Supplementary Data

A copper(II)-based porous metal–organic framework for efficient and rapid capture of toxic oxo-anion pollutants from water

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Material and methods. Chemicals were received commercially. 1,4,8,11-Tetraazacyclotetradecane-*N,N′,N″,N‴*-tetramethylenecinnamic acid (H_4L) was synthesized by following the reported method.[1,2] A Mattson Alpha Centauri spectrometer was used to determine FT-IR spectra. UV/vis spectrum was conducted with a Cary TU-1900 double beam UV/vis spectrophotometer. Elemental analyses (C, H and N) were recorded on a Euro vector EA3000 elemental analyzer. A Rigaku Dmax 2000 X-ray diffractometer with graphite monochromatized CuKα radiation (λ = 0.154 nm) was utilized to measure PXRD pattern. Thermogravimetric curve was determined on a Perkin-Elmer Model TG-7 analyzer. ICP data was conducted on a Leeman Laboratories Prodigy inductively coupled plasma-optical atomic emission spectrometry (ICP-AES). Scanning electron microscopy (SEM) was tested on Hitachi SU8010. Energy dispersive X-ray Spectroscopy (EDS) (EDX spectra and EDX mapping) was recorded on Hitachi SU8010 EDAX.

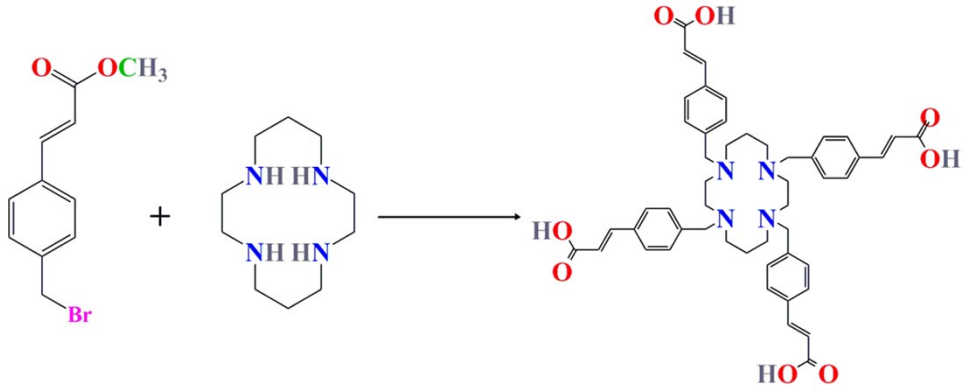
X-Ray crystallography. Crystallographic data was achieved on an Oxford Diffraction Gemini R Ultra diffractometer with graphite-monochromated MoKα radiation (λ = 0.71073 Å). Crystal structure was solved by the direct methods with SHELXS-2018, and refined with SHELXL-2018 program within WINGX.[3-5] Absorption corrections were accomplished with a multi-scan technique. Non-hydrogen atoms were refined anisotropically. Disordered solvents were removed with the SQUEEZE in PLATON.[6] Selected bond lengths and angles, and crystallographic data were summarized in Tables S1and S2.

Synthesis of 1. $CuCl_2{\cdot}2H_2O$ (7 mg, 0.04 mmol) and H_4L (8 mg, 0.01 mmol) were dissolved in a mixture of DMA (3 mL) and water (1 mL). The mixture was sealed in a Teflon reactor (15 mL) and heated at 80 °C for two days. After cooling to room temperature, green block-shaped crystals were achieved in a 65% yield. Anal. Calcd for $C_{66}H_{116}Cl_2Cu_3N_8O_{22}$ (*Mr* = 1635.18): C, 48.48; H, 7.15; N, 6.85. Found: C, 48.95; H, 7.77; N, 7.06. IR data (KBr, cm^{-1}): 3444.87 (w), 2935.40 (w), 1638.56 (s), 1510.96 (m), 1387.88 (s), 1267.77 (m), 1187.83 (w), 1063.12 (w), 1016.04 (w), 983.50 (w), 921.25 (w), 840.82 (w), 813.78 (w), 722.37 (w), 593.01 (w), 498.56 (w).

Anion exchange procedure. The sample of **1** (30 mg) was soaked in 5 mL aqueous

solution of $KMnO_4$ (3 mM, 4 mM, 5 mM and 6 mM) with stirring at room temperature. Anion exchange was monitored with UV/vis spectroscopy (545.5 nm). Similar $Cr_2O_7^{2-}$ exchange experiments were also determined in aqueous solutions of $K_2Cr_2O_7$ (1 mM, 2 mM and 3 mM) (352 nm). The sample of **1** (20 mg) was added to aqueous solution of $Cr_2O_7^{2-}$ (0.4 mM, 3 mL).

