Supporting Information

Aggregation of metallocycles {Cu_8} and {Cu_{20}} by [Cu(bp)] units (H_2bp = bis(2-hydroxybenzyl)amine): structures and magnetic properties

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Experimental Section

Materials

Ligand Bis(2-hydroxybenzyl)amine (H_2bp) was synthesized according to the literature procedure.[11] Other reagents were purchased from commercial sources and used without further purification.

Physical measurements

IR spectra were recorded as KBr pellets on a Perkin-Elmer FT-IR spectrometer in the range 4000−450 cm^{-1}. Elemental analyses were performed with a Carlo ERBA 1106 analyzer. The variable-temperature magnetic susceptibilities were measured on a Quantum Design MPMS-7 SQUID magnetometer in a field of 0.1T.

Synthesis of **1** and **2**.

Safety Note! Caution! Perchlorate salts of metal complexes are potentially explosive and should be handled only in small quantities with sufficient care.

solid H_2bp (0.0115g, 0.05 mmol) was added to a stirred solution of $Cu(ClO_4)_2{\cdot}6H_2O$ (0.0370g, 0.1 mmol) or $Cu(Ac)_2{\cdot}H_2O$ (0.0100g, 0.05 mmol) in CH_2Cl_2/CH_3OH (5ml, 2:3 v/v). After stirring for 6 h at room temperature, the resulting solution was filtered and the filtrate was diffused by diethyl ether through vapour phase. A few days later, X-ray quality red block crystals of **1** and green needle crystals of **2** were afforded. The crystals were picked by hand, washed with EtOH and dried under vacuum at room temperature.

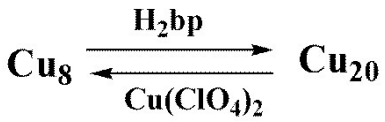
Complex **1**: Elemental analysis *calcd* (%) for $C_{56}H_{64}N_4O_{32}Cl_4Cu_8$: C34.40, H3.30, N2.87; found: C34.65, H3.59, N2.72; IR(KBr pellet): 3442, 3240, 3067, 2928, 1600, 1486, 1277, 1117, 1087, 939, 870, 758, 627, 478 cm^{-1}.

Complex **2**: Elemental analysis *calcd* (%) for $C_{280}H_{260}N_{20}O_{40}Cu_{20}{\cdot}52H_2O$: C 49.80, H 5.43, N4.15; found: C 50.21, H 4.80, N 3.88; IR(KBr pellet): 3427, 3242, 2929, 2866, 2348, 1596, 1483, 1454, 1270, 917, 865, 760, 622 cm^{-1}.

Interconversion of **1** and **2**

From Cu_8 to Cu_{20}: H_2bp (0.0183 g, 0.08 mmoL) was added to a solution of Cu_8 (0.0391 g, 0.02 mmol) in methanol (10 ml). The resulting solution was stirred for 6h, and then filtered. The green filtrate was diffused by diethyl ether through vapor phase. Six days later, X-ray quality green needle crystals were obtained. By the unit cell check, these green crystals were confirmed as complex Cu_{20}.

From Cu_{20} to Cu_8: Solid $Cu(ClO_4)_2 \cdot 6H_2O$ (0.0741 g, 0.2 mmoL) was added to a solution of Cu_{20} (0.0391 g, 0.01 mmol) in methanol (10 ml). The resulting solution was stirred for 6h, and then filtered. The orange-yellow filtrate was diffused by diethyl ether through vapor phase. One day later, X-ray quality red crystals were obtained. By the unit cell check, these red crystals were confirmed as complex Cu_8.



Scheme S1

Crystal Structure Determination

Crystal data and experimental details for **1** and **2** are given in Table S1. X-ray Diffraction data of complex **1** were collected on Agilent Supernova diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.7107 Å) at 298 K, and of complex **2** were obtained at 1W1A, Beijing Synchrotron Radiation Facility (λ = 0.75 Å) at 107 K. All calculations were performed with SHELX-97 crystallographic software package. The structures were solved by the standard direct method and refined in the anisotropic approximation. Hydrogen atoms were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors. For compound **2**, only a part of solvent molecules were determined by the SHELX-97 refinement, containing 14 H_2O, 4 CH_3OH and 2 CH_2Cl_2 molecules per formula unit. There are a number of seriously disordered solvent molecules with low occupancy, which could not be adequately modeled. The final refinements have been carried out with SQUEEZE data. The residual electron density was distributed to 2297 electrons per formula unit assigned to solvent molecules (3378 $Å^{-3}$) which can't be modeled by refinement.

Table S1 Crystal data and structure refinement for **1** and **2**

	1	**2**
Empirical formula	$C_{56}H_{64}N_4O_{32}Cu_8Cl_4$	$C_{286}H_{308}N_{20}O_{58}Cu_{20}Cl_4$
Formula weight	1955.23	6366.12
Crystal system	tetragonal	monoclinic
Space group	$P4_12_12$	C2/c
a (Å)	26.0104(6) A	43.225(9)
b (Å)	26.0104(6)	18.130(4)
c (Å)	14.1858(8)	44.879(9)
α (°)	90	90
β (°)	90	101.13(3)
γ (°)	90	90
Volume ($Å^3$)	9597.3(6)	34509(13)
Z	4	4
ρ_{calc} (g/cm^{-3})	1.353	1.225
$\mu(mm^{-1})$	1.915	1.229
θ range for data collection	2.98 to 24.99	1.59 to 22.67
Reflections collected	24740	39947
Independent reflections	8437	21613
Data/restraints/parameters	8437 / 0 / 470	21613 / 0 / 1749
Goodness of fit (GOF)	0.971	1.052
Final R indices [$I > 2\sigma(I)$]	0.0997	0.0779
R indices (all data)	0.1893	0.1044
Largest diff. peak / hole / $eÅ^{-3}$	1.135/-0.499	1.17/ -0.996

