

Supporting Information

N@C₆₀-porphyrin: a dyad of two radical centers

Guoquan Liu,[†] Andrei N. Khlobystov,[‡] Georgios Charalambidis,[§] Athanassios G. Coutsolelos,[§] G. Andrew D. Briggs,[†] and Kyriakos Porfyrakis^{†,*}

[†] Department of Materials, Oxford University, Oxford OX1 3PH, United Kingdom,

[‡] School of Chemistry, University of Nottingham, Nottingham NG7 2RD, United Kingdom,

[§] Department of Chemistry, University of Crete, Heraklion 71003, Greece.

Contents

- 1) General methods
- 2) Synthesis
- 3) Mass and NMR spectra
- 4) Simulation of the ESR spectra of CuTPP and dyad **2**
- 5) Linewidth broadening in mixtures of N@C₆₀ and CuTPP
- 6) Demetallation
- 7) Density Functional Theory Calculations
- 8) Supporting References

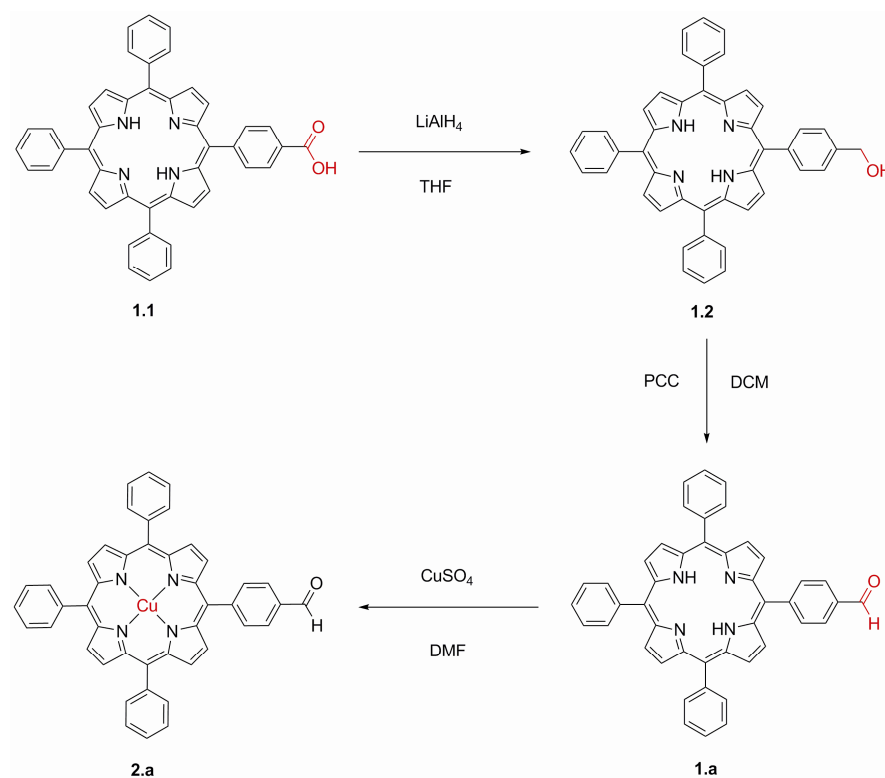
1) General Methods

Raw C₆₀ was supplied by MER corporation (99.5+%). N@C₆₀ was produced using the ion implantation method and enriched by HPLC in our lab. All other reagents and solvents unless specified were purchased from Sigma–Aldrich and were used without further purification. NMR spectra were obtained on a Bruker AV(III)500 spectrometer (500 MHz for ¹H; 125 MHz for ¹³C). Coupling constants (*J*) are denoted in Hz, and chemical shifts (δ), in ppm. Multiplicities are denoted as follows: s = singlet, d = doublet, m = multiplet. Mass spectrometry was carried out on a Bruker Ultraflex III MALDI-TOF spectrometer using DCTB as matrix (355 nm) and on a Bruker MicroTOF with electrospray ionization (ESI). Elemental analyses (C, H, N) were performed by the Elemental Analysis Service of London Metropolitan University. UV-vis spectra were recorded at room temperature in quartz cuvettes on a JASCO V-570 UV-VIS-NIR spectrophotometer. High Performance Liquid Chromatography (HPLC) for fullerene derivatives was carried out with a Cosmosil BuckyPrep M column and a 5PBB column (Nacalai Tesque Co. Ltd.). X-Band EPR measurements were performed on a Magnettech Miniscope MS200 and a Bruker EMX. Simulation of EPR spectra was performed using the EASYSPIN software package.¹

2) Synthesis

Syntheses of porphyrin-aldehyde are shown in scheme S1.

