

Synthesis of a self-assembled copper(II) metallo-rectangle with a guanosine-substituted terpyridine

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Supplementary Information

Synthesis of 2. To a stirred suspension of **1** (500 mg, 2.0 mmol) and K_2CO_3 (580 mg, 4.2 mmol) in dry degassed acetonitrile, 1,2-dibromoethane (586 mg, 3.1 mmol) was added under N_2 . The resulting reaction mixture was refluxed for 36 h after which time the solvent was removed under reduced pressure to yield an off-white solid. The solid residue was then purified by flash chromatography using alumina and eluting with hexane/ethylacetate (3.5: 1.5) to obtain **2** as a colourless crystalline solid. Yield 60%. 1H NMR in $CDCl_3$: δ 8.74-8.71 (m, 2H, terpy), 8.66-8.62 (d, $J = 8.0$ Hz, 2H, terpy), 8.07 (s, 2H, terpy), 7.91-7.86 (m, 2H, terpy), 7.39-7.35 (m, 2H, terpy), 4.63-4.56 (t, $J = 6.0$ Hz, 2H, OCH_2CH_2), 3.77-3.74 (t, $J = 6.0$ Hz, 2H, $BrCH_2CH_2$) ppm. ^{13}C NMR in $CDCl_3$ δ : 166.3, 157.3, 155.9, 149.1, 136.8, 123.9, 121.3, 107.3, 67.7, 28.6 ppm.

Synthesis of L¹. Compound **2** (113 mg, 0.35 mmol), guanosine (100 mg, 0.28 mmol) and Cs_2CO_3 (97.7 mg, 0.30 mmol) were added as solids to a flask which was degassed and purged with N_2 three times. Then dry (water less than 0.005%) DMSO (10 ml) was added by syringe and the resulting reaction mixture was heated to 140 °C for 24 h. During this time the solution changed from pale yellow to brownish. The solution was then cooled to room temperature and 10 ml of water added followed by neutralization of the mixture with aqueous HCl to pH 7. Further addition of water resulted in the precipitation of an off-white solid which was filtered and washed with water and dried under vacuum overnight to yield **L¹**. Yield 65%. 1H NMR in $DMSO-d_6$: δ 8.73-8.72 (m, 2H, terpy), 8.66-8.60 (d, $J = 8.0$ Hz, 2H, terpy), 8.1 (s, 1H, H8), 8.05 (s, 2H, terpy), 8.04-8.0 (m, 2H, terpy), 7.53-7.50 (m, 2H, terpy), 6.66 (s, 1H, NH_2), 6.04 (d, $J = 2.4$ Hz, 1H, guanosine-H1), 5.29-5.27 (dd, $J = 6.0, 2.4$ Hz, 1H, guanosine-H2), 5.07 (t, $J = 5.2$ Hz, 1H, OH), 5.04-5.0 (dd, $J = 6.4, 2.8$ Hz, 1H, guanosine-H3), 4.86-4.8 (t, $J = 4.8$ Hz, OCH_2CH_2), 4.7-4.66 (t, $J = 4.0$ Hz, 2H, NCH_2CH_2), 4.17-4.12 (m, guanosine-H4), 3.6-3.5 (m, 2H, guanosine-H5), 1.52 (s, 3H, CH_3), 1.32 (s, 3H, CH_3) ppm. Calculated M_w for $C_{30}H_{30}N_8O_6 =$

598.23 a.m.u. Found: $[M+H]^+ = 599.7$ a.m.u. ^{13}C NMR in CDCl_3 : δ 166.8, 161.3, 158.9, 157.0, 156.0, 152.4, 149.0, 139.1, 136.9, 123.9, 121.0, 116.8, 114.0, 107.5, 94.0, 85.8, 82.7, 81.6, 64.9, 63.6, 63.5, 27.6, 25.3 ppm.

