

## Supporting Information

The first example of rhombic dodecahedral CuBr clusters in a novel mixed-valence  
Cu(I,II)-benzimidazole complex

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### Experimental Section

**Materials and Apparatus.** All chemicals were reagent grade and commercially available, and were used without further purification. The infrared spectra were recorded as KBr pellets on a Shimadzu 8300 FT-IR spectrometer. Samples for elemental analysis were dried under a vacuum, and the analysis was performed with a CHNO-Rapid instrument. <sup>1</sup>H NMR spectra were recorded with a BRUKER 500 DRX spectrometer. The electronic spectra were recorded with a Hewlett-Packard HP-8453 Chemstation spectrophotometer in dimethylformamide (DMF) solutions. The EPR spectrum was obtained in the solid state at 298 K using a Bruker-ER 200-D-SRC spectrometer. The thermogravimetric analyses (TGAs) were performed on a TA2000/2960 thermogravimetric analyzer in the 298-1073 K temperature range at a heating rate of 10 K/min, under an N<sub>2</sub> gas flow of 20 L/min. A CHI 660C electrochemical workstation (Shanghai CH Instrument Company, China) was used for all of the electrochemical measurements such as cycle voltammetry (CV). A glassy carbon electrode (GCE) of 3-mm diameter was used as

working electrode; a platinum wire and a saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. These experiments were conducted at RT in a  $1.0 \times 10^{-4}$  M DMSO solution with 0.1 M sodium perchlorate as a supporting electrolyte. The solutions were deoxygenated by bubbling with nitrogen. The X-ray powder diffraction (XPRD) patterns of the samples were obtained on a BRUKER D8 ADVANCE X-ray diffractometer (German) using Cu-K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ).

### Synthesis

**Ligand 1,2-di(1H-benzoimidazol-2-yl)ethane-1,2-diol (TDB).** Ref<sup>35</sup>. 5 mL glycol was added to a mixture of tartaric acid (0.4994 g, 3.33 mmol) and o-phenylenediamine dihydrochloride (1.2059 g, 6.66 mmol). The mixture was irradiated for 4 minutes intermittently with WP700 LG microwave oven (output power 350W). When it was cooled to room temperature, 10 ml distilled water was added in and neutralized with an aqueous solution of NH<sub>3</sub>, then the free 1,2-di(1H-benzoimidazol-2-yl)ethane-1,2-diol was obtained. The yellowish solid product was collected by filtration, recrystallized twice from 2:1 EtOH:H<sub>2</sub>O. A white solid was collected and washed with Et<sub>2</sub>O and dried *in vacuo* (60% yield). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>):  $\delta$ =5.99 (d, 2H; alcohol-H); 7.50 (s, 4H benzimidazole-H); 7.13 (q, 4H, benzimidazole-H); 12.34 (s, 2H, benzimidazole-H); 5.33 (d, 2H; methine -H). IR (KBr pellet)  $\nu/\text{cm}^{-1}$ : 3438m, 3182br, 1622w, 1456s, 1142s, 1311w, 1275s, 1111w, 1076m, 846w, 741s.

**Complex I [(C<sub>7</sub>H<sub>5</sub>N<sub>2</sub>)(Cu<sup>I</sup>Cu<sup>II</sup>Br<sub>2</sub>)<sub>n</sub>].** A mixture of CuBr<sub>2</sub> (0.447 g, 2 mmol), TDB (0.588 g, 2 mmol) and distilled water (18 ml, 1mol) in a molar ratio of 1:1:500 was mixed in a 25 ml stainless-steel reactor with a Teflon liner and heated from room temperature (RT) to 448 K in 0.5 h. The temperature was kept constant at 448 K for 92 h, then cooled down naturally to RT. Light yellow gladiate crystals were collected in 15% yield. Elemental Analysis for C<sub>7</sub>H<sub>5</sub>N<sub>2</sub>Br<sub>2</sub>Cu<sub>2</sub>: calc. C 20.81; H 1.25; N 6.93; found: C 20.83; H 1.31; N 6.99. IR (KBr)  $\nu/\text{cm}^{-1}$ : 1618 w, 1498 m, 1460 m, 1437w, 1400s, 1364w, 1300 m, 1248m, 1125s, 1030w, 737s.

