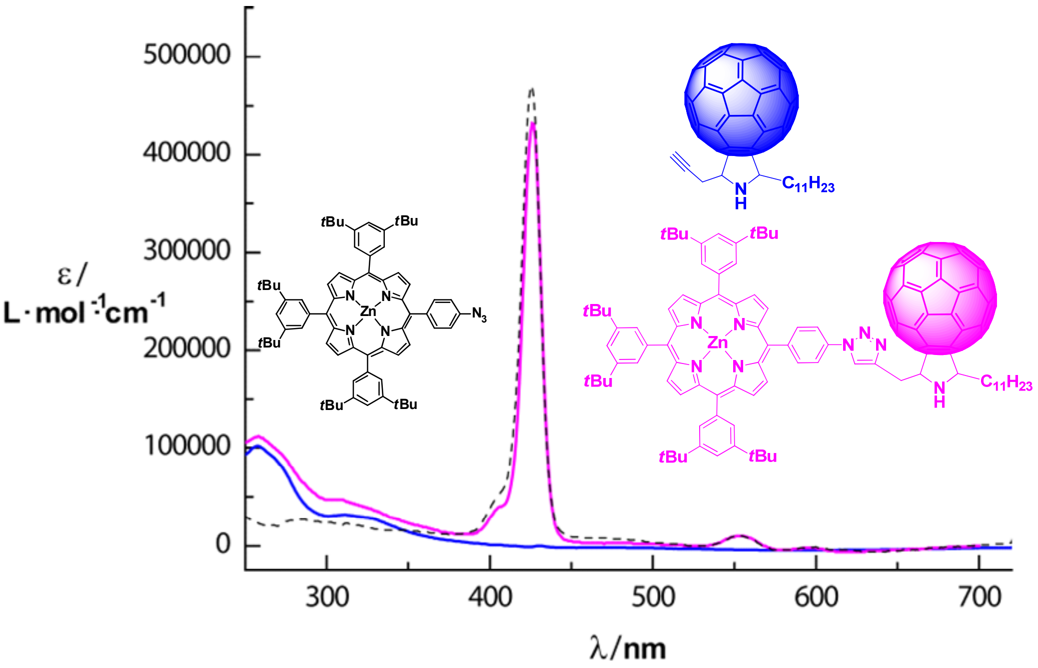
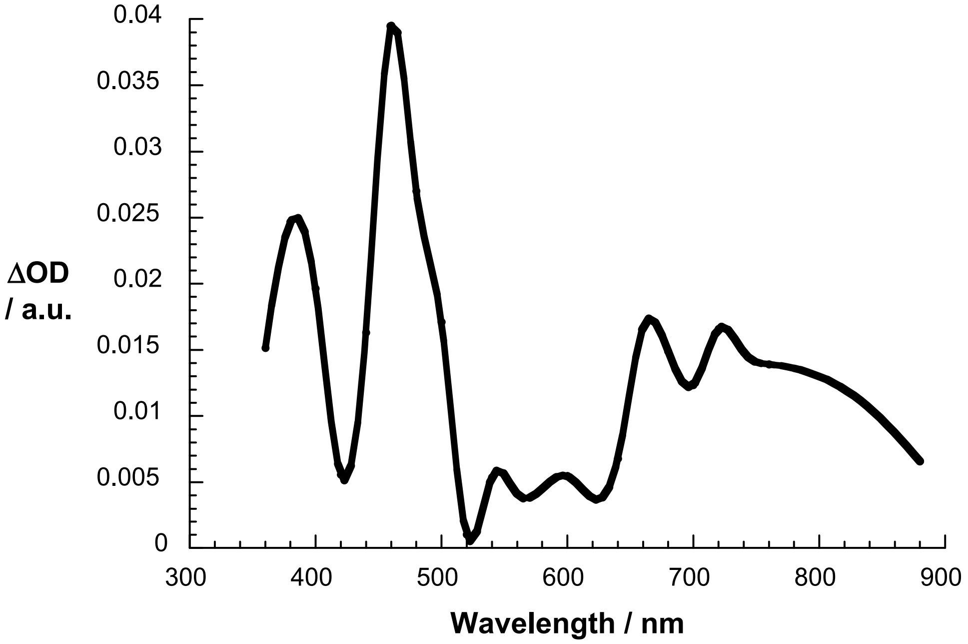


Figure S17. UV-vis spectra of compounds **3** (black), **5** (pink) and **6** (blue) recorded in $CHCl_3$ $1x10^{-6}$M, at room temperature.

Nanosecond Transient Absorption Measurements



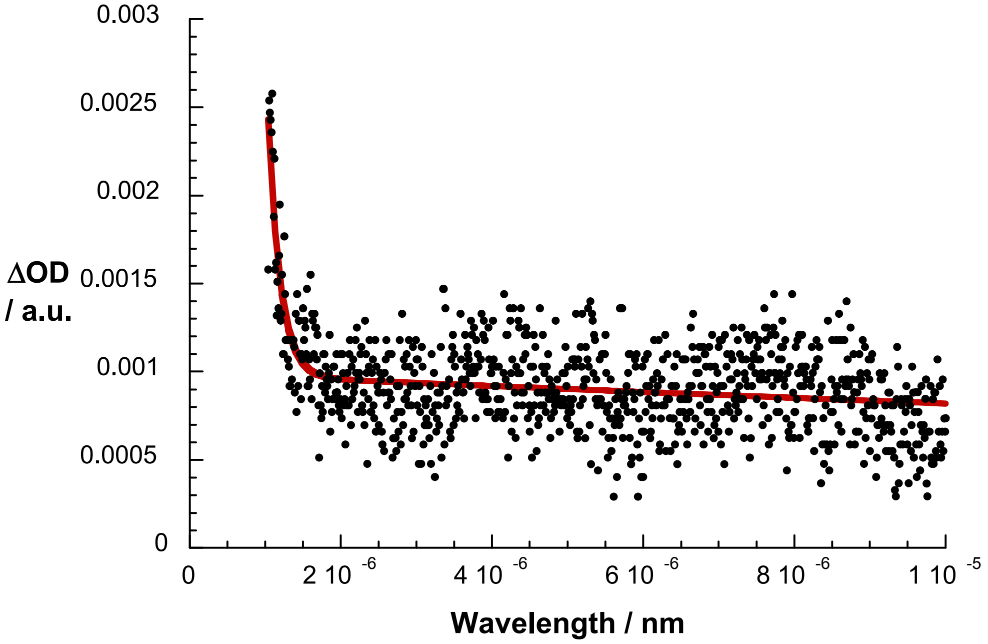


Figure S18. Upper part – differential absorption spectra (visible) obtained upon femtosecond flash photolysis (535 nm) of ZnP-C_{60}-C_{70} in THF with a time delay of 20 ns at room temperature. Lower part – time-absorption profile of the spectrum shown in the upper part at 380 nm monitoring the charge recombination.