Supporting Information

Large Pore 3-D Cubic Mesoporous (KIT-6) Hybrid Bearing Hard-soft Donor Combined Ligand for Enhancing U(VI) Capture: An Experimental and Theoretical Investigation

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SI-1 Characterization of DAPhen siloxane



Fig.S1 ¹H NMR spectra of N^2 , N^9 -bis(3-(triethoxysilyl)propyl)-1,10-phenanthroline-2,9dicarboxamide (DAPhen siloxane, inset shows its structure): Eluent: petroleum ether/ethyl acetate (1:1). Colorless wax. ¹H NMR (400 MHz, CDCl₃) δ 8.64-8.58 (m, 4H, N*H*, Ar*H*), 8.44 (d, J = 8.3 Hz, 2H, Ar*H*), 7.93 (s, 2H, Ar*H*), 3.83 (q, J = 6.9 Hz, 12H, CH₂CH₃), 3.67-3.62 (m, 4H, NHCH₂), 1.23-1.20 (m, 22H, CH₂CH₂CH₂, CH₂CH₃), 0.78 (t, J = 8.3Hz, 4H, CH₂Si).

SI-2. The calculated aqueous speciation of U(VI)

The aqueous speciation of U(VI) as a function of pH in the absence of sorbent was calculated according to the thermodynamic data listed in Table S1¹. To clarify whether there is precipitation or not, a solid phase, i.e. the schoepite phase, was also included in the speciation calculation. The distribution of aqueous and solid U(VI) species at different U(VI) concentrations $(1.00 \times 10^{-3} \text{ mol/L}, 5.00 \times 10^{-4} \text{ mol/L}, 1.00 \times 10^{-4} \text{ mol/L}, and 5.00 \times 10^{-5} \text{ mol/L})$ were given in Fig. S2.

Table S1 U(VI) solution reactions Species Reactions Log K (I=0) $UO_2^{2+} + H_2O = UO_2(OH)^+ + H^+$ $UO_2(OH)^+$ -5.25 $UO_2^{2+} + 2H_2O = UO_2(OH)_2^0 + 2H^+$ $UO_2(OH)_2^0$ -12.15 $UO_2^{2+} + 3H_2O = UO_2(OH)_3^{-} + 3H^{+}$ $UO_2(OH)_3$ -20.25 $UO_2^{2^+} + 4H_2O = UO_2(OH)_4^{2^-} + 4H^+$ $UO_2(OH)_4^{2-}$ -32.4 $2UO_2^{2+} + H_2O = (UO_2)_2(OH)^{3+} + H^+$ (UO₂)₂(OH)³⁺ -2.7 $2UO_2^{2^+} + 2H_2O = (UO_2)_2(OH)_2^{2^+} + 2H^+$ (UO₂)₂(OH)₂²⁺ -5.62 $3UO_2^{2^+} + 4H_2O = (UO_2)_3(OH)_4^{2^+} + 4H^+$ $(UO_2)_3(OH)_4^{2+}$ -11.90 $3UO_2^{2^+} + 5H_2O = (UO_2)_3(OH)_5^+ + 5H^+$ $(UO_2)_3(OH)_5^+$ -15.55 $3UO_2^{2^+} + 7H_2O = (UO_2)_3(OH)_7^- + 7H^+$ -32.20 (UO₂)₃(OH)₇- $4UO_2^{2^+} + 7H_2O = (UO_2)_4(OH)_7^+ + 7H^+$ $(UO_2)_4(OH)_7^+$ -21.90 $H_2O + CO_2(g) = H_2CO_3$ -1.47 $UO_2^{2+} H_2CO_3 = UO_2 CO_3^{0} + 2H^+$ $UO_2 CO_3^0$ -6.74 $UO_2^{2+} 2H_2CO_3 = UO_2 (CO_3)_2^{2-} + 4H^+$ $UO_2 (CO_3)_2^{2-}$ -16.75 $UO_2^{2+} 3H_2CO_3 = UO_2 (CO_3)_3^{4-} + 6H^+$ $UO_2 (CO_3)_3^{4-}$ -28.20 $2UO_2^{2+}H_2CO_3 + 3H_2O = (UO_2)_2CO_3(OH)_3^{-} + 5H^{+}$ (UO₂)₂ CO₃(OH)₃⁻ -17.55 $3UO_2^{2+}H_2CO_3 + 3H_2O = (UO_2)_3CO_3(OH)_3^+ + 5H^+$ (UO₂)₃ CO₃(OH)₃⁺ -16.04 $3UO_2^{2+} 6H_2CO_3 = (UO_2)_3 (CO_3)_6^{6-} + 12H^+$ $(UO_2)_3 (CO_3)_6^{-6-1}$ -46.08 $UO_2^{2+} + 3H_2O = UO_3 \cdot 2H_2O(cr) + 2H^+$ Schoepite -5.9 100 100 A . UO₂ (CO₃)₃⁴ В UO₂ (CO₃)3 (UO,), CO,(OH), 80 (UO2)2 CO3(OH)3 80 UO. (UO₂)₃(OH)₅⁺ (UO₂)₃(OH)₅⁺ Schoe Percent (%) 00 00 Percent (%) 60 40 (OH)(UO2)4(OF (UO₂)₂(OH)₂² (UO₂)₄(OH)₇ 20 UO2 (CO3)22 20 UO₂ (CO₃)² UO.OH (UO_)_(OH) 0 9 6 8 10 7 8 9 10 pН pН 100 С 100 D UO₂ (CO₃)3 UO2 (CO3)3 (UO2)2 CO3(OH)3 UO224 (UO₂)₂ CO₃(OH)₃ 80 80 (UO₂)₃(OH)₅⁺ (UO_)_(OH)_ Percent (%) Percent (%) 09 09 60 40 (UO2)2(OH)22+ (UO_),(OH),² (UO₂)₂(OH) UO₂)₃(OH)₄ (UO₂)₄(OH)₇ 20 20 UO2 (CO3)22 (UO₂)₄(OH)₇ UO2 (CO3)2 UO.0 UO.OH C 9 6 8 10

