Supporting Information (SI)

Identification of oxygen sites in β-ketoenamine-linked covalent organic frameworks for highly efficient uranium adsorption through experimental and theoretical studies

Tao Wen,‡ Xinjie Ma,‡ Yingzhong Huo, Ruoxuan Guo, Sai Zhang, Yanan Han, Yang Liu, Yuejie Ai* and Xiangke Wang*

MOE Key Laboratory of Resources and Environmental Systems Optimization, College of Environment and Chemical Engineering, North China Electric Power University, Beijing 102206, P.R. China

*: Corresponding author. Fax (Tel): +86-10-61772890; Email: aiyuejie314@126.com (Y. Ai), xkwang@ncepu.edu.cn (X. Wang).

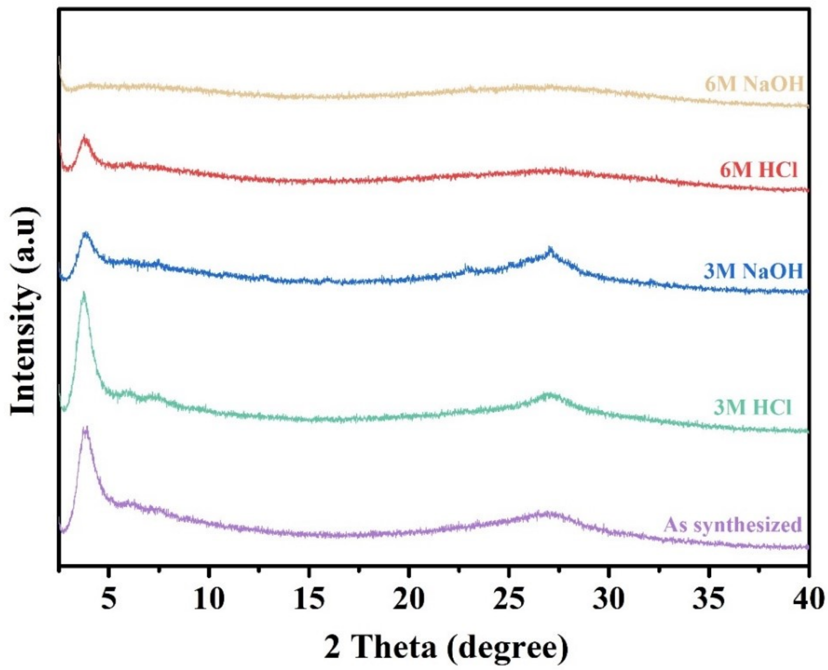

Fig. S1. PXRD patterns of DQTP COF before and after treatment under acid and alkali conditions

