

## Supporting Information

### **A unusual two-dimensional azido-Cu(II) network with benzoate derivative as coligand exhibiting ferromagnetic order and slow magnetic relaxation**

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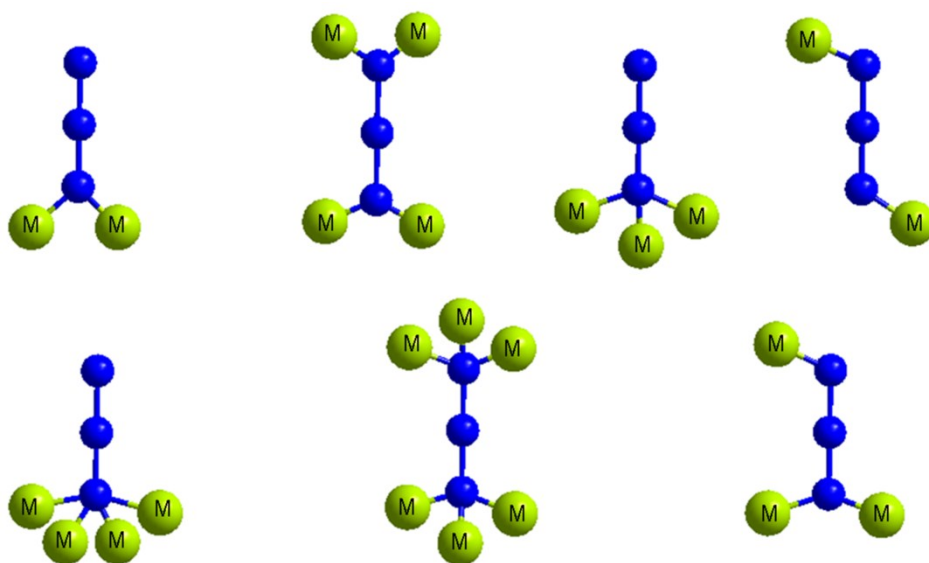
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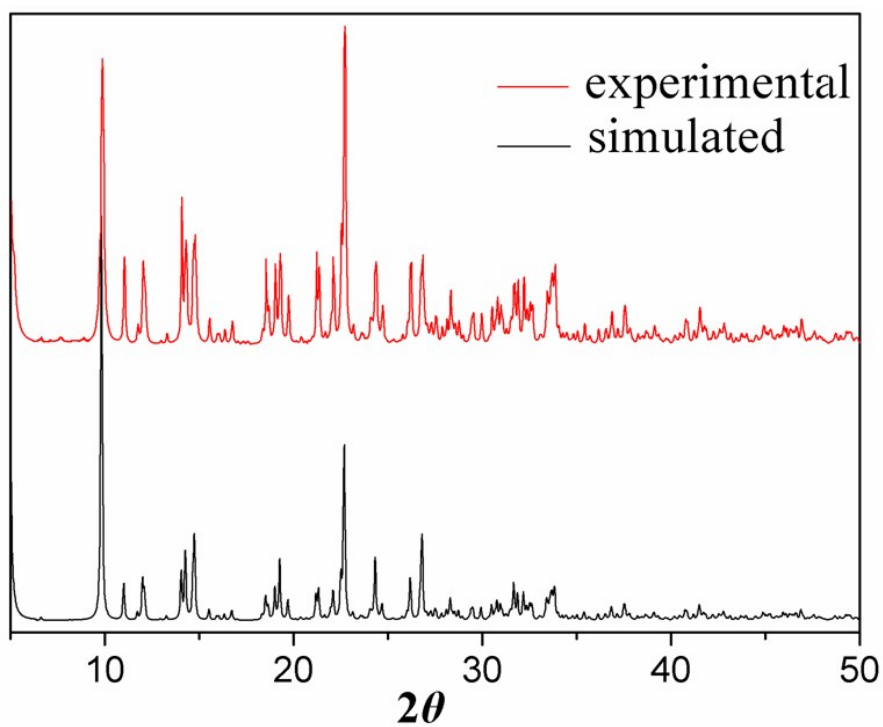
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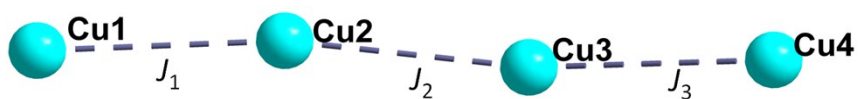
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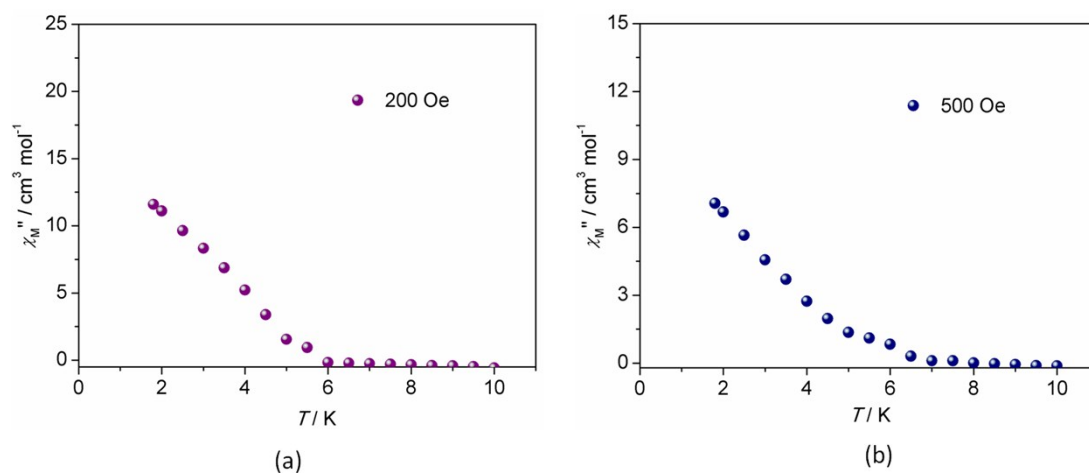
**Scheme S1** Coordination modes of azido.



