Electronic Supplementary Material (ESI) for ChemComm.

Supporting information

A Porous Zr-cluster-based Cationic Metal-Organic Framework for Highly Efficient $Cr_2O_7^{2-}$ Removal in Water

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1.1 Materials and characterization.

All the chemicals were commercially available and used without further purification. ^{1}H NMR spectra were recorded on a Bruker Advance DMX 500 spectrometer using tetramethylsilane (TMS) as an internal standard. Thermogravimetric analyses (TGA) were carried out on a Netzsch TG209F3 with a heating rate of 1 ˚C/min in N_2 atmosphere. Infrared spectrum (IR) was recorded on Thermo Fisher Nicolet iS10 spectrometer using KBr pallets. Powder X-ray diffraction (PXRD) patterns were collected in the 2θ = 5-50° range on an X'Pert PRO diffractometer with Cu Kα (λ = 1.542Å) radiation at room temperature.

1.2 Synthesis of MOF-867 and ZJU-101

Synthesis of MOF-867: To a 50 mL vial containing $ZrCl_4$ (116.7 mg, 0.5 mmol), 2,2'-bipyridine-5,5'-dicarboxylate (H_2bpydc) (122.1 mg, 0.5 mmol) was added DMF (18 mL) and glacial acetic acid (1 mL, 17.5 mmol). The resulting mixture was sonicated for 20 min until fully dissolved. The temperature was kept at 120 °C for 24 hours. The resulting white solid was isolated by filtration, and was washed with DMF and methanol repeatedly before being dried under vacuum.

Synthesis of ZJU-101: MOF-867 (ca. 200 mg) was placed in a vial with 20 mL solution of trifluoromethanesulphonate (10 folder molar excess of N atoms in **MOF-867**) in $CHCl_3$. The solution was stirred for 48 h at room temprature. The resulting solid was washed with $CHCl_3$, aqueous solution of 0.1mol/L $NaNO_3$ and acetone for several times, isolated by centrifugation, and dried under vacuum for at least 6 h.

1.3 Details of $Cr_2O_7^{2-}$ absorption test

Before adsorption, **MOF-867** and **ZJU-101** was dried overnight under vacuum at 60 ˚C and kept in a desiccator. Then the adsorbent (10 mg) was weighed precisely. During the adsorption process, adsorbents (10 mg) were used for the removal of dichromate with the concentration of 50 ppm. The dichromate solutions (20ml) containing the adsorbents were mixed well with magnetic stirring and maintained for a fixed time (5 min to 12 h) at 25 ˚C. The solution was separated from the adsorbent with a syringe filter (PTFE, 0.25 μm) for calculation of dichromate concentration by comparing the UV/vis absorbance (at λ=257 nm).

The pseudo second-order equation can be expressed as non-linear forms by Eq. (1):

$$Q_t = \frac{k_2 Q_e^2 t}{1 + k_2 Q_e t} \quad (1)$$

Where Q_e and Q_t are the amount of adsorbate (mg/g) onto adsorbent at the equilibrium and time t (min), respectively. Based on the pseudo second-order kinetic model, the initial adsorption rate h ($mg \cdot g^{-1} \cdot min^{-1}$) and half-adsorption time $t_{1/2}$(min) were calculated acording to the following equations:

$$h = k_2 Q_e^2 \quad (2)$$

$$t_{1/2} = \frac{1}{k_2 Q_e} \quad (3)$$

To obtain the adsorption capacity, **ZJU-101** (10 mg) and **MOF-867** was dispersed in 20 mL of $Cr_2O_7^{2-}$ solutions with a known concentration between 50 and 500 ppm respectively. 12 hours later, the solution was separated from the adsorbent with a syringe filter and UV/vis spectroscopy was used to analyze the residual concentrations of $Cr_2O_7^{2-}$. The equilibrium adsorption capacity Q_e was calculated according to Eq. (4):

$$Q_e = \frac{(C_0 - C_e)V}{m} \quad (4)$$

Where C_o 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.

