Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

Direct Observation of Fast Single-crystal-to-single-crystal Transformation from Cu^{II}-framework to Cu^{I}-chain Mediated by Ascorbic Acid: a Large Emission Shift of Two Valence-tautomeric Copper Coordination Polymers

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Section 1. Experimental Procedures

Materials and Methods. All reagents were analytical grade (99.7%) from commercial sources and were used directly without any further purification. Ligands H_3dpob, 4,4'-bpy and metal salts (CuI) were purchased from Ji Nan Henghua Sci. & Tec. Co. Ltd. (Shandong, China). Solvents for photophysical studies were dried and freshly distilled under dry nitrogen gas before using. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 240c elemental analyzer. IR spectra were recorded by Nicolet Impact 410 FT-IR spectrometer (range in 4000–400 cm^{-1}). UV-vis spectra were recorded on a Perkin-Elmer Lambda 20 spectrometer. The solid-state and solution photoluminescence analyses were carried out on an Edinburgh FLS920 fluorescence spectrometer in the range of 200–800 nm. An Edinburgh Xe 900 400 W Xenon arc lamp was used as exciting light source. The visible detector as well as the lifetime setup was red-sensitive photomultiplier (type r928). Low temperature analyses were carried out at 77 K with an Oxford Optistat DN^{TM} cryostat (with liquid nitrogen filling). Lifetime studies were performed using photon-counting system with a microsecond pulse lamp as the excitation source. Data were analyzed through the nonlinear least squares procedure in combination with an iterative convolution method. The emission decays were analyzed by the sum of exponential functions. The decay curve is well fitted into a double exponential function: $I = I_0 + A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$, where I and I_0 are the luminescent intensities at time $t = t$ and $t = 0$, respectively, whereas τ_1 and τ_2 are defined as the luminescent lifetimes. The average lifetime was calculated according to the following equation (1): $\frac{\tau_1^2 A_1\% + \tau_2^2 A_2\%}{\tau_1 A_1\% + \tau_2 A_2\%}$ (1).

Section 2. Synthesis of compounds 1 and 2

Synthesis of $[Cu_4(dpob)_2(4,4'\text{-}bpy)_2(H_2O)]_n$ (1)

A mixture of CuI (0.019 g, 0.10 mmol), 3,2',3'-H_3dpob (0.015 g, 0.05 mmol) and 4,4'-bpy (0.008g, 0.05 mmol) with a mole ratio of 2:1:1 was dissolved in 6 mL H_2O and 2 mL CH_3OH. When the pH value of the mixture was adjusted to ca. 6.0 with 0.1 M NaOH, the solution was transferred into a Teflon-lined stainless steel vessel (20 mL) under autogenous pressure and heated at 120 °C for 156 h. After slowly cooling to the room temperature, the mixture was washed with distilled water and yellow block-shaped crystals were filtered off and dried at room temperature (yield ca. 62%, based on H_3dpob ligand). Elemental analysis (%): Calc. for $C_{50}H_{34}Cu_4N_4O_{15}$ (*Mr*: 1184.97): C, 49.96 ; N, 4.66 ; H, 2.83 %. Found: C, 49.32 ; N, 4.58 ; H, 2.82 %. IR (cm^{-1}): 3454 (br, s), 1603 (vs), 1572 (vs), 1385 (vs), 1220 (s), 1075 (w), 982 (w), 806 (vs), 630 (m), 464 (m).

Synthesis of $[Cu(H_2dpob)(4,4'\text{-bpy})]_{2n}$ (2)

Coordination polymer **2** was obtained by immersing **1** in the aqueous solution of ascorboc acid (0.1 mol/L) at 80 °C for 3 h. The green crystals of **1** turned to yellow while maintaining their original shapes. Elemental analysis (%): Calc. for $C_{50}H_{34}Cu_2N_4O_{14}$ (*Mr*: 1041.91): C, 57.59 ; N, 5.37 ; H, 3.26 %. Found: C, 57.32 ; N, 5.34 ; H, 3.29 %. IR (cm^{-1}): 3427 (br, s), 1716 (vs), 1644 (vs), 1572 (vs), 1378 (s), 1246 (s), 969 (w), 825 (m), 499 (w).

Table S1 Attempted synthesis of 2.

