

Unprecedented metal-ion metathesis in a metal-carboxylate chains-based metal-organic framework

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Experimental section

Materials and physical measurements

All chemicals and reagents of analytical grade were commercially available and used without further purification. 5-(4-carboxybenzamido) isophthalic acid (H_3L) was synthesized according to the reported method.¹

The IR spectra were recorded on a Bruker TENSOR 27 spectrometer in the 500-4000 cm^{-1} range. Thermogravimetric Analyses (TGA) was carried out on a Netzsch STA 449 F3 instrument with a heating rate of 10 $^{\circ}C\ min^{-1}$ under N_2 atmosphere. Powder X-ray diffraction (PXRD) data were recorded using a Rigaku (D/Max-Ultima IV) diffractometer equipped with Cu- $K\alpha$ radiation, with a step size and a scan speed of 0.02 $^{\circ}$ and 5 $^{\circ}min^{-1}$, respectively. Simulated PXRD patterns were calculated with the Mercury program using the single crystal data. Scanning electron microscope energy-disperse X-ray spectroscopy (SEM-EDS) was conducted on a HITACHI S-4800 scanning electron microscope. Solid state photoluminescence spectra of complexes **1-Zn**, **1-Cu** and free H_3L ligand were measured on a Varian Cary Eclipse fluorescence spectrometer.

Synthesis of $[Zn_3L_2(DMF)_2]\cdot 2DMF$ (**1-Zn**)

A mixture of H_3L (16.1 mg, 0.04 mmol) and $Zn(NO_3)_2\cdot 6H_2O$ (18.6 mg, 0.063 mmol) in 4 mL DMF/ H_2O ($v = 1:1$) was sealed in a Teflon-lined stainless autoclave and heated at 80 $^{\circ}C$ under autogeneous pressure for 48 h, and then cooled to room temperature (cooling rate 0.1 $^{\circ}C\cdot\ min^{-1}$). Colorless block crystals were isolated in 85%

yield (based on H₃L). IR(cm⁻¹): 2817(m), 2773(m), 2729(w), 1804(w), 1766(s), 1708(s), 1691(s), 1651(s), 1622(m), 1597(s), 1550(m), 1439(m), 1400(m), 1363(m), 1218(m), 1174(w), 1016(m), 945(s), 882(s), 800(m), 727(s), 633(s).

Synthesis of **1-Cu**

To obtain the Cu²⁺-exchanged framework of [Zn₃L₂(DMF)₂] \cdot 2DMF, single crystals of the parent complex [Zn₃L₂(DMF)₂] \cdot 2DMF were soaked in a DMF/H₂O (*v:v* = 1:1) solution of Cu(NO₃)₂ \cdot 3H₂O (0.2mol/L) for 5 days. After decanting the solution, the Cu²⁺-exchanged crystals were washed thoroughly with DMF/H₂O and then soaked in fresh DMF at room temperature for ten days in order to remove the excess metal salt within the pores during which the DMF was replaced six times. For SEM-EDS analysis, the crystals were dried under vacuum. SEM-EDS analysis revealed that the framework Zn²⁺ could be completely exchanged by Cu²⁺, resulting in **1-Cu**. The reverse ion exchange was also investigated by soaking the fully exchanged **1-Cu** in a DMF/H₂O solution of Zn(NO₃)₂ \cdot 6H₂O (0.4M) for six months. SEM-EDS and ICP-AES analysis revealed that no copper ions could be exchanged by Zn²⁺, indicating the single-crystal to single-crystal process is irreversible.

X-ray Crystallography

Selected crystals were used for data-collection on a Bruker SMART ApexII diffractometer equipped with graphite-monochromatic Mo- $K\alpha$ radiation ($\lambda = 0.71073$ Å) at room temperature. Frames were collected at 0.5° intervals in φ and ω for 10s per frame such that a hemisphere of data was collected. Raw data collection and refinement were done using SMART. Data reduction was performed using SAINT+. Absorption corrections were applied using the SADABS program.² All the structures were solved using direct methods and then refined by full-matrix least-squares on F^2 with anisotropic displacement using SHELX-97.³ Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. All the hydrogen atoms attached to carbon atoms were placed in calculated positions and refined using a riding model.