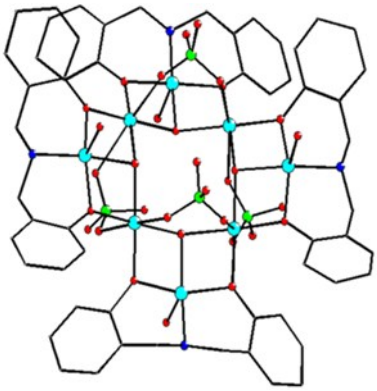


Fig. S1. Molecular structure of **1**. Green, Cl atom; cyan, Cu atom; red, O atom; blue, N atom.

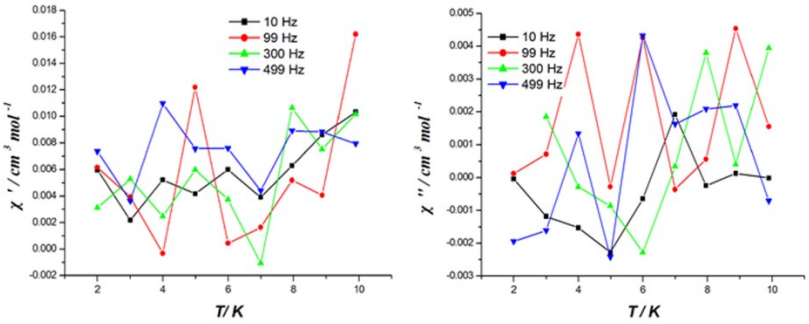


Fig. S2 In phase (χ′) and out-of-phase (χ″) components for **1** with increasing frequencies.

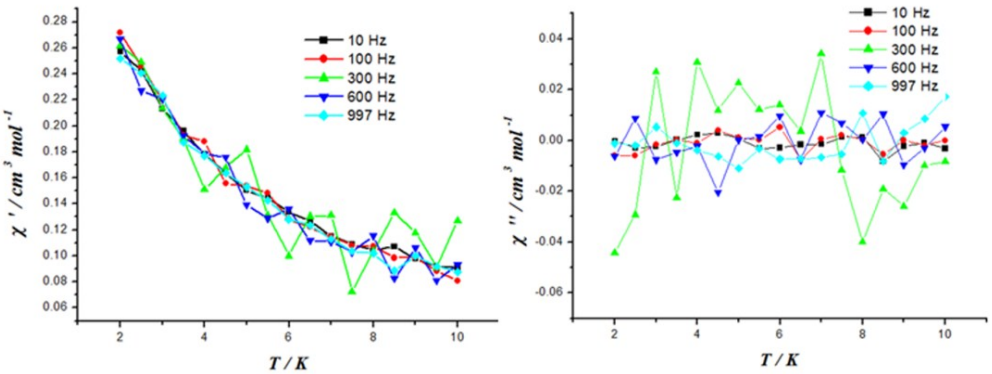


Fig. S3 In phase (χ′) and out-of-phase (χ″) components for **2** with increasing frequencies

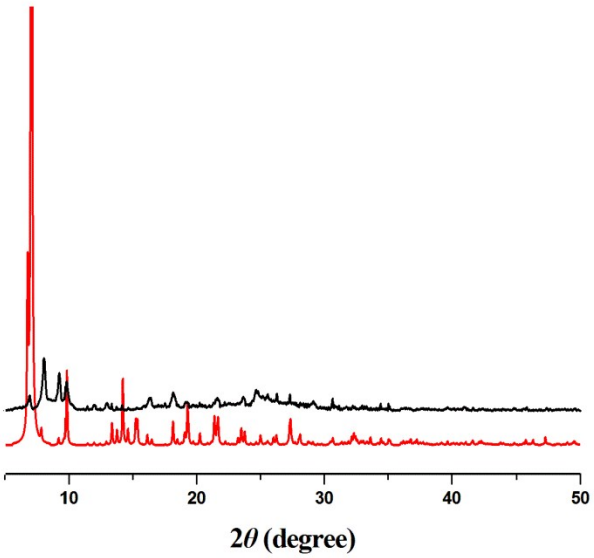


Fig. S4 the XRD pattern of complex **1**, red line is the simulation based on single crystal diffraction data.

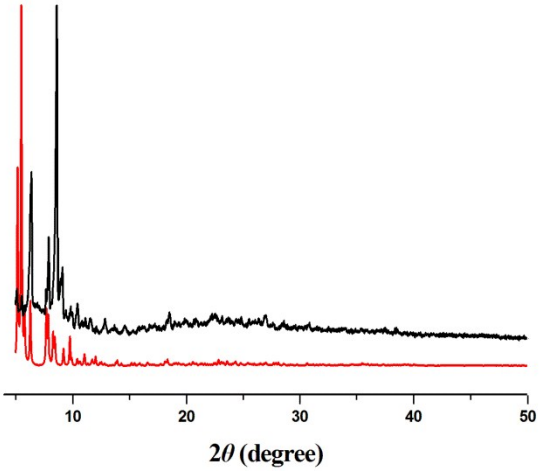


Fig. S5 the XRD pattern of complex **2**, red line is the simulation based on single crystal diffraction data.