

Supporting Information for

**An anionic manganese(II) metal-organic framework for efficient
UO₂²⁺ adsorption**

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1. Experimental Section

General Consideration.

All chemicals were purchased from commercial sources and used without further purification. Powder X-ray diffraction (PXRD) data were collected on a Rigaku Smartlab X-ray diffractometer with CuK α radiation ($\lambda = 1.5418 \text{ \AA}$). Thermogravimetric analysis (TG) was conducted on Mettler-Toledo TGA/DSC 1 analyzer in the temperature range of 25 °C to 800 °C under the flowing N₂. The temperature is increasing at 10 °C/min. Raman spectra were recorded using Laser Raman Spectrometer equipped with a 532 nm diode laser at Xi'an Jiaotong University Instrument Analysis Center. ICP-MS was tested Xi'an Jiaotong University Instrument Analysis Center using NexION 350D equipment. Infrared spectra were collected on a Thermo Fisher Nicolet 6700 FT-IR spectrometer using ATR (Attenuated Total Reflectance) method. Elemental analyses (C, H and N) were performed on a Vario MICRO cube elemental analyzer. Gas adsorption measurement was conducted by using Micromeritics ASAP 2020 Plus HD88 at Xi'an Jiaotong University Instrument Analysis Center.

Synthesis of **1**.

Into a 15 mL Teflon-lined stainless steel reactor, a slurry of MnCl₂·4H₂O (100 mg, 0.5 mmol), H₂ox·2H₂O (60 mg, 0.5 mmol), H₃izdc (imidazole-4,5-dicarboxylate, 80 mg, 0.5 mmol), KOH (168 mg, 3 mmol), KCl (100 mg, 1.3 mmol) and 11 mL CH₃CN/H₂O (1:1 in v/v) was stirred for 20 min in air before being heated at 160 °C for 48 hours. After cooling down, colourless block crystals were obtained. (115 mg, 48.7 % based on Mn). Anal. Calcd (%) for **1**: C, 25.87; H, 2.48; N, 11.20. Found: C, 26.01; H, 2.59; N, 11.23.

To remove the volatile guests, the powder of **1** was treated at 130 °C for 12 hours in vacuum to obtain the activated phase.

Determination of the guests.

To determine the guests, the crystals of **1** were digested by 1 M HNO₃ and heated at 60 °C for 30 min. The filtrate was analyzed by ICP-MS, which gives the concentrations of Mn²⁺ and K⁺ of 167 ppm and 121 ppm, respectively. This corresponds to a molar ratio of Mn²⁺ : K⁺ \approx 1 : 1.

Single crystal X-ray diffraction.

Crystal data were collected on a Bruker Apex CCD area-detector diffractometer using MoK α ($\lambda = 0.71073 \text{ \AA}$) radiation. The structure of **1** was solved using direct methods and refined with a full-matrix least-squares technique using OLEX2 program package.¹ The twin law (-1.0, 0.0, 0.0, 0.0, -1.0, 0.0, 0.0, 0.0, -1.0) has been applied for solving the crystal structure. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The hydrogen atoms were generated geometrically. SQUEEZE was applied to remove all the guest molecules. CCDC-1831034 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Water stability.

The experiments have been carried out by soaking ground powder of **1** in different pH conditions. After soaking for 24 hours, the powder was filtered and dried in the air. X-ray powder diffraction (PXRD) was performed to check the phase change. From Figure S3 we can see in the pH values ranging from 4.0 to 12.0, the crystallinity of **1** maintains; while above pH = 12, the disappear of the PXRD peaks indicates the loss of crystallinity. Furthermore, the bands in FT-IR spectrum of alkali treated sample of **1** is in good agreement with the fresh sample (Figure S4). Thus, we conclude that this material is stable in the pH range of 4 to 12.

Ion exchange experiments.

