Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary materials

A microporous cationic metal-organic framework for the efficient removal of dichromate and selective adsorption of dyes from water

Mingming Guo,[a] Huadong Guo,[a]* Siyu Liu,[a] Yingying Sun[a] and Xianmin Guo[a]*

[a] Department of Chemistry, Changchun Normal University, Changchun 130032, People's Republic of China

The evaluation of $NO_3^-/Cr_2O_7^{2-}$ exchange capacity of 1.

The anion-exchange capacity of **1** was evaluated by measuring the decolorization rate of aqueous $K_2Cr_2O_7$ solution, which was calculated by the following formula:

$$Q_e = \frac{(C_0 - C_e)V}{m}$$

where Ci and Ce (mg/L) are the initial and equilibrium Cr(VI) concentration, respectively. V (mL) is the volume of Cr(VI) solution, m(mg) is the mass of adsorbent.

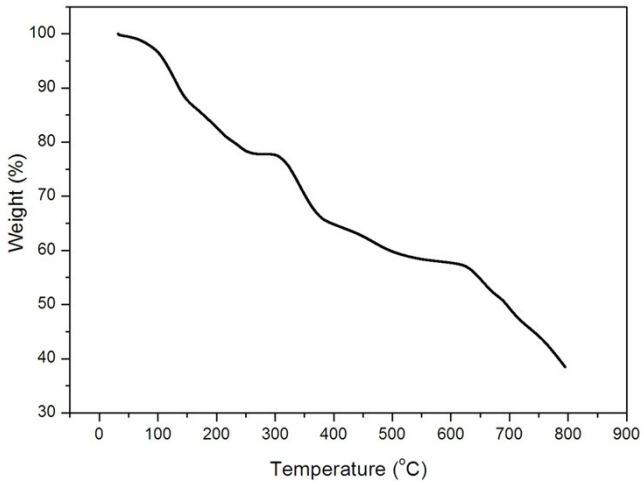

Fig. S1. The TGA curves of **1**. To characterize the thermal stabilities of compounds **1**, its thermal behavior was investigated by TGA. The experiments were performed on samples consisting of numerous single crystals of **1** under nitrogen atmosphere with a heating rate of 10°C/min. The weight loss in the range of 25-250°C is attributed to the release of free DMF molecule, coordinated water molecule and NO_3^- (obsd 21.6%, calcd 19.5%). The destruction of the framework occurs at ca. 300°.

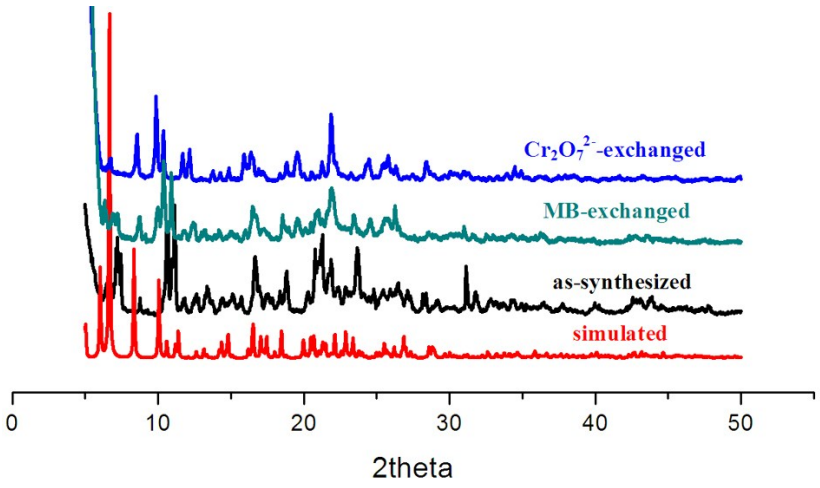

Fig. S2. PXRD patterns of the as-synthesized **1**, MB@**1** and $Cr_2O_7^{2-}$@**1**.

