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Supporting information

Porphyrinic metal-organic frameworks as molybdenum adsorbents for the $^{99}Mo/^{99m}Tc$ generator

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S1. Adsorption experiments

Adsorption kinetics of PCN-222 and PCN-224 was conducted as follows: 6±0.5 mg adsorbents and 1 ml of Mo solution at pH 3 (5 mg/ml) were added in Eppendorf tubes. After shaking from 5 to 1440 min, all tubes were centrifuged and the Mo concentration of the supernatant solutions was measured using ICP-OES.

To explore the influence of pH on Mo adsorption, experiments were carried out at a pH ranging from 2 to 10. First, 6±0.5 mg of the adsorbents and 1 ml of Mo solution (5 mg/ml) were added to Eppendorf tubes. After shaking for 24 h, all tubes were centrifuged and the molybdenum concentration of the supernatant solutions was measured using ICP-OES.

S2. Adsorption models

The experimental data were fitted using the Freundlich and Langmuir models. The linear mathematical equation of the Freundlich model can be described as

$$lnq_e = \frac{1}{n} lnC_e + lnK_F \quad \text{(S-1)}$$

The linear mathematical equation of the Langmuir model can be described as

$$\frac{C_e}{q_e} = \frac{1}{Q_m} C_e + \frac{1}{Q_m K_L} \quad \text{(S-2)}$$

Where C_e (mg/mL) and q_e (mg/g) are the Mo concentration and the Mo adsorption capacity at equilibrium, respectively. K_F is Freundlich constant and K_L is Langmuir constant. Q_m (mg/g) is the maximum adsorption capacity. The value of n reflects the sorption intensity, which is classified to be irreversible (n=0), favorable (0<1/n<1) and unfavorable (1/n>1).

The experimental dates were analyzed with the pseudo-first-order and the pseudo-second-order model to determine the adsorption kinetic process, as shown in Figure S1. The pseudo-first-order model can be described as follow:

$$\ln(q_e-q_t)=\ln q_e-K_1 t \quad \text{(S-3)}$$

The pseudo-second-order model can be described as follow:

$$\frac{t}{q_t}=\frac{1}{K_2 q_e^2}-\frac{t}{q_e} \quad \text{(S-4)}$$

Where K_1 is the pseudo-first-order constant and K_2 is the pseudo-second-order constant. q_t (mg/g) and q_e (mg/g) are Mo adsorption capacity at time t and equilibrium.

S3. Fabrication of ^{99}Mo/^{99m}Tc generator

20 mg of enriched MoO_3 (>99.95%) was sealed in a glass vial and irradiated for 3 h by neutrons at the reactor Institute of Energy Security and Environmental Safety Centre for Energy Research, Hungary. The 20 mg of the irradiated target (~68 MBq) and 355 mg of non-irradiated MoO_3 were dissolved in 20 mL of NaOH solution at room temperature. Then pH of the prepared solution was adjusted to 3 resulting in a total volume of molybdenum solution of 25 mL. Therefore, the molybdenum concentration was 10 mg/mL and the specific activity was 272 MBq/g.

A plastic column of 0.5 cm inner diameter (0.5 cm×10 cm) was equipped with two filters (20 μm pores) and ~100 mg of prepared MOFs. 50 mL of HCl solution (pH=3) was used to rinse the columns, which were fed using 5 ml (A_0) of molybdenum solution (5 mg/ml) under a flow rate of 0.3 ml/min. The eluted solution was collected and its activity was measured (A_1). 150 ml of saline solution was then passed through the columns to remove loose molybdenum species and the eluted solution was collected for

gamma counts measurement (A_2) using Wallac. Finally, the generator was eluted periodically at 24 hours intervals using the saline solution with different pH values (6.1, 7.9 and 9.6). The activity of all eluted fractions was analyzed by a germanium detector (Model LG22) and a NaI(T1) counter coupled to a 2048 analyzer (Wallac gamma counter, PerkinElmer). The gamma counts were recorded by measuring the 140 keV (^{99m}Tc) and 740 keV (^{99}Mo) γ-ray photon peaks.

The column mode adsorption capacity was calculated by the following equation:

$$q_d = \frac{(A_0 - C_1 - C_2) \times V}{m} \quad \text{(S-5)}$$

The zirconium breakthrough was measured by ICP-OES. The ^{99}Mo breakthrough was determined by using the following equation:

[^{99}Mo activity in eluted fraction]/[^{99}Mo activity +^{99m}Tc activity in eluted fraction]

The elution yield was calculated based on the following equation:

[^{99m}Tc activity in the eluted fraction]/ [expected ^{99m}Tc activity]