Synthesis of compound 3. To a methanolic suspension of L^1 (60 mg, 0.1 mmol) a clear methanolic solution of $\text{Cu}(\text{NO}_3)_2$ (24.1 mg, 0.1 mmol) was added at room temperature. The mixture turned immediately from light blue to a blue-green colour. The reaction mixture was stirred for further 15 min by which time all suspended solid had dissolved and a clear blue-green solution was obtained. The stirring was stopped and the solution left standing; slow evaporation of the solvent gave block shaped crystals corresponding to **3** after one week. Analysis calculated for $\text{C}_{60}\text{H}_{64}\text{Cu}_2\text{N}_{20}\text{O}_{26} \cdot 10(\text{H}_2\text{O})$: %C, 40.29; %H, 4.73; %N, 15.66. Found: %C, 40.07; %H, 4.24; %N, 15.30. ESI(+) MS: 1510 a.m.u. assigned to $[(\text{Cu})_2(\text{L}^1)_2(\text{NO}_3)_3]^+$. UV-vis spectrum: $\lambda_{\text{max}} = 334$ nm, 323 nm and 280 nm.

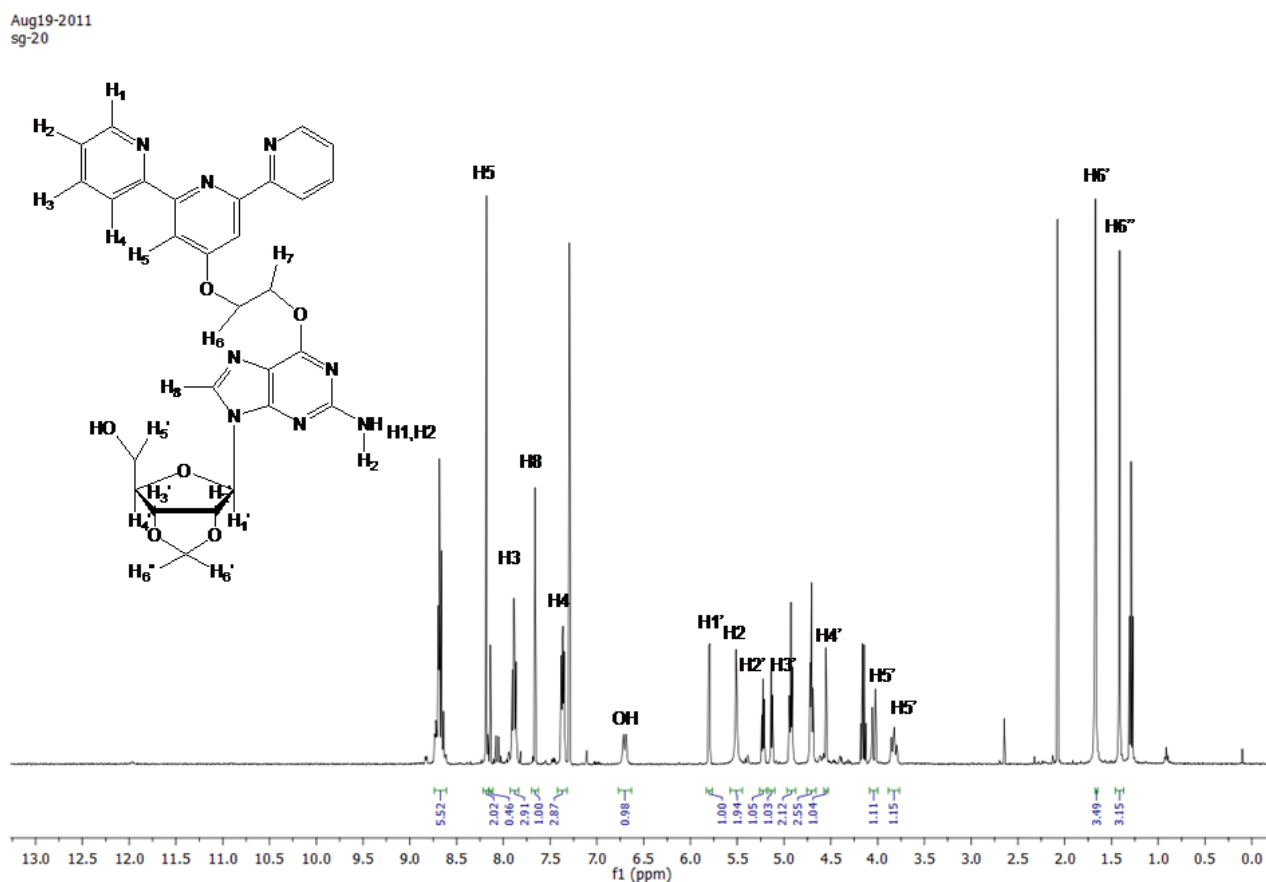


Fig. S1. ^1H NMR spectrum of L^1 in CDCl_3 at room temperature.