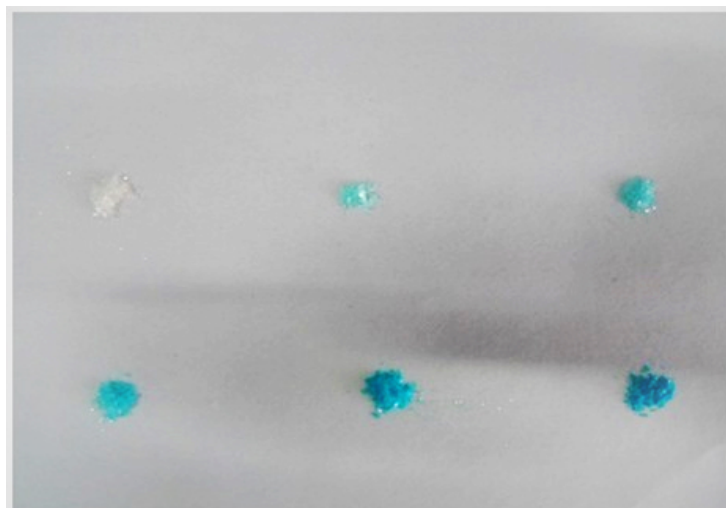


Fig. S1 Photographs of the ion exchange process showing the visual color change during the crystal-to-crystal transformation in five days (From left to right, the first row: origin crystal, the first day and the second day; the second row: from the third day to the fifth day).

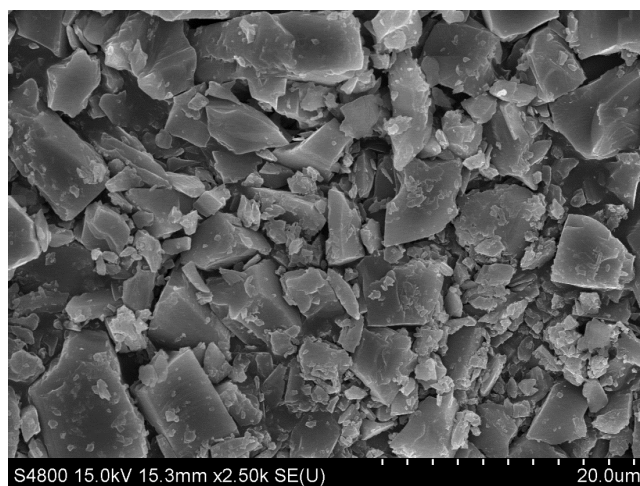


Fig. S2 SEM of complex **1-Zn**.

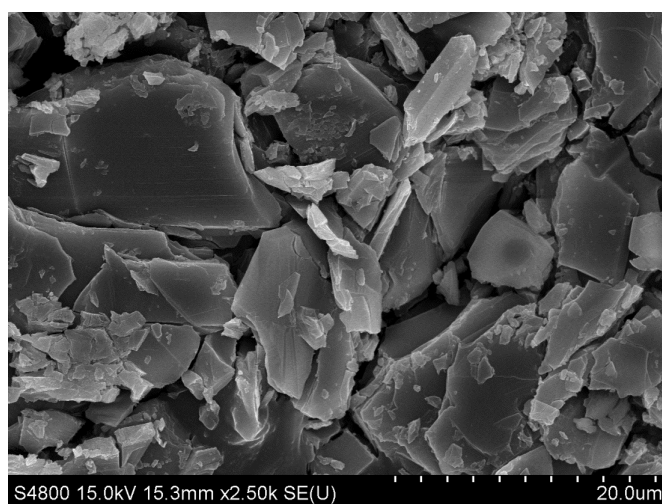
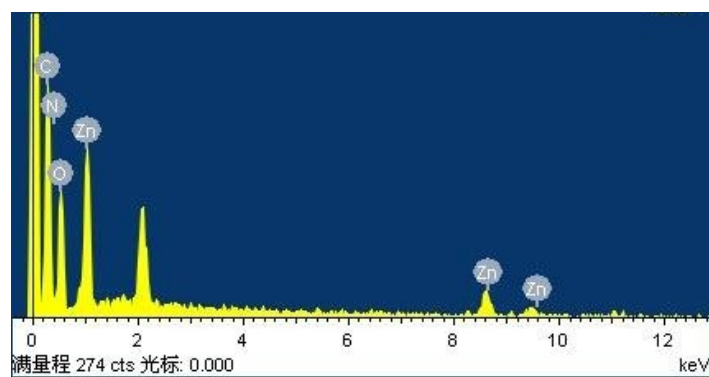
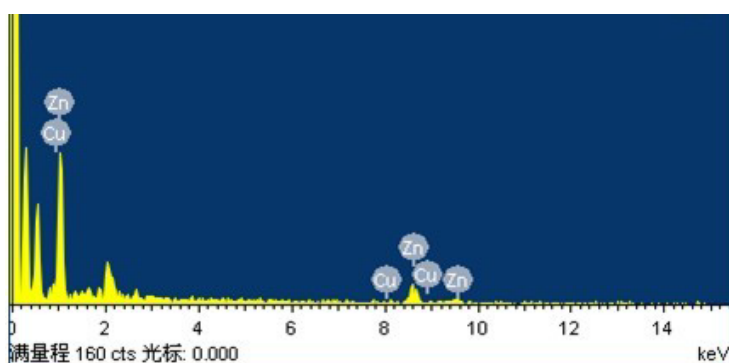


