Supplementary material (ESI) for Journal of Materials Chemistry

Supplementary Informations

Redox-active Si(100) surfaces covalently functionalised with [60]fullerene conjugates: new hybrid materials for molecular-based devices.

Fabrizio Cattaruzza,[a] Anna Llanes-Pallas,[a] Andrea G. Marrani,[b] Enrique A. Dalchiele,[b,c] Franco Decker,[b] Robertino Zanoni,[*b] Maurizio Prato,[a] and Davide Bonifazi[*a,d]

N-[2-(N-Boc)aminoethyl]-2-(4-dimethyl aniline)-3,4-fulleropyrrolidine (**3a**) (260 mg, 49%); λ_{max} (CH_2Cl_2)/nm 282 (ε/dm^3 mol^{-1} cm^{-1} 56 405), 309 (37 651), 330 (37 790), 433 (3 591); ν_{max}/cm^{-1} 3435.1, 2971.0, 2922.6, 2784.3, 1709.1, 1499.8, 1462.1, 1427.6, 1364.3, 1244.4, 1166.8, 1121.4, 1106.2, 1002.4, 752.5, 526.4, 477.9 ; δ_H (400 MHz, $CDCl_3$): 7.60 (2 H, d, J = 6.8 Hz), 6.73 (2 H, d, J = 8.4 Hz), 5.11 (2 H, d, J = 9.2 Hz), 5.04 (1 H, s), 4.14 (1 H, d, J = 9.6 Hz), 3.64 (2 H, br), 3.34 (1 H, br), 2.95 (6 H, s) , 2.70 (1 H, br), 1.51 (9 H, s) ; δ_C (50 MHz, $CDCl_3$): 156.59, 156.15, 154.22, 153.97, 150.53, 147.37, 146.99, 146.67, 146.57, 146.36, 146.32, 146.26, 146.20, 146.17, 146.15, 145.97, 145.84, 145.61, 145.48, 145.42, 145.35, 145.34, 145.28, 145.17, 144.76, 144.71, 144.45, 143.21, 143.01, 142.71, 142.62, 142.61, 142.33, 142.21, 142.18, 142.08, 142.06, 142.01, 141.89, 141.73, 141.58, 140.21, 140.16, 139.99, 139.69, 136.76, 135.83, 135.71, 130.43, 123.93, 112.36, 82.42, 79.57, 68.95, 66.82, 52.65, 40.53, 39.31, 28.72; *m/z* (ESI) 1026.2 $[M]^+$, 1048.2 $[M + Na]^+$; $C_{77}H_{27}N_3O_2$ requires 1026.06.

N-[2-(N-Boc)aminoethyl]-2-ferrocenyl-3,4-fulleropyrrolidine (**3b**) (300 mg, 54%); λ_{max} (CH_2Cl_2)/nm 282 (ε/dm^3 mol^{-1} cm^{-1} 60 557), 309 (40122), 331 (42 147), 432 (3 860); ν_{max}/cm^{-1} 3444.6, 2971.7, 2924.2, 1715.7, 1499.4, 1462.6, 1428.7, 1364.6, 1245.5, 1168.6, 1107.0, 1001.7, 755.4, 526.9, 478.3; δ_H (400 MHz, $CDCl_3$): 5.42 (1 H, br), 5.05 (1 H, s), 5.03 (1 H, m), 4.99 (1 H, m), 4.49 (2 H, s), 4.31 (5 H, s), 4.24 (1 H, s), 4.21 (1 H, m), 4.12 (1 H, d,

J = 9.2 Hz), 3.92 (1 H, m), 3.67 (1 H, m), 2.94 (1 H, dt, *J* = 11.6 Hz), 1.57 (9 H, s); δ_C (50 MHz, $CDCl_3$): 154.02, 153.12, 147.21, 146.19, 145.87, 145.46, 145.19, 144.64, 144.35, 143.04, 142.92, 142.55, 142.11, 141.79, 141.59, 140.14, 140.03, 139.36, 138.78, 136.24, 135.78, 86.38, 79.66, 69.49, 68.36, 68.26, 67.56, 67.45, 67.14, 53.68, 29.78, 28.65; *m/z* (ESI) 1091.1 $[M]^+$, 1113.1 $[M + Na]^+$; $C_{79}H_{26}FeN_2O_2$ requires 1090.91.

