Temperature-Induced Structural Transformations Accompanied by Changes in Magnetic Properties of Two Copper Coordination Polymers

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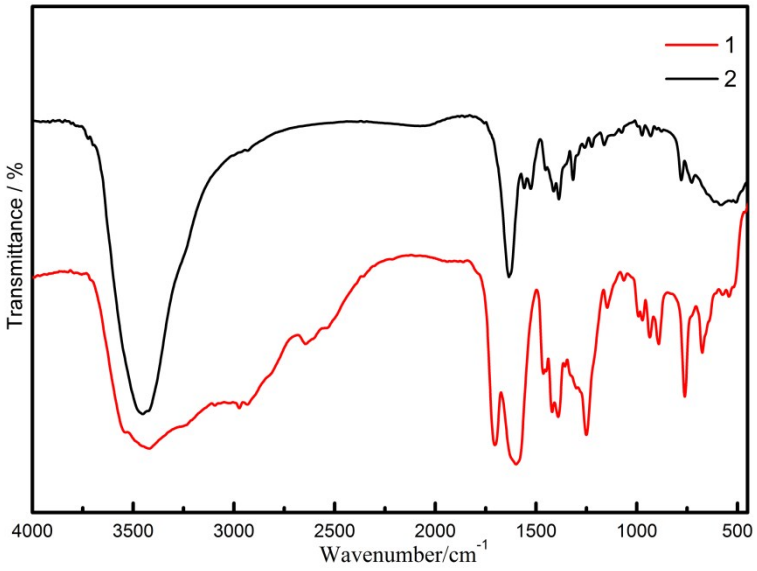

Fig. S1 IR spectra of **1** and **2**.

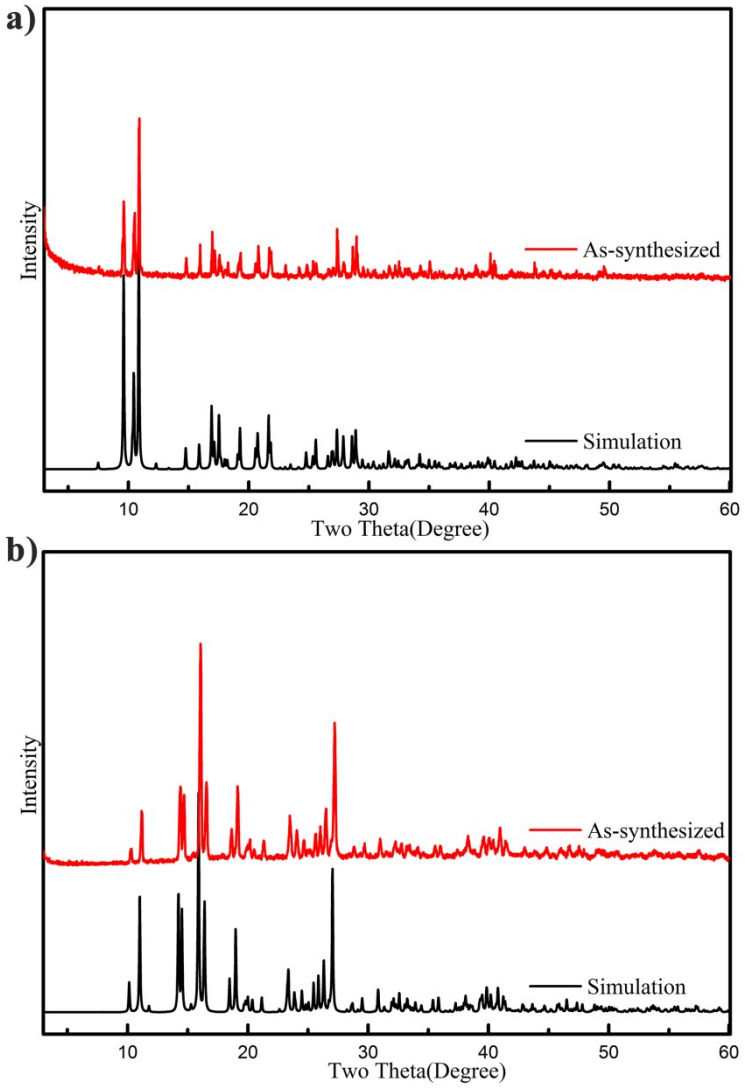

Fig. S2 Comparison of the simulated and experimental PXRD patterns: **1** (a) and **2** (b), respectively.