In isotherm sorption study, m mg powder sample of **1** was added to the 5 mL aqueous solution of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with starting concentration C_0 (ppm, based on U). The solution was stirred for 24 hours at room temperature and filtered. We then take 50 μL filtrate, which is filtrated by 0.22 μm PES polyether sulfone filter and diluted into 5 mL. The concentration of U was detected by ICP-MS to give C_e (ppm). Thus, the uranium capacity q (mg g^{-1}) can be given by eq S1:

$$q = \frac{(C_0 - C_e)V}{m} \quad (\text{S1})$$

In the kinetic study, 21.2 mg powder sample of **1** was added to the 20 mL aqueous solution of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with the concentration of 84 ppm (based on U). Then a small portion of 50 μL was taken out at certain time and filtrated by a 0.22 μm PES polyether sulfone filter. After diluted into 5 mL, the concentration of U was determined by ICP-MS.

In the selectivity experiment, 10.0 mg powder sample of **1** was added into 5 mL aqueous solutions of Ca²⁺, Na⁺, UO₂²⁺, K⁺, Mg²⁺, Cu²⁺, Ni²⁺ and Pb²⁺ with concentrations of 112, 282, 16.4, 69.7, 36.4, 101, 72 and 401 ppm, respectively (counter anions are Cl⁻ and NO₃⁻). Then the mixture was stirred for 24 hours, and small portion of 50 μL was taken out and filtered by a 0.22 μm PES polyether sulfone filter. After being diluted to 5 mL, the concentrations of the cations were determined by ICP-MS. To further compare the selectivities towards different cations, the distribution coefficient K_d (mL g⁻¹) and the relative cation removed percent R were given as following:

$$K_d = \frac{(C_0 - C_e)V}{mC_e} \quad (S2)$$

$$R = \frac{(C_0 - C_e)}{C_0} \times 100\% \quad (S3)$$

Exchange with larger cations.

Methylene blue (MB) molecule is one of the classical cationic probes the surface area described in text book. Considering the failure of the gas absorption experiment, we chose MB as probe to reveal the porosity of **1**. Firstly, we determined the working curve by the linear fitting of the light abs at 662 nm and the concentration of MB (Figure S8). To obtain the adsorption curve, ca. 10 mg **1** was soaking in 5 mL of MB solution with different concentrations and stirred for 24 h, the solution was then filtrated by a 0.22 μm PES polyether sulfone filter. Then the concentration of MB was determined by measuring the light absorbance at 662 nm. The linear fitting gives the parameter qm 39.70 mg g⁻¹, corresponding to surface area 97 m² g⁻¹, determined by using the Langmuir model (eq S4),

$$q = q_m \frac{C_e}{1 + \alpha C_e} \quad (S4)$$

where q_m is the maximum adsorption capacity (mg g⁻¹) and α is adsorption equilibrium constant.

Grand Canonical Monte Carlo (GCMC) Simulation.

The GCMC simulation was performed by using the sorption mudules of Material Studio 6.0 package. UO₂²⁺ ion was considered as rigid body and optimized using DMol3 modules, and ESP

charge was assigned to the ion. For the sorption simulation, the simulation box was set to be $1 \times 1 \times 1$ unit cells and the Q_{eq} fitted charge was assigned to the framework. The cut-off distance was set to be 18.5 Å. The system was described by the universal force field and electrostatic interaction was set to Ewald and van der Waals interaction was Atom based. The binding energy was obtained by the fixed loading task.

2. Supporting Tables

Table S1. Crystal data and structure refinement for **1**.

1	
formula	$\text{C}_{21}\text{H}_3\text{Mn}_5\text{N}_6\text{O}_{24}$
$M/\text{g mol}^{-1}$	997.99
crystal system	tetragonal
space group	$I-4c2$
a , Å	26.343(7)
b , Å	26.343(7)
c , Å	37.301(11)
V , Å ³	25885(16)
Z	16
$d_{\text{cal}}/\text{g cm}^{-3}$	1.024
temperature, K	150
2θ range	2.184 to 49.78
completeness	0.980
residual map, e Å ⁻³	1.00/-1.18
Goodness-of-fit on F^2 [a]	1.044
final indices [$I > 2\sigma(I)$] [b]	$R_1 = 0.0926$, $wR_2 = 0.2405$
R indices (all data)	$R_1 = 0.1094$, $wR_2 = 0.2546$
Flack parameter	0.37(4)

[a] $GOF = [\sum w(F_o^2 - F_c^2)^2 / (n_{\text{obs}} - n_{\text{param}})]^{1/2}$.

