Electronic Supplementary Information

The corrole and ferrocene marriage: 5,10,15-triferrocenylcorrolato Cu

Giuseppe Pomarico[‡], Andrea Vecchi[‡], Federica Mandoj[‡], Olga Bortolini[†], Daniel O. Cicero[‡], Pierluca Galloni[‡*] and Roberto Paolesse[‡*]

roberto.paolesse@uniroma2.it , galloni@scienze.uniroma2.it

‡ Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma Tor Vergata, via della Ricerca Scientifica 1, 00133 Rome, Italy

†Dipartimento di Scienze Chimiche e Farmaceutiche, Università di Ferrara, via Borsari 46, 44121 Ferrara, Italy

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Materials. Reagents and solvents (Sigma-Aldrich, Fluka, Merck and Carlo Erba) were of synthetic grade and used without further purification. Silica gel 60 (70–230 mesh) or neutral alumina (Brockmann grade III) were used for chromatography.

Instruments. ^{1}H spectra were recorded at 300 K either with a Bruker AV300 spectrometer operating at 300 MHz or with a Bruker Avance 600 MHz spectrometer operating at 600 MHz with a 5 mm inverse broad-band probe equipped with z-axis gradients. Chemical shifts are given in ppm

relative to residual solvent (7.26 ppm for ^{1}H and 77.3 ppm for ^{13}C). All data were processed with TopSpin. UV-vis spectra were measured in CH_2Cl_2 with a Varian Cary 50 spectrophotometer. High resolution mass spectra (HRMS) were acquired in positive-ion mode on an ESI-Q-TOF LC-MS (Agilent Accurate Mass 6520). Gas Temperature: 300°C, Vcap 3500 V, Fragmentor 175V, Skimmer 65 V, OCT1 RF Vpp 750 V. Sample was dissolved in DMF and then diluted with MeOH (final ratio 5% DMF 95% MeOH). Eluent, MeOH. Electrochemical experiments were carried out using a PalmSense potentiostat. CV and DPV experiments were carried out using a three-electrode scheme with SCE as the reference electrode and a platinum wire as the counter electrode. Tetrabutylammonimu perchlorate (TBAP) was crystallized three times from ethyl acetate. Benzonitrile (PhCN) was distilled over P_2O_5 under reduced pressure.

Synthesis of 5,10,15-TriFerrocenylCorrole – H_3TFcC, method A:

Ferrocenecarboxaldehyde (200 mg, 0.93 mmol) and pyrrole (622 µl, 8.96 mmol) were dissolved in 6 ml of CH_2Cl_2 and mixture bubbled with nitrogen for 5 minutes, then 5.5 µl of TFA were added and mixture stirred for 3 hours at room temperature. Chloranil (176 mg, 0.72 mmol) was added and reaction stirred at room temperature for 15 minutes. Solvent was reduced to a small volume and residue purified with a plug of alumina eluted with CH_2Cl_2. Fractions containing the corrole were collected and purified by PLC of silica gel eluted with CH_2Cl_2. First brownish band corresponded to H_3TFcC, (Rf = 0.36) followed by a green-brown fraction identified as the H_2TFcP (Rf = 0.11). Yield 5 mg (2%).

Synthesis of 5,10,15-TriFerrocenylCorrole - H_3TFcC, method B:

Ferrocenecarboxaldehyde (200 mg, 0.93 mmol) and pyrrole (324 µl, 4.65 mmol) were dissolved in 36 ml of methanol, then 36 ml of aqueous solution of HCl (0.25 M) were added and reaction stirred at room temperature for 3 hours. Mixture was extracted with chloroform and organic phase washed twice with water, dried over Na_2SO_4 and solvent removed under reduced pressure. Residue was dissolved with 90 ml of $CHCl_3$, chloranil (229 mg, 0.93 mmol) was added

and mixture stirred at room temperature for 10 minutes then mixture was purified as described in the method A. Yield 8 mg (3%).