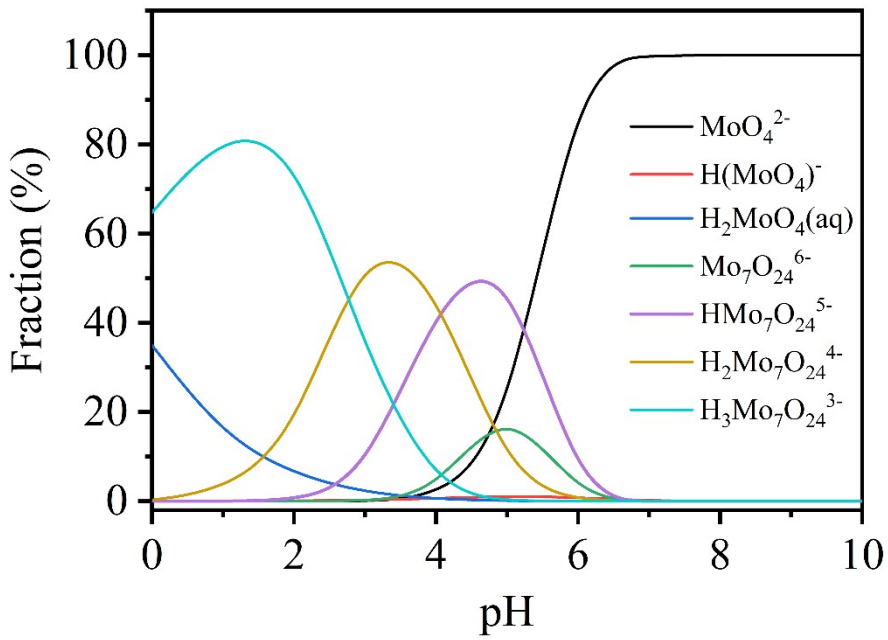

Figure S1. Molybdenum speciation in solution as a function of Ph by CHEAQS when molybdenum concentration is 5 mg/mL.

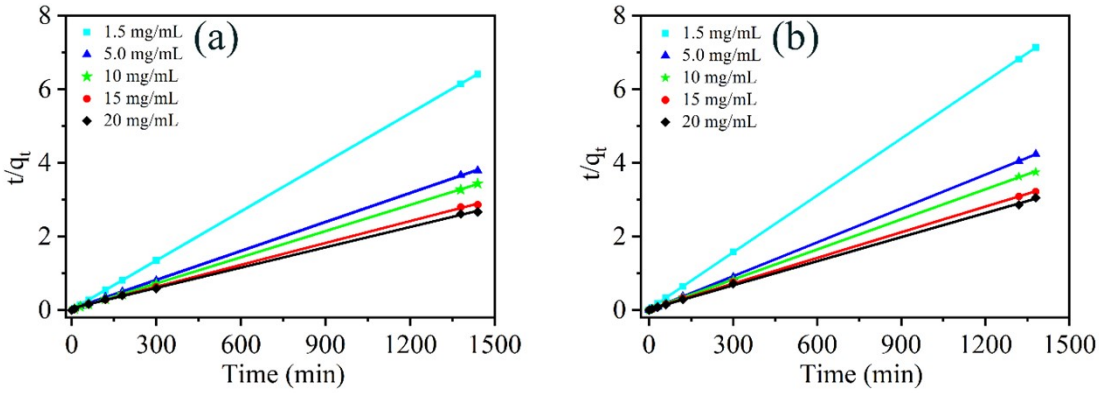

Figure S2. Mo adsorption kinetics of (a) PCN-222 and (b) PCN-224 fitted using the pseudo-second-order model.