[b] $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$, $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

Table S2. Results for the ion-exchange experiments.^a

Sample	Final U concn (ppb)	% removal
0.34 M NaCl (pH = 7) ^b	373	92
0.15 M NaNO ₃ (pH = 7) ^b	355	92
0.1 M NaH ₂ PO ₄ (pH = 4.6) ^b	83	98
0.01 M KOH (pH = 12) ^b	47	99

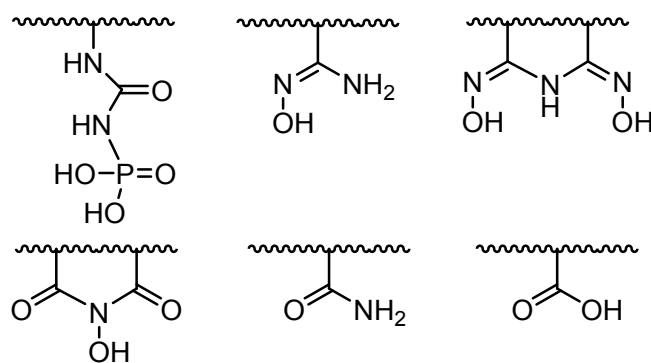
0.1 M NaHCO ₃ (pH = 8.3) ^b	3730	24
Simulated in lake water ^c	2600	84
Simulated in sea water ^d	954	82

^a The experiments were conducted using 5 mL solution and 10 mg of **1**. ^b The initial U concentration is 4920 ppb. ^c The concentration of Ca²⁺, Na⁺, UO₂²⁺, K⁺ and Mg²⁺ are 112, 282, 16.4, 69.7 and 36.4 ppm, respectively, pH value is 7.2. ^d The concentration of Ca²⁺, Na⁺, UO₂²⁺, K⁺ and Mg²⁺ are 302, 9855, 5.3, 359 and 1026 ppm, respectively, pH value is 7.2.

Table S3. The data for MB adsorption using **1**.

Number	1	2	3	4	5
m_{MOF}/mg	10.6	9.3	9.9	9.8	9.1
V/mL	5	5	5	5	5
C_0/ppm	48	36	24	12	6
Abs662/a.u.	4.2244	3.1573	2.0540	0.9880	0.4901
C_e/ppm	22.94	17.15	11.16	5.37	2.66
$q/\text{mg g}^{-1}$	11.82	10.14	6.49	3.38	1.83

3. Supporting Figures and Schemes



Scheme S1 Typical functional groups decorated in the uranium adsorption materials.

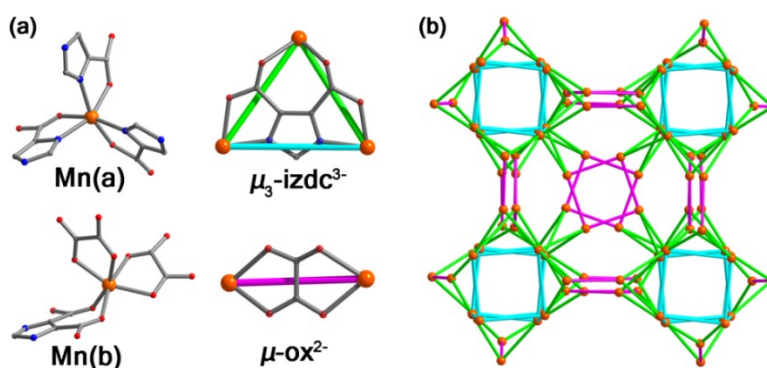


Figure S1. The coordination environments of the metal ions and ligands (a) and the topological connection (b) of **1**.