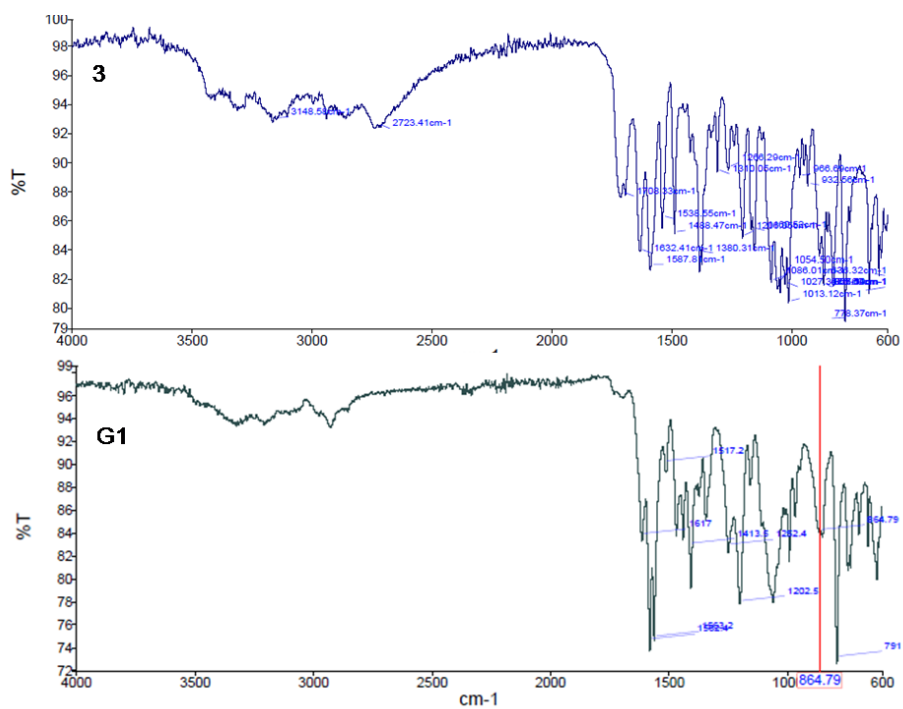


Fig. S2 IR spectra of guanosine (above) and L¹ (bottom) showing the disappearance of the C=O peak at 1708 cm⁻¹.