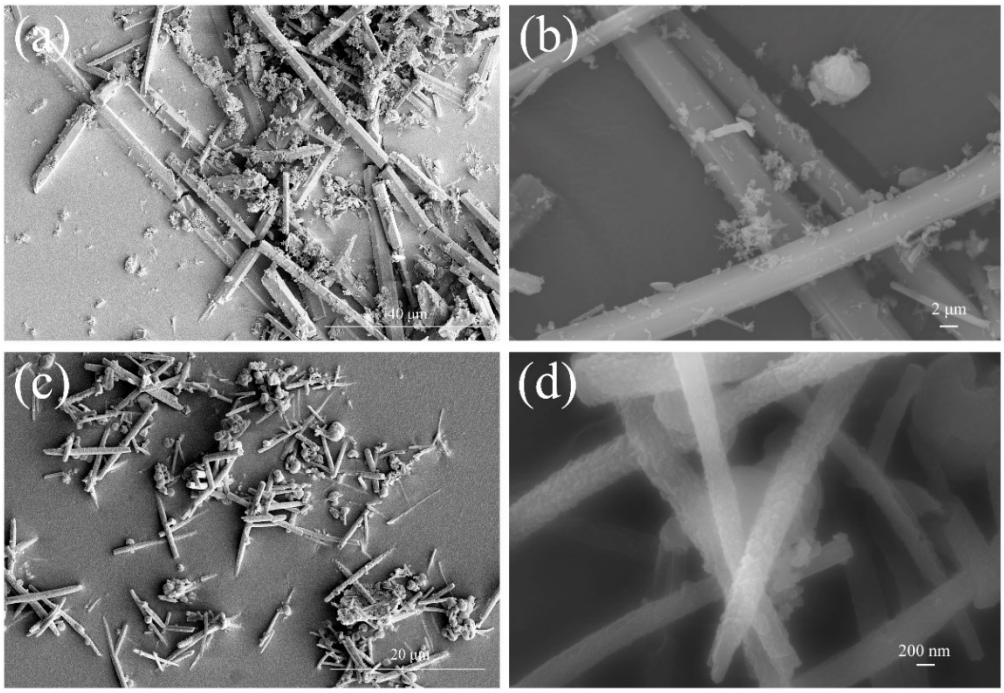

Figure S3. SEM images of (a, b) PCN-222 and (c, d) PCN-224

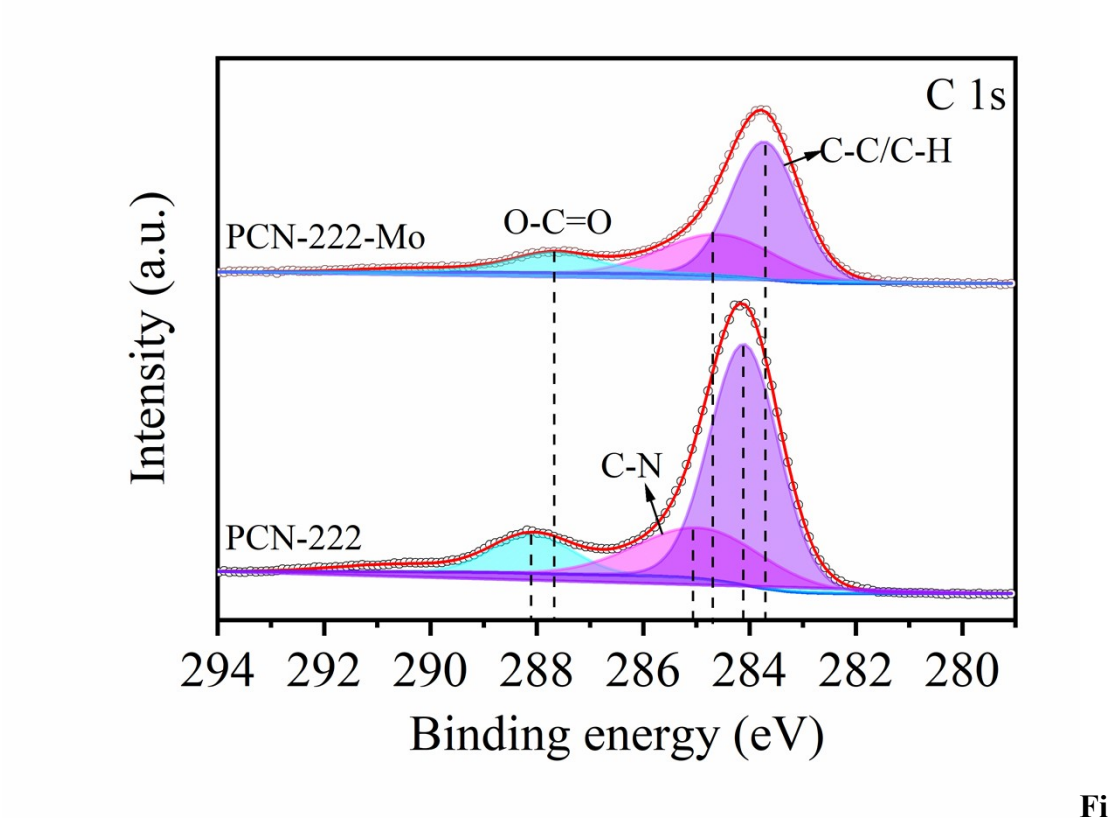

Figure S4. C 1s XPS spectra of PCN-222 before and after Mo adsorption.