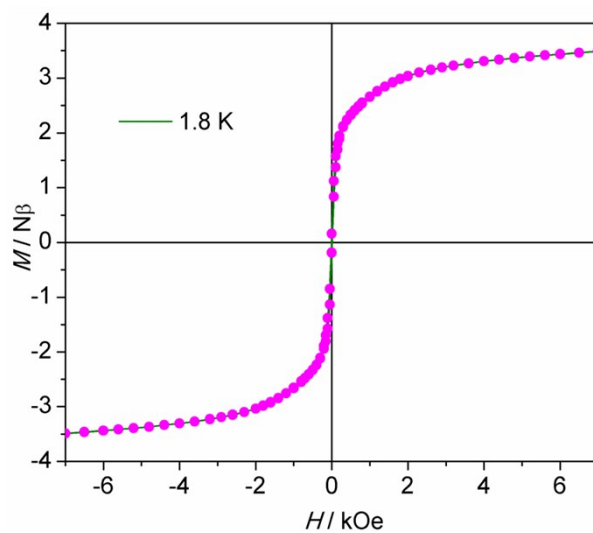
**Fig. S1** PXRD patterns for compound 1.



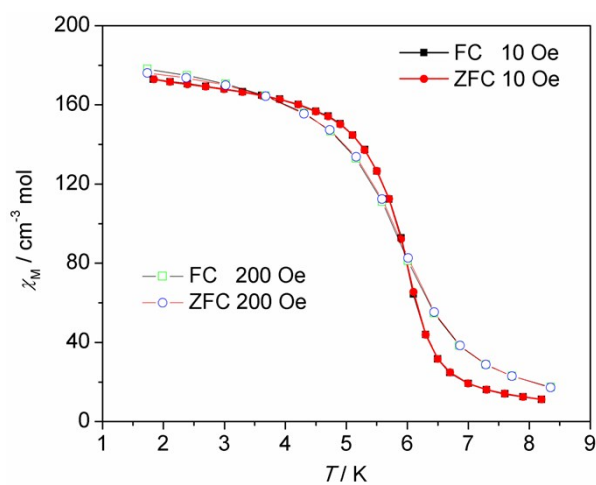
**Fig. S2** The magnetic pathways for the tetranuclear unit.