Anion selectivity. The sample of **1** (10 mg) was immersed in an aqueous solution of $KMnO_4$ (4 mM, 5 mL). $NaClO_4$, $NaNO_3$, NH_4PF_6 or KH_2PO_4 (4 mM/40 mM) was added to the mixture, respectively. After 5 h, the solution was monitored with UV/vis absorption spectroscopy. Similarly, the sample of **1** (10 mg) was soaked in an aqueous solution of $K_2Cr_2O_7$ (0.5 mM, 3 mL). $NaClO_4$, $NaNO_3$, NH_4PF_6 or KH_2PO_4 (0.5 mM/5 mM) was added to the mixture, respectively. After 9 h, the solution was monitored with UV/vis absorption spectroscopy.



Scheme S1 Synthetic procedure for H_4L.

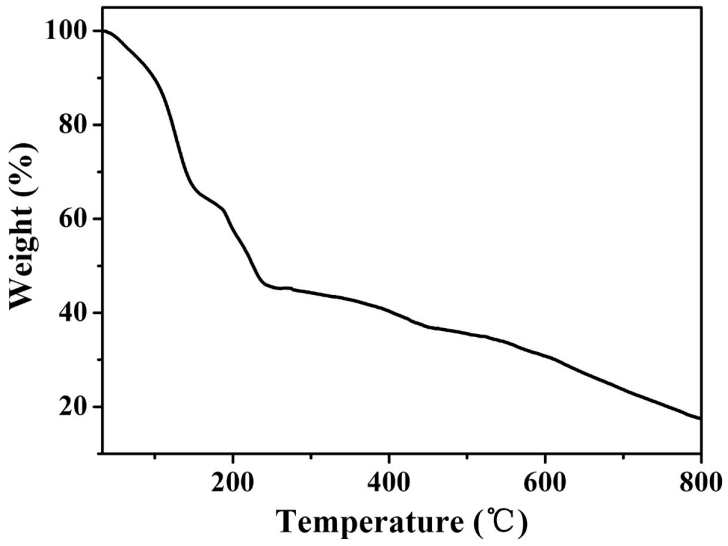
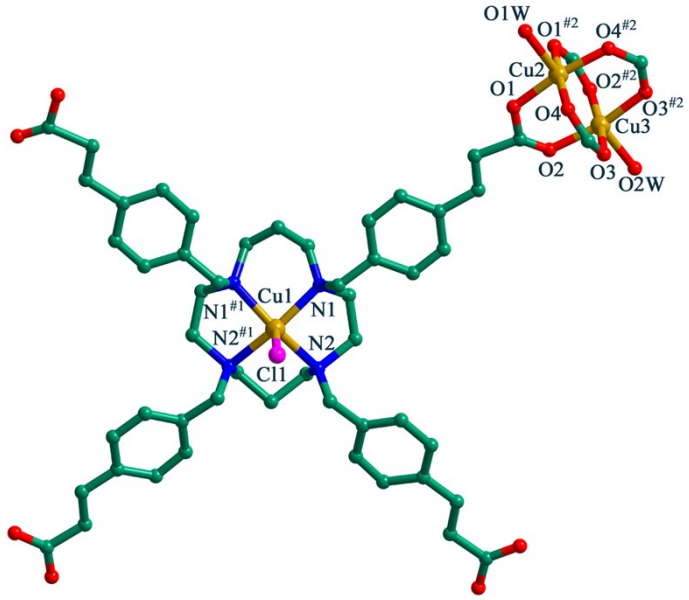
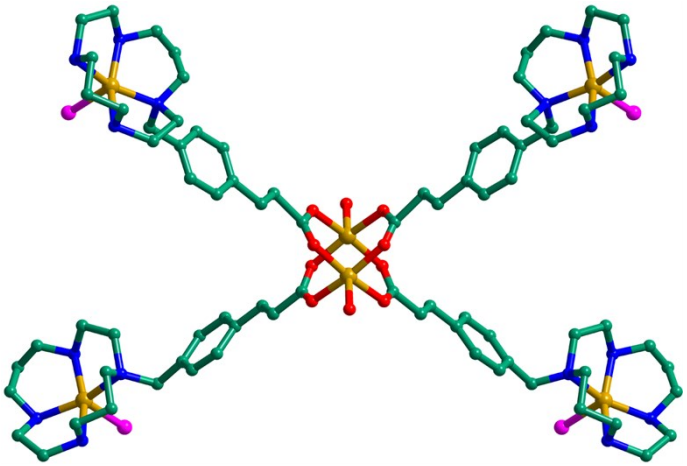


Fig. S1 Thermogravimetric curve of **1**.