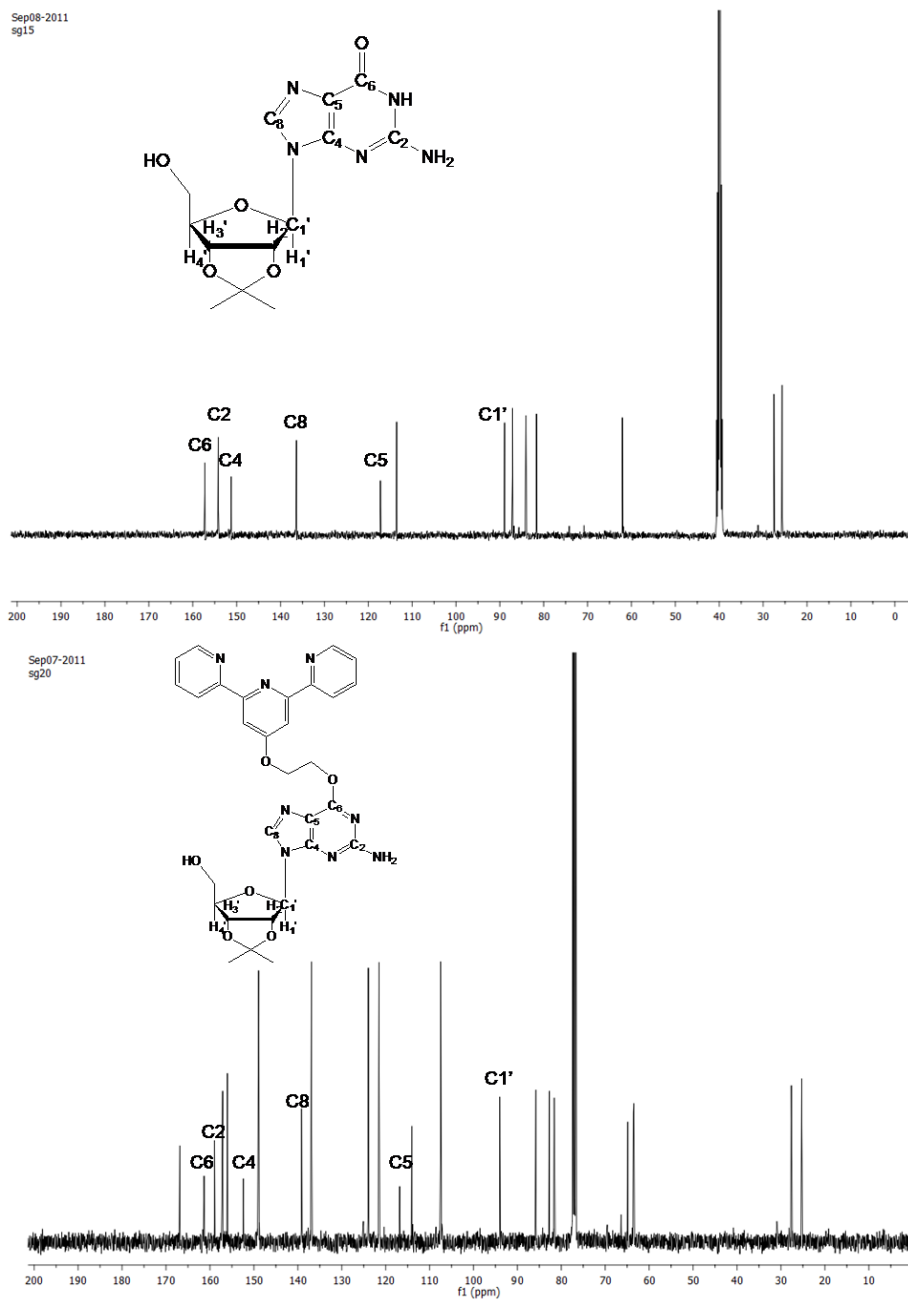


Fig. S3 ^{13}C NMR spectra of guanosine (above) and L¹ (bottom).

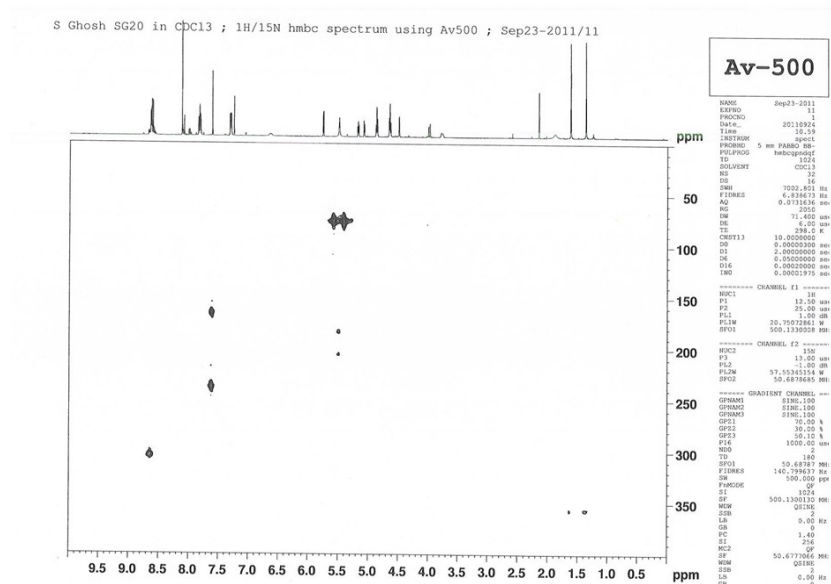


Fig. S4 HMBNMR of **L**¹ showing ¹H-¹⁵N correlation.