Synthesis of Copper[5,10,15-TriFerrocenylCorrolato] - CuTFcC: This complex was prepared by treating the reaction mixture (not purified) leading to H_3TFcC, obtained by method A or B with a methanolic solution of $Cu(AcO)_2$ and refluxing the final mixture for 10 minutes. Solvent was reduced to a small volume and passed through a silica gel plug eluted with $CHCl_3$. Fractions containing the corrole were collected and purified by silica gel column eluted with CH_2Cl_2/hexane 3:2. First fraction collected corresponds to the CuTFcP (Rf = 0.92), closely followed by the CuTFcC (Rf = 0.88). Fractions containing a mixture of porphyrin and corrole were further purified by PLC of silica gel eluted with CH_2Cl_2/hexane 3:2. Residue was crystallized by CH_2Cl_2/hexane. Yield 18 mg (6%). Mp > 300 °C. UV-vis (CH_2Cl_2): λ_{max}, nm (log ε): 422 (4.75), 674 (4.14). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.74 (d, 2 H, *J* = 3.97 Hz, *β*-pyrrole 3, 17), 8.52 (d, 2 H, *J* = 4.25 Hz, *β*-pyrrole 8, 12), 8.22 (d, 2 H, *J* = 4.45 Hz, *β*-pyrrole, 7, 13), 7.95 (d, 2 H, *J* = 3.15 Hz, *β*-pyrrole 2,18), 5.11 (m, 4 H, *α*-Cp C-5, C-15), 5.10 (m, 2 H, *α*-Cp C-10), 4.69 (m, 2 H, *β*-Cp, C-10), 4.66 (m, 4 H, *β*-Cp, C-5, C-15), 4.24 (s, 5 H, CpH, C-10), 4.21 (s, 10 H, CpH, C-5, C-15). ^{13}C NMR (150.7 MHz, $CDCl_3$): δ = 152.2 (C 9, 11)*, 150.7 (C 6, 14)*, 144.3 (C 4, 16)$^\#$, 143.6 (C 1, 19)$^\#$, 132.4 (C 7, 13), 130.2 (C 8, 12), 128.4 (C 3, 17), 119.4 (C 2, 18), 87.8 (e-Cp, *meso* 10), 85.4 (a-Cp, *meso* 5, 15), 74.1 (f-Cp *meso* 10), 73.4 (b-Cp *meso* 5, 15), 71 (h-Cp, *meso* 10), 70.9 (Cp, *meso* 5,15), 69.8 (c-Cp *meso* 5, 15 + g-Cp *meso* 10).

$^{*,\#}$ Signal assignments may be exchanged.
a-h See the corresponding atoms on figure S2-S5