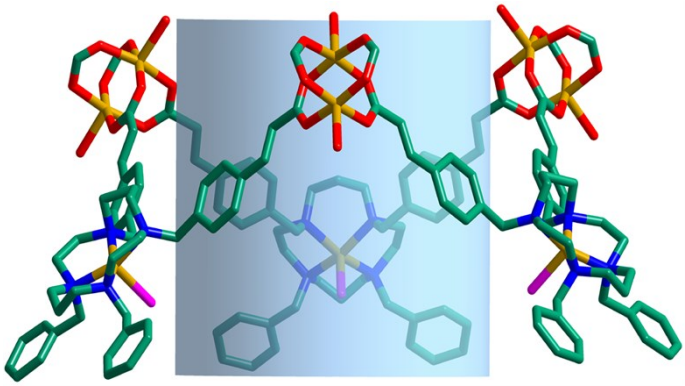
The weight loss before 156 °C is probably ascribed to the removal of four DMA molecules and ten water molecules (calculated: 34.75%, observed: 34.49%).



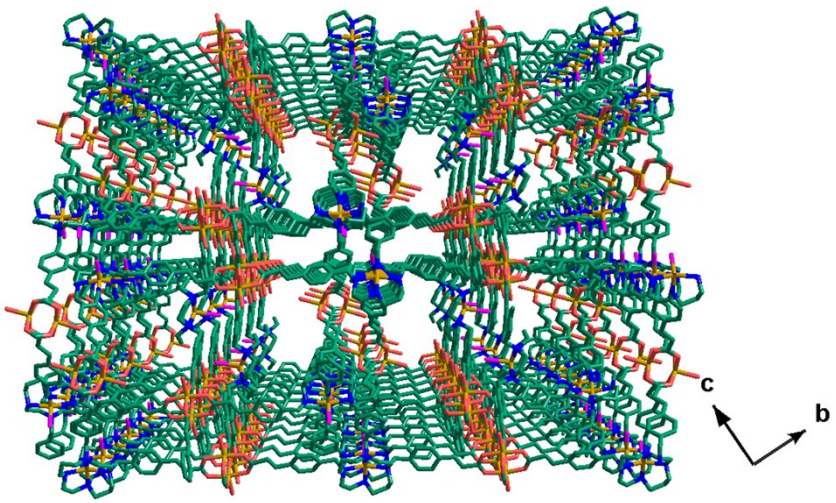
(a)



(b)



(c)



(d)

Fig. S2 (a) Coordination environments of Cu(II). (b) Structure of $[Cu_2(COO)_4(H_2O)_2]$ unit. (c) 1D nanotubular channel. (d) Packing structure of **1**.

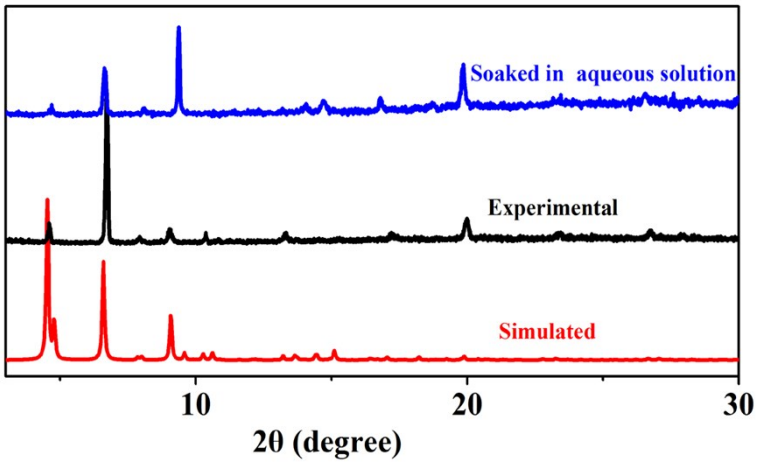


Fig. S3 The simulated (red) and experimental (black) PXRD patterns of **1** and the one after immersion in water (blue).

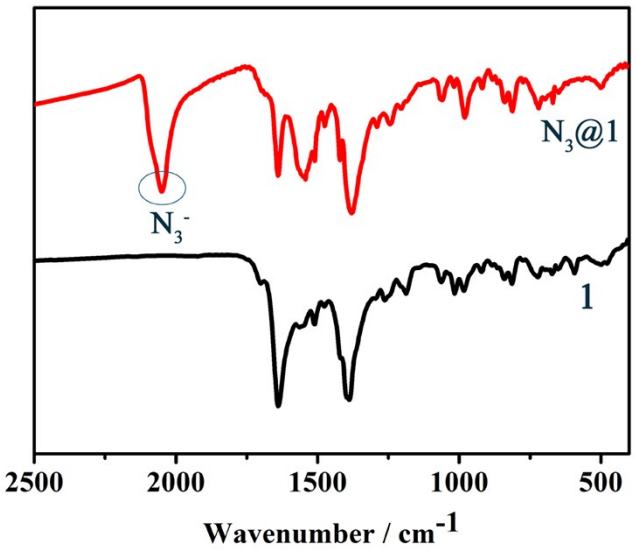


Fig. S4 IR spectra of **1** and **N_3@1**.