N-[2-(N-Boc)aminoethyl]-2-(5-(4-phenyl)-10,15,20-tris(3,5-di-tert-butylphenyl)porphyrin)-3,4-fulleropyrrolidine (**3c**) (548 mg, 55%); λ_{max} (CH_2Cl_2)/nm 311 (ε/dm^3 mol^{-1} cm^{-1} 663 967), 424 (5 908 218), 552 (315 253), 591 (129 027); ν_{max}/cm^{-1} 3433.4, 2961.3, 1719.5, 1589.6, 1493.1, 1461.7, 1423.3, 1391.6, 1361.7, 1261.7, 1163.1, 1098.2, 1022.5, 1001.3, 797.1, 716.0, 526.4; δ_H (400 MHz, $CDCl_3$): 8.99 (6 H, br), 8.89 (2 H, br), 8.06 (10 H, br), 7.76 (3 H, s), 5.14 (1 H, br), 4.64 (1 H, d, *J* = 6.8 Hz), 3.89 (1 H, br), 3.69 (1 H, br), 3.56 (2 H, d, *J* = 6.8 Hz), 3.14 (1 H, br), 2.66 (1 H, br), 1.51 (63, br); δ_C (50 MHz, $CDCl_3$): 150.33, 150.16, 149.57, 148.56, 148.47, 148.43, 146.59, 145.42, 145.19, 145.17, 144.49, 144.33, 144.31, 142.19, 141.79, 141.68, 141.46, 141.21, 138.63, 135.73, 134.18, 132.28, 131.44, 130.05, 130.02, 129.99, 129.51, 122.67, 122.54, 120.76, 120.67, 119.81, 95.67, 81.56, 67.99, 52.81, 35.14, 31.86, 29.76, 28.57; *m/z* (ESI) 1942.1 $[M + Na]^+$; $C_{137}H_{92}N_6O_2Zn$ requires 1919.63.

Characterization: ^{1}H-NMR and ESI spectra.

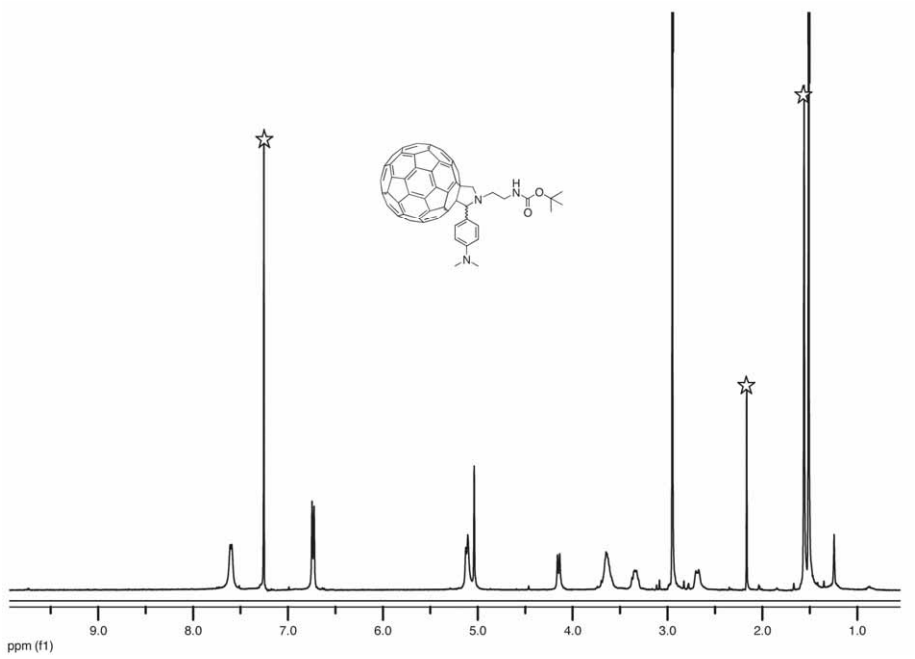

Fig. S1. ^{1}H-NMR spectrum (400 MHz) of **3a**. Residual solvent peaks ($CHCl_3$, acetone and H_2O at 7.26, 2.17 and 1.56 ppm, respectively) are indicated with a star.