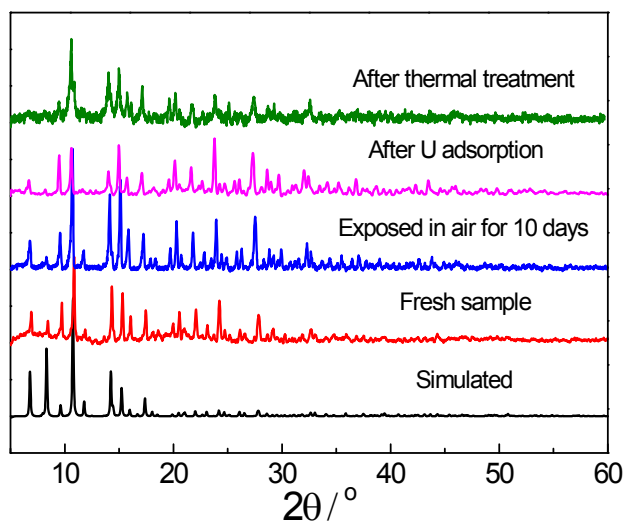


Figure S2. PXRD patterns of indicated samples.

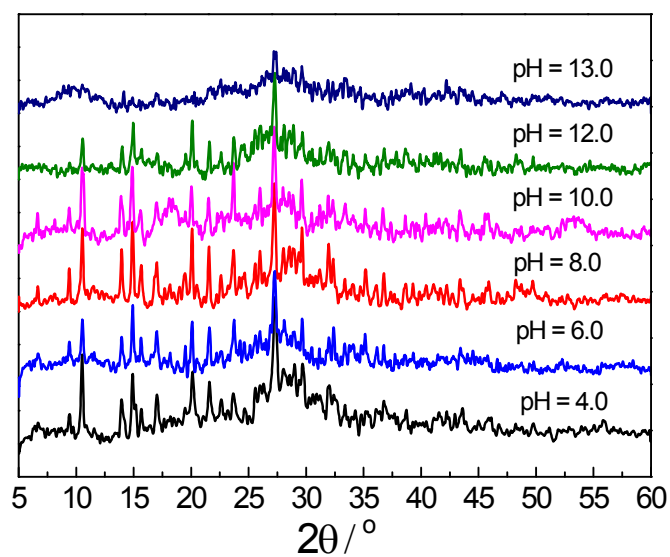


Figure S3. PXRD patterns of the samples after soaking in the aqueous solution with different pH values.

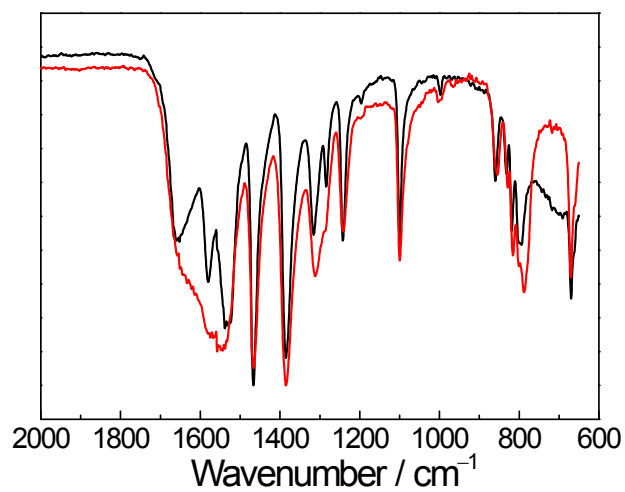


Figure S4. FT-IR of **1** (black) and **1** after soaking in aqueous solution of KOH with pH value of 12.0 for 24 hours (red).

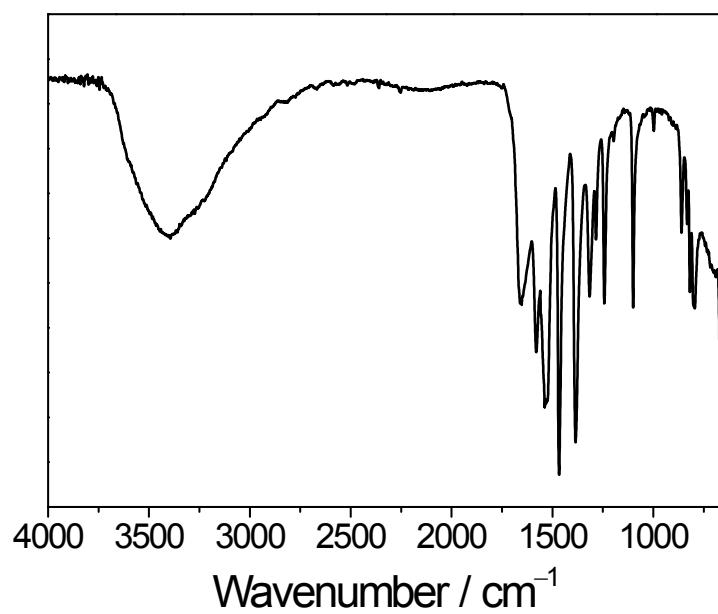


Figure S5. IR spectra of **1**.