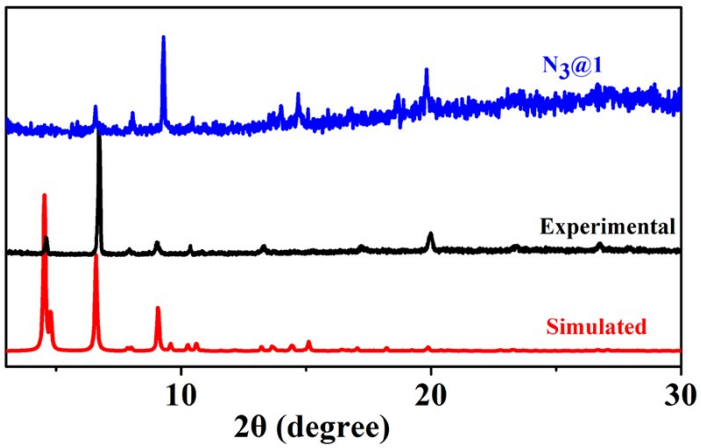
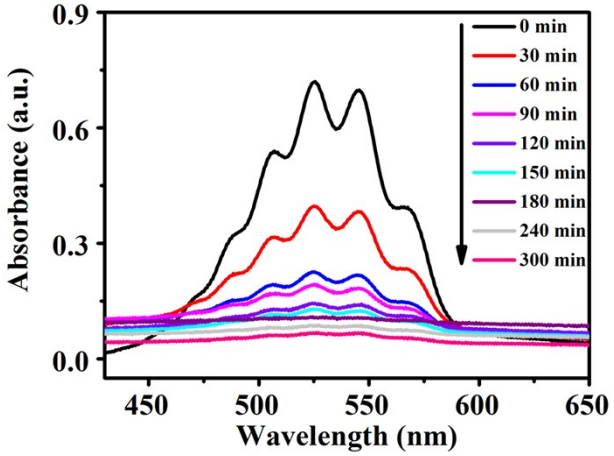
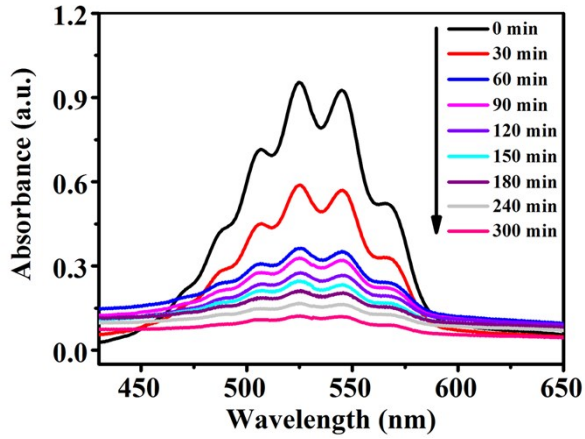


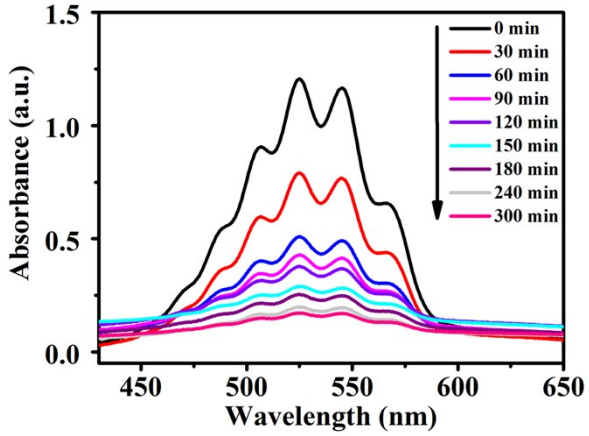
Fig. S5 PXRD patterns of the simulated (red), the experimental (black) and the anion exchange with N_3^- (blue).



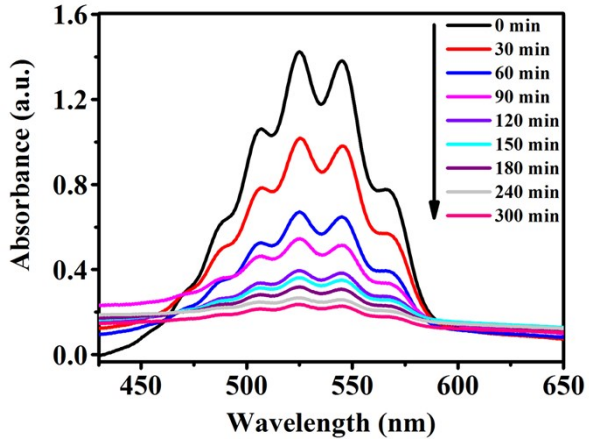
(a)



(b)



(c)



(d)

Fig. S6 Uv-vis adsorption spectra of MnO_4^- in the anion exchange process (3 mM (a), 4 mM (b), 5 mM (c) and 6 mM (d)).