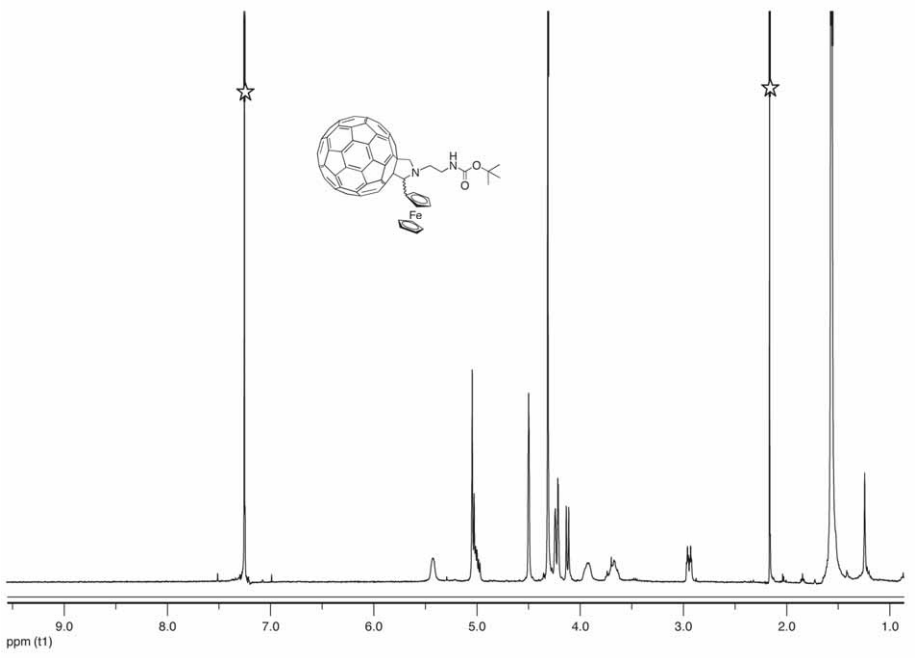

Fig. S2. ^{1}H-NMR spectrum (400 MHz) of **3b.** Residual solvent peaks ($CHCl_3$ and acetone at 7.26 and 2.17 ppm, respectively) are indicated with a star.

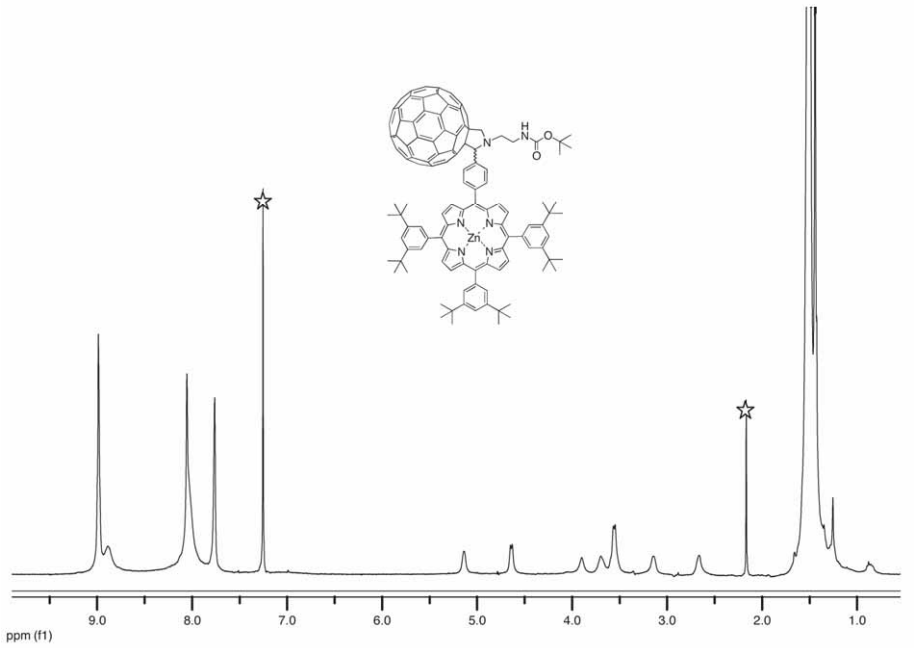

Fig. S3. ^{1}H-NMR spectrum (400 MHz) of **3c**. Residual solvent peaks ($CHCl_3$ and acetone at 7.26 and 2.17 ppm, respectively) are indicated with a star.