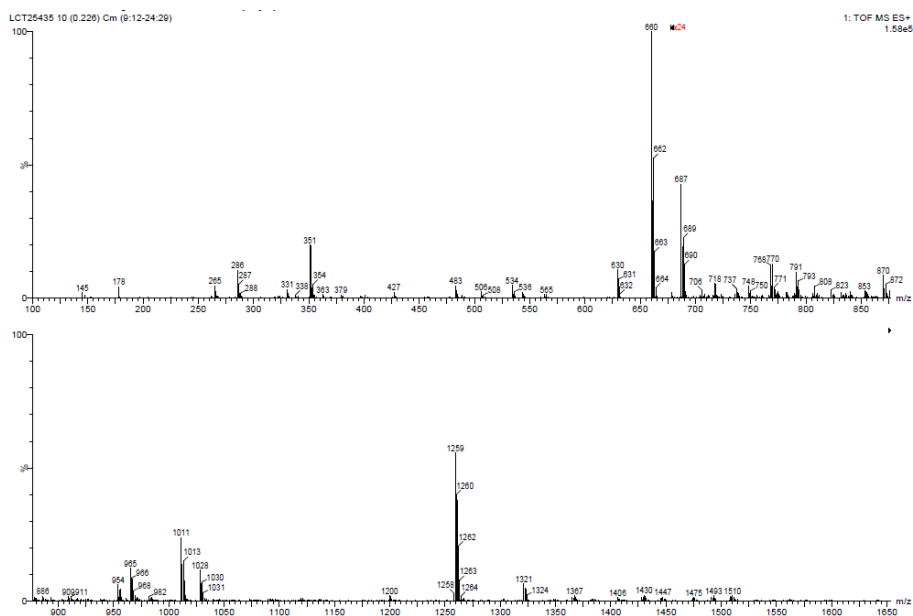


Fig. S5 ESI(+)-Mass Spectrum for complex **3** showing the a peak at 1510 a.m.u. assigned to $[(\text{Cu})_2(\text{L}^1)_2(\text{NO}_3)_3]^+$.

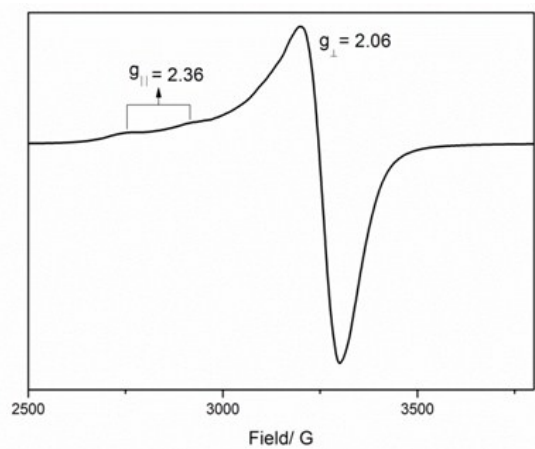


Fig. S6 X-band EPR spectra of **3** recorded as a frozen glass in DMSO at 5K.

The X-ray crystal structure of **3**

The included solvent in the structure of **3** was found to be highly disordered, and the best approach to handling this electron density was found to be the SQUEEZE routine of PLATON.^[1] This suggested a total of 103 electrons per unit cell. The crystal was grown from a mixture of methanol [CH₄O, 18 electrons] and water [H₂O, 10 electrons], and before the use of SQUEEZE the electron density distribution most resembled a mixture of these two solvents. 4MeOH and 3H₂O equates to 102 electrons and so this was used as the solvent present. The atom list for the unit cell is thus low by 4(CH₄O) and 3(H₂O), i.e. C₄H₂₂O₇.

The N–H and O–H hydrogen atoms of the amino and water moieties were located from ΔF maps and refined freely subject to an X–H distance constraint of 0.90 Å. The O–H hydrogen atoms on O(41) and O(91)/O(91') could not be located from ΔF maps and so were added in idealised positions at an O–H distance of 0.90 Å and allowed to rotate about the C–O bond to find the orientation that best fits with the electron density (the SHELX HFIX 147 command). The hydrogen atom on O(91') however, never found a settled position, and so was fixed in an arbitrary position (with an idealised C–O–H angle). As these O–H hydrogen atoms were not located from ΔF maps, their positions should be treated with some caution.