Fig.S2 Aqueous speciation of U(VI) in an open system equilibrated with $p(CO_2) = 10^{-3.5}$ as a function of pH. A, $C[U(VI)]_{total} = 1.00 \times 10^{-3} \text{ mol/L}$; B, $C[U(VI)]_{total} = 5.00 \times 10^{-4} \text{ mol/L}$; C, $C[U(VI)]_{total} = 1.00 \times 10^{-4} \text{ mol/L}$; D, $C[U(VI)]_{total} = 5.00 \times 10^{-5} \text{ mol/L}$ in water solution. (The species less than 1% were not denoted in the figures for clarity)

As can be seen from Figure S1, the distribution of U(VI) species show a dependency on pH values and U(VI) total concentration. At pH < 4.5 and C[U(VI)]_{total} = 5.00×10^{-5} mol/L, for example, free uranyl ion (UO₂²⁺) was the dominant species. With increasing of pH, UO₂²⁺ underwent hydrolysis, and multinuclear hydroxide complexes were the dominant species at pH > 5. The charge of the species is also dependent on the solution pH. The U(VI) hydroxide complexes are mainly positive charge in the pH range of ~5-7, and mainly negative charge in the pH range above ~7. Besides, schoepite (UO₃ • 2H₂O) precipitates from the solution at C[U(VI)]_{total} = 1.00×10^{-3} mol/L and pH = $5.7 \sim 7.4$, while no precipitation occurs at other test C[U(VI)]_{total} and pH.

In this study, the sorption experiments were mainly performed at pH 5.0 and U(VI) concentration of $< 5.0 \times 10^{-4}$ mol/L, in which $UO_2^{2^+}$, $(UO_2)_2(OH)_2^{2^+}$, $(UO_2)_3(OH)_5^+$, $(UO_2)_4(OH)_7^+$ are the dominant species, and no insoluble species were observed during 3 h keeping at room temperature.

SI-3. The sorption data fitting by kinetic models

In order to clarify the sorption process of U(VI) in KIT-6-DAPhen, the pseudo-first-order kinetic model and the pseudo-second-order kinetic model were applied to analyse the experimentally observed kinetic data. The linear form of the two models are expressed as followed respectively.