Scheme S1



meso-5-(4-hydroxymethylphenyl)-10,15,20-triphenylporphyrin (1.2). To a solution of *meso*-5-(4-benzoic acid)-10,15,20-triphenylporphyrin (**1.1**) (47 mg, 0.07 mmol) in dry THF (20 ml), LiAlH_4 (12 mg, 0.28 mmol) was added. The solution was stirred at room temperature for about 30 min and was then quenched by EtOAc. The crude product was purified by column chromatography (silica, EtOAc, $R_f = 0.95$) to afford **1.2** with a yield of 65%. ESI-MS 645.3 m/z [M] $^+$. ^1H NMR (500 MHz, CDCl_3): δ /ppm 8.86 (8H, s), 8.24-8.23 (8H, m), 7.82-7.75 (11H, m), 5.09 (2H, s), -2.75 (2H, s) ppm.

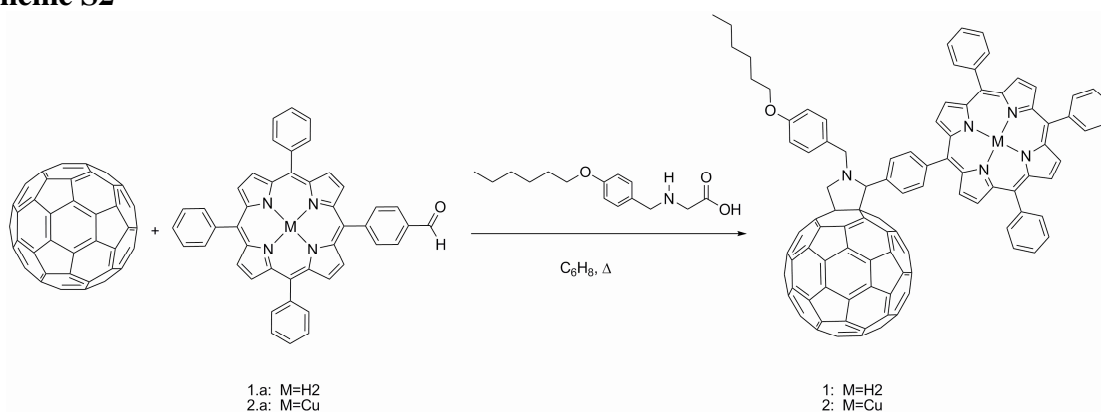
meso-5-((4-formylphenyl)-10,15,20-triphenylporphyrin (1.a). To a solution of **1.2** (31 mg, 0.048 mmol) in dry DCM (20 ml), PCC (22 mg, 0.096 mmol) was added. The solution was stirred at room temperature for about 60 min and 20 ml silica-gel was added. The crude product was purified by column chromatography (silica, DCM with 0.1% Et₃N, R_f = 0.75) to afford **1.a** with a yield of 90%. ESI-MS 643.2 *m/z* [*M*]⁺. UV-vis (acetone): 482, 515, 550, 592, 648 nm. ¹H NMR (500 MHz, CDCl₃): δ/ppm 10.41 (1H, s), 8.90 (2H, d, *J*=4.7Hz), 8.88 (4H, s), 8.80 (2H, d, *J*=4.7Hz), 8.43 (2H, d, *J*=8.0Hz), 8.31 (2H, d, *J*=8.1Hz) 8.25-8.23 (4H, m), 7.83- 7.72 (9H, m) -2.75 (2H, s) ppm.

meso-5-((4-formylphenyl)-10,15,20-triphenylporphyrin copper (II) (2.a). **2.a** was synthesized according to the Adler procedures.² To a solution of **1.a** (20 mg, 0.03 mmol) in DMF (5 ml), anhydrous CuSO₄ (52 mg, 0.33 mmol) was added. The mixture solution was allowed to reflux for about 10 min, and completion of the reaction was checked by UV-vis absorption. The resultant solution was cooled in an ice-water bath and chilled distilled water was then added. The precipitate was filtered and washed with water to afford the title compound with a yield of 92%. MALDI-MS 703.2 *m/z* [*M*]⁺. UV-vis (acetone): 501, 540, 579 nm.

