

Electronic Supplementary Information

A metal-organic framework based on an asymmetric ligand built from 1,2,4-triazole and tetrazole

Yves Boland,^a Bernard Tinant,^a Damir A. Safin,^a Jacqueline Marchand-Brynaert,^a Rodolphe Clérac,^{b,c} and Yann Garcia^{a,*}

^a*Institute of Condensed Matter and Nanosciences, MOST - Inorganic Chemistry, Université Catholique de Louvain, Place L. Pasteur 1, 1348 Louvain-la-Neuve, Belgium. Fax: +32(0) 1047 2330; Tel: +32(0) 1047 2831; E-mail: yann.garcia@uclouvain.be*

^b*CNRS, CRPP, UPR 8641, F-33600 Pessac, France*

^c*Univ. Bordeaux, CRPP, UPR 8641, F-33600 Pessac, France*

Physical measurements: Infrared spectrum (KBr) was recorded with a FTIR-8400S SHIMADZU spectrophotometer in the range 400–3600 cm⁻¹. Raman spectra were obtained with a FTIR Nicolet Magna 860 with Raman unit and Nd:YVO₄ (λ = 1064 nm) laser. Diffuse reflectance spectrum was obtained with a Varian Cary 5E spectrometer using polytetrafluoroethylene (PTFE) as a reference. Simultaneous thermogravimetric (TG) and differential thermal (DTA) analyses were performed by a SDT 2960 Simultaneous DTA-TGA instrument in a dynamic air atmosphere (100 mL min⁻¹) from laboratory temperature to 1000 °C with a 10 °C min⁻¹ heating rate. Elemental analyses were performed on a Perkin Elmer 2400 CHN microanalyser. Magnetic susceptibility measurements were performed using a Quantum Design MPMS-XL SQUID magnetometer. The measurements were performed on a polycrystalline sample introduced in a polyethylene bag (3 × 0.5 × 0.02 cm). dc measurements were conducted from 300 to 1.8 K and between – 70 kOe and 70 kOe applied dc fields. A *M* vs. *H* measurement was performed at 100 K to confirm the absence of ferromagnetic impurities. Experimental data shown in Figure S5 were corrected for the sample holder and for the diamagnetic contribution of the sample.

Synthesis of [CuL(OH)]BF₄ (I): The compound **L** (0.300 g, 1.67 mmol) was dissolved in water (20 mL). Then a 50% wt. aqueous solution of Cu(BF₄)₂ (0.133 g, 0.28 mmol) was added. A blue precipitate appeared instantaneously. Then water (60 mL) was added and the precipitate was dissolved by heating the solution. The solution was allowed to cool and small blue crystals suitable for a single crystal X-ray analysis were obtained on standing after three months. Yield: 0.49 g (50%). *Anal.* Calc. for C₆H₁₀BCuF₄N₇O (346.54): C 20.80, H 2.91, N 21.93. Found: C 20.94, H 2.83, N 21.82.

X-Ray crystallography: The X-ray intensity data were collected at 100(2) K with a MAR345 image plate using Mo-K α ($\lambda = 0.71069$ Å) radiation. The crystal was chosen, mounted in inert oil and transferred quickly to the cold gas stream for flash cooling. Crystal data and data collection parameters are summarized hereafter. The unit cell parameters were refined using all the collected spots after the integration process. The data were not corrected for absorption, but the data collection mode partially takes the absorption phenomena into account. The structure was solved by direct methods with SHELX97.¹ The structure was refined by full-matrix least-squares on F^2 using SHELX97.¹ All non-hydrogen atoms were refined with anisotropic temperature factors. All hydrogen atoms were localized by Fourier-difference synthesis and included in the refinement with a common isotropic temperature factor. Figures were generated using the program Mercury.²

Crystal data for I: C₆H₁₀CuN₇O, BF₄; $M_r = 346.57$ g mol⁻¹, orthorhombic, space group $P2_12_12_1$, $a = 6.566(2)$, $b = 10.457(3)$, $c = 17.386(5)$ Å, $V = 1193.7(6)$ Å³, $Z = 4$, $\rho = 1.929$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 1.889$ mm⁻¹, $T = 100$ K, reflections: 4859 collected, 1848 unique, $R_{\text{int}} = 0.055$, $R_1(\text{all}) = 0.0438$, $wR_2(\text{all}) = 0.1013$.