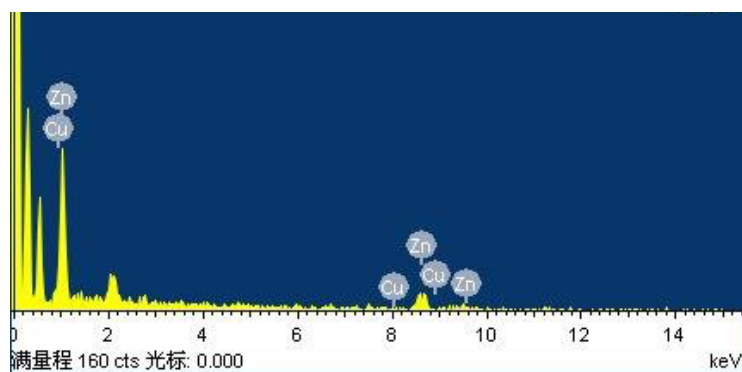
Fig. S3 SEM of complex **1-Cu**.



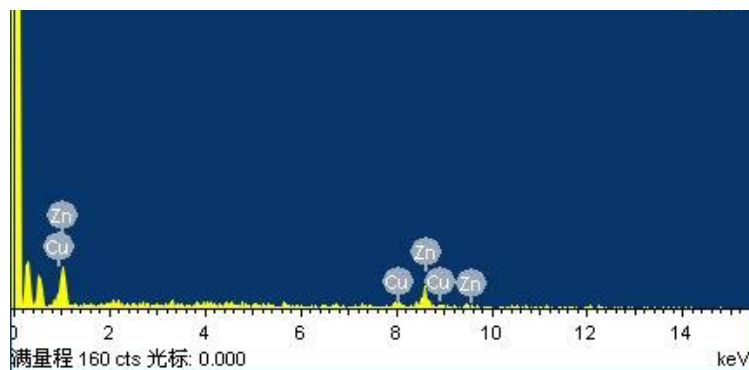
(a)



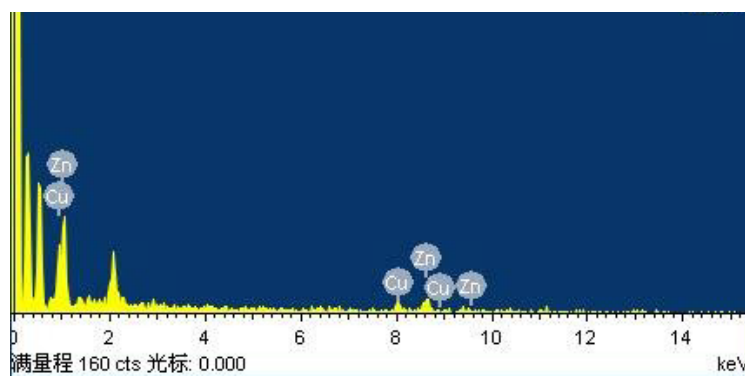
(b)