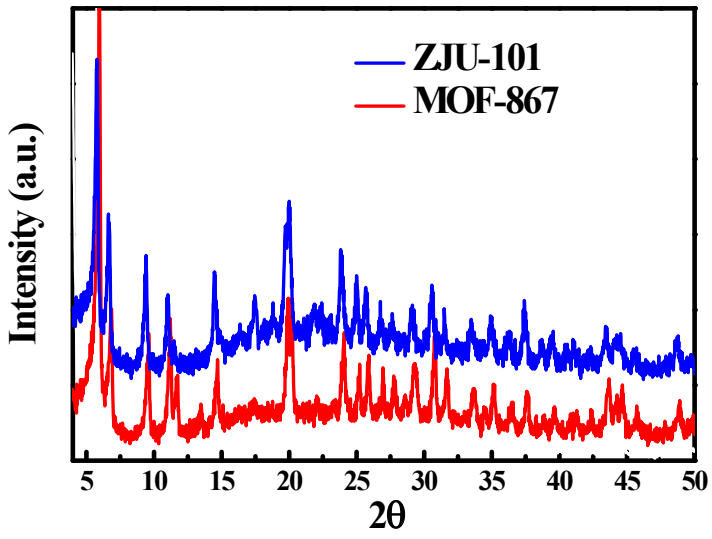

Figure S1. PXRD data for **MOF-867** and **ZJU-101**.

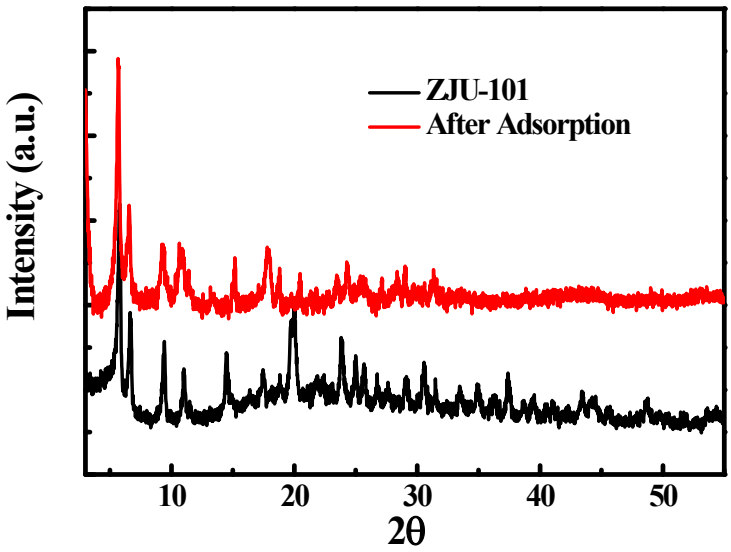

Figure S2. PXRD data for **ZJU-101** and **ZJU-101**after adsorption.

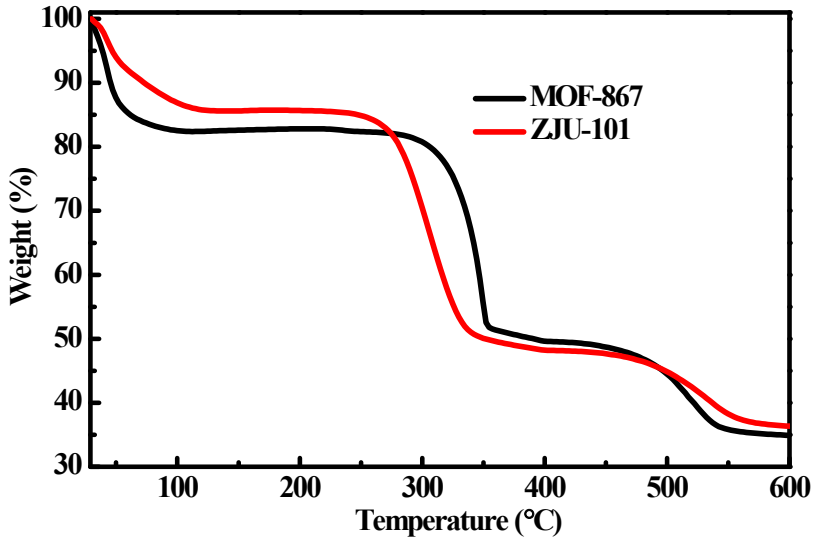

Figure S3. TGA curves of **MOF-867** and **ZJU-101** under a nitrogen atmosphere at a heating rate of 1 $K \cdot min^{-1}$.