CCDC 883200 (I) contains the supplementary crystallographic data. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

References

- 1 G. M. Sheldrick, *Acta Crystallogr.*, 2008, **A64**, 112.
- 2 I. J. Bruno, J. C. Cole, P. R. Edgington, M. Kessler, C. F. Macrae, P. McCabe, J. Pearson and R. Taylor, *Acta Crystallogr.*, 2002, **B58**, 389.

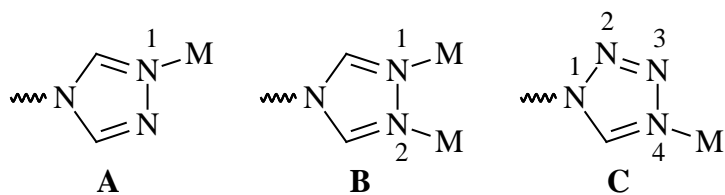


Chart S1

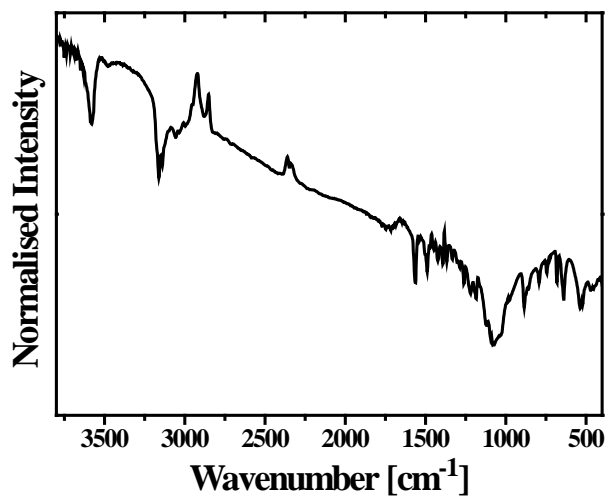


Fig. S1 Normalized FTIR spectrum of I at room temperature.

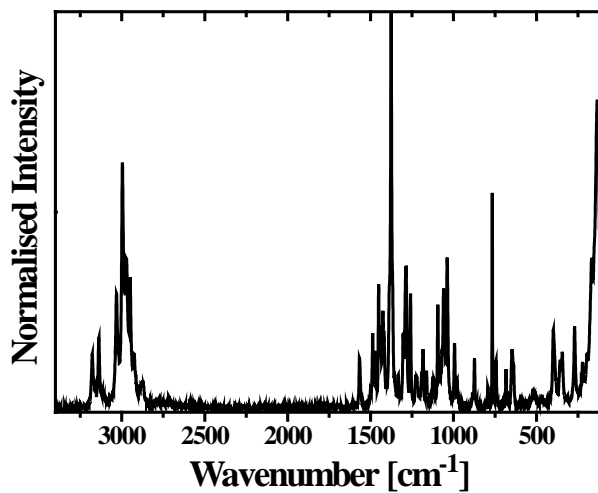


Fig. S2 Normalized Raman spectrum of I at room temperature.

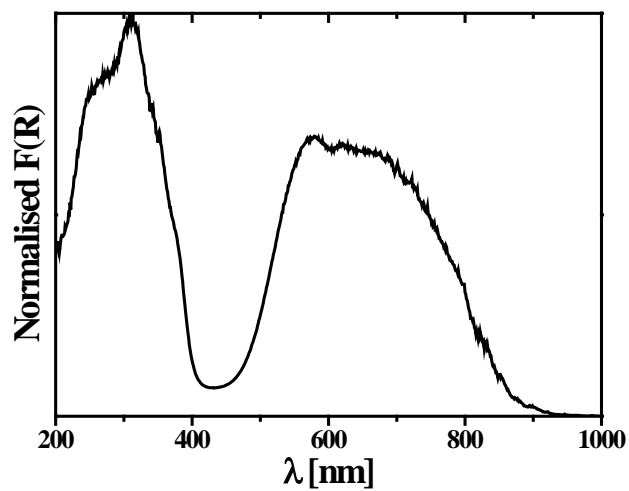


Fig. S3 Normalized Kubelka-Munk spectrum of **I** at room temperature.