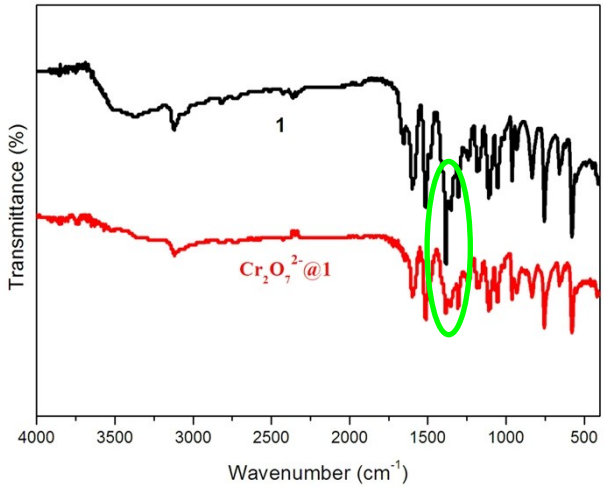

Fig. S3. IR spectra for: as-synthesized **1** and **$Cr_2O_7^{2-}$@1** obtained in a 200 mg/L $K_2Cr_2O_7$ aqueous solution for 0.5 hour. The peaks of NO_3^- significantly reduced, indicating that the NO_3^- ions were replaced by $Cr_2O_7^{2-}$ anion ions.

The evaluation of adsorption effeciency of 1 to $Cr_2O_7^{2-}$ impacted by 5-fold of Cl^-, Br^-, I^-, NO_3^- and SO_4^{2-}.

10 mg of **1** was immersed in 15 mL of solutions of $K_2Cr_2O_7$ (50 mg L^{-1}) together with 5-fold molar excess of Cl^-, Br^-, I^-, NO_3^- and SO_4^{2-} together, then agitated in a magnetic stirring for 2 hours. As shown in Fig. S4, the adsorption effeciency decreased to 45%, below the values when single disturbing ions were added (ca. 90%). Obviously, with the anions increasing exponentially, the competition exclusion between them affects the adsorption of $Cr_2O_7^{2-}$.

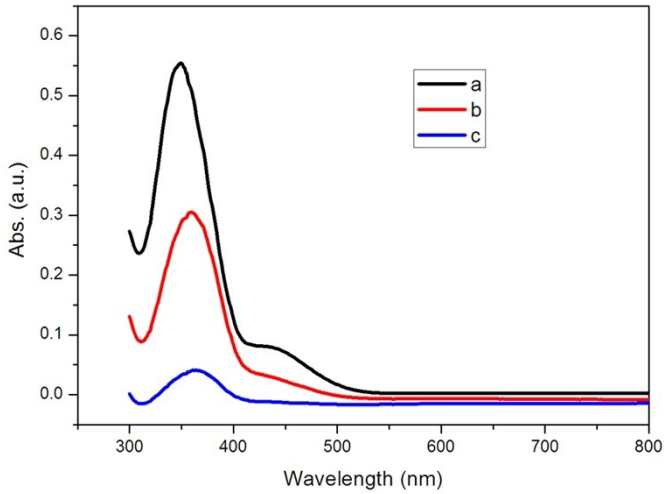

Fig. S4. (a) UV-vis adsorption spectra of $Cr_2O_7^{2-}$ solution without **1**. (b) UV-vis adsorption spectra of $Cr_2O_7^{2-}$ solution after ion-exchange by adding 5-fold of Cl^-, Br^-, I^-, NO_3^- and SO_4^{2-}. (c) UV-vis adsorption spectra of $Cr_2O_7^{2-}$ solution after ion-exchange without adding disturbing anions.

The releasing process of $Cr_2O_7^{2-}$/NO^{3-} exchange for 1.

The releasing process was carried out to evaluate the regeneration ability of the ion exchanger. The samples were centrifuged, rinsed with water, and dried in air after 10 mg of **1** being submerged in 15 mL dichromate solution (50 mg/L) for 2 h; then the solid was placed in the same volume solution in the presence of a 200-fold molar

excess of KNO_3. The UV-Vis measurement showed that the release efficiency of $Cr_2O_7^{2-}$ was ca. 69% after 24 h (Fig. S5).