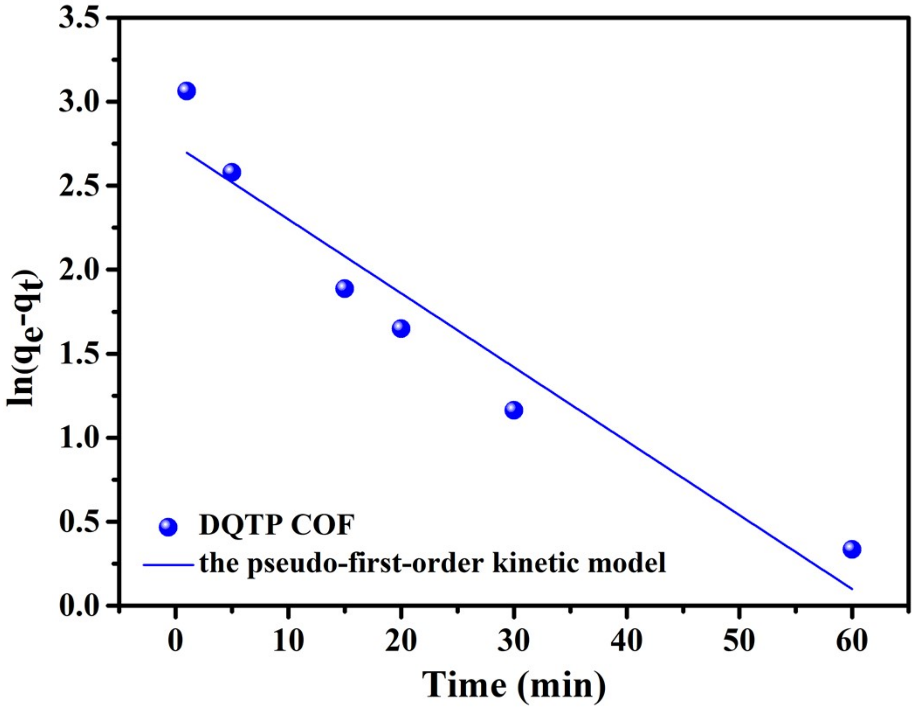

Fig. S2. The pseudo-first-order kinetic model for the adsorption. Conditions: $C_{U(VI)}$ = 10 ppm, m/V= 0.2 g/L, pH=6.0 ± 0.1, T = 298 K.

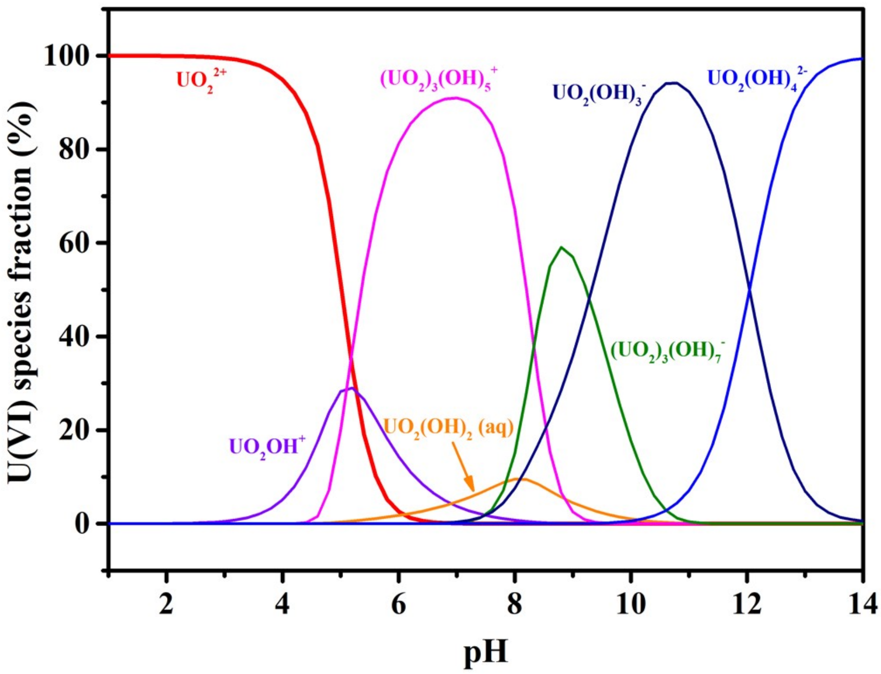

Fig. S3. The U(VI) species fraction at different pH values.