Trial	Compound 1	Concentration	Temperature	Time	Result
1	10mg	0.01	25°C	24h	Compound 1
2	10mg	0.01	50°C	24h	Compound 1
3	10mg	0.01	80°C	24h	Compound 1
4	10mg	0.05	25°C	24h	Compound 1
5	10mg	0.05	50°C	24h	Compound 1
6	10mg	0.05	80°C	24h	Compound 1
7	10mg	0.1	25°C	24h	Compound 1
8	10mg	0.1	50°C	24h	Compound 1
9	10mg	0.1	80°C	24h	Compound 2
10	10mg	0.1	80°C	12h	Compound 2
11	10mg	0.1	80°C	6h	Compound 2
12	10mg	0.1	80°C	3h	Compound 2

Section 3. X-ray Crystallography

The X-ray diffraction data taken at room temperature for coordination polymers **1** and **2** are collected on a Rigaku R-AXIS RAPID IP diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0. 71073 Å). The structures of **1** and **2** are solved by direct methods and refined on F^2 by the full-matrix least squares using the SHELXTL-97 crystallographic software. Anisotropic thermal parameters are refined to all of the non-hydrogen atoms. The hydrogen atoms are held in calculated positions on carbon atoms and nitrogen atoms and that are directly included in the molecular formula on water molecules. The CCDC 1444337 and 1444338 contain the crystallographic data **1** and **2** of this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/ deposit.

Table S2 Crystal data and structure refinement parameters of compounds **1**–**2**.

Identification code	Compound **1**	Compound **2**
Empirical formula	$C_{50}H_{34}Cu_4N_4O_{15}$	$C_{50}H_{34}Cu_2N_4O_{14}$
Formula mass	1184.97	1041.91
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a (Å)	7.4800(15)	7.8383(6)
b (Å)	25.630(5)	9.4782(6)
c (Å)	12.470(3)	14.9216(13)
α (°)	90.00	91.826(6)
β (°)	98.05(3)	95.897(6)
γ (°)	90.00	103.056(6)
V (Å^3)	2182.4(8)	1072.46(14)
Z	2	1
D_c/(g cm^{-3})	1.803	1.613
μ (Mo Kα)/mm^{-1}	2.005	1.071
F(000)	1196	532
Crystal size	0.26 x 0.24 x 0.20 mm	0.26 x 0.24 x 0.20 mm
θ range (°)	3.07 – 27.48	3.15 – 27.56
Limiting indices	$-8 \leq h \leq 9$	$-9 \leq h \leq 10$
	$-30 \leq k \leq 30$	$-12 \leq k \leq 10$
	$-16 \leq l \leq 16$	$-19 \leq l \leq 19$

Data/Restraints/Parameters	4994 / 6 / 338	4897 / 0 / 316
GOF on F^2	1.076	1.007
Final R indices [$I > 2\sigma(I)$]		
R_1[a]	0.0839	0.0504
wR_2[b]	0.2165	0.1071
R indices (alldata)		
R_1	0.0988	0.0803
wR_2	0.2322	0.1221
CCDC	1444337	1444338

[a] $R_1 = \Sigma||F_o| - |F_c||/ \Sigma|F_o|$; [b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$.

Table S3 Selected bond lengths [Å] and angles [°] for **1**.

