Electronic Supplementary Information

A porous cationic metal-organic framework based on tetranuclear hydroxyl-copper(II) cluster for fast and highly efficient dichromate trapping through a singlecrystal to single-crystal process

Xiu-Xiu Lv, Lu-Lu Shi, Ke Li, Bao-Long Li*, Hai-Yan Li

State and Local Joint Engineering Laboratory for Functional Polymeric Materials, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, PR China. E-mail: libaolong@suda.edu.cn

Experimental Section

1. General

Reagents and solvents employed were commercially available and used as received. Elemental analyses (EA) for C, H, and N were performed on a Perkin- Elmer 240C analyzer. FT-IR spectra were obtained on a Bruker VERTEX 70 FT-IR spectrophotometer in the 4000–400 cm⁻¹ region. Powder X-ray diffraction (PXRD) was performed on a D/MAX-3C diffractometer with the Cu K α radiation (λ = 1.5406 Å) at room temperature. The UV-vis spectra were measured on a Varian Cary 500 UV-vis spectrophotometer.

2. Synthesis of $\{[Cu_4(OH)_2(mtrb)_2(1,4-bda)_2]Br_2 \cdot 6H_2O\}_n$ (1-Br)

A mixture of mtrb (0.2 mmol), 1,4-H₂bda (0.1 mmol), CuBr₂ (0.4 mmol), NaOH (0.18 mmol) and H₂O (10 mL) was placed in a Teflon-lined stainless steel vessel, heated to 90 °C for one days, then cooled to room temperature over 24 h. The blue crystals $\{[Cu_4(OH)_2(mtrb)_2(1,4-bda)_2]Br_2 \cdot 6H_2O\}_n$ (1-Br) were obtained (Yield: 39% based on 1,4-H₂bda). Anal. Calc. for C₄₄H₅₄Br₂Cu₄N₁₂O₁₆ (1-Br): C, 37.19; H, 3.83; N, 11.83; Found: C, 37.08; H, 3.78; N, 11.76. IR (cm⁻¹, KBr) 3440vs, 3119w, 1568vs, 1430w, 1385s, 1278w, 1208w, 1083w, 1046w, 867w, 796w, 730w, 711w, 641w.

3. Synthesis of $\{[Cu_4(OH)_2(mtrb)_2(1,4-bda)_2]Cr_2O_7 \cdot 6H_2O\}_n (1-Cr_2O_7)$

The crystals of {[$Cu_4(OH)_2(mtrb)_2(1,4-bda)_2$] $Br_2•6H_2O$ }_n (1-Br) (0.02 mmol) were immersed in a 10 mL Cr₂O₇₂₋ (1.0 × 10⁻² mol/L) aqueous solution 1.0 and kept for 6 days. After decanting the solution, the resultant green crystals {[$Cu_4(OH)_2(mtrb)_2(1,4-bda)_2$] $Cr_2O_7•6H_2O$ }_n (1-Cr₂O₇) were washed thoroughly with deionized water and dried in air. The air-dried {[$Cu_4(OH)_2(mtrb)_2(1,4-bda)_2$] $Cr_2O_7•6H_2O$ }_n (1-Cr₂O₇) were characterized by FT-IR spectroscopy, PXRD and single-crystal X-ray diffraction. IR (cm⁻¹, KBr): 3442vs, 3120w, 1572vs, 1430w, 1385s, 1278w, 1208w, 1083w, 1046w, 941w, 771w, 731w, 641w.