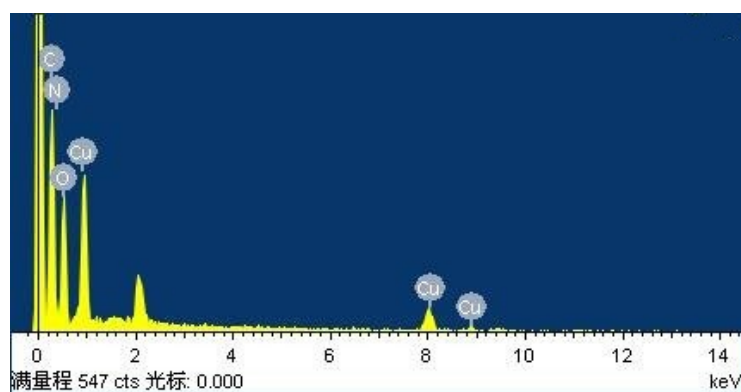
(c)



(d)



(e)

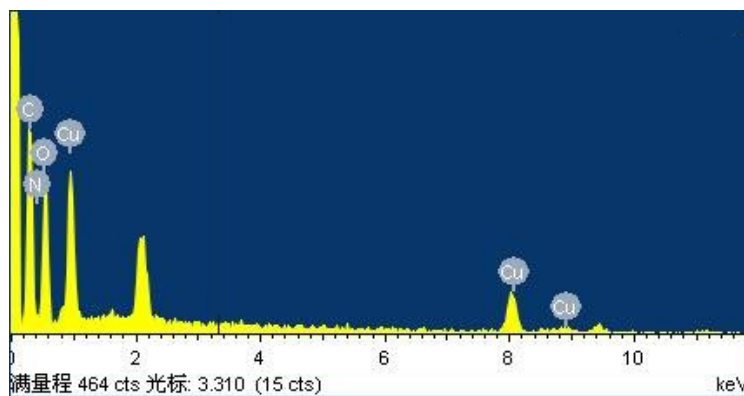


(f)

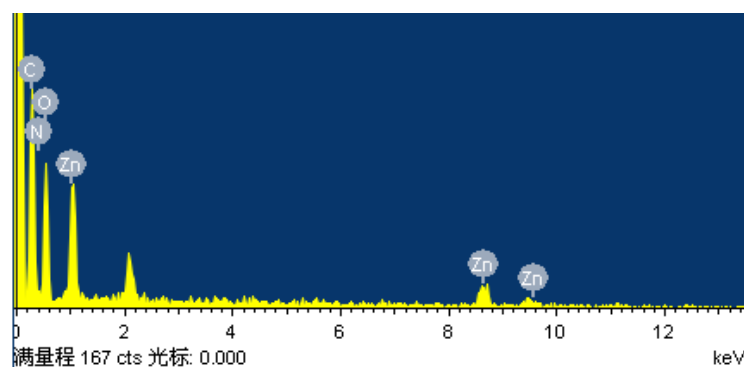
Fig. S4 EDS tests before and after the single-crystal-to-single-crystal transformation process: (a) Complex **1-Zn** (before metal ion-exchange); metal ion exchanged on: (b) the first day; (c) the second day; (d) the third day; (e) the fourth day; (f) the fifth day (**1-Cu**).

Table S1 Metal ion ratio during the ion exchange process monitored by ICP-AES

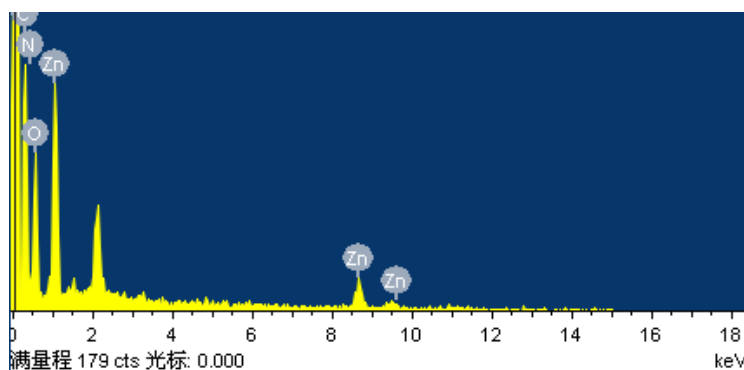
Sample	Time	Metal molar ratio (%)	
		Zn	Cu
1-Zn soaked in DMF/H ₂ O solution of Cu(NO ₃) ₂ ·3H ₂ O (0.2 M)	0 h	100	0
	8 h	85	15
	12 h	78	22
	24 h	55	45
	32 h	38	62
	36 h	35	65
	56 h	25	75
	96 h	11	89
	5 days	3	97
	21 days	1	99
	1-Zn soaked in DMF/H ₂ O solution of CuCl ₂ ·4H ₂ O (0.2 M)	12 days	2