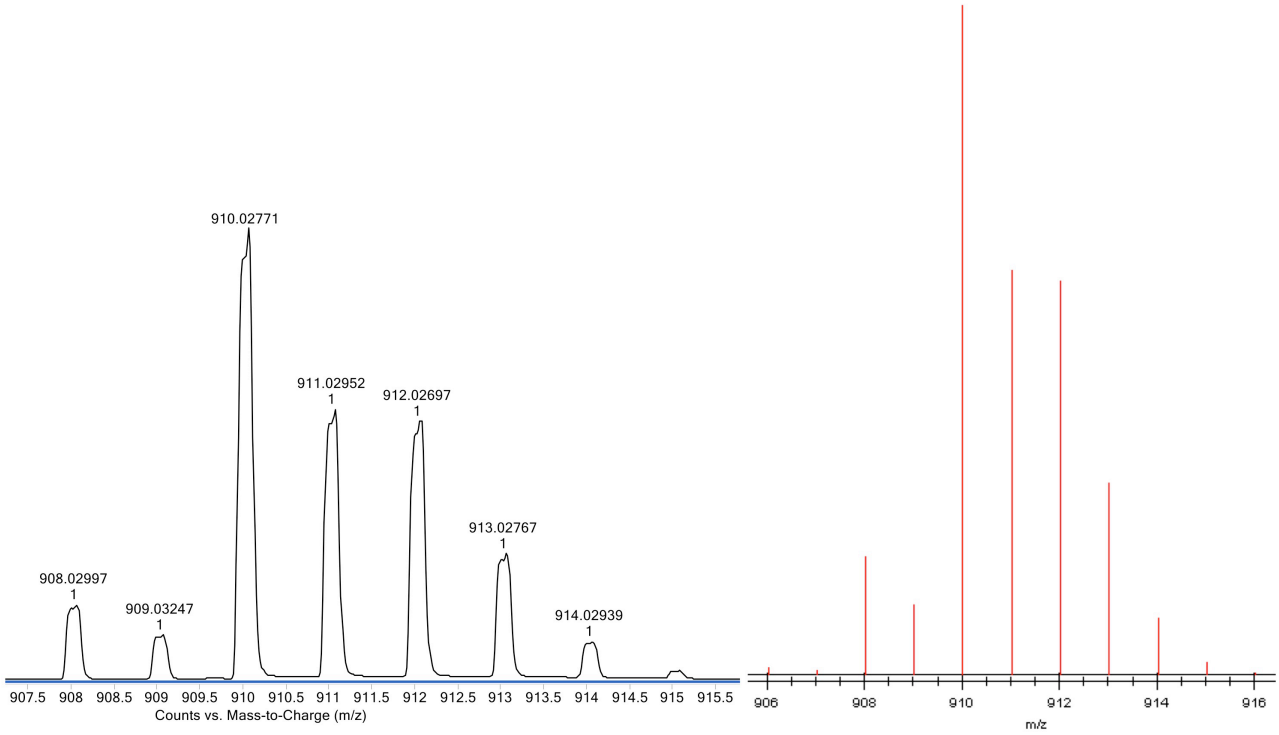

Figure S1. Experimental (left) and calculated (right) HRMS of CuTFcC.