Bond length	(Å)	Bond angles	(°)	Bond angles	(°)
Cu(1)-O(8)	1.930(4)	O(8)-Cu(1)-N(1)	173.1(2)	O(8)#3-Cu(2)-O(5)#2	90.18(19)
Cu(1)-N(1)	2.000(5)	O(8)-Cu(1)-O(4')#1	96(2)	O(8)-Cu(2)-O(5)#2	89.82(19)
Cu(1)-O(4’)#1	2.03(15)	N(1)-Cu(1)-O(4')#1	88.1(17)	O(8)#3-Cu(2)-O(5)#4	89.82(19)
Cu(1)-O(6)#2	2.045(5)	O(8)-Cu(1)-O(6)#2	89.68(18)	O(8)-Cu(2)-O(5)#4	90.18(19)
Cu(1)-O(1)	2.258(5)	N(1)-Cu(1)-O(6)#2	92.5(2)	O(5)#2-Cu(2)-O(5)#4	180.0(2)
Cu(1)-O(4)#1	2.29(13)	O(4')#1-Cu(1)-O(6)#2	120(5)	O(8)#3-Cu(2)-O(1)	100.11(16)
Cu(2)-O(8)#3	1.927(4)	O(8)-Cu(1)-O(1)	84.03(18)	O(8)-Cu(2)-O(1)	79.89(16)
Cu(2)-O(8)	1.927(4)	N(1)-Cu(1)-O(1)	89.3(2)	O(5)#2-Cu(2)-O(1)	95.16(19)
Cu(2)-O(5)#2	1.985(5)	O(4')#1-Cu(1)-O(1)	144(5)	O(5)#4-Cu(2)-O(1)	84.84(19)
Cu(2)-O(5)#4	1.985(5)	O(6)#2-Cu(1)-O(1)	95.49(19)	O(8)#3-Cu(2)-O(1)#3	79.89(16)
Cu(2)-O(1)	2.417(4)	O(8)-Cu(1)-O(4)#1	99.0(14)	O(8)-Cu(2)-O(1)#3	100.11(16)
Cu(2)-O(1)#3	2.417(4)	N(1)-Cu(1)-O(4)#1	86.2(13)	O(5)#2-Cu(2)-O(1)#3	84.84(19)
Cu(3)-O(2)#5	1.947(4)	O(4')#1-Cu(1)-O(4)#1	7(3)	O(5)#4-Cu(2)-O(1)#3	95.16(19)
Cu(3)-O(2)	1.947(4)	O(6)#2-Cu(1)-O(4)#1	113(3)	O(1)-Cu(2)-O(1)#3	180.0(2)
Cu(3)-N(2)#6	2.060(5)	O(1)-Cu(1)-O(4)#1	151(3)	O(2)#5-Cu(3)-O(2)	180.000(1)
Cu(3)-N(2)#7	2.060(5)	O(8)#3-Cu(2)-O(8)	180.00(1)	O(2)#5-Cu(3)-N(2)#6	86.68(19)
		O(2)-Cu(3)-N(2)#7	86.68(19)	O(2)-Cu(3)-N(2)#6	93.32(19)
		N(2)#6-Cu(3)-N(2)#7	180.00(1)	O(2)#5-Cu(3)-N(2)#7	93.32(19)

Symmetry transformations used to generate equivalent atoms: #1: –x, –y+2, –z; #2: –x, –y+1, –z+1.

Table S4 Selected bond lengths [Å] and angles [°] for **2**.

Bond length	(Å)	Bond angles	(°)
Cu(1)-N(1)	1.904(2)	N(1)-Cu(1)-N(2)	168.56(11)
Cu(1)-N(2)	1.909(2)	N(1)-Cu(1)-O(4)	97.77(9)
Cu(1)-O(4)	2.489(2)	N(2)-Cu(1)-O(4)	92.89(9)

Symmetry transformations used to generate equivalent atoms: #1: –x, –y+2, –z; #2: –x, –y+1, –z+1.

Section 4. The PXRD patterns of 1 and 2.

In order to check the phase purity of **1** and **2**, the X-ray powder diffraction (PXRD) pattern was checked at room temperature. The simulated and experimental PXRD patterns of **1** and **2** are in good agreement with each other (Fig. S1), indicating the phase purity of the products. The differences in intensity may be due to the preferred orientation of the powder samples.

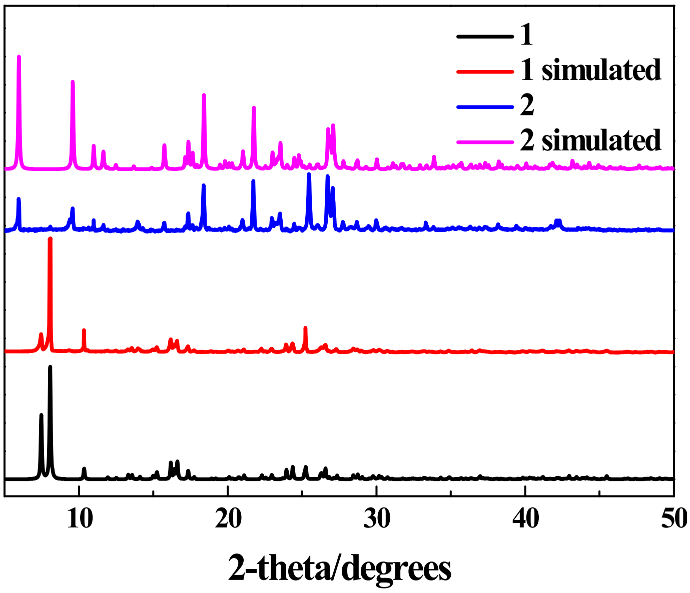


Fig.S1 The PXRD patterns of **1** and **2**with the relevant simulated patterns.