Synthesis of fullerene dyads

Dyads of C₆₀ and porphyrin (**1** and **2**) were synthesized according to the Prato reaction procedure (Scheme S2). Dyads **1N** and **2N** were obtained accordingly using N@C₆₀/C₆₀ (approximate molar ratio 0.5/1000) as the starting material.

Scheme S2



C₆₀-H₂TPP (dyad 1)

A mixture consisting of C₆₀ (22 mg, 0.03 mmol), **1.a** (29.0 mg, 0.045 mmol) and 2-(4-(hexyloxy)benzylamino)acetic acid (16.0 mg, 0.06 mmol) in degassed toluene (100 mL) was allowed to react for 15 min at 110 °C under N₂ atmosphere. Purification of the resulting mixture by HPLC (5PBB, toluene) afforded the pure title compound with a yield of 28%. MALDI-MS 1566.7 *m/z* [*M*]⁺. UV-vis (toluene): 317, 421, 483, 515, 550, 591, 647 nm. ¹H NMR (500 MHz, CS₂, C₆D₆ as insert) δ/ppm 9.01(6H, broad s), 8.97 (2H, broad s), 8.83 (2H, broad s), 8.51(2H, broad s), 8.41(6H, broad s), 7.99 (9H, broad s), 7.86(2H, d, *J*=6.7 Hz), 7.21(2H, d, *J*=6.5 Hz), 5.60 (1H, s), 5.14(1H, d, *J*=8.7 Hz), 5.06 (1H, d, *J*=12.8 Hz), 4.42 (1H, d, *J*=8.9 Hz), 4.24 (2H, t, *J*=5.6 Hz), 4.03 (1H, d, *J*=13.6 Hz), 2.08 (2H, m), 1.78 (2H, m), 1.65 (4H, m), 1.23-1.08 (3H, m), -2.66 (2H, s). ¹³C NMR

(126 MHz, CS₂, DMSO-*d*₆ as insert): δ /ppm 158.18, 155.50, 153.16, 152.78, 152.49, 146.59, 146.17, 145.66, 145.59, 145.50, 145.44, 145.41, 145.25, 145.08, 144.90, 144.75, 144.73, 144.69, 144.61, 144.55, 144.54, 144.46, 144.09, 144.01, 143.70, 143.65, 142.50, 142.30, 142.06, 142.02, 141.93, 141.89, 141.67, 141.58, 141.51, 141.47, 141.45, 141.41, 141.34, 141.28, 141.05, 140.97, 139.60, 139.59, 139.45, 138.69, 136.34, 135.95, 135.43, 135.11, 134.00, 130.36, 129.45, 128.40, 127.69, 127.03, 126.14, 119.48, 119.42, 118.49, 114.16, 80.53, 76.27, 67.88, 67.20, 66.13, 55.99, 31.54, 29.24, 25.76, 22.77, 14.05.

C₆₀-CuTPP (dyad **2)**

Following the synthetic procedures for **1**, **2a** was reacted with C₆₀ and 2-(4-(hexyloxy)benzylamino)acetic acid to afford the pure title compound with a yield of 25%. MALDI-MS 1628 *m/z* [*M*][−]. UV–vis (toluene): 316, 419, 501, 541, 581 nm.

3) Mass and NMR spectra

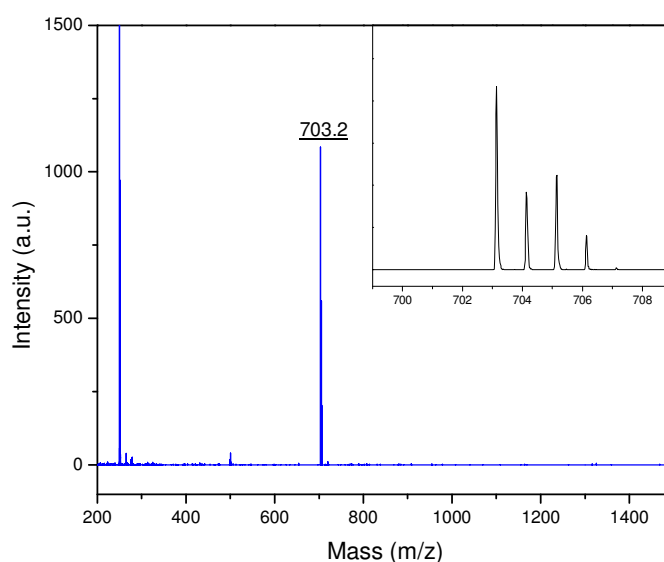


Figure S1: MALDI mass spectrum of derivative **2a** (the inset shows the corresponding isotopic distribution in the molecular ion peak).