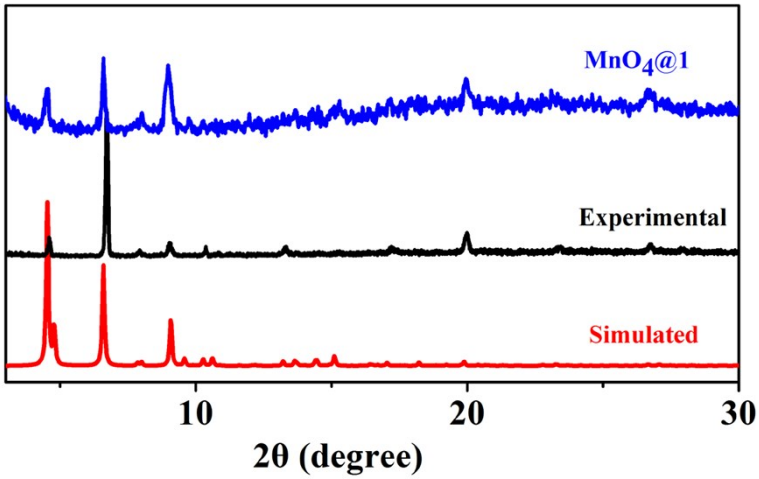
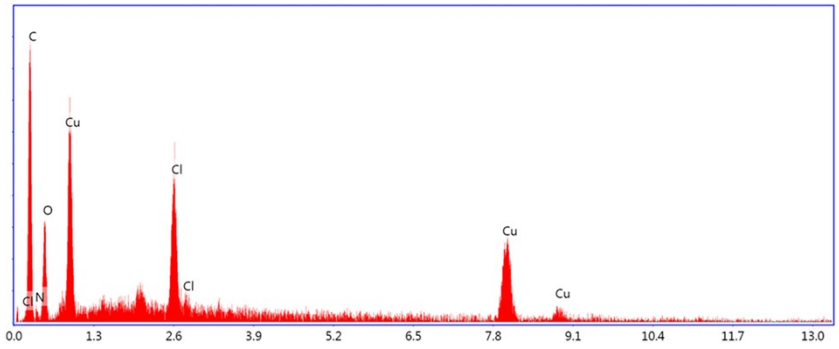
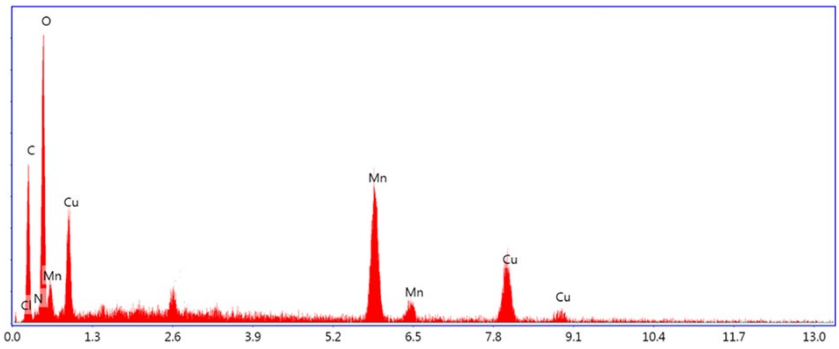


Fig. S7 PXRD patterns of the simulated (red), the experimental (black) and after anion exchange with MnO_4^- (blue).

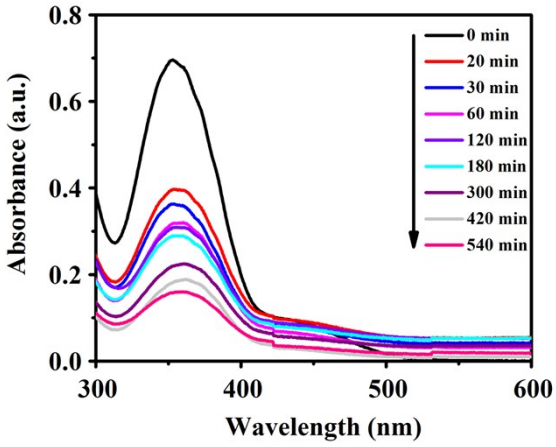


(a)

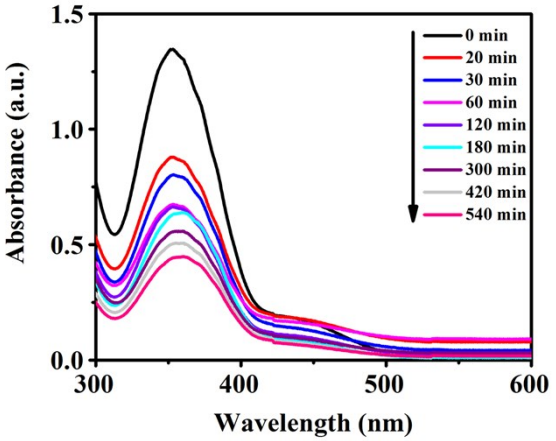


(b)