4. Crystallographic Studies

X-ray single crystal diffraction data collections for **1-Br** and **1-Cr₂O**₇ were performed on an Agilent Gemini Atlas diffractometer with graphite monochromated Mo K*a* radiation ($\lambda = 0.71073$ Å). Intensities were collected and reduced on the program CrysAlisPro (Agilent Technologies, Version 1.171.36.32, 2013), and a multi-scan absorption correction was applied. The structures were solved by direct methods and refined with the full-matrix least-squares technique (SHELXTL package). The disordered water molecules in **1-Br** were removed with the SQUEEZE procedure in PLATON. The disordered water molecules in **1-Cr₂O**₇ were obtained from successive Fourier syntheses. Crystal data for C₄₄H₄₂Br₂Cu₄N₁₂O₁₀ ({[Cu₄(OH)₂(mtrb)₂(1,4bda)₂]Br₂}_n): *M*r = 1312.88, monoclinic, *P*₂/_c, *a* = 9.6552(2) Å, *b* = 17.1958(5) Å, *c* = 20.8804(6) Å, β = 94.231(2), *V* = 3457.31(16) Å³, *Z* = 2, *D*_c = 1.261 g/cm³, μ = 2.419 mm⁻¹, *F*(000) = 1312, S = 1.061, *R*₁ = 0.0660, wR₂ = 0.2029. Crystal data for C₄₄H₅₄Cr₂Cu₄N₁₂O₂₃ (**1-Cr₂O**₇): *M*r = 1477.15, monoclinic, *P*₂/_c, *a* = 9.6691(3) Å, *b* = 17.4598(5) Å, *c* = 20.4487(6) Å, β = 94.891(2), *V* = 3439.59(18) Å³, *Z* = 2, *D*_c = 1.426 g/cm³, μ = 1.593 mm⁻¹, *F*(000) = 1500, S = 1.027, *R*₁ = 0.0579, wR₂ = 0.1699.

5. Anion Exchange Studies

(a) Molar ratio 1:1 (1-Br to $Cr_2O_7^{2-}$)

{[Cu₄(OH)₂(mtrb)₂(1,4-bda)₂]Br₂•6H₂O}_n (1-Br) (30 mg, 0.021 mmol) was immersed in a 8.4 mL 2.5×10^{-3} mol/L Cr₂O₇²⁻ aqueous solution and the mixture was mildly shaken at room temperature for 48 h. The anion exchange process was monitored by liquid UV-vis spectroscopy based on typical absorption of Cr₂O₇²⁻ at 257 nm. 0.10 mL Cr₂O₇²⁻ aqueous solution was pipetted at different time interval and was diluted using 2 mL deionized water to measure the UV-vis adsorption intensity.

The equilibrium adsorption capacity $q_e (mg/g)$ is calculated by the following equation.

$$q_e = \frac{(C_i - C_e)V}{W} \quad (1)$$

Where C_i and C_e (mg/L) were the initial and final concentrations of $Cr_2O_7^{2-}$, respectively. V (L) was the volume of the solution, and m (g) was the mass of sorbent.

(b) Molar ratio 2:1 (1-Br to $Cr_2O_7^{2-}$)

{[Cu₄(OH)₂(mtrb)₂(1,4-bda)₂]Br₂•6H₂O}_n (1-Br) (60 mg, 0.042 mmol) was immersed in a 8.4 mL 2.5×10^{-3} mol/L Cr₂O₇²⁻ aqueous solution and the mixture was mildly shaken at room temperature for 24 h. The anion exchange process was monitored by liquid UV-vis spectroscopy based on typical absorption of Cr₂O₇²⁻ at 257 nm. 0.10 mL Cr₂O₇²⁻ aqueous solution was pipetted at different time interval and was diluted using 2.0 mL deionized water to measure the UV-vis adsorption intensity.

(c) Selective capture of Cr₂O₇²⁻

{[Cu₄(OH)₂(mtrb)₂(1,4-bda)₂]Br₂•6H₂O}_n (1-Br) (30 mg, 0.021 mmol) was immersed in a 4.2 mL aqueous solution containing 2.5×10^{-3} mol/L Cr₂O₇²⁻ and 2.5×10^{-2} mol/L ClO₄⁻, or 2.5×10^{-3} mol/L Cr₂O₇²⁻ and 2.5×10^{-2} mol/L BF₄⁻, or 2.5×10^{-3} mol/L Cr₂O₇²⁻ and 2.5×10^{-2} mol/L Cr₂O₇²⁻ and 2.5×10^{-2} mol/L Cr₂O₇²⁻ and 2.5×10^{-2} mol/L NO₃⁻, or 2.5×10^{-3} mol/L Cr₂O₇²⁻ and 2.5×10^{-2} mol/L Br⁻, or 2.5×10^{-3} mol/L Cr₂O₇²⁻ and 5.0×10^{-3} mol/L SO₄²⁻, respectively. The mixture was mildly shaken at room temperature for 24 h. The resultant solids were used for IR measurement. The resultant solutions were all monitored by UV–vis absorbance measurement.