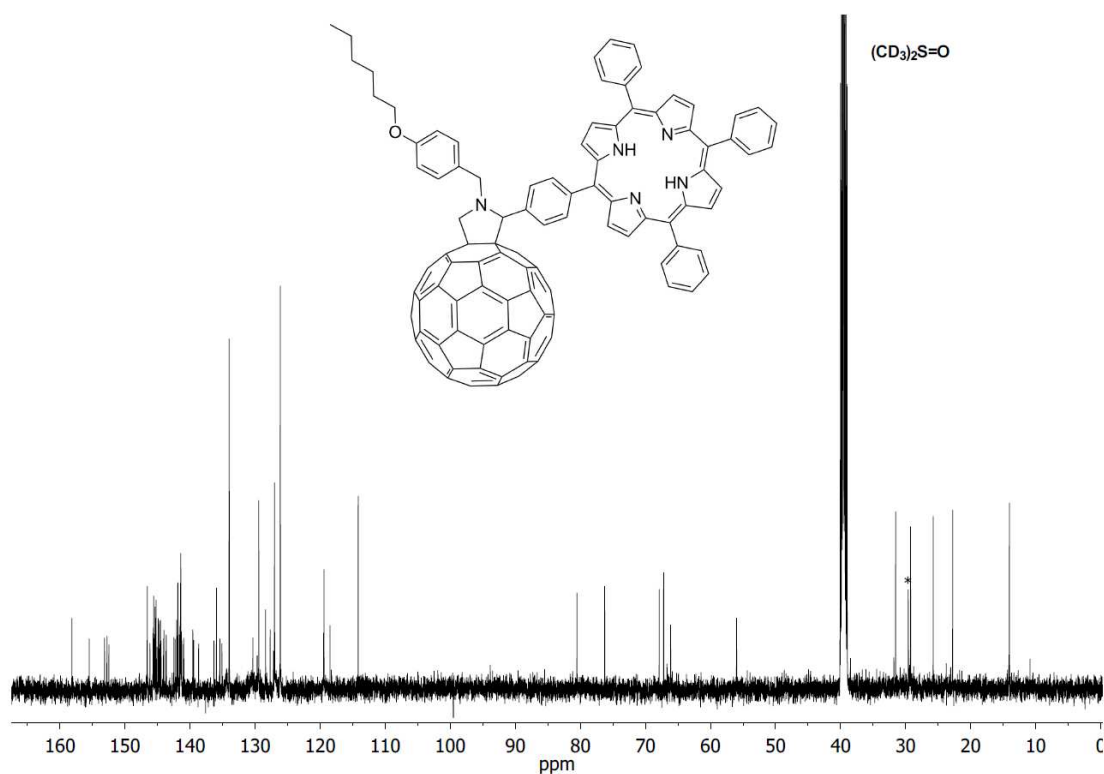


Figure S2: ^{13}C NMR spectrum (125.8 MHz, $\text{CS}_2/\text{C}_6\text{D}_6=1:1$) of dyad **1**. Minor impurity is marked (*).