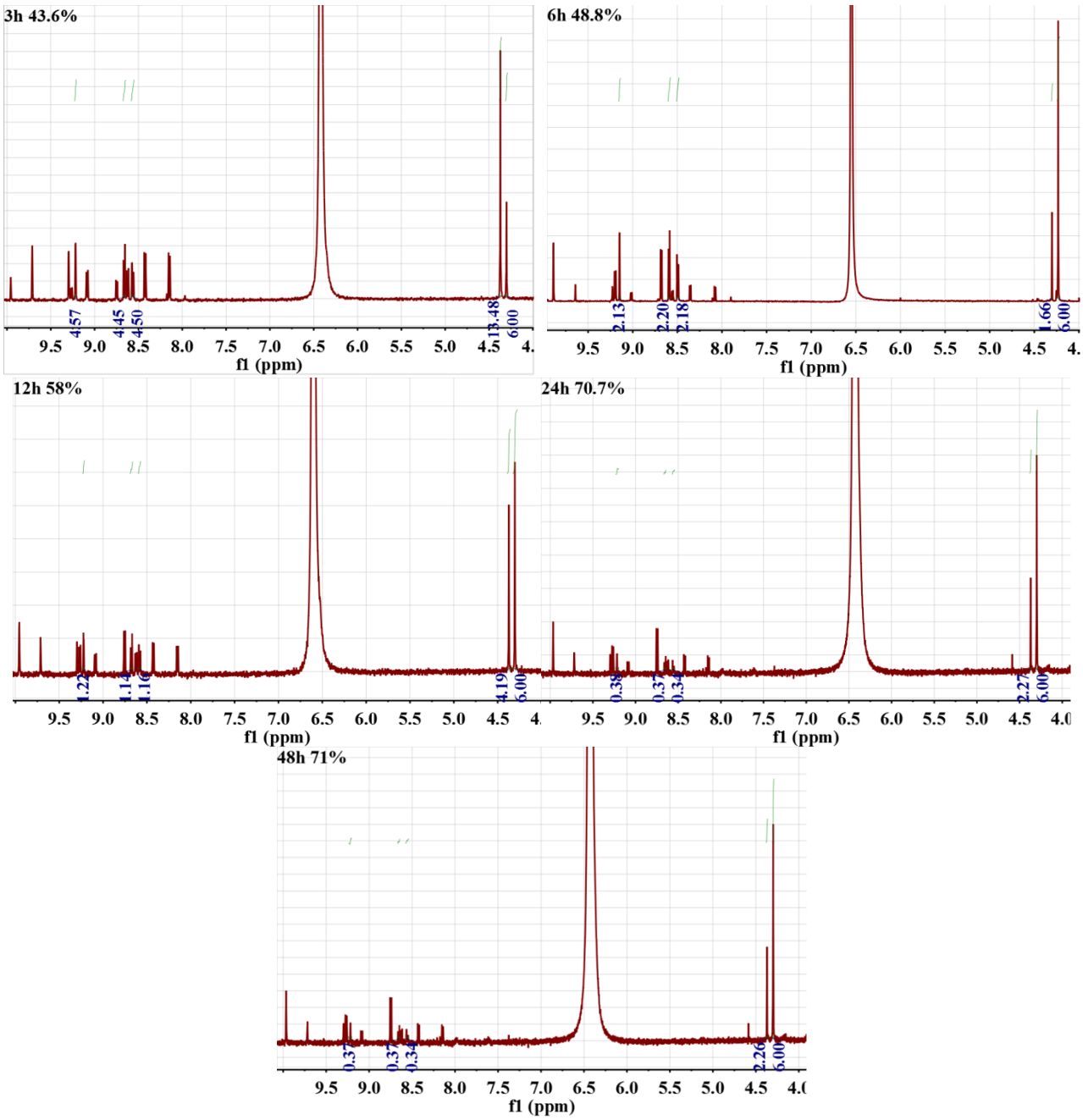

Figure S4. NMR analysis of **ZJU-101** at different times**.**

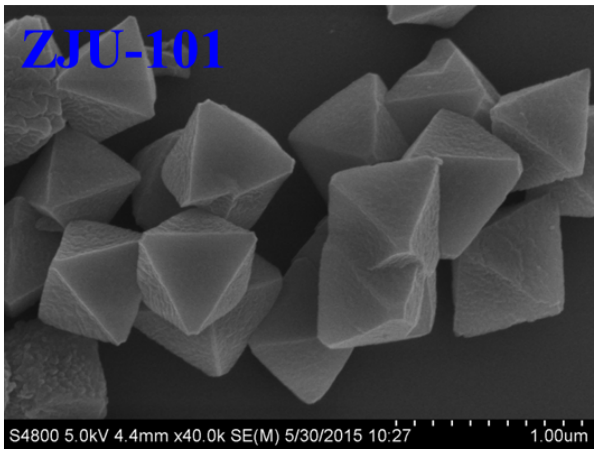

Figure S5. SEM photos for **ZJU-101**.

Table S1. Adsorption capacities for dichromate on various porous materials.

MOF-type Adsorbents	*Maximum capacities (mg/g)*	*References*	*Other types Adsorbents*	*Maximum capacities (mg/g)*	*References*
$Zn_{0.5}Co_{0.5}$-SLUG-35	68.5	1	**Amino starch**	12.12	5