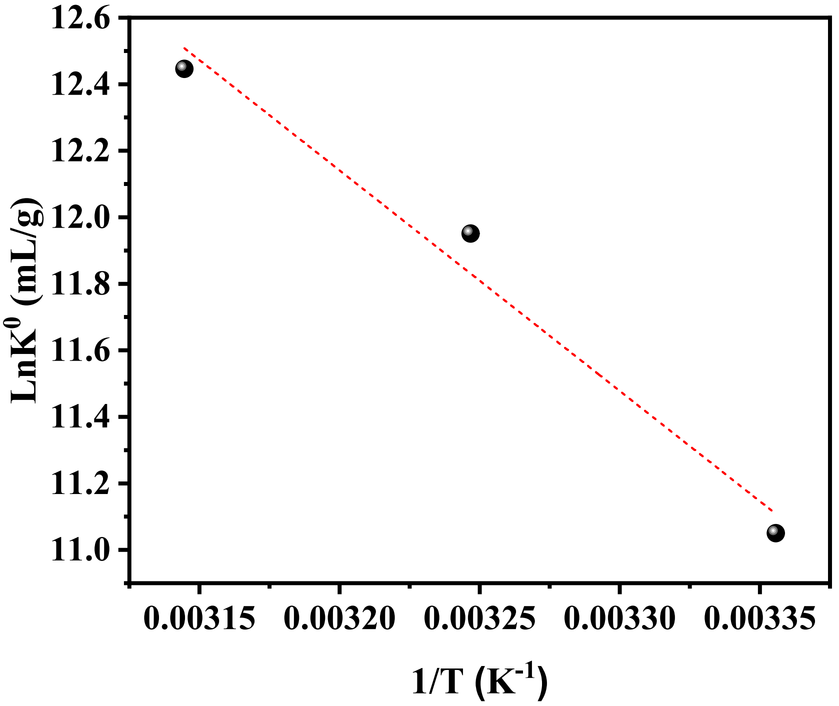

Fig. S4. The linear plot of ln K^0 vs. 1/T for U(VI) adsorption on DQTP COF at 298, 308, and 318 K. m/V= 0.2 g/L, pH=6.0 ± 0.1.

The Gibbs free energy change (ΔG^0, kJ mol^{-1}), enthalpy change (ΔH^0, kJ mol^{-1}) and enthalpy change (ΔS^0, J mol^{-1} K^{-1}) of the ion-exchange process can be calculated by combining the two following equations:

$$\ln K^0 = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \qquad (1)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \qquad (2)$$

where T (K) is the absolute temperature, and R is the universal gas constant (8.314 J mol^{-1} K^{-1}). The ion-exchange constant, K^0, can be determined by plotting $\ln K_d^U$ vs. $1/T$ and further extrapolating C_e to 0.

Table S1 Comparison of adsorption capacity with other COFs.

Adsorbent	Experimental conditions	Adsorption capacity(mg/g)	Reference
COF-PDAN-AO	pH=4, T=298K, m/V=0.5 g/L	410	[1]
TP-COF-AO	pH=6, T=298K, m/V=0.5 g/L	436	[2]
HDU-102-AO	pH=5, T=298K, m/V=0.2 g/L	389.08	[3]
HDU-102	pH=5, T=298K, m/V=0.2 g/L	250.49	[3]
COF-1	pH=7, T=298K, m/V=0.4 g/L	411	[4]
TpPa-1	pH=6, T=298K, m/V=0.5 g/L	120	[5]
TpBpy	pH=5, T=298K, m/V=0.2 g/L	115.45	[6]
TpPy	pH=6, T=298K, m/V=0.2 g/L	291.79	[6]
TpDb-AO	pH=6, T=298K, m/V=0.5 g/L	380	[7]
JUC-505-AO	pH=5, T=298K, m/V=0.025 g/L	395	[8]
JUC-505-COOH	pH=6, T=298K, m/V=0.025 g/L	464	[8]
CNT/COF-OH	pH=5, T=298K, m/V=0.25 g/L	518.2	[9]
MOF@COF	pH=6.5, T=298K, m/V=0.02 g/L	536.73	[10]
DQTP COF	pH=6, T=298K, m/V=0.2 g/L	517.62	This work