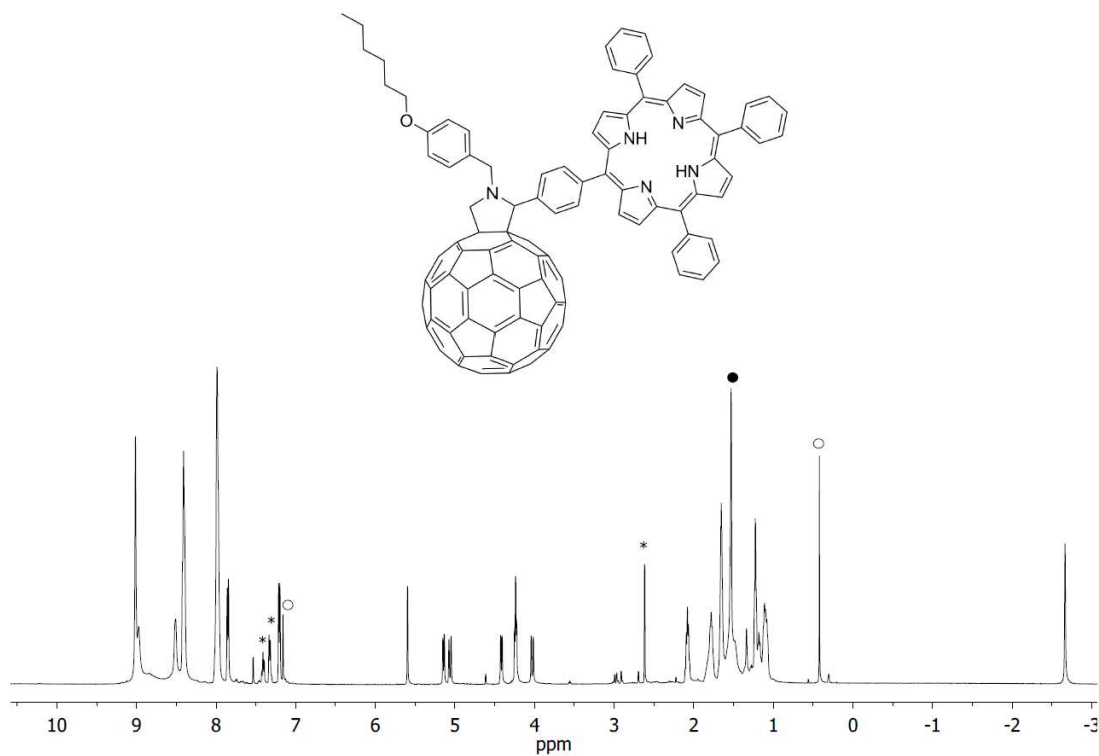


Figure S3: ^1H NMR spectrum (500 MHz, CS_2 with C_6D_6 as inset) of dyad **1**. Remnant toluene is marked (*); C_6D_6 is marked (o); H_2O is marked (•).

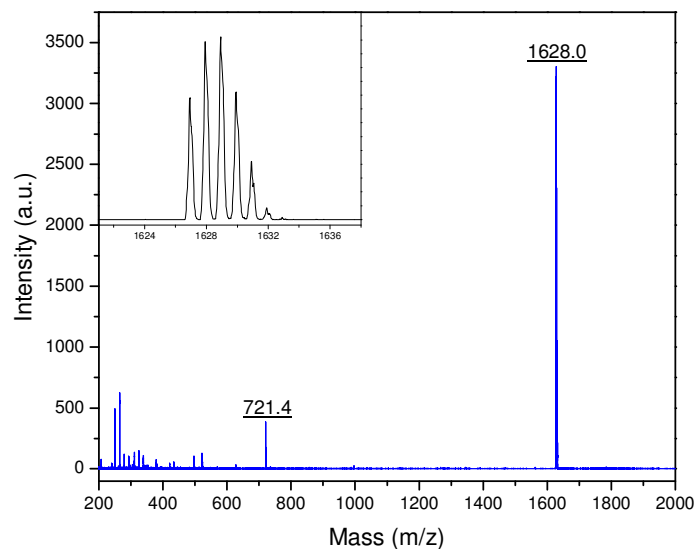


Figure S4: MALDI mass spectrum of dyad **2** (the inset shows the corresponding isotropic distribution).