**X-ray Crystallography.** The data of the complex was collected on a Bruker Smart Apex II diffractometer equipped with 1K CCD instrument by using a graphite monochromator utilizing Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at RT. Cell parameters were determined using SMART software<sup>1</sup>. Data reduction and corrections were performed using SAINTPlus. Absorption corrections were made via SADABS<sup>2</sup>. The structures were solved by direct methods with the program SHELXS-97 and refined by full-matrix least-squares methods on all  $F^2$  data with SHELXL-97<sup>3</sup>. Non-H atoms were refined anisotropically. Hydrogen atoms attached C were added theoretically and treated as riding on the concerned atoms. The final cycle of full-matrix least-squares refinement was based on observed reflections and variable parameters. Crystallographic data of complex are shown in Table S1. Selected bond lengths and bond angles were given in Table S2. The CIF files deposited in the Cambridge Crystallographic Data Center (CCDC reference number 810807) can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html); or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, U.K. [fax: (t44)-1223/336-033; e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)].

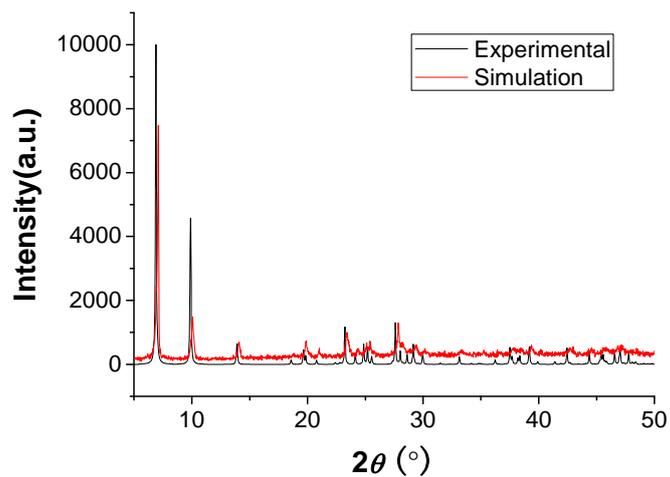
**Table S1** Crystallographic data for complexes **I**

CCDC numbers	810807	Empirical formula	[C <sub>7</sub> H <sub>5</sub> Br <sub>2</sub> Cu <sup>I</sup> Cu <sup>II</sup> N <sub>2</sub> ]
Formula weight	404.03	Temperature (K)	298(2)
Crystal system	Monoclinic	Space group	C <sub>2/m</sub>
a (Å)	25.745(6)	b (Å)	9.538(2)
c (Å)	3.9843(10)	β(°)	95.716(4)
V (Å <sup>3</sup> )	973.6(4)	Crystal size/mm	0.20×0.10×0.05
Z	4	Dcalc (g cm <sup>-3</sup> )	2.756
μ/mm <sup>-1</sup>	12.524	F(000)	756
Theta range	1.59 to 25.0	Goodness-of-fit on F <sup>2</sup>	1.127
Limiting indices	-30<h<22	Reflections collected	2138
	-11<k<10	Reflections Unique	897
	-4<l<4	R <sub>int</sub>	0.0266
Final R indices[I > 2σ(I)]	R1 = 0.057 ωR2 = 0.1604	R indices(all data)	R1 = 0.081 ωR2 = 0.1901
Largest diff. Peak, hole(e Å <sup>-3</sup> )	0.862 and -0.981		

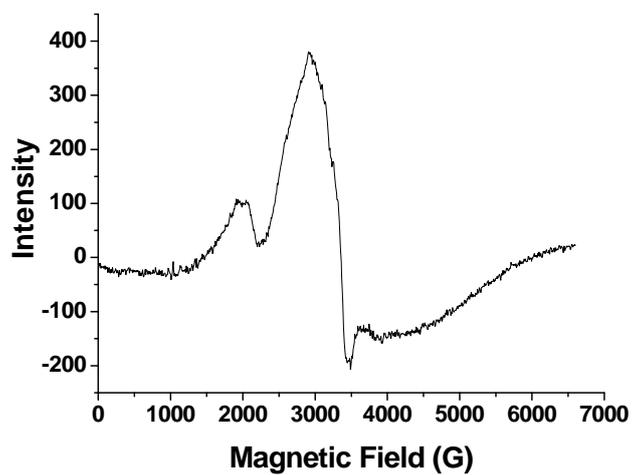
**Table S2** Selected bond distances (Å) and angles (°) for complex **I**