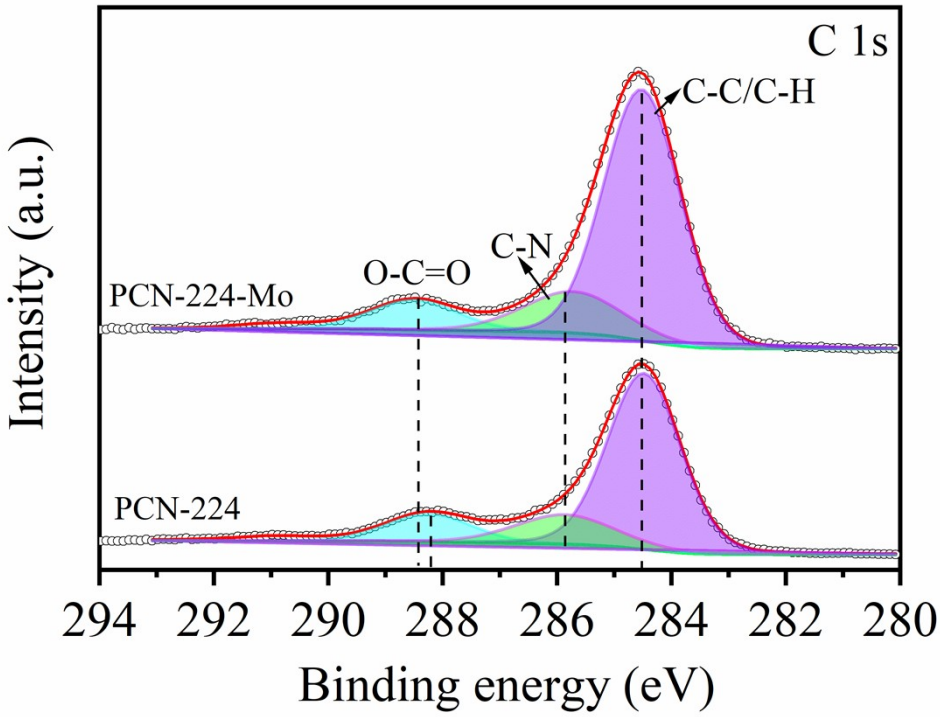

Figure S5. C 1s XPS spectra of PCN-224 before and after Mo adsorption.

Table S1. Parameters calculated from the pseudo-first-order and pseudo-second-order model for Mo adsorption on PCN-222

C_0 (mg/mL)	Pseudo-first order			Pseudo-second order		
	q_e, calcd (mg/g)	K_1 (min^{-1})	R^2	q_e, calcd (mg/g)	K_2 (g/mg·min)	R^2
1.62	11.22	0.0035	0.828	224.72	0.0018	1.000
5.57	58.47	0.0024	0.780	380.23	0.0093	0.999
10.91	166.98	0.0207	0.981	421.94	0.0005	0.999
16.20	109.95	0.0019	0.784	505.05	0.0001	0.999
21.46	146.55	0.0020	0.784	543.48	0.00006	0.999

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able S2. Parameters calculated from the pseudo-first-order and pseudo-second-order model for Mo adsorption on PCN-224

C_0 (mg/mL)	Pseudo-first order			Pseudo-second order		
	q_e, calcd (mg/g)	K_1 (min^{-1})	R^2	q_e, calcd (mg/g)	K_2 (g/mg·min)	R^2
1.55	34.08	0.0082	0.807	194.18	0.0001	1.000
5.51	35.21	0.0112	0.660	325.73	0.0019	0.999
10.54	39.35	0.0020	0.592	367.65	0.0006	0.999
15.69	77.45	0.0032	0.998	434.78	0.0002	0.999
20.93	79.43	0.0031	0.750	458.72	0.0002	0.999

Table S3. Parameters calculated from the Langmuir and Freundlich model fit for Mo adsorption

Samples	Langmuir Parameters			Freundlich Parameters		
	Q_m	K_L	R^2	1/n	K_F	R^2
PCN-222	503	12.25	0.903	0.18	304	0.961
PCN-224	452	1.99	0.945	0.22	240	0.997

Table S4. The surface area of PCN-222 and PCN-224

Samples	BET (m^2/g)	V (cm^3/g)
PCN-222	1882	1.22
PCN-224	1467	0.56
PCN-222-Mo	471	0.31
PCN-224-Mo	13	0.002

Table S5. Elution performances of PCN-222 based $^{99}Mo/^{99m}Tc$ generator

Elution No.	Time of growth (h)	Elution yield (%)	^{99}Mo breakthrough
1	24	28.4	5.9
2	25	30.1	7.1
3	22	33.8	6.5
4	24	30.2	5.0

Table S6. Elution performances of PCN-224 based $^{99}Mo/^{99m}Tc$ generator

Elution No.	Time of growth (h)	Elution yield (%)	^{99}Mo breakthrough
1	23	7.9	19.7
2	25	9.9	14.4
3	22	5.9	15.1
4	24	6.5	14.2

Table S7. Elution performances of PCN-224 based $^{99}Mo/^{99m}Tc$ generator using eluent having different pH values.

Elution No.	pH	Time of growth (h)	Elution yield (%)	^{99}Mo breakthrough (%)	Zr breakthrough (ppm)
1	6.1	24	2.7	16.6	0.067
2		71	2.9	25.8	0.009
3	7.9	24	3.0	23.9	0.066
4		24	3.4	26.3	0.006
5	9.6	24	3.3	8.4	0.006