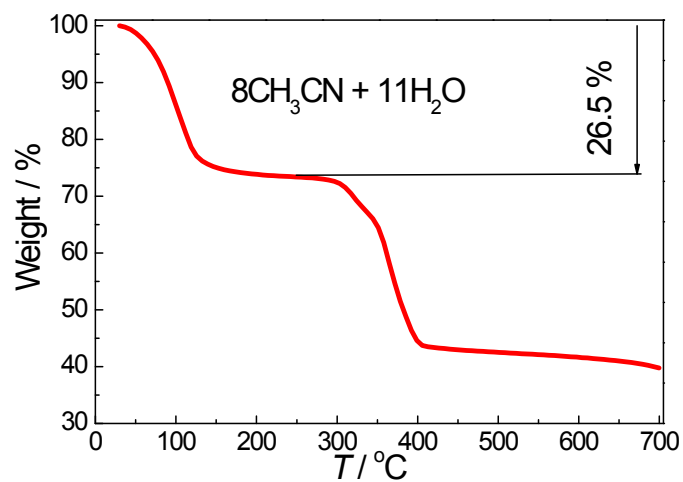


Figure S6. TG curve of 1.

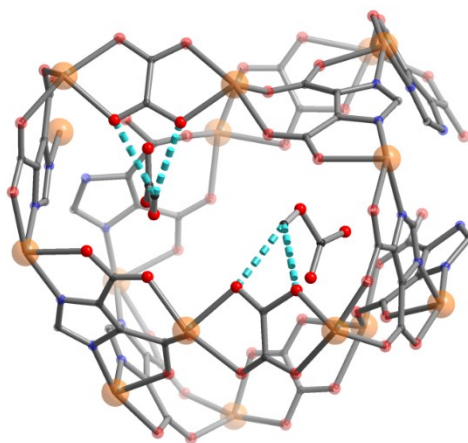


Figure S7. The hydrogen bonds between the framework carboxylate_O atoms and the HCO₃⁻ simulated by GCMC.

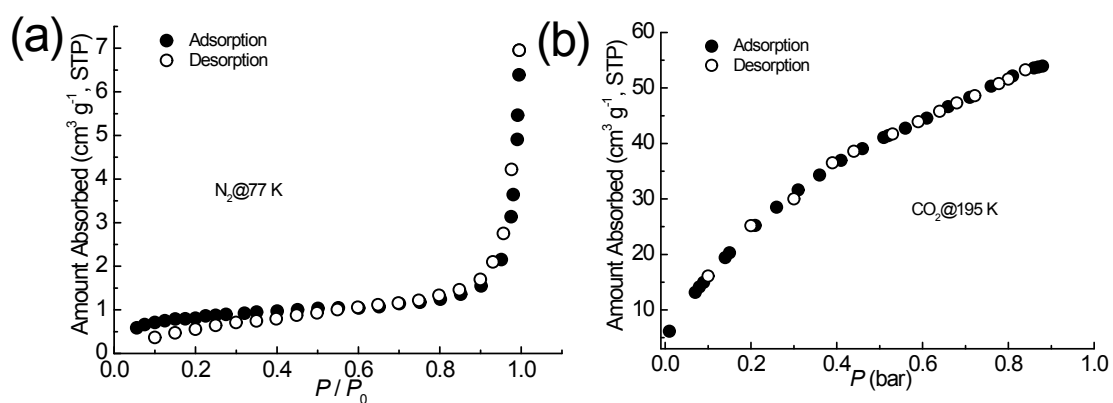


Figure S8. (a) N₂ adsorption isotherm of 1 at 77 K. (b) CO₂ adsorption isotherm of 1 at 195 K.