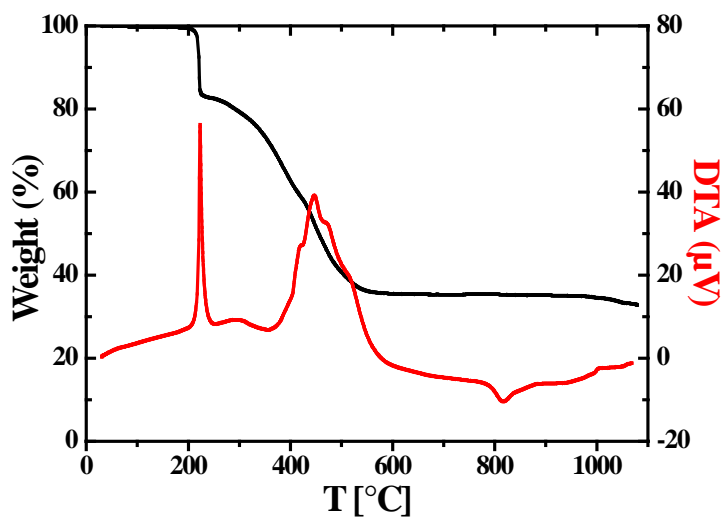


Fig. S4 Simultaneous TG/DTA analyses of **I** performed in a dynamic air atmosphere.

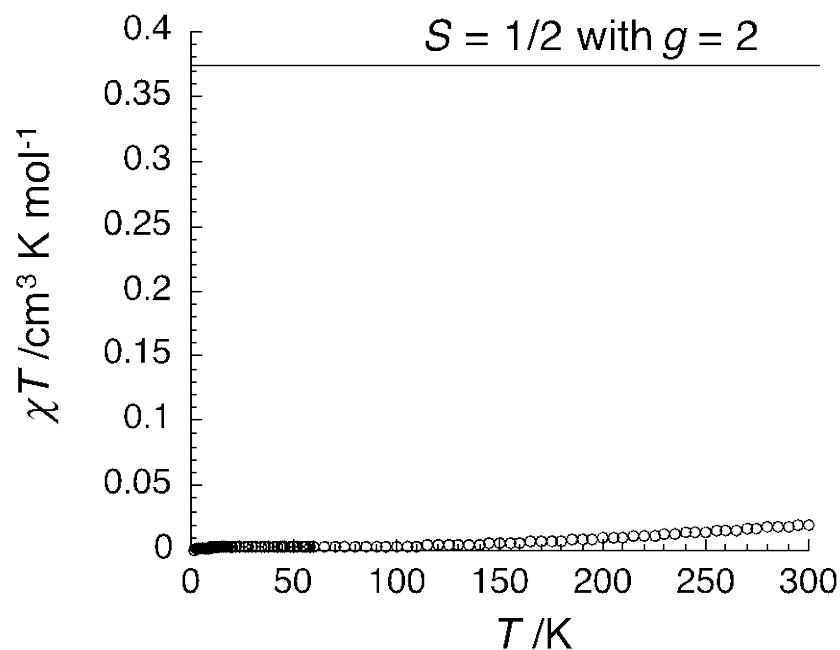


Fig. S5 Temperature dependence of the χT product for a polycrystalline sample of **I** at 1000 Oe. Even at room temperature, the magnetic properties of compound **I** are dominating by strong Cu•••Cu antiferromagnetic coupling through the μ -OH, μ -N1,N2 triazole and μ -N2,N3 tetrazole bridges. The compound is thus globally diamagnetic and the first magnetic excited state of the chain is only very slightly populated at 300 K. Similar magnetic properties have been observed in related materials: E. Aznar, S. Ferrer, J. Borrás, F. Lloret, M. Liu-González, H. Rodríguez-Prieto and S. García-Granda, *Eur. J. Inorg. Chem.*, 2006, 5115–5125 ; J.-H. Zhou, R.-M. Cheng, Y. Song, Y.-Z. Li, Z. Yu, X.-T. Chen, Z.-L. Xue and X.-Z. You, *Inorg. Chem.*, 2005, **44**, 8011–8022 ; T. Otieno, S. J. Rettig, R. C. Thompson and J. Trotter, *Inorg. Chem.*, 1995, **34**, 1718-1725.