Table S1. Distances (Å) and angles (º) of hydrogen bonds for **1**.

D-H	d(D-H)	d(H···A)	<DHA	d(D···A)	A
O1-H1	0.820	1.887	167.17	2.692	O12 [x-1/2, y+1/2, z]
O3-H3	0.820	2.108	142.02	2.800	O13A [x, -y+1, z-1/2]
O3-H3	0.820	1.848	147.70	2.579	O14B [-x+1, -y+1, -z+1]
O9-H9A	0.871	1.747	169.23	2.608	O10 [-x+3/2, -y+1/2, -z+1]
O9-H9B	0.873	1.966	164.40	2.817	O11 [-x+1, -y, -z+1]
O10-H10C	0.850	1.892	165.11	2.723	O5
O10-H10D	0.856	1.966	155.88	2.769	O2 [-x+1, -y+1, -z+1]
O12-H12C	0.853	2.524	149.93	3.290	O9 [x, -y, z-1/2]
O12-H12C	0.853	2.475	117.17	2.963	O15 [-x+1, -y, -z+1]
O12-H12D	0.850	2.101	153.13	2.884	O7
O15-H15A	0.850	2.392	125.05	2.963	O12 [-x+1, -y, -z+1]
O15-H15A	0.850	2.502	117.47	2.991	O14B
O15-H15B	0.850	2.442	133.89	3.092	O8
O16-H16A	0.849	2.085	147.11	2.836	O11
O16-H16B	0.850	2.149	166.19	2.981	O14B
C10-H10A	0.970	2.361	157.89	3.280	O10 [-x+3/2, -y+1/2, -z+1]

Table S2. Distances (Å) and angles (º) of hydrogen bonds for **2**.

D-H	d(D-H)	d(H···A)	<DHA	d(D···A)	A
O9-H9A	0.872	2.5	121.51	3.048	O7 [-x+1, -y+1, -z+1]
O9-H9A	0.872	2.587	113.06	3.037	O11 [-x+1, -y+1, -z+1]
O9-H9B	0.871	1.963	168.03	2.821	O5 [x, y+1, z]
O10-H10A	0.851	1.899	140.31	2.611	O4 [-x+1, -y+1, -z]
O10-H10B	0.85	2.248	118.13	2.753	O2 [x-1, y, z]
O11-H11A	0.871	1.894	148.79	2.678	O5 [-x, -y, -z+1]
O11-H11B	0.869	1.794	168.19	2.651	O4 [x-1, y, z+1]
C2-H2B	0.97	2.506	138.38	3.295	O2 [-x+2, -y+1, -z+1]

