Supporting Information

Click chemistry for the efficient preparation of functionalized [60]fullerene hexakis-adducts

Julien Iehl, Rossimiriam Pereira de Freitas, Béatrice Delavaux-Nicot,

and Jean-François Nierengarten

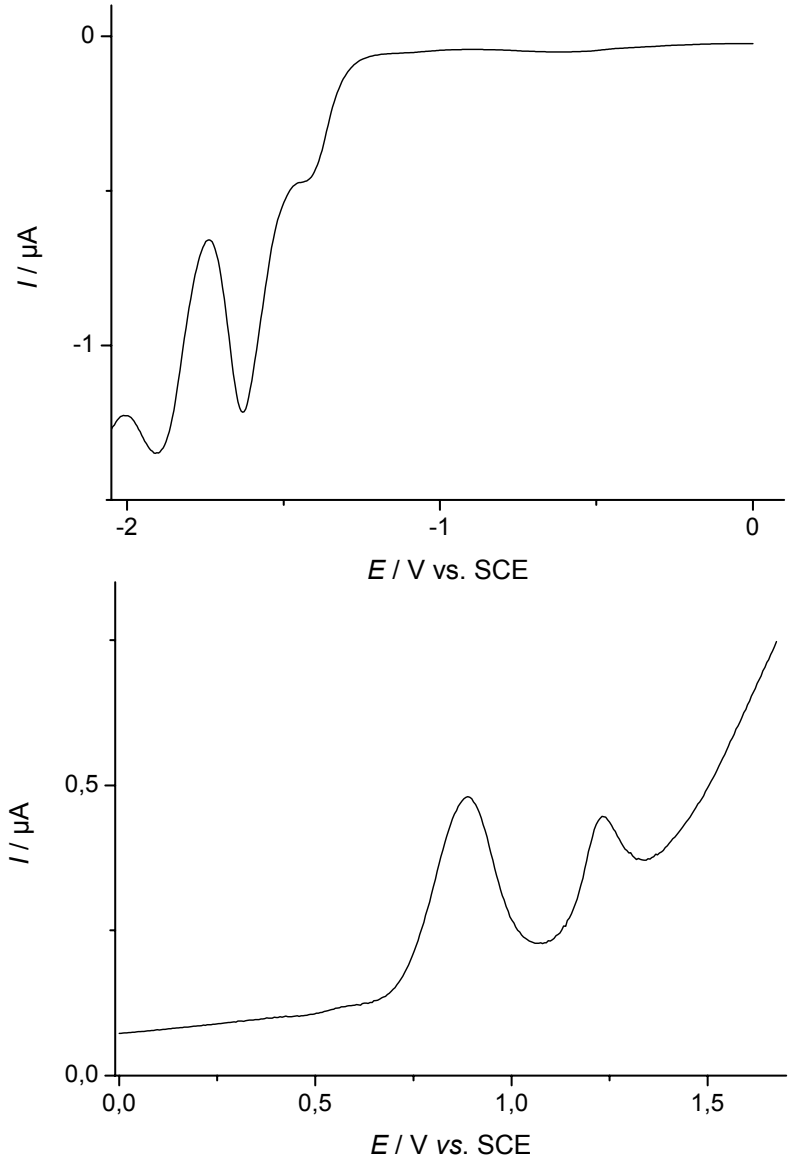

Figure S1. OSVWs of compound **5f** on a Pt electrode in CH_2Cl_2 at room temperature. Top: cathodic scan showing three reductions: the first one is centered on the fullerene core and the two following ones on the peripheral Zn(II)-porphyrin subunits. Bottom: anodic scan showing the two oxidations of the Zn(II)-porphyrins.

Experimental section

General. All reagents were used as purchased from commercial sources without further purification. Compound **4f** was prepared according to previously reported procedures.[1] All reactions were performed in standard glassware. Evaporation was done using water aspirator and drying *in vacuo* at 10^{-2} Torr. Column chromatography: Merck silica gel 60, 40-63 μm (230-400 mesh). TLC: Precoated glass sheets with silica gel 60 F_{254} (Merck), visualization by UV light.