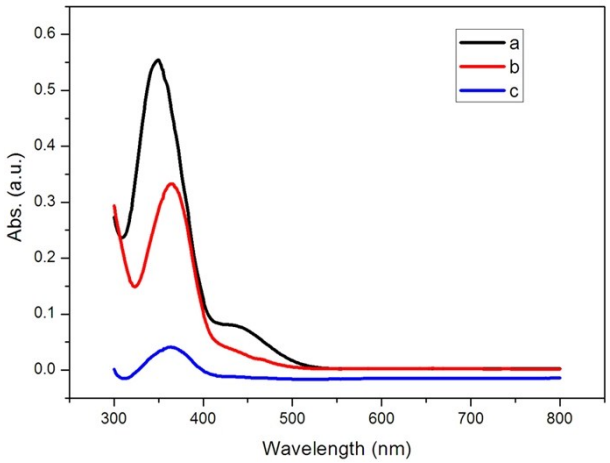

Fig. S5. (a) UV-vis adsorption spectra of $Cr_2O_7^{2-}$ solution without **1**. (b) UV-vis adsorption spectra of $Cr_2O_7^{2-}$ solution after the releasing process in the presence of a 200-fold molar excess of KNO_3. (c) UV-vis adsorption spectra of $Cr_2O_7^{2-}$ solution after ion-exchange with **1**.

Table S1. Crystal and Structure Refinement Data for Compounds **1**.

param	**1**
formula	$C_{31}H_{31}CdN_8O_8P$
fw	787.01
space group	$P2_1/c$
a	17.9427(8)
b	26.5356(12)
c	8.4262(4)
α (deg)	90
β(deg)	101.4620(10)
γ (deg)	90
V	3931.9(3)

Z	4
D_{calcd} (g cm^{-3})	1.330
F(000)	1600
GOF on F^2	1.108
R_1/wR_2[I≥2sigma(I)]	0.0337/0.0830
R_1/wR_2 (all data)	0.0373/0.0845

Table S2. Bond lengths [Å] and angles [°] for **1**.

Cd(1)-N(1)	2.2892(19)	Cd(1)-N(4)#4	2.2976(18)
Cd(1)-N(6)#2	2.3490(18)	Cd(1)-O(2)	2.6241(15)
Cd(1)-O(3)	2.4855(18)	Cd(1)-O(4)	2.3822(17)
N(1)-Cd(1)-N(4)#4	168.35(7)	N(1)-Cd(1)-N(6)#2	104.30(7)
N(4)#4-Cd(1)-N(6)#2	86.15(7)	N(1)-Cd(1)-O(2)#5	91.57(6)
N(4)#4-Cd(1)-O(2)#5	94.95(6)	N(6)#2-Cd(1)-O(2)#5	82.41(6)
N(1)-Cd(1)-O(4)	84.64(7)	N(4)#4-Cd(1)-O(4)	92.57(6)
N(6)#2-Cd(1)-O(4)	78.61(6)	O(2)#5-Cd(1)-O(4)	159.05(6)
N(1)-Cd(1)-O(3)	82.59(7)	N(4)#4-Cd(1)-O(3)	90.15(6)
N(6)#2-Cd(1)-O(3)	154.32(6)	O(2)#5-Cd(1)-O(3)	72.59(5)
O(4)-Cd(1)-O(3)	126.99(6)	N(1)-Cd(1)-O(2)	83.86(6)
N(4)#4-Cd(1)-O(2)	84.50(6)	N(6)#2-Cd(1)-O(2)	153.10(6)
O(2)#5-Cd(1)-O(2)	123.48(3)	O(4)-Cd(1)-O(2)	76.68(6)
O(3)-Cd(1)-O(2)	50.92(5)		

Symmetry transformations used to generate equivalent atoms: #2 -x+2,-y,-z+1; #4 x-1,y,z; #5 x,-y+1/2,z+1/2.