(a)



(b)



(c)

Fig. S5 (a) EDS of complex **1-Cu** in a concentrated DMF/H₂O solution containing Zn(NO₃)₂·6H₂O (0.4 M) after 6 months; (b) EDS of complex **1-Zn** in a concentrated DMF/H₂O solution containing Ni(NO₃)₂·6H₂O (0.2 M) under 80 °C after 36 h; (c) EDS of complex **1-Zn** in a concentrated DMF/H₂O solution containing Co(NO₃)₂·6H₂O after under 80 °C after 36 h.

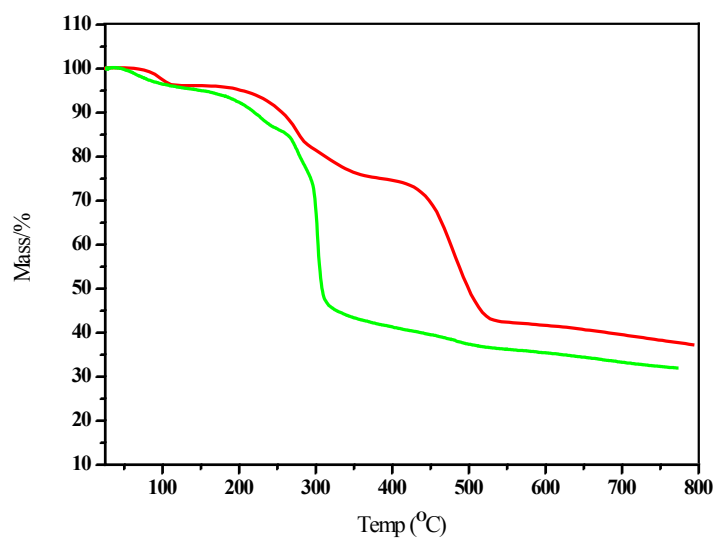


Fig. S6 TGA curves of $[\text{Zn}_3\text{L}_2(\text{DMF})_2]\cdot 2\text{DMF}$ (**1-Zn**, red) and **1-Cu** (green).

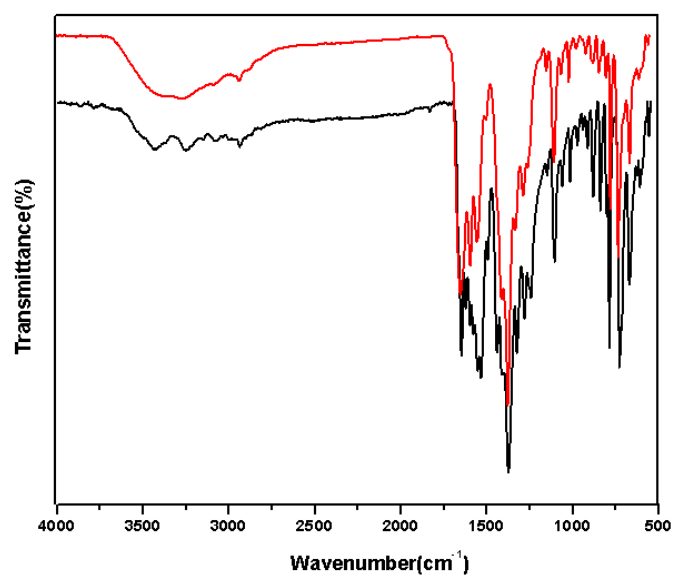


Fig. S7 FT-IR spectra of **1-Zn** (black), **1-Cu** (red).

References

1. J. G. Duan, Z. Yang, J. F. Bai, B. S. Zheng, Y. Z. Li and S. H. Li, *Chem. Commun.*, 2012, **48**, 3058.
2. (a) SMART, Version 5.05; Bruker AXS, Inc.: Madison, WI, 1998; (b) SAINT-Plus, Version 7.03; Bruker AXS Inc.: Madison, Wisconsin, 2004; (c) G. M. Sheldrick, SADABS (Version 2.03) and TWINABS (Version 1.02), University of Göttingen, Germany, 2002.
3. G. M. Sheldrick, *SHELXS-97*; University of Göttingen: Germany, 1997.