The C(82)-based sugar group was found to be disordered. Two orientations were identified of ca. 75 and 25% occupancy, their geometries optimised, the thermal parameters of adjacent atoms restrained to be similar, and only the non-hydrogen atoms of the major occupancy orientation were refined anisotropically (the remainder were refined isotropically).

The N(120) and N(130)-based nitrate anions were found to be disordered. In each case two orientations were identified, (of ca. 64:36 and 68:32% occupancy respectively), their geometries optimised, the thermal parameters of adjacent atoms restrained to be similar, and only the atoms of the major occupancy orientations were refined anisotropically (the remainder were refined isotropically).

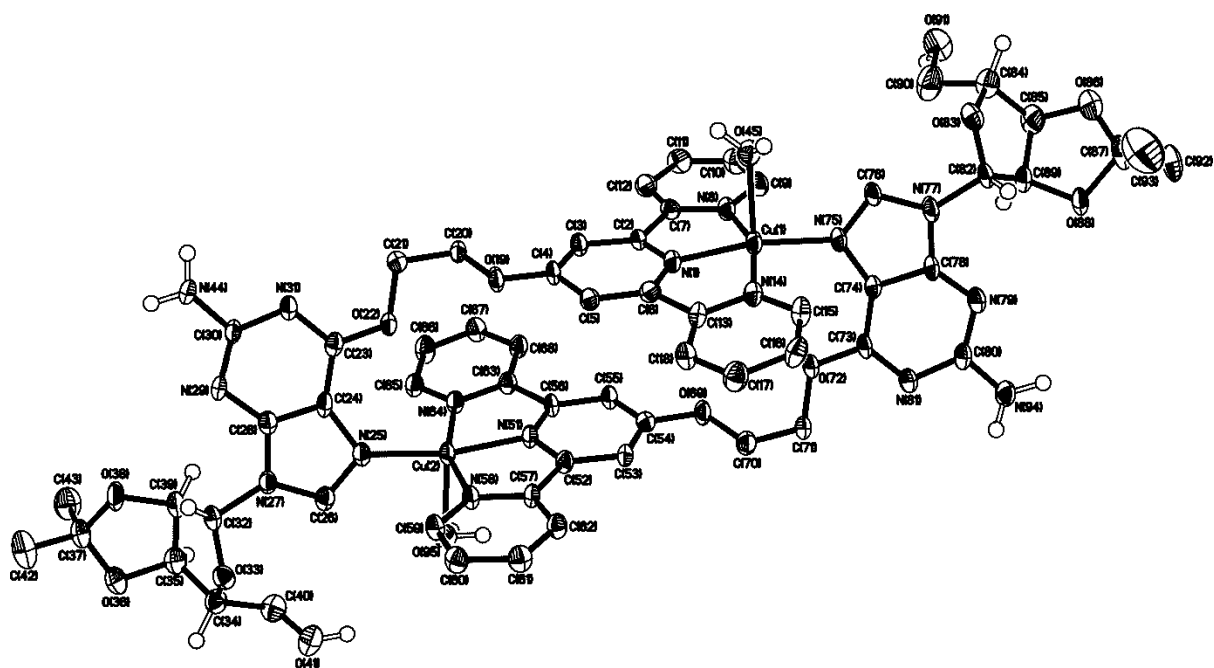


Fig. S6 The crystal structure of **3** (30% probability ellipsoids).

Table S1. Selected bond lengths (Å) and angles (°) for **3**.

Cu(1)–N(1)	1.920(4)	Cu(2)–N(51)	1.946(4)
Cu(1)–N(8)	2.023(5)	Cu(2)–N(58)	2.057(4)
Cu(1)–N(14)	2.058(4)	Cu(2)–N(64)	2.057(4)
Cu(1)–O(45)	2.259(4)	Cu(2)–O(95)	2.246(4)
Cu(1)–N(75)	1.963(4)	Cu(2)–N(25)	1.965(4)
N(1)–Cu(1)–N(8)	79.87(18)	N(51)–Cu(2)–N(58)	79.56(16)
N(1)–Cu(1)–N(14)	79.86(18)	N(51)–Cu(2)–N(64)	79.43(17)
N(1)–Cu(1)–O(45)	96.92(18)	N(51)–Cu(2)–O(95)	102.44(18)
N(1)–Cu(1)–N(75)	168.5(2)	N(51)–Cu(2)–N(25)	166.64(19)
N(8)–Cu(1)–N(14)	159.07(16)	N(58)–Cu(2)–N(64)	158.75(15)
N(8)–Cu(1)–O(45)	90.86(17)	N(58)–Cu(2)–O(95)	92.06(15)
N(8)–Cu(1)–N(75)	100.42(18)	N(58)–Cu(2)–N(25)	100.07(16)
N(14)–Cu(1)–O(45)	96.72(17)	N(64)–Cu(2)–O(95)	95.56(16)
N(14)–Cu(1)–N(75)	98.40(18)	N(64)–Cu(2)–N(25)	99.62(17)
O(45)–Cu(1)–N(75)	94.54(17)	O(95)–Cu(2)–N(25)	90.92(17)