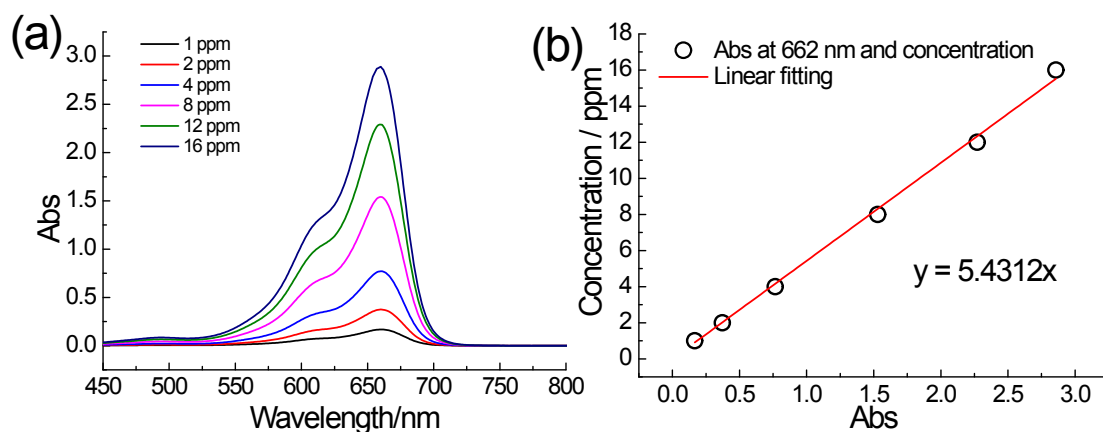


Figure S9. (a) The UV-vis spectrum of MB in aqueous solution with different concentrations. (b) The working curve determined by the linear fitting of the light abs at 662 nm and the concentration of MB.

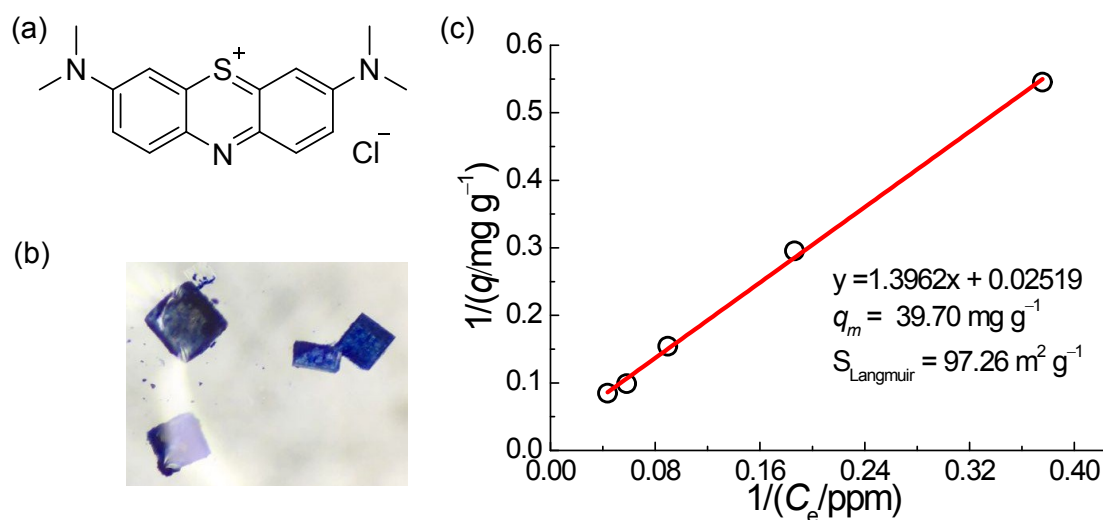


Figure S10. (a) The dimensionality of MB molecule with consideration of van der Waals radii. (b) The photograph of the crystal after soaking in MB solution with high concentration. (c) The MB adsorption after treated using Langmuir model.

4. Reference

1. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann. *J. Appl. Cryst.* 2009, **42**, 339–341.