4) Simulation of the ESR spectra of CuTPP and dyad **2**

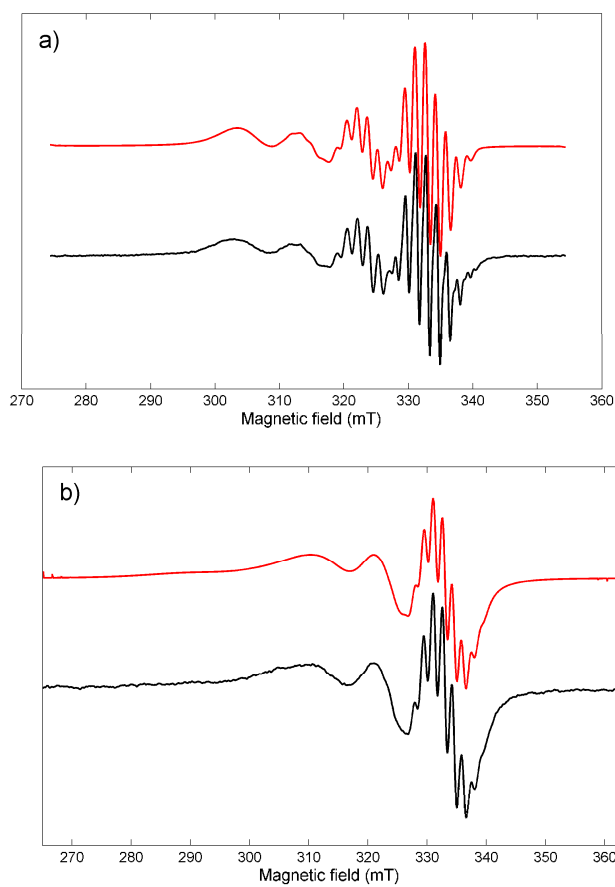


Figure S5: Simulation of the ESR spectra (the red traces) of CuTPP (a) and dyad **2** (b) in solution.

Table S1: Simulated ESR parameters for CuTPP and dyad **2**. * Hyperfine interaction tensor with nitrogen was taken from the literature,³ and was fixed in the simulation.

	g_{\perp}, g_{\parallel}	$A_{\perp}(^{63}\text{Cu})$ (MHz)	$A_{\parallel}(^{63}\text{Cu})$ (MHz)	$A_{\perp}(^{14}\text{N})^*$ (MHz)	$A_{\parallel}(^{14}\text{N})^*$ (MHz)	Correlation time (ps)
CuTPP	2.053, 2.176	-90.5	-576	43.5	49.2	79
dyad 2	2.053, 2.174	-90.5	-574	43.5	49.2	355

5) Linewidth broadening in mixtures of N@C₆₀ and CuTPP

Concentration of N@C₆₀ (1.0×10^{-3} M, nitrogen filling ratio of ca. 0.001) and the whole volume (0.1 mL) were fixed, and the concentration of CuTPP varied. ESR spectra were recorded at room temperature (295K). As shown in Fig. S5, the linewidth broadening of N@C₆₀ is linearly proportional to the concentration of CuTPP.⁴

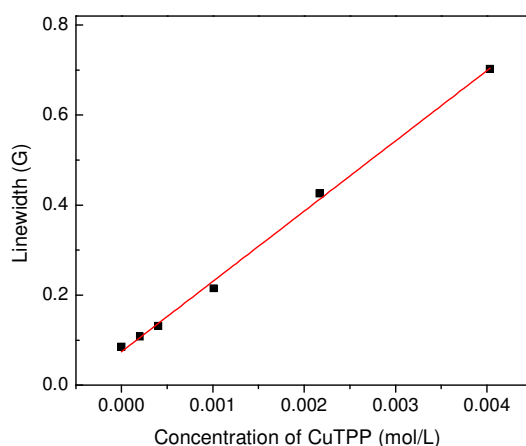


Figure S6: Linewidth (peak to peak) of N@C₆₀ mixed with CuTPP in CS₂.

6) Demetallation

Dyad **2** or **2N** (1.6×10^{-7} mol) was dissolved in 4 mL of CH₂Cl₂ under sonication. A mixture of trifluoroacetic acid and 2% sulphuric acid (1 mL/0.02 mL) was added and the mixture was stirred for about 5 min. Mixture of ice/water was added and the aqueous phase was extracted with CH₂Cl₂. The extraction was washed with saturated solution of NaHCO₃ and then with water to adjust the PH to nearly neutral. The organic phase was evaporated and redissolved in toluene or CS₂.