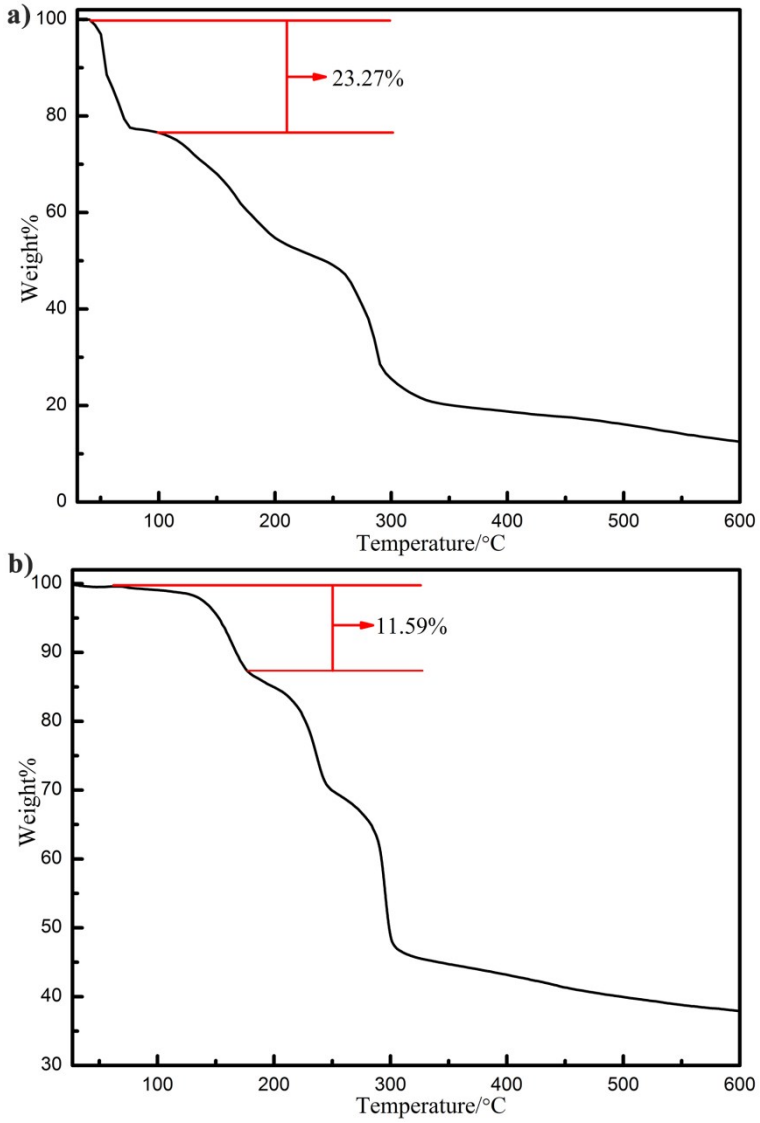

Fig. S3 The TG curves of **1** (a) and **2** (b) on crystalline samples in a N_2 atmosphere in the range of 25–600 ºC.

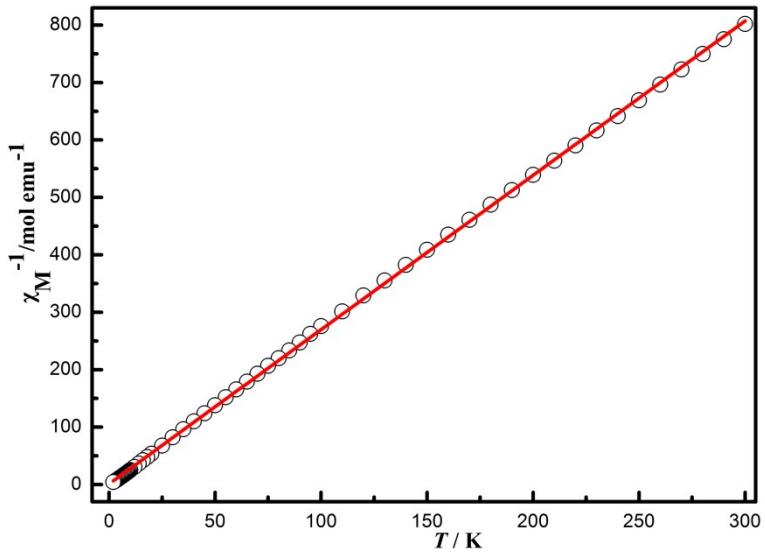

Fig. S4 Temperature dependence of the magnetic susceptibility in the form of χ_M^{-1} *vs T* for **1** at an applied field of 1000 Oe between 1.8 and 300 K. The red solid line was generated from the best fitting by the Curie-Weiss expression.