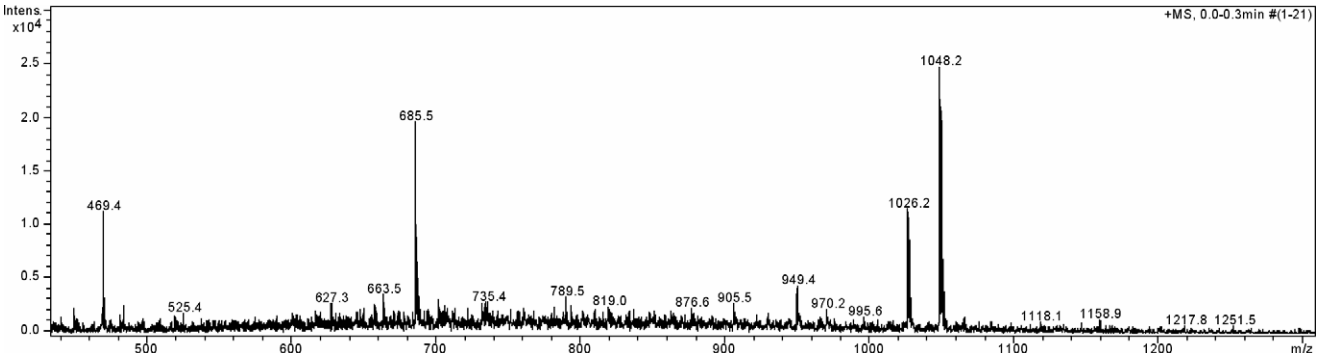

Fig. S4. ESI-MS spectrum of **3a**.

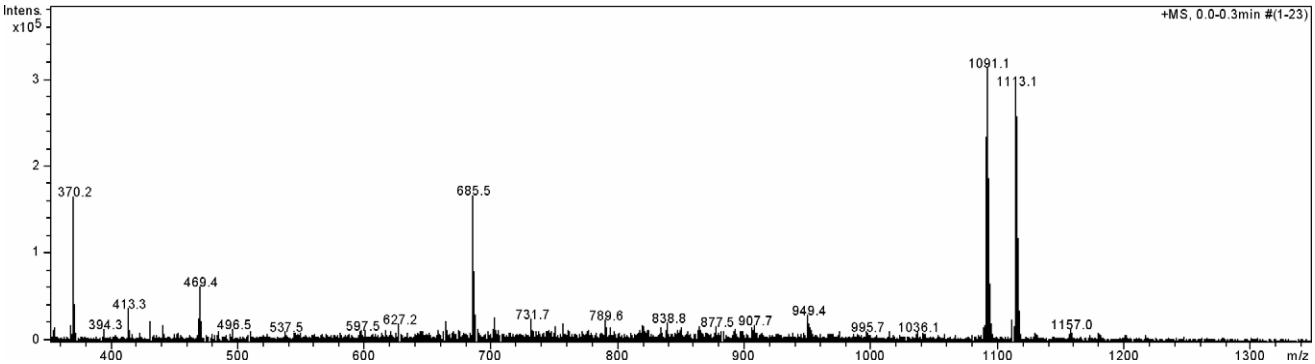

Fig. S5. ESI-MS spectrum of **3b**.

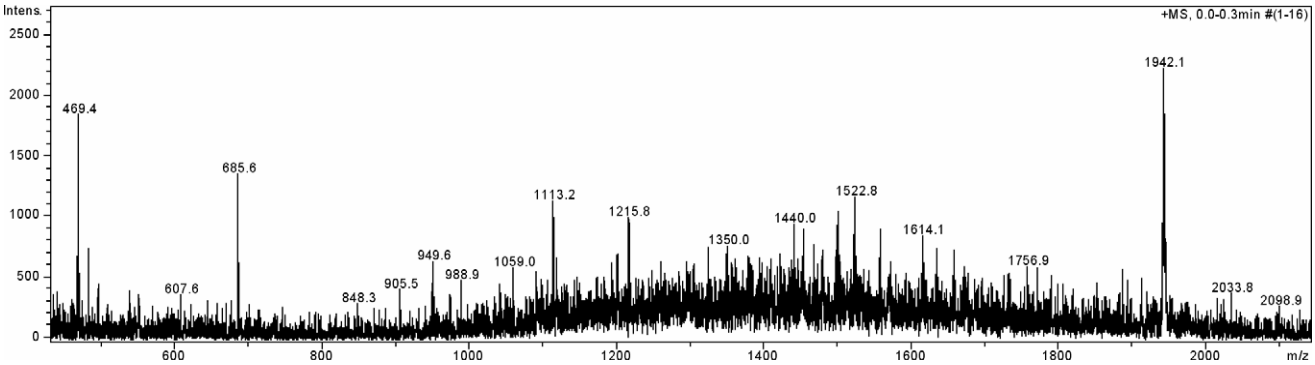

Fig. S6. ESI-MS spectrum of **3c**.