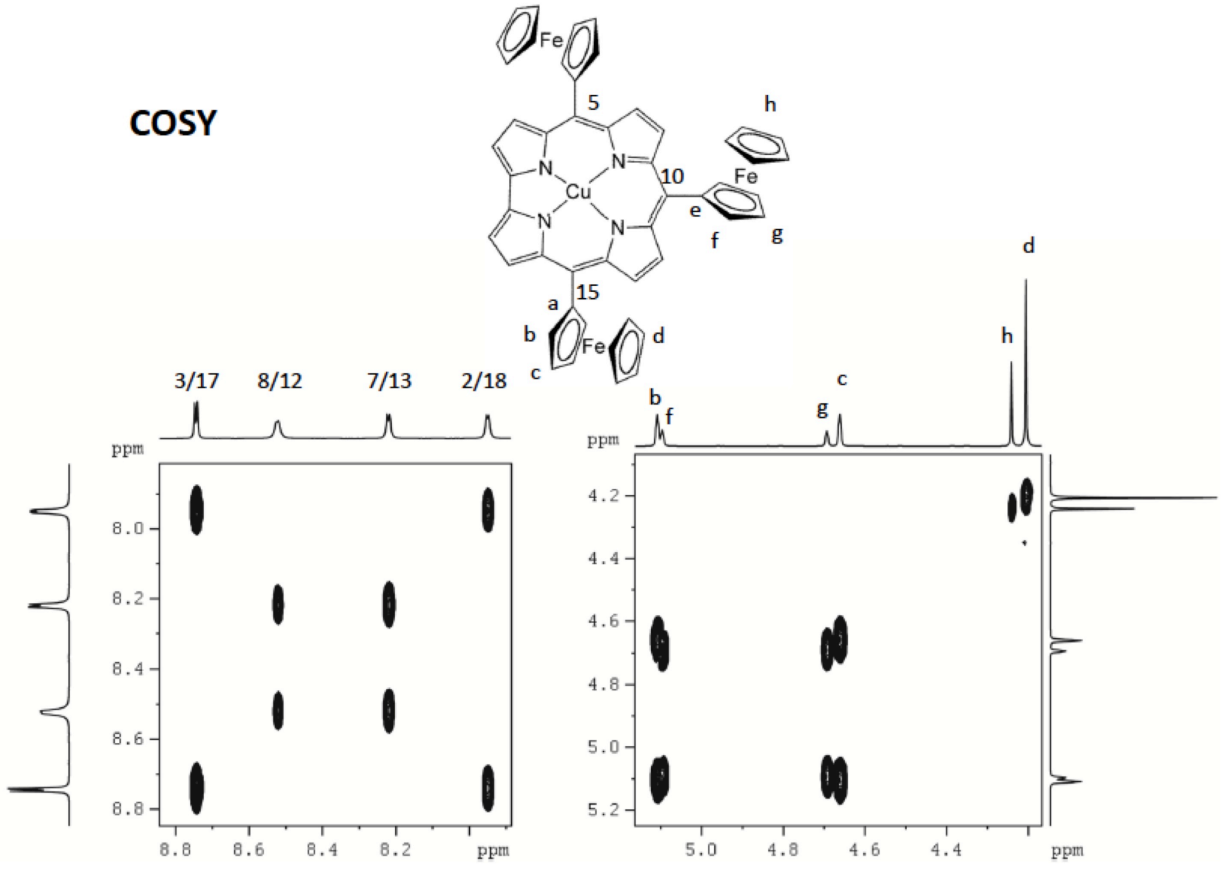

Figure S2. COESY spectrum of CuTFcC

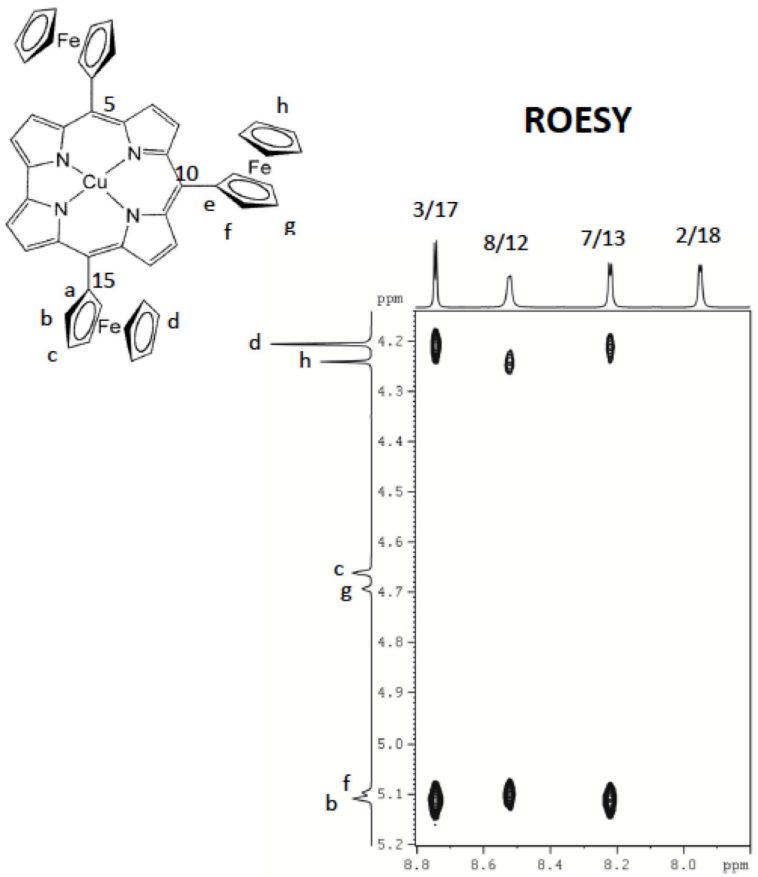

Figure S3. ROESY spectrum of CuTFcC