**Fig. S3**  $\chi''_M$  vs  $T$  plots under the 200 Oe (a) and 500 Oe (b) applied fields for **1**.



**Fig. S4** Hysteresis loop for compound **1** at 1.8 K.



**Fig. S5** FC and ZFC plots at 10 Oe and 200 Oe for compound **1**.

**Table S1** Crystal data and structure refinement details for compounds **1**

<b>1</b>	
Empirical formula	C <sub>32</sub> H <sub>17</sub> Cu <sub>4</sub> F <sub>12</sub> N <sub>9</sub> O <sub>9</sub>
Formula weight	1153.70
Crystal system	triclinic
Space group	<i>P</i> -1
<i>a</i> (Å)	8.1340(4)
<i>b</i> (Å)	13.4990(7)
<i>c</i> (Å)	18.0200(9)
$\alpha$ (°)	91.257(9)
$\beta$ (°)	90.449(9)
$\gamma$ (°)	98.596(9)
<i>V</i> (Å <sup>3</sup> )	1955.7(17)
<i>Z</i>	2
$\mu$ (mm <sup>-1</sup> )	2.269
Unique reflections	7970
Observed reflections	11001
<i>R</i> <sub>int</sub>	0.0611
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0822, <i>wR</i> <sub>2</sub> = 0.1862
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.1912, <i>wR</i> <sub>2</sub> = 0.2490

**Table S2** Selected bond lengths (Å) and bond angles (°) for **1**

<b>1</b>					
Cu(1)-O(5)	1.909(7)	Cu(3)-O(4)	1.899(8)	O(5)-Cu(1)-O(9)	94.9(3)
Cu(1)-O(1)	1.915(7)	Cu(3)-O(7)	1.900(8)	O(3)-Cu(2)-O(9)	88.0(3)
Cu(1)-O(9)	1.923(7)	Cu(3)-N(7)	1.938(9)	Cu(2)-O(9)-Cu(4)#1	106.5(3)
Cu(1)-N(4)	1.959(8)	Cu(3)-N(1)	1.964(9)	Cu(1)-O(9)-Cu(4)#1	117.4(3)
Cu(2)-O(3)	1.906(7)	Cu(4)-O(9)#1	2.364(7)	Cu(2)-O(9)-Cu(1)	120.7(3)
Cu(2)-O(9)	1.916(7)	Cu(4)#2-N(4)	2.041(9)	Cu(3)-N(7)-Cu(4)	121.0(5)
Cu(2)-O(6)	1.947(8)	Cu(4)-O(2)#3	1.937(7)	Cu(2)-N(1)-Cu(3)	116.5(5)
Cu(2)-N(1)	1.958(9)	Cu(4)-N(7)	2.021(9)	Cu(1)-N(4)-Cu(4)#2	122.5(4)
#1 -x+1,-y+1,-z+1		#2 x,y-1,z		#3 x,y+1,z	

**Table S3** Remnant magnetizations and coercive fields for related Cu(II) compounds

Compounds	Remnant magnetization	Coercive field	Refs.
[C(NH <sub>2</sub> ) <sub>3</sub> ][Cu(HCOO) <sub>3</sub> ]	—	5 Oe	Ref. 1
[Cu(p-mpa)(N <sub>3</sub> )]	—	13 Oe	Ref. 2
[Cu(trz)(N <sub>3</sub> )]	0.0028 Nβ	200 Oe	Ref. 3
[Cu(2-na)(N <sub>3</sub> )]	0.005 Nβ	12 Oe	Ref. 4
[Cu(2-na)(N <sub>3</sub> )]	0.047 Nβ	10 Oe	Ref. 4
[Cu(2-na)(N <sub>3</sub> )(C <sub>2</sub> H <sub>5</sub> OH)]	0.002 Nβ	37 Oe	Ref. 4
[Cu <sub>4</sub> (4-tfmba) <sub>4</sub> (N <sub>3</sub> ) <sub>3</sub> (OH)]	0.157 Nβ	11 Oe	This work