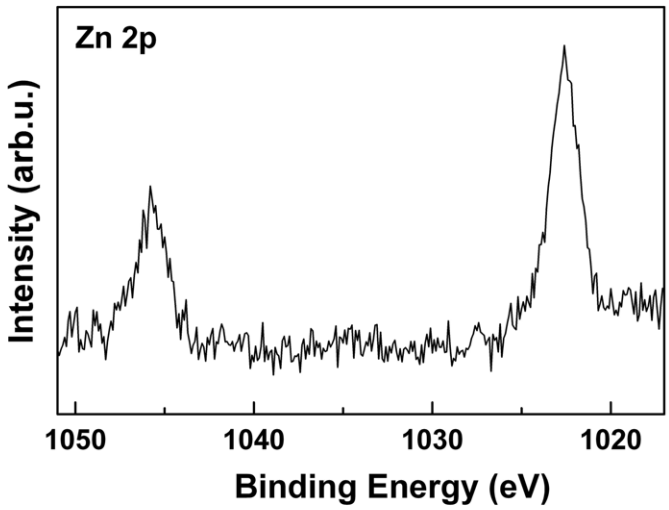

Fig. S7. XPS spectrum taken for [**4c**-Si(100)] in the Zn 2p region.

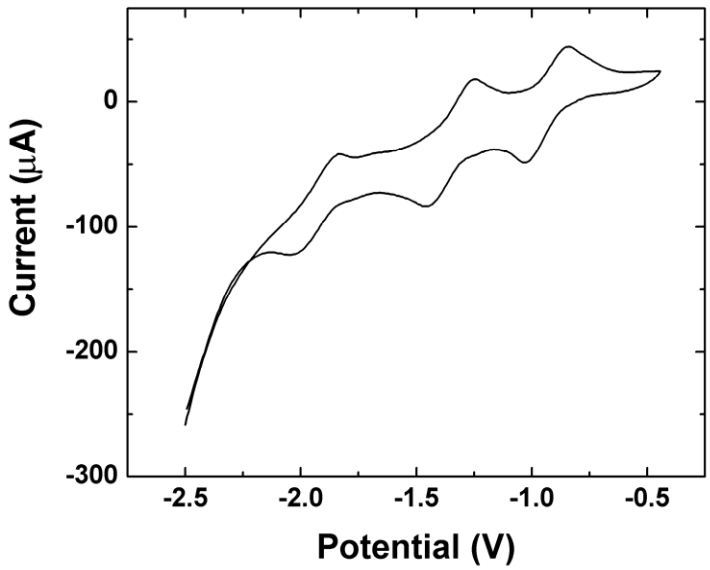

Fig. S8. Cyclic voltammogram of molecule **3b** in CH_3CN (+ 0.1 M Et_4NClO_4) solution on a bare Pt electrode.

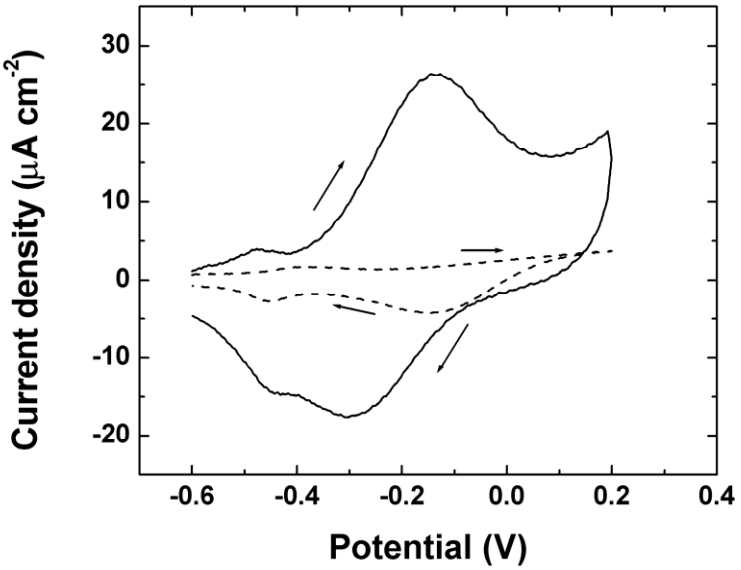

Fig. S9 CV traces of [**4b**-*n*Si(100)] in CH_3CN (+ 0.1 M Et_4NClO_4), under dark conditions (---) and under laser illumination (–). Scan rate: 1 V s^{-1}.