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

<i>Bond lengths</i>					
Cu(1)···Cu(1)b	3.2889(12)	N(1)–N(2)b	1.362(7)	N(4)–C(5)	1.347(7)
Cu(1)–N(1)	2.017(4)	N(9)–N(10)	1.339(6)	N(9)–C(13)	1.351(8)
Cu(1)–N(2)	2.003(4)	N(10)–N(11)c	1.316(7)	N(12)–C(13)	1.315(9)
Cu(1)–N(10)	2.580(5)	N(11)–N(12)b	1.385(7)	F(1)–B(1)	1.366(8)
Cu(1)–N(11)	2.645(5)	N(1)–C(5)	1.311(6)	F(2)–B(1)	1.384(8)
Cu(1)–O(1)	1.911(4)	N(2)–C(3)	1.299(6)	F(3)–B(1)	1.407(8)
Cu(1)–O(1)b	1.921(4)	N(4)–C(3)b	1.344(7)	F(4)–B(1)	1.394(9)
<i>Bond angles</i>					
Cu(1)–O(1)–Cu(1)c	118.2(2)	N(2)–Cu(1)–N(11)	95.16(17)	C(13)–N(12)–N(11)c	106.6(5)
Cu(1)–N(1)–C(5)	134.8(4)	N(2)–Cu(1)–O(1)b	90.83(17)	N(10)–N(9)–C(13)	108.6(5)
Cu(1)–N(1)–N(2)b	117.6(3)	N(10)–Cu(1)–N(11)	172.80(16)	N(1)–C(5)–N(4)	109.4(5)
Cu(1)–N(2)–C(3)	133.0(4)	N(10)–Cu(1)–O(1)b	95.18(17)	N(2)–C(3)–N(4)c	109.9(5)
Cu(1)–N(2)–N(1)c	119.2(3)	N(11)–Cu(1)–O(1)b	84.14(17)	N(9)–C(13)–N(12)	108.6(5)
Cu(1)–N(10)–N(9)	131.4(4)	O(1)–Cu(1)–N(1)	93.72(17)	N(9)–N(10)–N(11)c	107.5(4)
Cu(1)–N(10)–N(11)c	116.5(3)	O(1)–Cu(1)–N(2)	87.18(17)	N(10)b–N(11)–N(12)b	108.8(5)
Cu(1)–N(11)–N(10)b	105.8(3)	O(1)–Cu(1)–N(10)	78.97(17)	F(1)–B(1)–F(2)	110.1(6)
Cu(1)–N(11)–N(12)b	145.4(4)	O(1)–Cu(1)–N(11)	101.95(17)	F(1)–B(1)–F(3)	111.1(5)
N(1)–Cu(1)–N(2)	178.74(18)	O(1)–Cu(1)–O(1)b	173.74(18)	F(1)–B(1)–F(4)	109.4(6)
N(1)–Cu(1)–N(10)	89.02(19)	C(3)–N(2)–N(1)c	107.7(4)	F(2)–B(1)–F(3)	109.3(5)
N(1)–Cu(1)–N(11)	83.80(18)	C(5)–N(1)–N(2)b	107.3(4)	F(2)–B(1)–F(4)	108.5(5)
N(1)–Cu(1)–O(1)b	88.36(17)	C(5)–N(4)–C(3)b	105.8(4)	F(3)–B(1)–F(4)	108.5(6)
N(2)–Cu(1)–N(10)	92.01(17)				

b = x - 1/2, -y + 3/2, -z + 1; c = x + 1/2, -y + 3/2, -z + 1