Compound 1. Malonyl dichloride (1.75 mL, 18 mmol) was added to a solution of 3-bromopropan-1-ol (5 g, 35.96 mmol) and pyridine (2.90 mL, 35.96 mmol) in CH_2Cl_2 (250 mL) at 0°C under N_2. After 1 h, the mixture was allowed to warm up to room temperature, then stirred for 18 h, filtered, and evaporated.. Column chromatography (SiO_2, CH_2Cl_2/Hexane 80/20) gave **1** (5.20 g, 83%) as a pale yellow oil. IR (neat): 1729 (C=O); ^{1}H NMR ($CDCl_3$, 300 MHz): 2.19 (q, J = 6 Hz, 4H), 3.39 (s, 2H), 3.45 (t, J = 6 Hz, 4H), 4.29 (t, J = 6 Hz, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz): 29.1, 31.4, 41.3, 63.2, 166.2.

Compound 2. A mixture of **1** (3.757 g, 57.8 mmol) and NaN_3 (3.758 g, 57.81 mmol) in anhydrous DMF (50 mL) was stirred at room temperature for 16 h under N_2. The mixture was diluted with Et_2O, washed with water then brine, dried over $MgSO_4$, and concentrated. Column chromatography (SiO_2, CH_2Cl_2) gave **2** (3.71 g, 95%) as a colourless oil. IR (neat): 2092 (N_3), 1731 (C=O); ^{1}H NMR ($CDCl_3$, 300 MHz): 1.88 (q, J = 6 Hz, 4H), 3.36 (m, 6H), 4.20 (t, J = 6 Hz, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz): 27.9, 41.2, 47.9, 62.3, 166.2; Anal. Calcd for $C_9H_{14}O_4N_6$: C, 40.00 ; H, 5.22 ; N, 31.10. Found: C, 39.84 ; H, 4.92 ; N, 30.59.

Compound 3. CBr_4 (28.92 g, 87.2 mmol), **2** (2.355 g, 8.72 mmol), and DBU (2.61 mL/17.44 mmol) were added successively to a solution of C_{60} (0.628 g, 0.87 mmol) in ODCB (200mL). The mixture was stirred for 72 h and evaporated. Column chromatography (SiO_2, CH_2Cl_2/Hexane, 90/10) gave **3** (1.26 mg, 62%) as an orange glassy product. IR (neat): 2092 (N_3), 1739 (C=O); ^{1}H NMR ($CDCl_3$, 300 MHz): 1.91 (q, J = 6 Hz, 24H), 3.33 (t, J = 6 Hz,

[1] S. Prathapan, T. E. Johnson and J. S. Lindsey, *J. Am. Chem. Soc*. 1993, **115**, 7519.

24H), 4.31 (t, J = 6 Hz, 24H); ^{13}C NMR ($CDCl_3$, 75 MHz): 28.0, 45.2, 47.9, 63.8, 69.0, 141.1, 145.8, 163.5.

General Procedure for the click reactions. $CuSO_4.5H_2O$ (0.1 equiv.) and sodium ascorbate (0.3 equiv.) were added to a mixture of **3** (1 equiv.) and the appropriate terminal alkyne (13 equiv.) in CH_2Cl_2/H_2O (1:1). The resulting mixture was vigorously stirred for 12 h at rt under N_2. The organic layer was diluted with CH_2Cl_2, washed with water, dried over $MgSO_4$ (**5a-e**) or Na_2CO_3 (**5f**) and concentrated. The product was then purified as outlined in the following text.