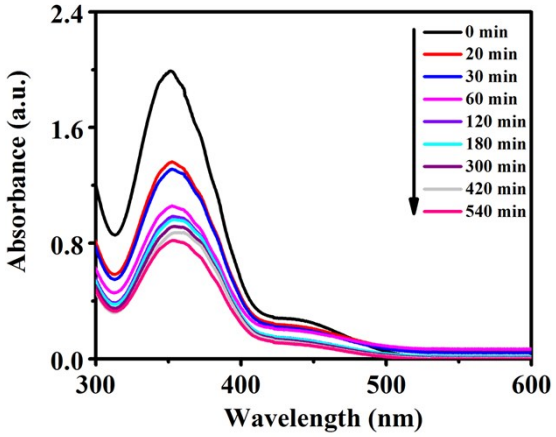
Fig. S8 EDX spectra of **1** (a) and **MnO_4@1** (b).



(a)



(b)



(c)

Fig. S9 Uv-vis adsorption spectra of $Cr_2O_7^{2-}$ in the anion exchange process (1 mM (a), 2 mM (b) and 3 mM (c)).

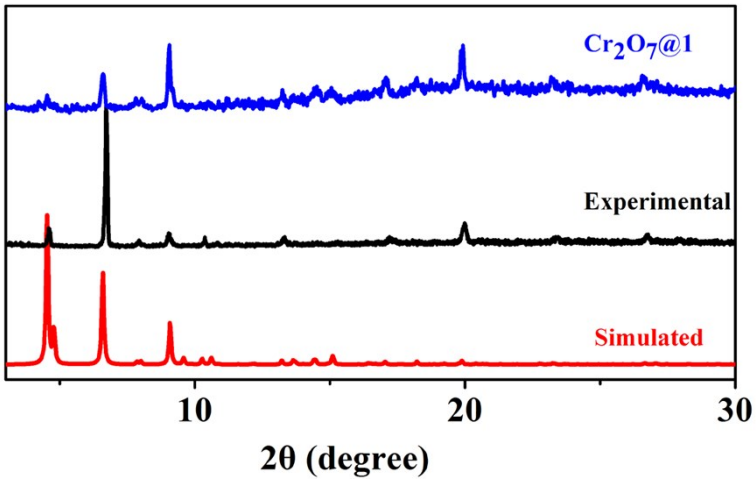
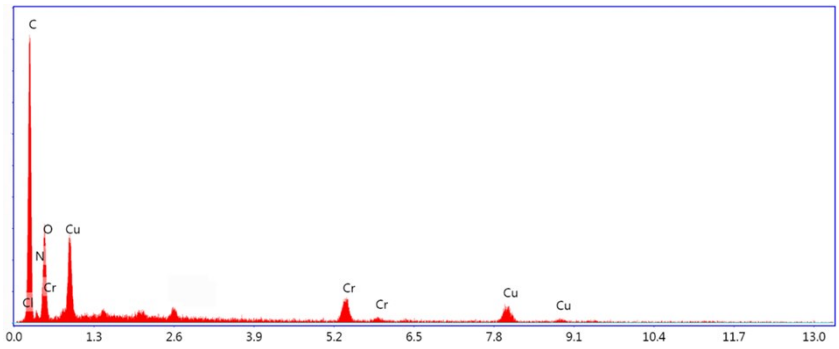


Fig. S10 PXRD patterns of the simulated (red), the experimental (black) and after $Cr_2O_7^{2-}$ exchange (blue).

(a)



(b)

Fig. S11 EDX spectra of **1** (a) and **Cr_2O_7@1** (b).

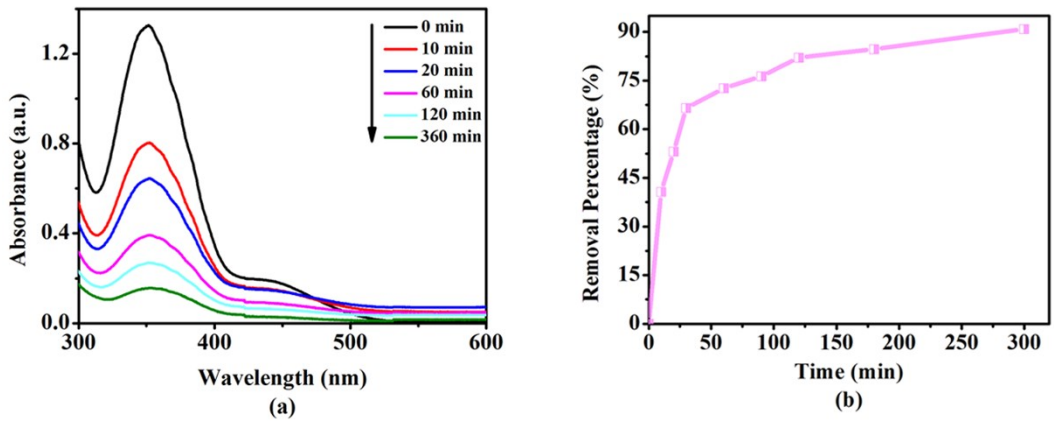


Fig. S12 (a) UV/vis absorption spectra of $Cr_2O_7^{2-}$ removed by **1** at different time intervals. (b) Absorption kinetics of $Cr_2O_7^{2-}$ (0.4 mM).