Computational Details

The calculations were performed using density functional theory with the spin-unrestricted hybrid Becke's 3 parameters for exchange and Lee-Yang-Parr's correlation functional (B3LYP)² in conjunction with Ahlrichs' triple- ζ def2-TZVP basis set.³ The magnetic pathways between molecule fragments were investigated using the broken symmetry approach implemented in the ORCA 2.8.0 software package.⁴

Herein, the coupling constants were estimated from the difference in energy between the highspin (HS) and broken symmetry (BS) state where the phenomenological Hamiltonian is expressed as

$$H = -2JS_1.S_2$$

Where J is estimated from the spin projected approach, which is valid for the weak coupling limit

$$J = -(E_{HS} - E_{BS}) / (S_A + S_B)^2$$

Thus, fragments with positive J would be ferromagnetically coupled while those with a negative value for J are antiferromagnetically coupled as the highest and lowest spin state are lowest in energy, respectively.

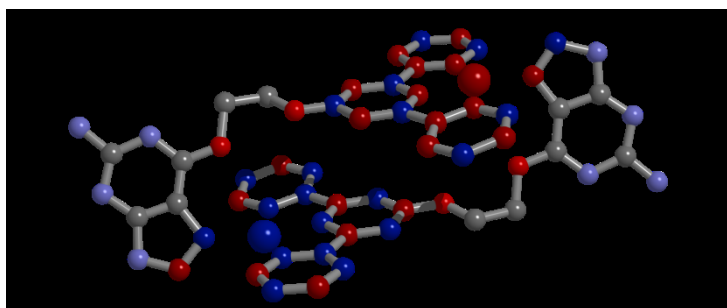


Fig. S7 Graphic representation of the spin density for the model **4**. Spin contributions from copper and the central terpyridine ligands are labelled red and blue for spin up and spin down, respectively. Hydrogens omitted for clarity.

Table S2. Summary of significant Mulliken Spin contributions for model 4.

Atom	Mulliken Spin Density	Atom	Mulliken Spin Density
Cu (1)	0.59731	Cu (2)	-0.596715
N (1)	0.114983	N (25)	-0.082499
C (2)	-0.005211	N (51)	-0.112615
C (3)	0.004968	C (52)	0.005245
C (4)	-0.004846	C (53)	-0.00518
C (5)	0.005599	C (54)	0.0051
N (8)	0.103898	C (55)	-0.005657
C (10)	0.006775	N (58)	-0.105139
C (11)	-0.005088	C (59)	0.008648
N (14)	0.091442	C (60)	-0.007608
C (15)	-0.006636	C (61)	0.005117
C (16)	0.00651	N (64)	-0.092561
N (75)	0.082339	C (65)	0.007194
C (76)	-0.005394	C (66)	-0.006205

References

1. A.L. Spek (2008) PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands. See also A.L. Spek, *J. Appl. Cryst.*, 2003, **36**, 7–13.
2. (a) A.D. Becke, *J.Chem.Phys.* 98 (1993) 5648-5652; (b) P.J. Stephens, F.J. Devlin, C.F. Chabalowski, M.J. Frisch, *J. Phys. Chem.* 1994, **98**, 11623-11627
3. (a) A.D. Becke, *J. Chem. Phys.* 1993, **97**, 5648-5652
4. F. Neese: The ORCA program system (*WIREs Comput Mol Sci* 2012, **2**, 73-78)