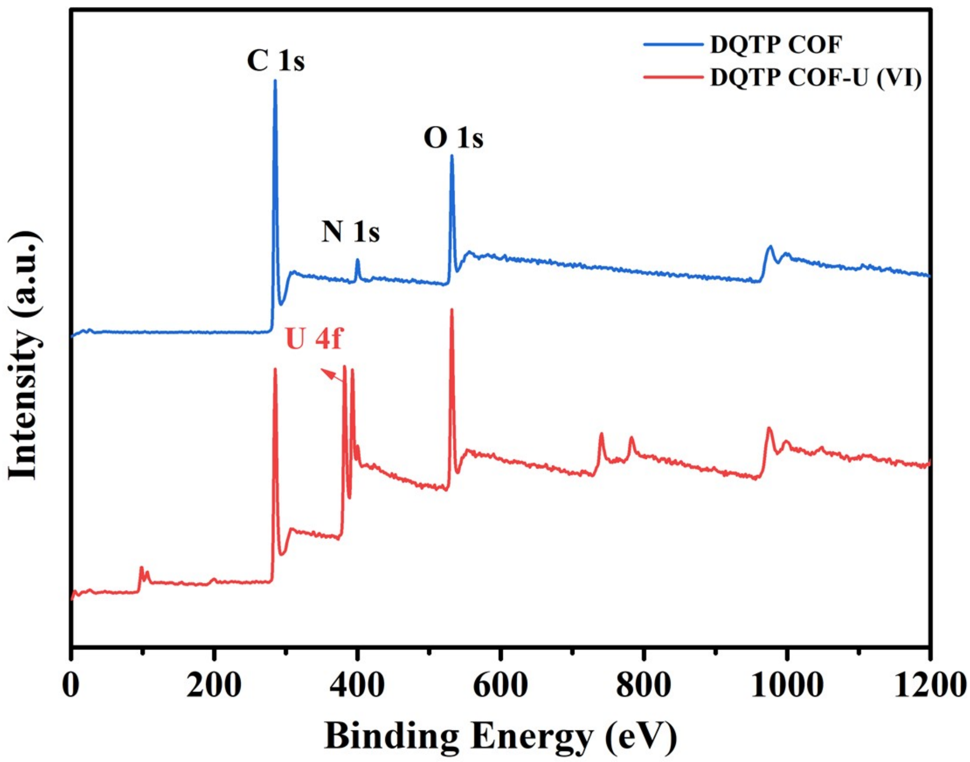

Fig. S5. XPS survey spectrum of DQTP COF before and after U(VI) adsorption

Reference

[1] Li F, Cui W, Jiang W, et al. Stable sp carbon-conjugated covalent organic framework for detection and efficient adsorption of uranium from radioactive wastewater[J]. Journal of Hazardous Materials, 2020, 392.

[2] Zhang C R, Cui W R, Jiang W, et al. Simultaneous sensitive detection and rapid adsorption of UO_2^{2+} based on a post-modified sp(2) carbon-conjugated covalent organic framework[J]. Environmental Science: Nano, 2020, 7(3): 842-850.

[3] Wang C, Xi W, Guo R, et al. A novel amidoxime-functionalized covalent organic framework for removal of U(VI) from uranium-containing wastewater with appreciable efficiency and selectivity[J]. Journal of Radioanalytical and Nuclear Chemistry, 2022, 331(6): 2469-2478.

[4] Yang S, Yin J, Li Q, et al. Covalent organic frameworks functionalized electrodes for simultaneous removal of UO_2^{2+} and ReO_4^- with fast kinetics and high capacities by electro-adsorption[J]. Journal of Hazardous Materials, 2022, 429.

[5] Li Z D, Zhang H Q, Xiong X H, et al. U(VI) adsorption onto covalent organic frameworks-TpPa-1[J]. Journal of Solid State Chemistry, 2019, 277: 484-492.

[6] Guo R X, Liu Y, Huo Y Z, et al. Chelating effect between uranyl and pyridine N containing covalent organic frameworks: A combined experimental and DFT approach[J]. Journal of Colloid and Interface Science, 2022, 606: 1617-1626.

[7] Sun Q, Aguila B, Earl L D, et al. Covalent organic frameworks as a decorating platform for utilization and affinity enhancement of chelating sites for radionuclide sequestration[J]. Advanced Materials, 2018, 30(20): 1705479.

[8] Li Z, Zhu R, Zhang P, et al. Functionalized polyarylether-based COFs for rapid and selective extraction of uranium from aqueous solution[J]. Chemical Engineering Journal, 2022, 434: 134623
[9] Liu X, Wang X, Jiang W, et al. Covalent organic framework modified carbon nanotubes for removal of uranium (VI) from mining wastewater[J]. Chemical Engineering Journal, 2022, 450.
[10] Zhong X, Liu Y X, Liang W, et al. Construction of core-shell MOFs@COF hybrids as a platform for the removal of UO_2^{2+} and Eu^{3+} ions from solution [J]. ACS Applied Materials and Interfaces, 2021, 13(11): 13883-13895.