The pseudo-first-order equation:
$$\ln(q_e - q_t) = \ln q_e - k_1 t$$
 (S1)

The pseudo-second-order equation:
$$\frac{t}{q_t} = \frac{l}{k_2 q_e^2} + \frac{t}{q_e}$$
(S2)

Intraparticle diffusion model:
$$q_t = k_{id}t^{1/2}$$
 (S3)

where $q_e(mg/g)$ and $q_t(mg/g)$ are the quantities of the sorbed U(VI) at equilibrium and at time *t* respectively; $k_1 (1 \text{ min}^{-1})$, $k_2 (g/(mg \text{ min}))$, and $k_{id}(mg g^{-1} h^{-1})$ are the sorption rate constants of pseudo-first-order, pseudo-second-order, and intraparticle diffusion models, respectively. The model parameters and the correlation coefficient obtained by all the three model are shown in Table S2.



Fig. S3 The pseudo-first-order kinetic (left), pseudo-second-order kinetic (middle), and intraparticle diffusion model linearized plots for U(VI) sorption on KIT-6 and KIT-6-DAPhen.

 Table S2 Kinetics model constants and correlation coefficients for U(VI) sorption by

 KIT-6 and KIT-6-DAPhen

	Kinetics mo	del							
	Pseudo-first-order			Pseudo-se	Pseudo-second-order			Intraparticle diffusion	
	$q_e(mg/g)$	$k_l(\min^{-1})$	R^2	$q_e(mg/g)$	$k_2(g mg^{-1} min^{-1})$	R^2	k_{id} (mg g ⁻¹ h ⁻¹)	R^2	
KIT-6	28.3	0.026	0.81	148.8	3.3×10 ⁻³	> 0.99	7.1	0.90	
KIT-6-DAPhen	84.8	0.012	0.80	246.9	7.9×10 ⁻⁴	> 0.99	4.7	0.98	

SI-4. The sorption data fitting by isotherm models

The Langmuir model assumes that the sorption of metal ions occurs on a homogenous surface by monolayer sorption and there no interaction between adsorbed ions, with homogeneous binding sites and equivalent sorption energies. The linear equation of the Langmuir isotherm model is expressed as followed:

$$\frac{\mathbf{c}_e}{q_e} = \frac{1}{q_m k_L} + \frac{\mathbf{c}_e}{q_m} \tag{S4}$$

where q_m is the maximum sorption capacity corresponding to complete monolayer coverage (mg/g) and k_L is a constant indirectly related to sorption capacity and energy of sorption (L/mg), which characterizes the affinity of the adsorbate with the adsorbent. The linearized plot was obtained when we plotted c_e/q_e against c_e and q_m and k_L could be calculated from the slope and intercept.

The Freundlich equation is an empirical equation based on sorption on a heterogeneous surface. The isotherm assumes that adsorbent surface sites have a spectrum of different binding energies. The linear equation can be expressed by:

$$\ln q_e = \ln k_F + \frac{1}{n} \ln c_e \tag{S5}$$

where k_F and n are the Freundlich constants related to the sorption capacity and the sorption intensity, respectively. The linear plot was obtained by plotting $\ln q_e$ against $\ln c_e$, and the values of k_F and n were calculated from the slope and intercept of the straight line.

Dubinin-Radusckevich (D-R) isotherm describes sorption on a single type of uniform pores, and its linear expression can be defined as:

$$\ln q_e = \ln Q_m - \beta \varepsilon^2 \tag{S6}$$

where Q_m (mol/g) represents theoretical monolayer saturation capacity, β (mol²/kJ²) is a constant correlated to sorption energy, and ε is the Polanyi potential (KJ/mol) related to the equilibrium concentration, illustrated as:

$$\varepsilon = \operatorname{RT}\ln(1 + \frac{1}{C_e}) \tag{S7}$$

where R is the universal gas constant (kJ/(mol K)) and T is the absolute temperature (K). The mean free energy *E* (kJ/mol) which is used to estimate the sorption type can be calculated from constant β :

$$E = (-2\beta)^{-0.5}$$
(S8)

 Q_m and β for U(VI) sorption in KIT-6 and KIT-6-DAPhen were obtained from the linear plot of $\ln q_e$ against ε^2 .



Fig. S4 Langmuir isotherm (left), Freundlich isotherm (middle) and Dubinin–Radusckevich isotherm (right) linearized plots for U(VI) sorption on KIT-6 and KIT-6-DAPhen.