(d) Release and cycle experiment

The release experiment was carried out right after the completion of an ion-exchange process of $Cr_2O_7^{2-}$ at molar ratio 1:1 (**1-Br** to $Cr_2O_7^{2-}$). The **1-Cr_2O_7** was filtered and washed with water several times before release operation. The **1-Cr_2O_7** was immersed in a 8.4 mL 0.50 mol/L Br⁻ aqueous solution (**200-fold molar excess**) and the mixture was mildly shaken at room temperature for 48 h. The cycle experiments were done by performing ion-exchange, release, and filtering in turn for 3 cycles. The measurements were performed after completion of ion-exchange and release. The processes were all monitored by UV–vis absorbance measurement.

Table S1 Selected bond lengths and angles for 1-Br and 1-Cr₂O₇ (Å and °).

1-Br			
Cu(1)-O(1)	1.947(4)	Cu(1)-O(5)	1.918(4)
Cu(1)-N(1)	2.034(5)	Cu(1)-N(4A)	2.360(5
Cu(1)-N(5B)	1.984(5	Cu(2)-O(2C)	1.968(4)
Cu(2)-O(4D)	1.993(4)	Cu(2)-O(5)	1.928(4)
Cu(2)-O(5C)	2.264(4)	Cu(2)-N(2)	2.006(5)
O(1)-Cu(1)-O(5)	92.37(17)	O(1)-Cu(1)-N(1)	176.19(19)
O(1)-Cu(1)-N(4A)	94.49(18)	O(1)-Cu(1)-N(5B)	87.32(19)
O(5)-Cu(1)-N(1)	87.41(17)	O(5)-Cu(1)-N(4A)	92.05(16)
O(5)-Cu(1)-N(5B)	167.23(18)	N(1)-Cu(1)-N(4A)	89.31(19)
N(1)-Cu(1)-N(5B)	92.05(19)	N(4A)-Cu(1)-N(5B)	100.70(18)
O(2C)-Cu(2)-O(4D)	93.41(18)	O(2C)-Cu(2)-O(5)	171.86(17)
O(2C)-Cu(2)-O(5C)	94.17(15)	O(2C)-Cu(2)-N(2)	86.21(18)
O(4D)-Cu(2)-O(5)	94.72(17)	O(4D)-Cu(2)-O(5C)	91.55(15)
O(4D)-Cu(2)-N(2)	163.92(18)	O(5)-Cu(2)-O(5C)	85.45(15)
O(5)-Cu(2)-N(2)	86.02(18)	O(5C)-Cu(2)-N(2)	104.52(17)
		1-Cr ₂ O ₇	
Cu(1)-O(1A)	1.948(3)	Cu(1)-O(5)	1.927(3)
Cu(1)-N(1)	2.031(4)	Cu(1)-N(4B)	1.989(4)
Cu(1)-N(5C)	2.347(4)	Cu(2)-O(2D)	1.956(3)
Cu(2)-O(4)	2.015(4)	Cu(2)-O(5)	1.924(3)
Cu(2)-O(5E)	2.253(3)	Cu(2)-N(2)	2.022(4)
O(1A)-Cu(1)-O(5)	91.87(14)	O(1A)-Cu(1)-N(1)	176.20(16)
O(1A)-Cu(1)-N(4B)	87.46(16)	O(1A)-Cu(1)-N(5C)	94.65(15)
O(5)-Cu(1)-N(1)	87.55(15)	O(5)-Cu(1)-N(4B)	166.98(16)
O(5)-Cu(1)-N(5C)	93.10(14)	N(1)-Cu(1)-N(4B)	92.26(16)
N(1)-Cu(1)-N(5C)	89.13(16)	N(4B)-Cu(1)-N(5C)	99.92(15)
O(2D)-Cu(2)-O(4)	92.63(16)	O(2D)-Cu(2)-O(5)	171.38(15)
O(2D)-Cu(2)-O(5E)	93.42(13)	O(2D)-Cu(2)-N(2)	85.96(15)
O(4)-Cu(2)-O(5)	95.92(15)	O(4)-Cu(2)-O(5E)	92.74(14)
O(4)-Cu(2)-N(2)	162.64(16)	O(5)-Cu(2)-O(5E)	85.10(13)
O(5)-Cu(2)-N(2)	86.20(15)	O(5E)-Cu(2)-N(2)	104.61(14)

Symmetry transformations used to generate equivalent atoms: A 1-X, -1/2+Y, 1/2-Z; B X, 3/2-Y, 1/2+Z; C -X, 1-Y, 1-Z; D X, 1/2-Y, -1/2+Z for 1-Br; A X, 3/2-Y, 1/2+Z; B X, 1/2-Y, 1/2+Z; C 1-X, 1/2+Y, 1/2-Z; D -X, -1/2+Y, 1/2-Z; E -X, 1-Y, 1-Z for 1-Cr₂O₇.