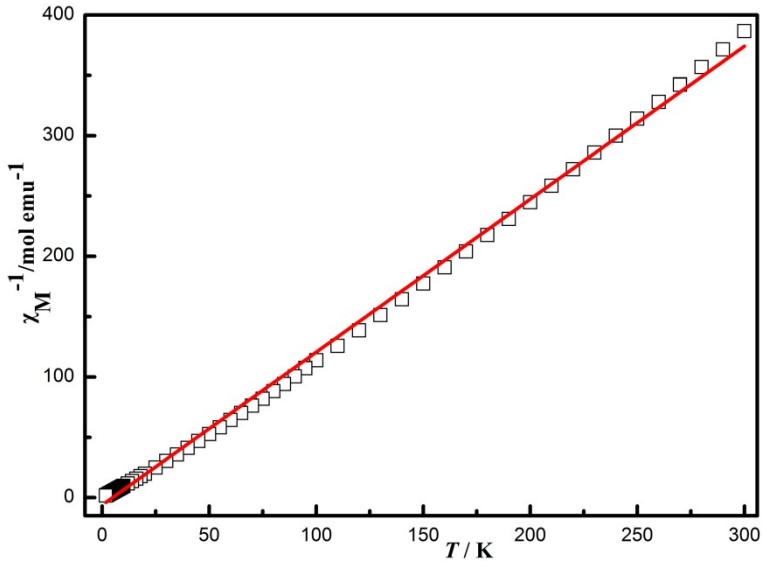

Fig. S5 Temperature dependence of the magnetic susceptibility in the form of χ_M^{-1} *vs T* for **1** at an applied field of 1000 Oe between 1.8 and 300 K. The red solid line was generated from the best fitting by the Curie-Weiss expression.

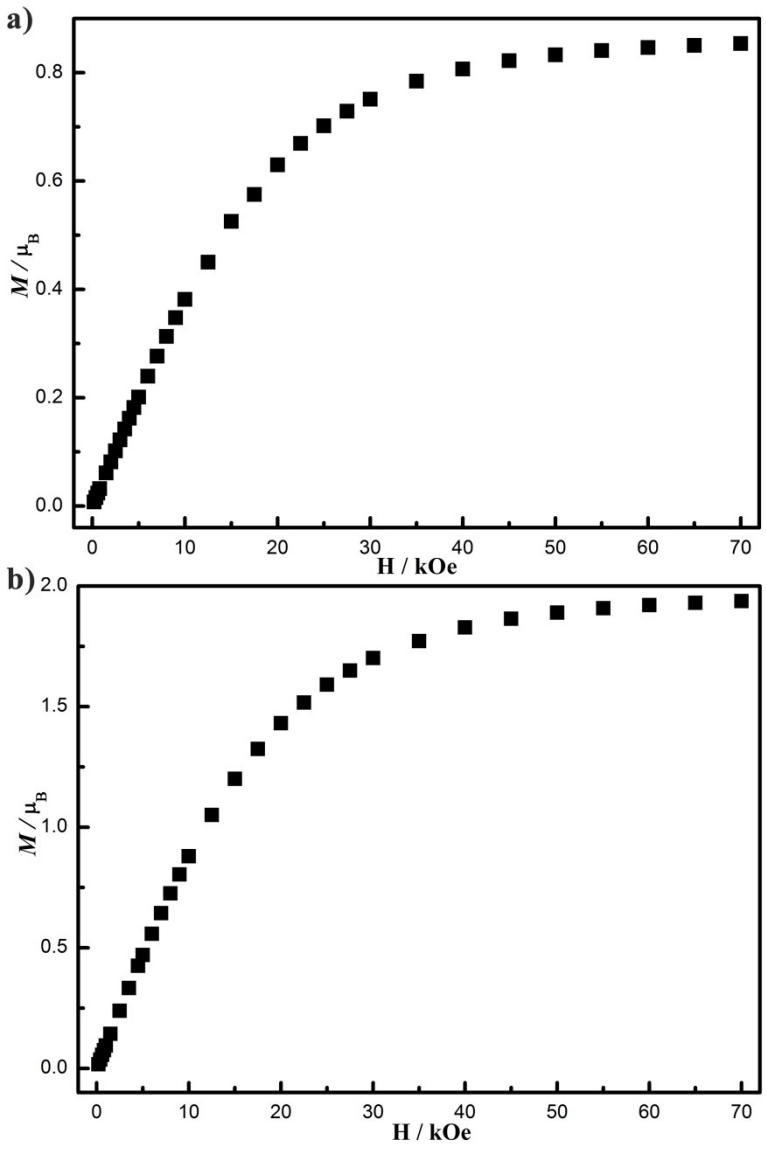

Fig. S6 The field dependence of magnetization measurement for CPs **1** (a) and **2** (b) at 2 K and 0 - 70 kOe, respectively.