Compound 5a. This compound was prepared from **3** (218 mg, 0.09 mmol), **4a** (124 mg, 1.22 mmol), $CuSO_4.5H_2O$ (1.48 mg, 0.009 mmol) and sodium ascorbate (5.54 mg, 0.028 mmol) in CH_2Cl_2/H_2O (1:1, 6 mL). Column chromatography (SiO_2, CH_2Cl_2 containing 0.5% of methanol) followed by gel permeation chromatography (Biobeads SX-1, CH_2Cl_2) gave **5a** (259 mg, 78%) as an orange glassy product. IR (neat): 1739 (C=O); ^{1}H NMR ($CDCl_3$, 300 MHz): 2.29 (m, 24H), 4.34 (t, J = 6 Hz, 24H), 4.41 (t, J = 6 Hz, 24H), 7.32 (m, 36H), 7.76 (m, 24H), 7.82 (s, 12H); ^{13}C NMR ($CDCl_3$, 75 MHz,): 29.3, 45.4, 46.8, 63.7, 69.2, 120.1, 125.6, 128.1, 128.6, 130.4, 141.2, 145.8, 147.8, 163.4; MALDI-TOF-MS: 3556 (M^+, calcd. for $C_{210}H_{144}N_{36}O_{24}$: 3555.68).

Compound 5b. This compound was prepared from **3** (380 mg, 0.163 mmol), **4b** (280 mg, 2.12 mmol), $CuSO_4.5H_2O$ (2.6 mg, 0.016 mmol) and sodium ascorbate (9.5 mg, 0.048 mmol) in CH_2Cl_2/H_2O (1:1, 8 mL). Column chromatography (SiO_2, CH_2Cl_2 containing 2% of methanol) followed by gel permeation chromatography (Biobeads SX-1, CH_2Cl_2) gave **5b** (390 mg, 61%) as an orange glassy product. IR (neat): 1741 (C=O); ^{1}H NMR ($CDCl_3$, 300 MHz): 2.27 (m, 24H), 3.76 (s, 36H), 4.36 (m, 48H), 6.86 (d, J = 8 Hz, 24H), 7.66 (d, J = 8 Hz, 24H), 7.72 (s, 12H); ^{13}C NMR ($CDCl_3$, 75 MHz): 29.2, 45.4, 46.7, 55.2, 63.7, 69.1, 114.1, 119.2, 123.1, 126.9, 141.2, 145.8, 147.6, 159.5, 163.3; MALDI-TOF-MS: 3916 (M^+, calcd. for $C_{222}H_{168}N_{36}O_{36}$: 3916.00).

Compound 5c. This compound was prepared from **3** (380 mg, 0.163 mmol), **4c** (505 mg, 2.12 mmol), $CuSO_4.5H_2O$ (2.6 mg, 0.016 mmol) and sodium ascorbate (9.5 mg, 0.048 mmol) in CH_2Cl_2/H_2O (1:1, 8 mL). Column chromatography (SiO_2, CH_2Cl_2 containing 1% of methanol) followed by gel permeation chromatography (Biobeads SX-1, CH_2Cl_2) gave **5c**

(477 mg, 56%) as an orange glassy product. IR (neat): 1744 (C=O); ^{1}H NMR ($CDCl_3$, 300 MHz): 2.41 (m, 24H), 4.39 (t, J = 6 Hz, 24H), 4.55 (t, J = 6 Hz, 24H), 7.76 (s, 12H), 8.09 (s, 12H), 8.18 (m, 24H); ^{13}C NMR ($CDCl_3$, 75 MHz): 29.1, 45.1, 47.2, 63.5, 69.0, 121.1, 121.6, 122.7 (q, J = 270 Hz), 125.6, 132.0 (q, J = 30 Hz), 132.5, 140.9, 145.3, 145.7, 163.2; ^{19}F NMR ($CDCl_3$, 282 MHz): 63.1; MALDI-TOF-MS: 5187 (M^+, calcd. for $C_{234}H_{120}N_{36}O_{24}F_{72}$: 5187.64).