 Table S3 comparison of parameters of Langmuir, Freundlich and Dubinin–Radusckevich isotherms

	Isotherm model									
	Langmuir			Freundlich			Dubinin-Radusckevich			
	$Q_m(mg/g)$	<i>b</i> (mL/mg)	R^2	$k_F(L^n/mol^{n-1}g)$	n	R^2	$Q_m (mg/g)$	$\beta (mol^2/kJ^2)$	E (kJ/mol)	R^2
KIT-6	142.9	0.248	0.99	21.5	2.07	0.71	681.7	3.9×10 ⁻³	11.3	0.77
KIT-6-DAPhen	327.9	0.148	0.98	85.6	2.72	0.87	1992	4.4×10 ⁻³	10.7	0.84



Fig. S5 TGA profile of DAPhen.

Coexistent ion	Reagent	Reagent purity
U	$UO_2(NO_3)_2$ ·6H ₂ O	Standard reagent
Co	Co(NO ₃) ₂ ·6H ₂ O	AR
Ni	Ni(NO ₃) ₂ ·6H ₂ O	AR
Zn	Zn(NO ₃) ₂ ·6H ₂ O	AR
Sr	Sr(NO ₃) ₂	AR
La	La(NO ₃) ₃ ·6H ₂ O	AR
Nd	Nd(NO ₃) ₃ ·6H ₂ O	AR
Sm	Sm(NO ₃) ₃ ·6H ₂ O	99.9% metal basis
Gd	Gd(NO ₃) ₃ ·6H ₂ O	AR
Yb	Yb(NO ₃) ₃ ·5H ₂ O	99.9% metal basis

Table S4 Compositions of the coexistent ions solution.



Fig. S6 XRD patterns (left) and N_2 sorption/desorption isotherms (right) of KIT-6-DAPhen before and after U(VI) sorption

Table S5 The desorption of U(VI) from KIT-6-DAPhen

[HNO ₃] ^a (mol/L)	0.05	0.1	0.2	0.5
Efficiency (%)	88.2	91.2	93.2	~100

^a denotes the concentration of HNO₃ in eluent.

MOs	U			N/O	
215MO	U: 6d _{xy} (1.36)	$N_L:2p_y(10.40)$	$N_L:2p_y(10.28)$		
	$5f_x(1.24)$	2p _z (3.98)	2p _z (4.34)		
		$2p_x(3.68)$	$2p_x(3.35)$		
		3s(2.28)	3s(2.25)		
223MO	U:5f _{z3} (3.17)	O _L :2p _y (14.23)	$O_L:2p_y(14.41)$	$O_N:2p_y(1.79)$	$O_{N}:2p_{y}(1.78)$
		2p _x (10.19)	2p _x (10.85)		
226MO	U:5f _{z3} (7.55)	$N_L:2p_y(1.91)$	$N_L:2p_y(1.92)$	$O_N:2p_y(14.65)$	$O_{N}:2p_{y}(14.71)$
	$5f_{z2y}(2.44)$	2px(1.11)	2px(1.08)	$2p_x(2.63)$	$2p_x(2.48)$
227MO	U:5f _{z3} (23.66)	$O_L: 2p_y(2.16)$	$O_L: 2p_y(2.39)$	$O_N:2p_y(2.86)$	$O_N:2p_y(2.91)$
		2p _x (1.93)	$2p_x(2.20)$	$2p_z(2.38)$	2p _z (2.35)
228MO	U:5f _x (1.56)	O _L :2p _y (14.69)	O _L :2p _y (14.27)		
		2p _x (14.32)	$2p_x(14.49)$		
236MO	U:5f _{z3} (1.04)	O _L :2p _z (8.90)	$O_L:2p_z(1.70)$	$O_N:2p_z(6.48)$	O _N :2p _z (12.02)
237MO	U:5f _{z3} (2.30)	O _L :2p _z (13.46)	$O_L:2p_z(4.57)$	$O_N:2p_z(5.59)$	
238MO	U:5f _{z3} (8.01)	$O_L:2p_z(2.04)$	O _L :2p _z (13.97)	$O_N:2p_z(3.08)$	$O_{N}:2p_{z}(5.69)$
244MO	$U:6d_{xy}(1.46)$			$O_N:2p_y(16.83)$	$O_N:2p_y(16.97)$
	5f _x (2.83)			2p _x (5.67)	2p _x (5.59)

Table S6 Contribution (%) of uranium (U) and the nitrogen (N_L) and oxygen (O_L) atoms of ligand, and the oxygen atom of nitrate anion (O_N) to the delocalized canonical MOs for the complex [UO₂L(NO₃)]⁺.

References

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