Section 5. The coordination modes and structural information of H_3dopb ligand

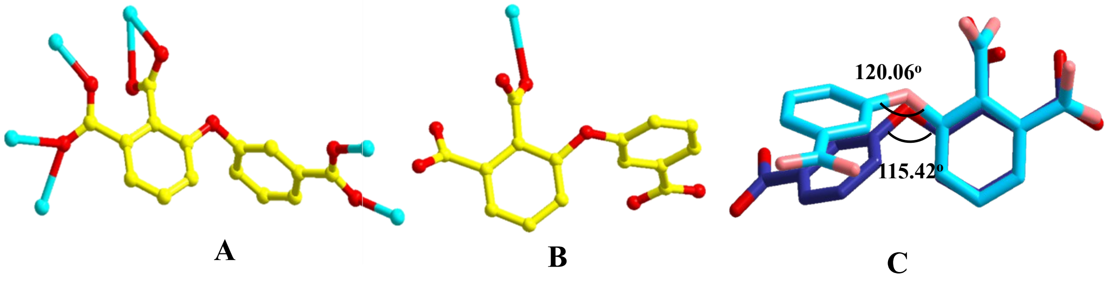
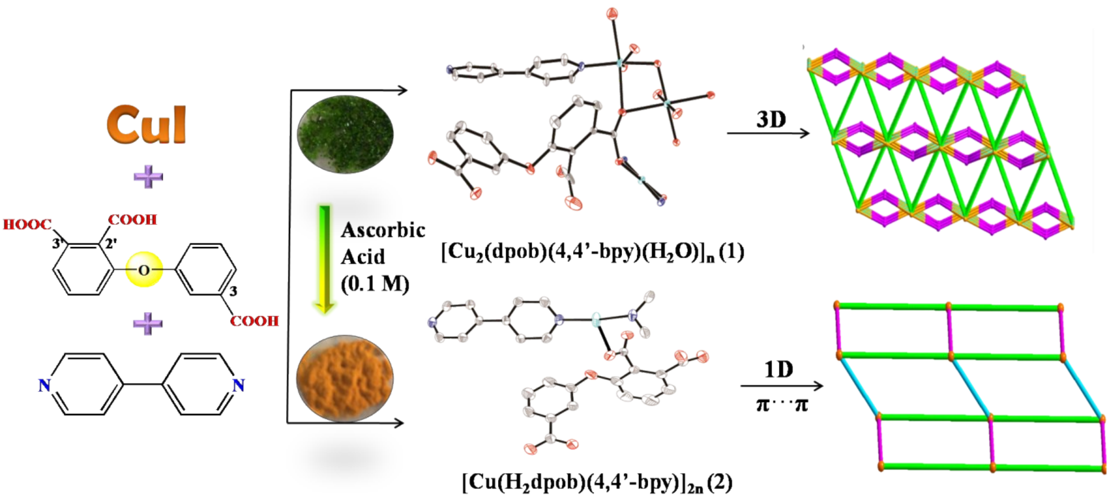


Fig. S2 The coordination modes of the H_3dpob ligand found in compound **1** (mode A,) and **2** (mode B)

Table S5 Thel angles for 4,4’-bpy and H_3dpob ligands.

Angle	**1**	**2**
The plane of pyridine rings in 4,4'-bpy	31.62	27.37
The plane of benzene rings in H_3dpob	89.79	66.58
The benzene-O-benzene in H_3dpob	115.42	120.06
2'-carboxylic group and benzene ring	73.92	72.00
3'-carboxylic group and benzene ring	40.16	43.97
3-carboxylic group and benzene ring	4.60	1.69

Section 6. Structural Information for 1 and 2.



Scheme S1 The reaction routes and structures of compounds **1** and **2**.