Compound 5d. This compound was prepared from **3** (465 mg, 0.2 mmol), **4d** (473 mg, 2.6 mmol), $CuSO_4.5H_2O$ (3.2 mg, 0.02 mmol) and sodium ascorbate (12 mg, 0.06 mmol) in CH_2Cl_2/H_2O (1:1, 10 mL). Column chromatography (SiO_2, CH_2Cl_2 containing 2% of methanol) followed by gel permeation chromatography (Biobeads SX-1, CH_2Cl_2) gave **5d** (569 mg, 63%) as an orange glassy product. IR (neat): 1741 (C=O); ^{1}H NMR ($CDCl_3$, 300 MHz): 2.23 (m, 24H), 3.82 (s, 36H), 4.33 (m, 48H), 7.00-7.08 (m, 24H), 7.58 (d, J = 5 Hz, 12H), 7.61 (d, J = 5 Hz, 12H), 7.70-7.80 (m, 24H), 8.11 (s, 12H); ^{13}C NMR ($CDCl_3$, 75 MHz): 29.3, 45.6, 46.8, 55.3, 63.9, 69.3, 105.8, 119.2, 120.0, 124.2, 124.3, 125.7, 127.4, 128.9, 129.7, 134.3, 141.4, 145.9, 148.0, 157.9, 163.5. MALDI-TOF-MS: 4539 ($[M + Na]^+$, calcd. for $C_{270}H_{192}N_{36}O_{36}Na$: 4539.70).

Compound 5e. This compound was prepared from **3** (256 mg, 0.109 mmol), **4e** (300 mg, 1.42 mmol), $CuSO_4.5H_2O$ (1.7 mg, 0.011 mmol) and sodium ascorbate (6.5 mg, 0.032 mmol) in CH_2Cl_2/H_2O (1:1, 5 mL). Column chromatography (SiO_2, CH_2Cl_2 containing 2% of methanol) followed by gel permeation chromatography (Biobeads SX-1, CH_2Cl_2) gave **5e** (428 mg, 81%) as an orange glassy product. IR (neat): 1741 (C=O); ^{1}H NMR ($CDCl_3$, 300 MHz): 2.31 (m, 24H), 4.05 (s, 60H), 4.27 (s, 24H), 4.36 (m, 48H), 4.71 (s, 24H), 7.55 (s, 12H); ^{13}C NMR ($CDCl_3$, 75 MHz): 29.2, 45.3, 46.6, 55.3, 63.8, 66.7, 69.1, 69.6, 75.4, 119.3, 141.1, 145.8, 146.8, 163.3. MALDI-TOF-MS: 4850 (M^+, calcd. for $C_{258}H_{192}N_{36}O_{24}Fe_{12}$: 4850.75).

Compound 5f. This compound was prepared from **3** (85 mg, 0.036 mmol), **4f** (393 mg, 0.474 mmol), $CuSO_4.5H_2O$ (0.6 mg, 0.004 mmol) and sodium ascorbate (2 mg, 0.01 mmol) in CH_2Cl_2/H_2O (1:1, 2 mL). Column chromatography (SiO_2, CH_2Cl_2 containing 2% of methanol) followed by gel permeation chromatography (Biobeads SX-1, CH_2Cl_2) gave **5f** (331 mg, 74%) as a purple glassy product. IR (neat): 1744 (C=O); ^{1}H NMR ($CDCl_3$, 300 MHz): 1.76 (s, 144H), 1.82 (s, 72H), 2.26 (m, 24H), 2.49 (m, 72H), 2.59 (s, 36H), 4.25 (m,

24H), 4.40 (m, 24H), 7.15 (m, 72H), 7.91 (s, 12H), 8.17 (m, 48H), 8.68 (m, 96H); ^{13}C NMR ($CDCl_3$, 75 MHz): 21.4, 21.6, 21.7, 29.7, 45.2, 46.6, 63.8, 69.4, 118.6, 118.8, 119.2, 120.2, 123.8, 127.5, 129.2, 130.6, 130.8, 131.1, 131.7, 131.9, 134.8, 137.2, 139.0, 139.1, 139.2, 141.4, 143.0, 146.0, 147.7, 149.6, 149.9, 163.4.