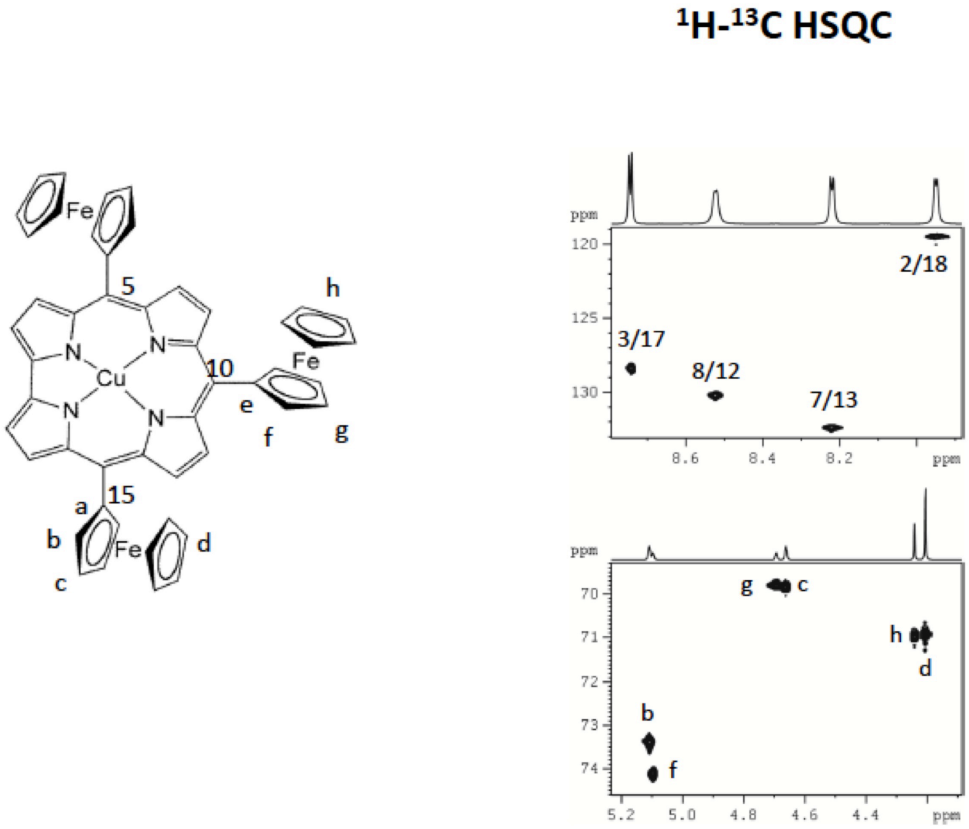

Figure S4. HSQC spectrum of CuTFcC

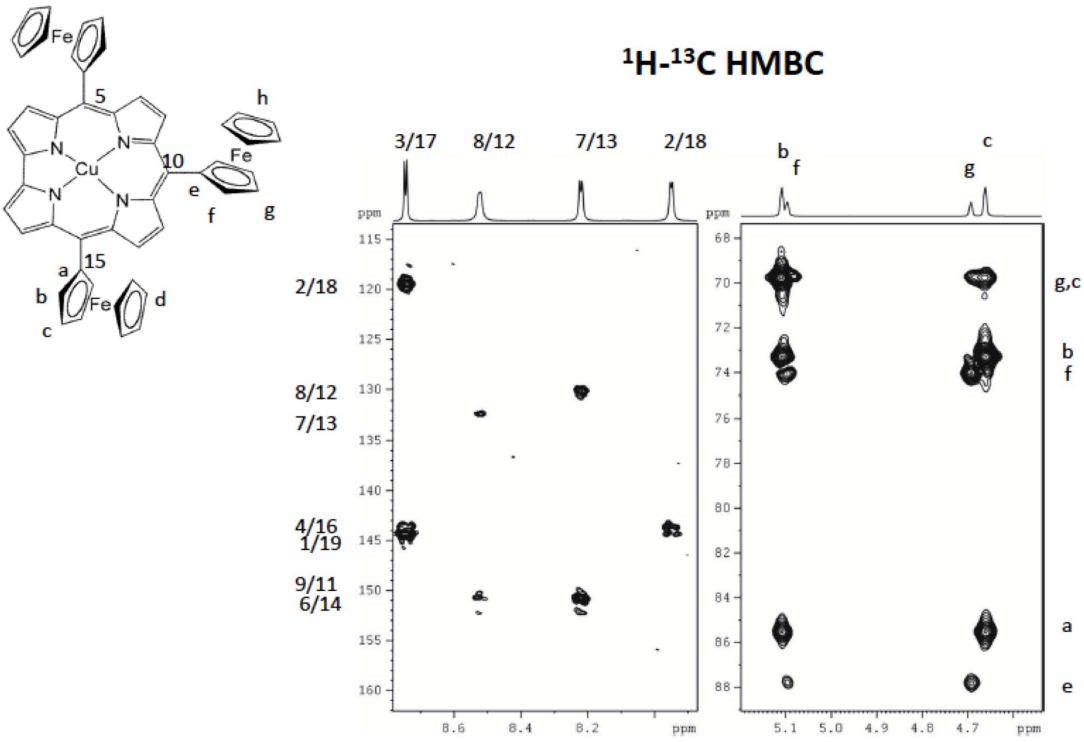