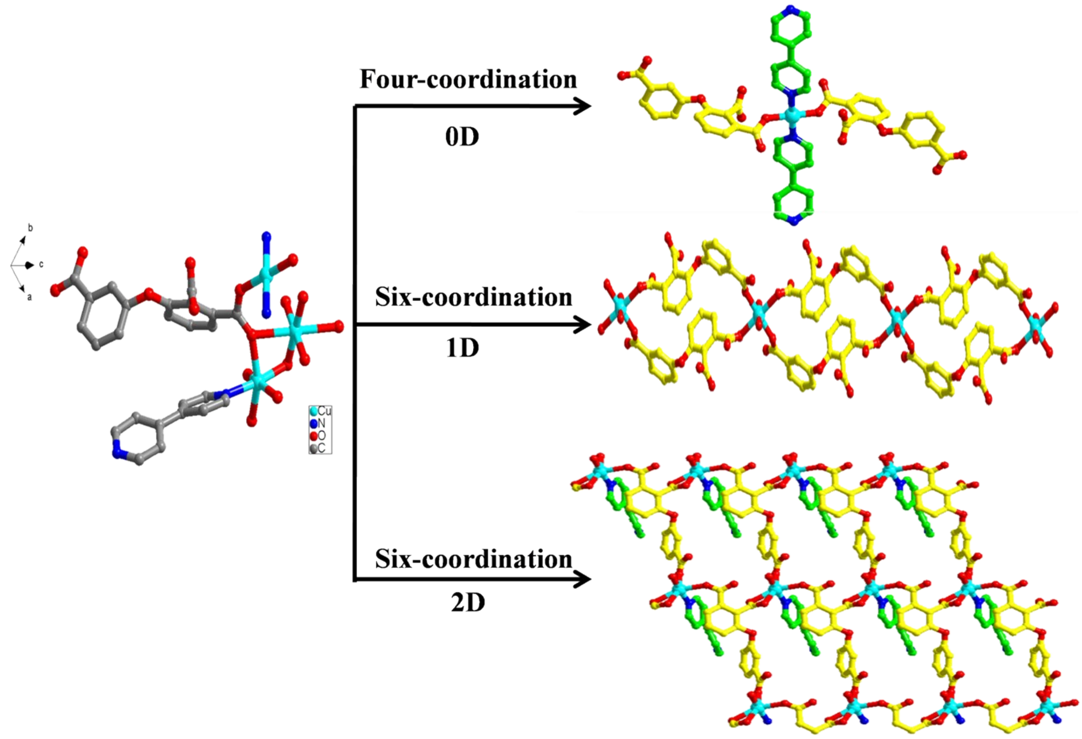


Fig.S3 The trinuclear structure of **1 (**hydrogen atoms and free water molecules were omitted for clarity).

Cu3 ion is in a quadrangle coordination environment built from two nitrogen atoms of 4,4'-bpy ligands and two oxygen atoms from carboxylic groups of two dpob^{3-}in the monodentate coordination mode, forming a 0D structure unit. Both Cu1 and Cu2 ions are six-coordinated geometry but exhibit two types of coordination environments. Cu2 ion locates in a distorted octahedral coordination sphere with four oxygen atoms from four carboxylic groups and two coordinated water molecules, two Cu2 ions are interconnected by dpob^{3-} ligand to afford a 1D beaded chain. Cu3 ion is coordinated with four oxygen atoms of three dpob^{3-} ligands, one nitrogen atoms from bpy ligand and one coordinated water molecule, resulting in an octahedron motif, which displays a 2D layer structure.

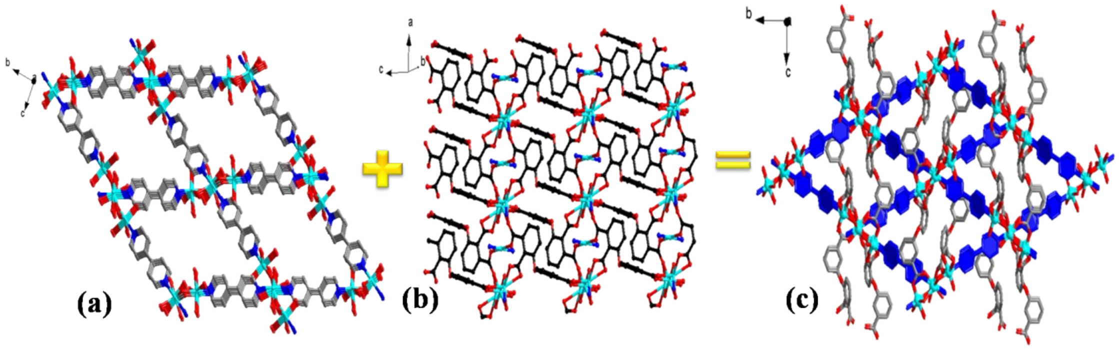


Fig.S4 (a) 3D structure of **1** is built by 4,4'-bpy ; (b) 2D structure of **1** is built by H_3dopb; (c) 3D + 2D → 3D framework of **1** viewing from the *a* axis;