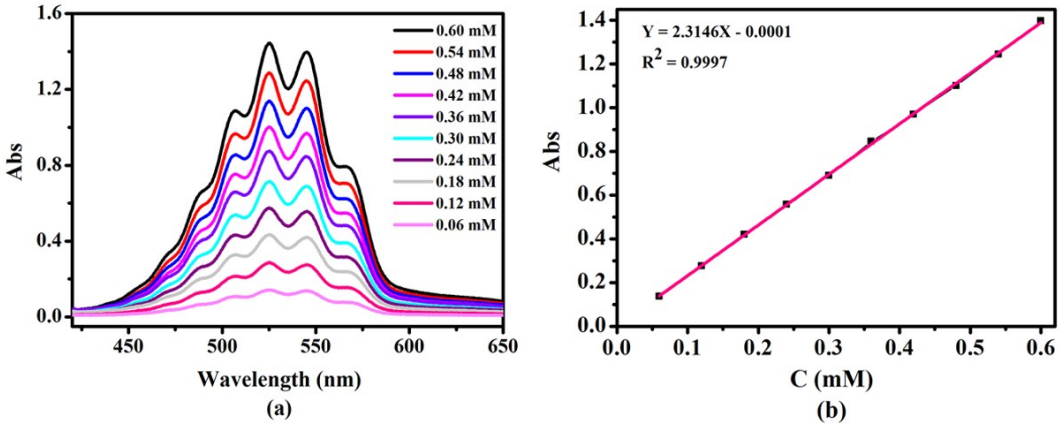


Fig. S13 (a) Calibration plot of standard MnO_4^- determined by UV/vis spectra. (b) Fitting plot of MnO_4^- concentration *vs* Abs value.

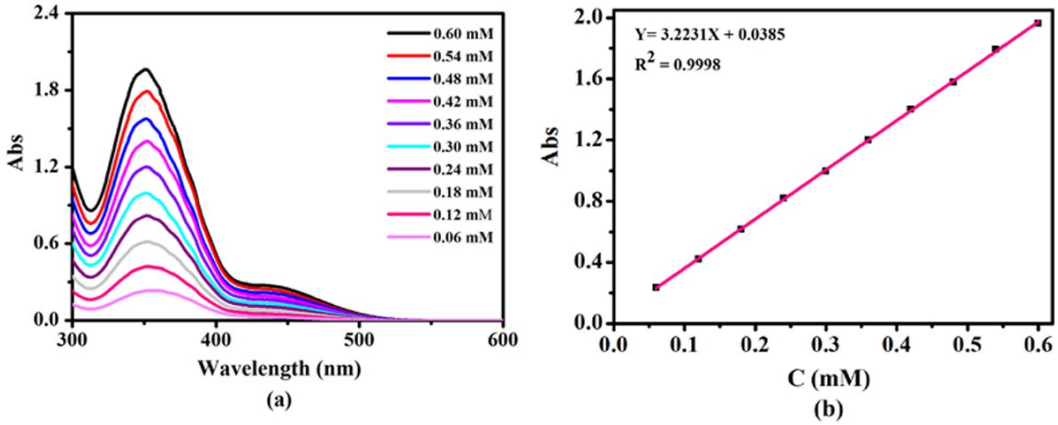


Fig. S14 (a) Calibration plot of standard $Cr_2O_7^{2-}$ determined by UV/vis spectra. (b) Fitting plot of $Cr_2O_7^{2-}$ concentration *vs* Abs value.

Table S1 Selected Bond Distances (Å) and Angles (°) for **1**.