D-H-A	d(D-H)	d(H···A)	D(D···A)	<(DHA)
O(5)-H(5)-O(6)	0.85(2)	1.98(4)	2.739(6)	148(7)
O(6)-H(6A)-O(9)	0.85	2.24	2.955(19)	142.2

O(5)-H(6A)-O(10)	0.85	2.44	3.07(3)	131.6
O(6)-H(6B)-O(16) ⁱ	0.85	2.63	3.07(4)	113.4
O(6)-H(6B)-O(17) ⁱ	0.85	2.07	2.86(3)	155.1
O(6)-H(6B)-O(18) ⁱ	0.85	2.31	3.150(17)	170.4
C(11)-H(11)-O(12)	0.93	2.45	3.262(11)	146.2
C(3)-H(3B)-O(19) ⁱⁱ	0.97	2.65	3.40(2)	133.7
C(3)-H(3B)-O(20) ⁱⁱ	0.97	2.56	3.45(2)	153.3
C(21)-H(21A)-O(10)	0.97	2.51	3.35(3)	145.2

Symmetry transformations used to generate equivalent atoms: i X, 1+Y, Z; ii 1-X, -Y, 1-Z.

Table S3 Adsorption capacities for dichromate on various porousmaterials.

MOF-type Adsorbents	Maximum capacity	The single-crystal to single-crystal process	Reference
Zno.5Coo.5SLUG-35	68.5 mg/g or 0.43	No	1
	mol/mol		
2D Ag based-MOFs	60.0 mg/g	Νο	2
3D Dy-MOFs	62.9 mg/g	Νο	3
3D Ag-based MOF	0.73 mol/mol	Yes	4
FIR-53	74.2 mg/g	Yes	5
FIR-54	103.1 mg/g	Νο	5
ZJU-101	245 mg/g	Νο	6
3D Ni based MOF	166 mg/g	Νο	7
1-Br	128 mg/g or 0.84	Yes	This work
	mol/mol		
Other types	Maximum capacities (mg/g)		Reference
Adsorbents			
Amino starch	12.12		8
β-CD and quaternary	61.05		9
ammonium groups			
modified cellulose			
Hexadecylpyridinium	14.31		10

bromide modified		
natural zeolites		
Modified magnetic	58.48	11
chitosan chelating		
resin		
Amino-functionalized	153.85	12
titanate nanotubes		

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Fig. S1 The coordination environment of Cu(II) atoms in 1-Br.



Fig. S2 The coordination mode of 1,4-bda ligand: One 1,4-bda ligand connects two tetranuclear $[Cu_4(\mu_3\text{-}OH)_2]$ clusters in 1-Br.



Fig. S3 One mtrb ligand connects three tetranuclear $[Cu_4(\mu_3-OH)_2]$ clusters in 1-Br.



Fig. S4 Each tetranuclear $[Cu_4(\mu_3\text{-}OH)_2]$ cluster connects six mtrb ligands in 1-Br.



Fig. S5 The 10-connected $[Cu_4(\mu_3\text{-}OH)_2]$ tetranuclear copper(II) cluster in 1-Br.



Fig. S6 UV/Vis spectra of $Cr_2O_7^{2-}$ aqueous solution during exchange with equimolar 1-Br and 36.7 ppm $Cr_2O_7^{2-}$ aqueous solution.



Fig. S7 UV-vis spectra of $Cr_2O_7^{2-}$ aqueous solution during anion exchange with double molar amount of **1-Br** and 36.7 ppm $Cr_2O_7^{2-}$ aqueous solution.



Fig. S8 PXRD patterns for simulated and measured of **1-Br**, simulated and measured of **1-Cr₂O₇**, molar ratio 1:1 and 2:1 (**1-Br** to $Cr_2O_7^{2-}$) anion exchange.



Fig. S9 The $[Cu_4(OH)_2(mtrb)_2(1,4-bda)_2]_n$ 3D network in $1-Cr_2O_7$.



Fig. S10 UV-vis spectra of the mixed aqueous solution during anion exchange.



Fig. S11 IR spectra for 1-Br, $1-Cr_2O_7$ and 1-Br immersed in the mixed aqueous solution during anion exchange.