Table S3. Structural and magnetic data for selected dinuclear copper(II)-carboxylato compounds.

Compound[a]	Cu-O (Å) Equatorial	Axial	Cu···Cu (Å)	Cu-O-Cu (°)	J_{exp} (cm^{-1})
$[Cu_2(phen)_2(\mu\text{-}OH)(\mu\text{-}OH_2)(\mu\text{-}O_2CCH_3)](BF_4)_2\cdot(H_2O)_{0.5}$[S1]	1.925–2.008	2.374, 2.390	3.002	102.1	120.8
$[Cu_2(bpy)_2(\mu\text{-}OH)(\mu\text{-}O_2CCH_3)(\mu\text{-}Cl)]Cl\cdot(H_2O)_{0.5}$[S1]	1.936–2.029	2.632, 2.657	3.040	103.3	145.3
$[Cu_2(bpy)_2(\mu\text{-}OH)(\mu\text{-}OH_2)(\mu\text{-}O_2CCH_3)](ClO_4)_2$[S2]	2.006–2.010	2.379, 2.405	3.035	103.8	19.3
$[Cu_2(phen)_2(\mu\text{-}OH)(\mu\text{-}OH_2)(\mu\text{-}O_2CCH_3)](ClO_4)_2$[S3]	1.933–2.020	2.360, 2.375	2.989	101.3	120.0
$[Cu_2(bpy)_2(\mu\text{-}OH)(\mu\text{-}OH_2)(\mu\text{-}O_2CCH_2CH_3)](ClO_4)_2$[S3]	1.920–2.005	2.382, 2.415	3.037	104.5	148.9
$[Cu_2(\mu\text{-}O_2CH)(\mu\text{-}OH)(\mu\text{-}Cl)(dpyam)_2](ClO_4)\cdot0.5H_2O$[S4]	2.072-2.478	1.916, 1.975	3.036	104.8	79.1
$[Cu_2(\mu\text{-}O_2CH)(\mu\text{-}OH)(\mu\text{-}OCH_3)(dpyam)_2](ClO_4)$[S4]	2.169-2.175	1.918, 1.961	3.023	104.0	62.5
$[Cu_2(\mu\text{-}O_2CH)(\mu\text{-}OH)(\mu\text{-}Cl)(dpyam)_2](PF_6)$[S5]	2.183	1.918	3.061	105.8	79.7
$[Cu_2(\mu\text{-}O_2CH)(\mu\text{-}OH)(\mu\text{-}OCOH)(dpyam)_2](PF_6)$[S5]	2.144-2.200	1.934	3.113	107.2	47.8
$[Cu_2(\mu\text{-}O_2C_2H_5)(\mu\text{-}OCOC_2H_5)(\mu\text{-}OH)(dpyam)_2](ClO_4)$[S5]	1.931-1.959	2.236, 2.318	3.006	101.8	24.1
$[Cu_2(phen)_2(\mu\text{-}OH)(\mu\text{-}OH_2)(\mu\text{-}O_2CCH_2CH_3)](NO_3)_2$[S6]	1.925–2.029	2.344, 2.368	3.026	103.6	98.4
$[Cu_2(phen)_2(\mu\text{-}OH)(\mu\text{-}OH_2)(\mu\text{-}O_2CC(CH_3)_3)](ClO_4)_2\cdot(CH_3CH_2OH)$[S6]	1.911–2.015 1.893–2.012	2.379, 2.419 2.369, 2.425	3.010 3.034	103.8 105.3	151.2
$[Cu_2(bpy)_2(\mu\text{-}OH)(\mu\text{-}OH_2)(\mu\text{-}O_2CCH_2CH_3)(\mu\text{-}O_2SOCF_3)](CF_3SO_3)(DMF)_{0.5}$[S6]	1.906–2.019	2.351, 2.354	3.341	122.3	104.5
$[Cu_2(bpy)_2(\mu\text{-}OH)(\mu\text{-}OH_2)(\mu\text{-}O_2CCH_3)](CF_3SO_3)_2$[S7]	1.921–2.009	2.323, 2.394	3.024	103.4	102.1
$[Cu_2(4,4'\text{-}dmbpy)_2(\mu\text{-}OH)(\mu\text{-}OH_2)\text{-}(\mu\text{-}O_2CH)](ClO_4)_2$[S7]	1.908–1.999	2.324, 2.409	3.077	107.3	72.6
$[Cu_2(4,4'\text{-}dmbpy)_2(\mu\text{-}OH)(\mu\text{-}OH_2)(\mu\text{-}O_2CCH_3)](ClO_4)_2$[S7]	1.918–1.999	2.323, 2.442	3.055	105.6	90.2
$[Cu_2(5,5'\text{-}dmbpy)_2(\mu\text{-}OH)(\mu\text{-}OH_2)(\mu\text{-}O_2CCH_3)](ClO_4)_2$[S7]	1.929–2.003	2.329, 2.346	2.984	101.1	104.3
$[Cu_2(5,5'\text{-}dmbpy)_2(\mu\text{-}OH)(\mu\text{-}OH_2)(\mu\text{-}O_2CC(CH_3)_3)](ClO_4)_2$[S7]	1.921–2.012	2.320, 2.333	3.008	102.4	98.7
$[Cu_2(5,5'\text{-}dmbpy)_2(\mu\text{-}OH)(\mu\text{-}OH_2)(\mu\text{-}O_2CCH_3)](CF_3SO_3)_2$[S7]	1.923–2.003	2.310, 2.323	3.007	102.6	92.1
$[Cu_2(5,5'\text{-}dmbpy)_2(\mu\text{-}OH)(\mu\text{-}OH_2)(\mu\text{-}O_2CCH_2CH_3)](CF_3SO_3)_2$[S7]	1.931–1.996	2.321, 2.339	2.979	100.8	103.1
$[Cu_2(bpym)(OH)(HCO_2)(SO_4)(H_2O)_2]\cdot3H_2O$[S8]	1.912-2.051	2.333, 2.420	3.003	103.5	116
$[Cu_2(OH)(O_2CPh)_2(tmen)_2](PF_6)$[S9]	1.941-2.100	2.140, 2.190	3.259	114.9	22.6