2-D Ag-based-MOFs	60.0	2	**β-CD and quaternary ammonium groups modified cellulose**	61.05	6
3-D Dy-MOFs	62.9	3	**Hexadecylpyridinium bromide modified natural zeolites**	14.31	7
FIR-53	74.2	4	**Modified magnetic chitosan chelating resin**	58.48	8
FIR-54	103.1	4	**NH_2-TNTs**	153.85	9
ZJU-101	243	This Work			

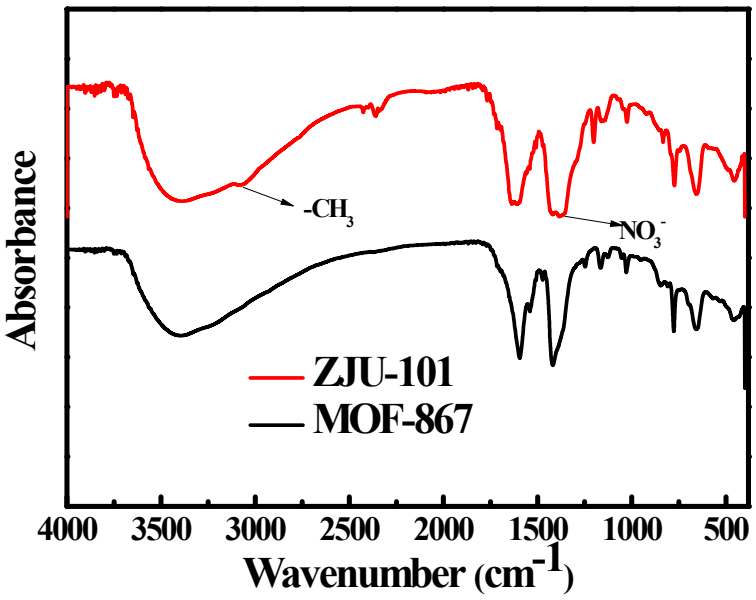

Figure S6. FT-IR spectra of **MOF-867** and **ZJU-101**.

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