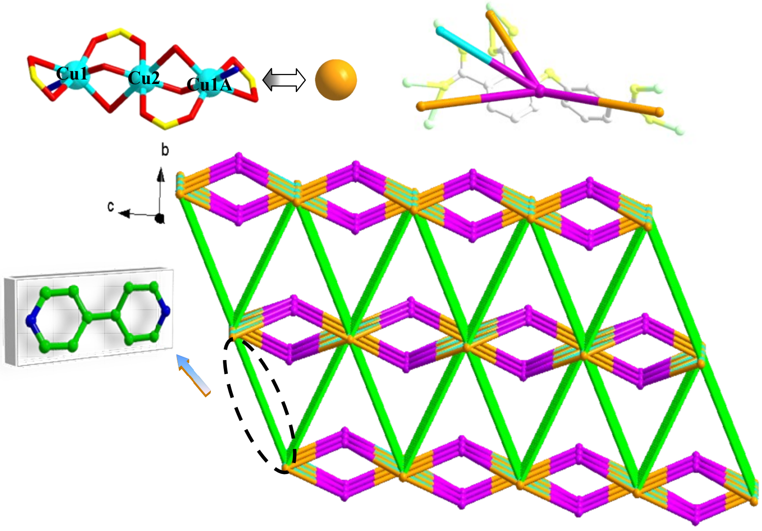


Fig. S5 Schematic representation of the underlying network topology of **1**(color code: $\{Cu_3O_4(CO)_4\}$, orange ball; H_3dpob, purple ball; 4,4'-bpy, green line).

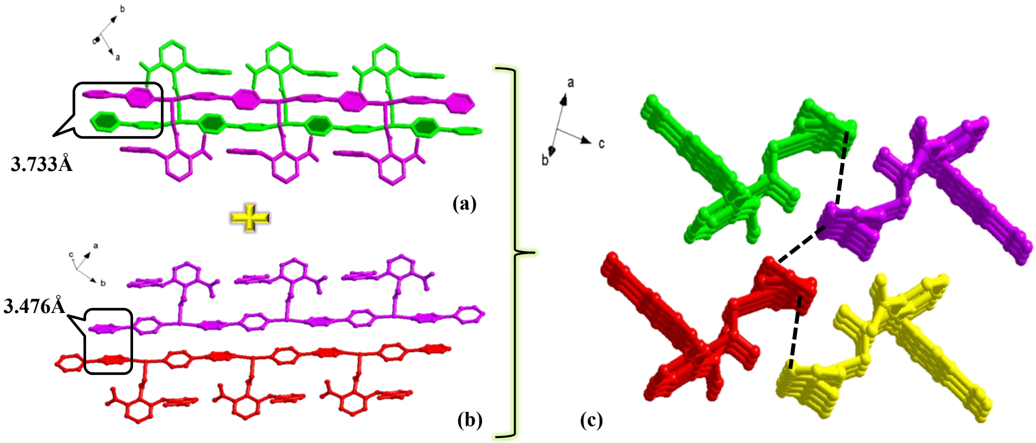


Fig.S6 (a) 1D dimer chain of **2**; (b) 1D parallel chain of **2**; (c) 2D framework of **2** *via* π-π stacking interactions.

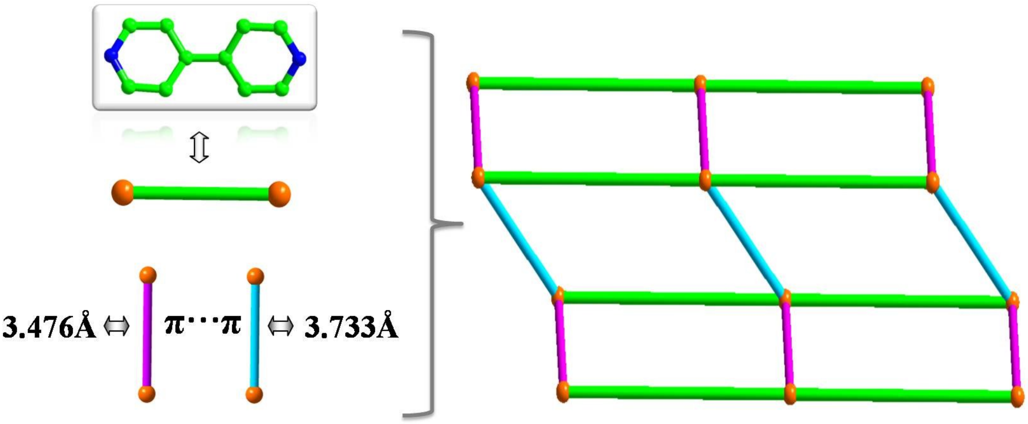


Fig. S7 Schematic representation of the underlying network topology of **2** (color code: Cu, orange ball; 4,4'-bpy, green line).

Section 7. IR spectra of 1, 2 and ligands H_3dpob, bpy.