$[Cu_2(\mu_5\text{-btb})(\mu\text{-OH})(\mu\text{-}H_2O)]$[S10]	1.905-1.956	2.651	3.083	107.4	82.9
$[Cu_2(tmen)_2(OH)(O_2CFc)](ClO_4)_2$[S11]	1.905-2.047	2.049, 2.076	3.363	123.9	29
$[Cu_2(phen)_2(OH)(O_2CCH_2CH_3)](NO_3)_2\cdot H_2O$[S12]	1.917-2.012	2.018, 2.021	3.015	103.6	109
$[Cu_2(phen)_2(OH)(O_2CCH_3)](NO_3)_2\cdot H_2O$[S12]	1.922-2.027	2.0271, 2.031	3.017	103.4	111
$[Cu_2(adip)(H_2O)_3]$ (**This work**)	1.935-1.989	2.393	3.196	107.6	26.8

[a] Abbreviations: bpy = 2,2′-bipyridine, phen = 1,10′-phenanthroline, dpyam = di-2-pyridylamine, 4,4′-dmbpy = 4,4′-dimethyl-2,2′-bipyridine, 5,5′-dmbpy = 5,5′-dimethyl-2,2′-bipyridine, bpym = 2,2′-bipyrimidine, tmen = *N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine, H_3btb = benzene-1,2,3-tricarboxylic acid.

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