Figure S5. HMBC spectrum of CuTFcC

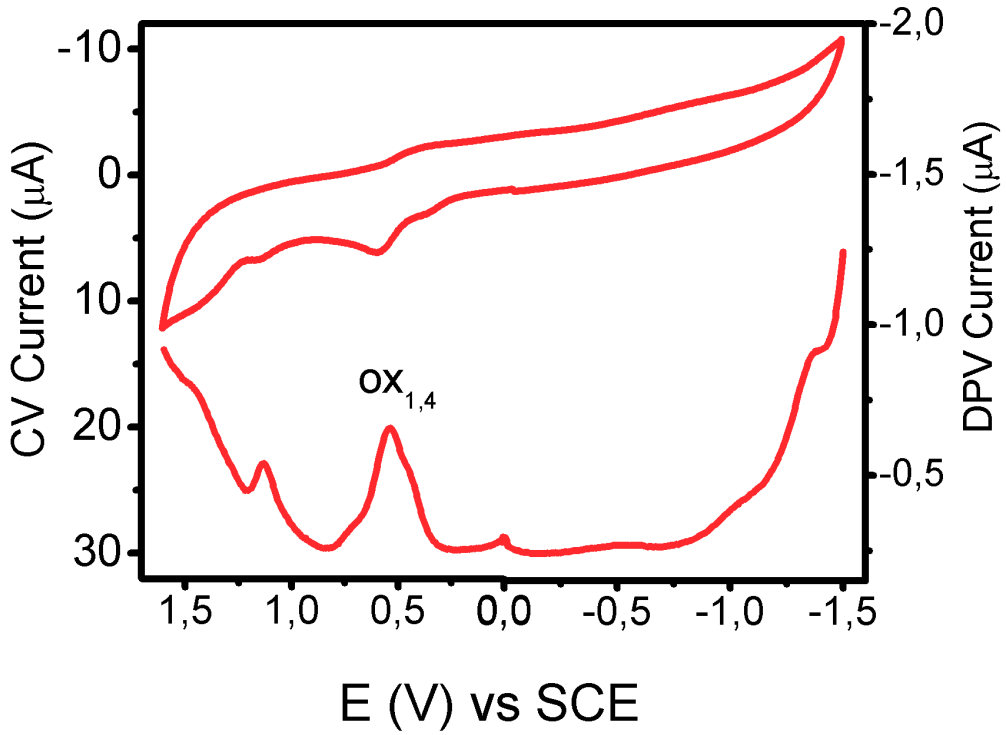

Figure S6. Electrochemistry (CV and DPV) of CuTFcP in PhCN/TBAP