1			
Cu(1)-N(1)	2.116(4)	O(1)$^{\#2}$-Cu(2)-O(1)	90.3(2)
Cu(1)-N(2)	2.135(4)	O(1)-Cu(2)-O(4)$^{\#2}$	171.2(2)
Cu(1)-Cl(1)	2.432(2)	O(1)$^{\#2}$-Cu(2)-O(4)	171.2(2)
Cu(2)-O(1)	1.931(3)	O(1)$^{\#2}$-Cu(2)-O(4)$^{\#2}$	89.52(15)
Cu(2)-O(4)	1.959(3)	O(4)-Cu(2)-O(4)$^{\#2}$	89.4(2)
Cu(2)-O(2W)	2.188(5)	O(1)-Cu(2)-O(2W)	95.30(18)
Cu(3)-O(2)	1.997(4)	O(1)$^{\#2}$-Cu(2)-O(2W)	95.30(18)
Cu(3)-O(3)	1.971(3)	O(4)-Cu(2)-O(2W)	93.44(16)
Cu(3)-O(1W)	2.163(7)	O(4)$^{\#2}$-Cu(2)-O(2W)	93.43(16)
N(1)-Cu(1)-N(2)	87.95(17)	O(2)-Cu(3)-O(2)$^{\#2}$	89.6(2)
N(1)-Cu(1)- N(2)$^{\#1}$	160.0(2)	O(3)-Cu(3)-O(2)	88.73(15)
N(1)-Cu(1)-N(1) $^{\#1}$	87.6(2)	O(3)$^{\#2}$-Cu(3)- O(2)	167.8(2)
N(1)$^{\#1}$-Cu(1)-N(2)	160.0(2)	O(3)-Cu(3)-O(2)$^{\#2}$	167.8(2)
N(1)$^{\#1}$-Cu(1)-N(2)$^{\#1}$	87.95(17)	O(3)$^{\#2}$-Cu(3)-O(2)$^{\#2}$	88.72(15)
N(2)-Cu(1)- N(2)$^{\#1}$	89.6(3)	O(2)-Cu(3)-O(1W)	96.2(2)
N(1)-Cu(1)-Cl(1)	101.70(15)	O(2)$^{\#2}$-Cu(3)-O(1W)	96.2(2)
N(1)$^{\#1}$-Cu(1)-Cl(1)	101.70(15)	O(3)-Cu(3)-O(1W)	96.01(19)
N(2)-Cu(1)-Cl(1)	98.29(19)	O(3)$^{\#2}$-Cu(3)-O(1W)	96.01(19)
N(2)$^{\#1}$-Cu(1)-Cl(1)	98.30(19)	O(3)$^{\#2}$-Cu(3)-O(3)	90.4(2)
O(1)-Cu(2)-O(4)	89.52(15)		

Symmetry transformations used to generate equivalent atoms:

$^{\#1}$ -*y*+1, -*x*+1, *z*; $^{\#2}$ -*x*+*y*, *y*, *z*; $^{\#3}$ -*y*+2/3, *x*-*y*+1/3, *z*+1/3; $^{\#4}$ -*x*+*y*+1/3, -*x*+2/3, *z*-1/3.

Table S2 A comparison of the adsorption capacity of **1** for the MnO_4^- anion with other reported adsorbents.

Adsorbents	Q_t (mg/g)	Selectivity	Ref.
1	106	ClO_4^-, NO_3^-, PF_6^-, $H_2PO_4^-$	This work
$[Ag_4(L_1)_6](BF_4)_4$	75.2	Cl^-,Br^-,NO_3^-	7
$\{[Ag_2(H_2O)(L_2)_2]\cdot(BF_4)_2\}_n$	83.4	Cl^-,Br^-,NO_3^-	7
$\{[Zn_2(BDC)_{1.5}(L_3)(DMF)]NO_3\}_n$	104	various anions	8
$\{[Cd(L_5)_2]\cdot(ClO_4)_2\}_n$ (IPM-206)	113	PF_6^-, $CF_3SO_3^-$	9
$[Ag(L_4)](NO_3)(H_2O)(CH_3CN)$ (**1**·NO_3)	297.9	various anions	10

Table S3 A comparison of the adsorption capacity of **1** for the $Cr_2O_7^{2-}$ anion with other reported adsorbents.

Adsorbents	Q_t (mg/g)	Selectivity	Ref.
1	70	ClO_4^-, NO_3^-, PF_6^-, $H_2PO_4^-$	This work
Cu-BTC	48	–	11
$Zr_6O_4(OH)_4(BPYDC)_6$ (MOF-867)	53.4	–	12
$[Zn_2(Tipa)_2(OH)]\cdot3NO_3\cdot12H_2O$ (FIR-53)	74.2	Cl^-,Br^-,NO_3^-	13
$[Ag(L_4)](CF_3CO_2)(H_2O)$	207	various anions	14
TJNU-243	273	various anions	15
TJNU-244	269	various anions	15
TJNU-334	293	various anions	15

Table S4 Crystallographic Data and Structural Refinement for **1**.

Compound	**1**
Formula	$C_{66}H_{116}Cl_2Cu_3N_8O_{22}$
Mr	1635.18
Crystal system	Trigonal
Space group	*R-3m*
a (Å)	38.907(3)
b (Å)	38.907(3)

c (Å)	44.043(3)
α(°)	90
β(°)	90
γ(°)	120
V (Å^3)	57737(9)
Z	18
D_{calc} (g cm^{-3})	0.847
F(0 0 0)	15570
R_{int}	0.118
GOF on F^2	0.969
$R1^a$ [I>2σ(I)]	0.1076
wR_2^b (all data)	0.3465

$^aR_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^bwR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma w(F_o^2)^2]\}^{1/2}$

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