Br1-Cu2	2.5096(19)	Br1-Cu1 <sup>ii</sup>	2.572(4)
Br1-Cu1	2.764(5)	Br2-Cu1 <sup>iii</sup>	2.372(4)
Br2-Cu2 <sup>vi</sup>	2.464(3)	Br2-Cu2	2.525(3)
Cu2-Br2 <sup>ii</sup>	2.464(3)	Cu2...Cu1 <sup>iv</sup>	2.841(5)
Cu2...Cu1 <sup>v</sup>	2.881(5)	Cu2...Cu2 <sup>i</sup>	3.000(5)
Cu2-Br1-Cu2 <sup>i</sup>	73.40(10)	Cu2-Br1-Cu1 <sup>ii</sup>	111.78(10)
Cu2 <sup>i</sup> -Br1-Cu1 <sup>ii</sup>	69.04(11)	Cu2-Br1-Cu1 <sup>iii</sup>	69.04(11)
Cu2 <sup>i</sup> -Br1-Cu1 <sup>iii</sup>	111.78(10)	Cu1 <sup>ii</sup> -Br1-Cu1 <sup>iii</sup>	79.05(16)
Cu2-Br1-Cu1	115.81(10)	Cu2 <sup>i</sup> -Br1-Cu1	64.98(9)
Cu1 <sup>ii</sup> -Br1-Cu1	96.54(15)	Cu1 <sup>iii</sup> -Br1-Cu1	83.46(15)
Cu2-Br1-Cu1 <sup>iv</sup>	64.98(9)	Cu2 <sup>i</sup> -Br1-Cu1 <sup>iv</sup>	115.81(10)
Cu1 <sup>ii</sup> -Br1-Cu1 <sup>iv</sup>	83.46(15)	Cu1 <sup>iii</sup> -Br1-Cu1 <sup>iv</sup>	96.54(15)
Cu1-Br1-Cu1 <sup>iv</sup>	179.11(15)	Cu1 <sup>iii</sup> -Br2-Cu1 <sup>v</sup>	118.1(2)
Cu1 <sup>iii</sup> -Br2-Cu2 <sup>vi</sup>	71.92(12)	Cu1 <sup>v</sup> -Br2-Cu2 <sup>vi</sup>	71.92(12)
Cu1 <sup>iii</sup> -Br2-Cu2	72.00(10)	Cu1 <sup>v</sup> -Br2-Cu2	72.00(10)
Cu2 <sup>vi</sup> -Br2-Cu2	105.99(11)	Br2 <sup>ii</sup> -Cu2-Br1	114.31(7)
Br2 <sup>ii</sup> -Cu2-Br1 <sup>i</sup>	114.31(7)	Br1-Cu2-Br1 <sup>i</sup>	106.60(10)
Br2 <sup>ii</sup> -Cu2-Br2	105.99(10)	Br1-Cu2-Br2	107.65(7)
Br1 <sup>i</sup> -Cu2-Br2	107.65(7)		

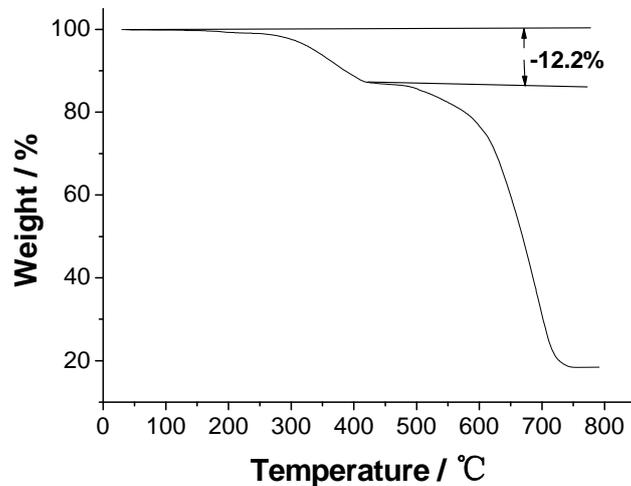
i: -x+2,-y+2,-z+1; ii: x,y,z+1; iii: -x+2,y,-z; iv: -x+2,y,-z+1; v: -x+2,-y+2,-z; vi: x,y,z-1



**Fig. S1** The PXRD patterns of experimental(black) and simulation(red) in RT for complex *I*.



**Fig. S2** The EPR spectrum of complex *I* in the solid state in RT



**Fig. S3** TG spectrum of complex *I*

**References:**

- 1 SMART (Version 5.0) and SAINT (Version 6.02); Bruker AXS Inc.: Madison, Wisconsin, USA, 2000.
- 2 G. M. Sheldrick, SADABS; University of Gottingen: Germany, 2000.
- 3 G. M. Sheldrick, SHELXS97 and SHELXL97; University of Gottingen: Germany, 1997.