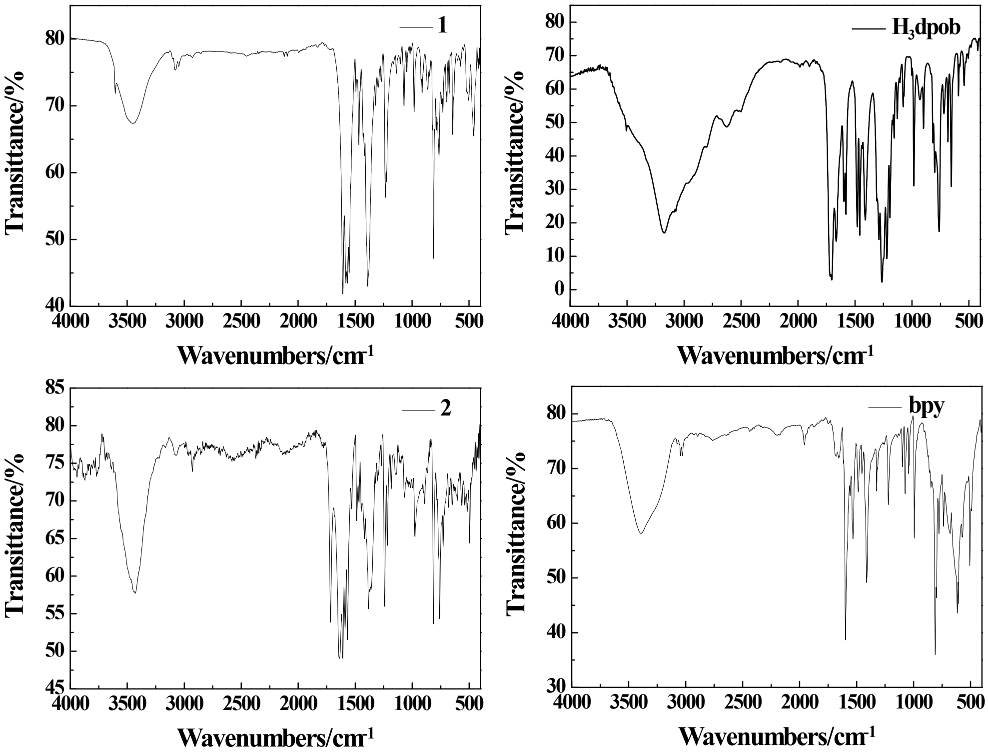


Fig.S8 IR spectra of **1** and **2**

Section 8. The TGA for 1 and 2.

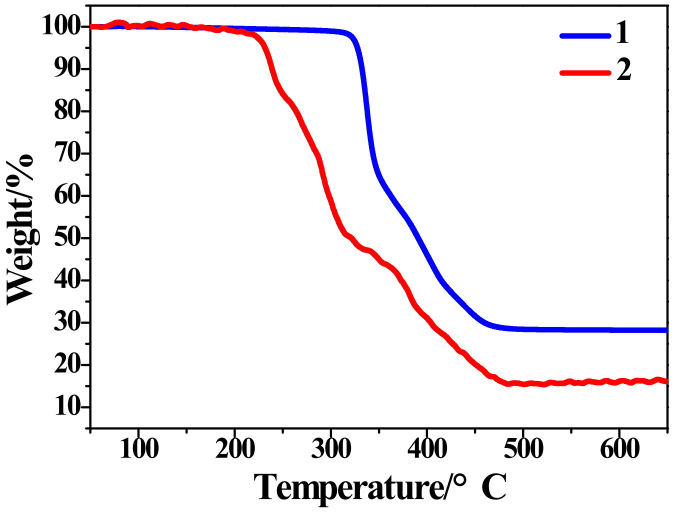


Fig.S9 Thermal gravimetric curves for **1** and **2**.

Thermogravimetric experiments were conducted to study the thermal stability of compounds **1** and **2**(Fig. S7, ESI†). In the TGA curve of **1**, there is one continuous weight-loss step. The weight loss of 72.89% in the temperature range of 322–476 °C corresponds to one 4,4'-bpy, one dpob^{3-} anion and release of one coordinated water molecule, which is in accordance with the calculated value of 73.33%. For **2**, the main weight loss from 215 °C to 487 °C is attributed to two 4,4'-bpy and two H_2dpob^{-} anions (obsd: 84.68%; calcd: 84.64%). The thermal stability of **1** is significantly better than **2**, which is attributed to the compact 3D architecture of **1**, which is more stable than the 1D structure of **2**.The remaining weight of 27.91% for **1** and 15.32% for **2**, correspond to the percentage (calcd: 26.67% and 15.36%) of Cu and O components, indicating that the final product is CuO.