## 1. Physical measurements

Elemental analysis was performed on a Perkin-Elmer 2400 CHN elemental analyzer. The FT-IR spectra were recorded in the range 400-4000 cm<sup>-1</sup> using KBr pellets on an EQUINOX55 FT/IR spectrophotometer. The phase purity of the bulk or polycrystalline samples was verified by powder X-ray diffraction (PXRD) measurements performed on a Rigaku RU200 diffractometer at 60 kV, 300 mA and CuKα radiation ( $\lambda = 1.5406 \text{ \AA}$ ), with a scan speed of 5° min<sup>-1</sup> and a step size of 0.02° in 2θ. Magnetic measurements were obtained on poly-crystalline samples (17.44 mg for **1**) using a Quantum Design MPMS-XL7 SQUID magnetometer at temperatures between 1.8 and 300 K for direct current (dc) applied fields with an applied field of 1 kOe (restrained in eicosane to prevent torqueing at high fields). Magnetization vs field (M/H) variations were measured between 7 and -7 kOe at different temperatures. Alternating current (ac) susceptibility measurements for compound **1** were performed using an oscillating ac field of 3.5 Oe with the frequency at 1, 10, 100 and 1000 Hz. The experimental susceptibilities were corrected for the diamagnetism of the constituent atoms (Pascal's tables).

## 2. Synthesis

All reagents and solvents employed were commercially available and used as received without further purification.

**CAUTION!** Although we did not encounter this in our experiments, azido-based compounds of metal ions are potentially explosive. Only a small amount of the materials should be prepared, and

they should be handled with care.

**[Cu<sub>4</sub>(4-tfmba)<sub>4</sub>(N<sub>3</sub>)<sub>3</sub>(OH)] (1):** A mixture of Cu(NO<sub>3</sub>)<sub>2</sub> · 3H<sub>2</sub>O (0.072 g, 0.3 mmol), 4-Htfmba (0.076 g, 0.4 mmol) and NaN<sub>3</sub> (0.013 g, 0.2 mmol) in water (8 mL) was heated in a stainless steel reactor with a Teflon liner (15 mL) at 110 °C for 3 days, followed by slow cooling (5 °C·h<sup>-1</sup>) to room temperature. Dark green flake crystals of **1** were obtained and collected. (Yield 68%, based on Cu<sup>2+</sup>). Anal. Calcd. For Cu<sub>4</sub>C<sub>32</sub>H<sub>17</sub>F<sub>12</sub>N<sub>9</sub>O<sub>9</sub> (1152.70): C, 33.31; H, 1.47; N, 10.93%. Found: C, 33.28; H, 1.46; N, 10.90%. Main IR (KBr, cm<sup>-1</sup>): 2106 (s), 1632 (s), 1533 (s), 1428 (m), 1333 (s), 1164 (w), 1136 (m), 784 (w), 709 (w).

### 3. Crystallographic data collection and refinement

Single-crystal diffraction data for **1** was collected on a Rigaku SCX mini CCD diffractometer using graphite-mono-chromatized MoK $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at room temperature. The data integration and reduction were processed with SAINT software. Absorption correction based on multi-scan was performed using the SADABS program.<sup>5a</sup> The structures were solved by the direct method using SHELXTL and refined by a full-matrix least-squares method on  $F^2$  with the SHELXL-97 program.<sup>5b</sup> All non-hydrogen atoms were refined anisotropically. A summary of the crystallographic data, data collection, and refinement parameters are provided in Table S1, selected bond lengths and angles are listed in Table S2.

### 4. References

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