7) Density Functional Theory (DFT) Calculations

Geometry of dyad **2** was optimized using hybrid DFT method at the B3LYP level with the Gaussian03 programme.⁵ Split-valence 6-31G (d, p) basis set was used for C, H, N and O, and TZVP for the transitional metal Cu. Full geometry optimization was carried out by means of energy gradient techniques. Geometry of dyad **2N** was obtained based on that of dyad **2** by adding a nitrogen atom to the center of the carbon cage. Energy of dyad **2N** was calculated at two different spin states ($S=2$ and $S=1$) with tight SCF convergence criterion (RMS density matrix $\leq 1.0 \times 10^{-8}$, MAX density matrix $\leq 1.0 \times 10^{-6}$, energy deviation $\leq 1.0 \times 10^{-6}$). Their electronic energies are both -6608.144871 Hartree. The optimized structure and spin density distribution were visualized using GaussView.⁶ All calculations were set to be in the gas phase.

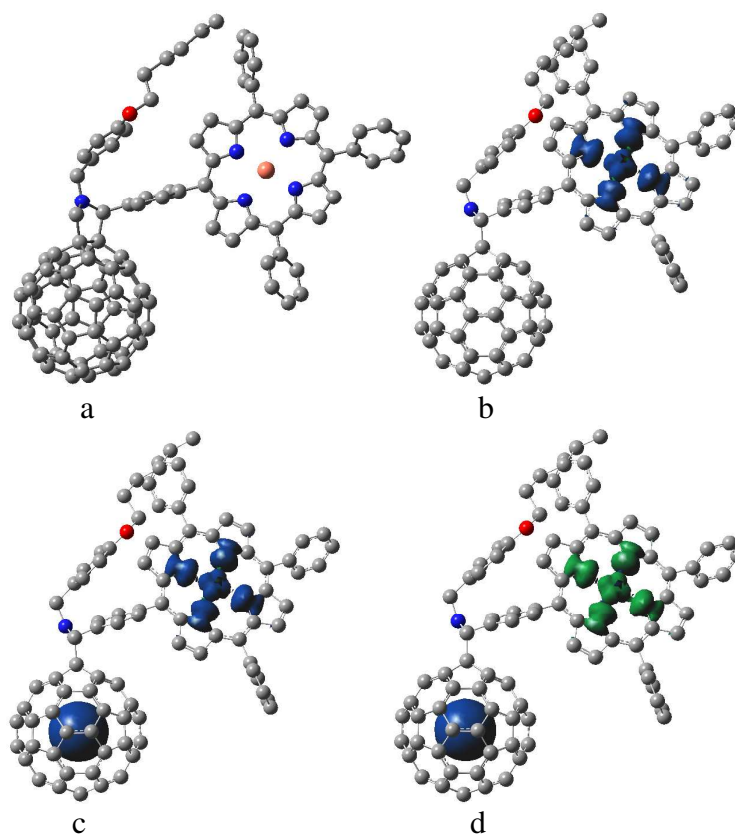


Figure S7: (a) Optimized geometry of dyad **2** (which produces a distance of 1.26 nm between the Cu ion and the centre of the fullerene cage); (b) Spin density distribution of dyad **2**; (c) Spin density distribution of dyad **2N** with $S=2$; (d) Spin density distribution of dyad **2N** with $S=1$. All contour levels are 1×10^{-3} e/a.u..

Table S2: Mulliken atomic spin densities in dyad **2N** (atoms with values smaller than 0.01 are omitted).

	$S=2$ (sum of spin densities=4)	$S=1$ (sum of spin densities=2)
N@C ₆₀ moiety		
N	2.97131	2.97131

CuTPP moiety		
Cu	0.57123	-0.57123
N1	0.10637	-0.10637
N2	0.10591	-0.10591
N3	0.10556	-0.10557
N4	0.10507	-0.10507

8) Supporting Information References

- (1) Stoll, S.; Schweiger, A. *J. Magn. Reson.* **2006**, *178*, 42.
- (2) Adler, A. D.; Longo, F. R.; Kampas, F.; Kim, J. *J. Inorg. Nucl. Chem.* **1970**, *32*, 2443.
- (3) Assour, J. M. *J. Chem. Phys.* **1965**, *43*, 2477.
- (4) Berner, B.; Kivelson, D. *J. Phys. Chem.* **1979**, *83*, 1406.
- (5) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A.; Gaussian, Inc.: Wallingford CT, 2004.
- (6) Dennington, R.; Keith, T.; Millam, J.; Version 5 ed.; Semichem Inc.: Shawnee Mission KS, 2009.