Section 9. Photophysical studies for 1 and 2.

Experiment of Photoluminescence (PL) investigations.

The fluorescence properties of coordination polymers **1** and **2** in the solid state and in various solvent suspensionwere investigated at room temperature or 77 K. The **1** and **2** suspension were prepared by introducing 1.0 mg of **1** and **2** fine powder into 50 mL of DMSO, DMF, CH_3CN, CH_3OH, CH_3CH_2OH, Acetone, THF, Toluene respectively. After sonication treatment, aging for over 24 h and shaking, the luminscence spectra were measured.

UV-vis spectrum

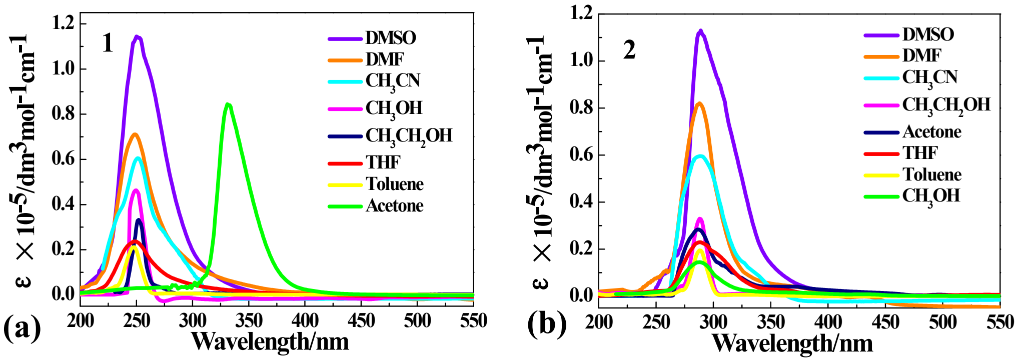


Fig.S10 The UV-vis spectra for**1** and **2**.

Table S6 Luminescent data for **1** and **2** in the solid state at 298 K and 77K

Compoud	Temperature(K)	Excitation (λ_{ex}, nm)	Emission (λ_{em}, nm)	CIE (x, y)	τ_1 (μs)	τ_2 (μs)	<τ>(μs)
1	298	300	499	(0.21,0.36)	1.07 (57.38%)	11.07 (46.62%)	9.92
	77	300	504	(0.23,0.53)	1.05 (51.24%)	18.12 (48.76%)	17.14
2	298	360	558	(0.46,0.53)	1.14 (47.40%)	13.20 (52.60%)	12.15
	77	360	596	(0.57,0.43)	1.89 (49.25%)	26.84 (50.75%)	25.24
H_3dpob	298	300	403	(0.22,0.19)	—	—	—
4,4'-bpy	298	300	481	(0.21,0.32)	—	—	—

Table S7 Luminescent data for **1** and **2** introduced in different solvents at 298 K

Compound	Solvent	Excitation (λ_{ex} nm)	Emission (λ_{em}, nm)	τ_1 (μs)	τ_2 (μs)	<τ>(μs)
1	DMSO	300	362	0.87 (53.62%)	7.37 (46.38%)	6.59
	DMF	300	345	1.09 (64.09%)	8.09 (35.91%)	6.73
	CH_3CN	300	350	1.19 (64.62%)	7.97 (35.38%)	6.52
	CH_3OH	300	346	0.90 (79.18%)	7.59 (20.82%)	5.51
	CH_3CH_2OH	300	353	0.96 (87.76%)	8.34 (12.24%)	5.00
	Acetone	300	503	1.20 (59.87%)	10.86 (40.13%)	9.49
	THF	300	359	0.85 (83.03%)	6.85 (16.97%)	4.58
	Toluene	300	361	0.83 (82.54%)	7.56 (17.46%)	5.26
2	DMSO	360	558	0.88 (42.67%)	13.23 (57.33%)	12.65
	DMF	360	554	0.69 (58.70%)	12.52 (41.30%)	11.66
	CH_3CN	360	554	2.50 (21.24%)	11.03 (78.76%)	10.54
	CH_3OH	360	551	0.91 (54.71%)	11.23 (45.29%)	10.31
	CH_3CH_2OH	360	552	0.80 (44.62%)	10.36 (55.38%)	9.80
	Acetone	360	554	2.43 (19.21%)	8.64 (80.79%)	8.25
	THF	360	554	0.80 (79.09%)	10.02 (20.91%)	7.88
	Toluene	360	550	0.73 (75.10%)	9.21 (24.90%)	7.57