Supporting Information

The construction of core-shell MOFs@COFs hybrids as a platform for UO_2^{2+} and Eu^{3+} ions removal from solution

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1. Materials

2-aminoterephthalic acid (NH_2-BDC, 99%), titanium isopropoxide (TPOT, 99%), N, N-dimethylformamide (DMF, 99.5%), methanol (CH_3OH, 99.5%), acetic acid (99.7%), mesitylene (98%), dioxane (99.5%), 1, 3, 5-triformylphloroglucinol (Tp, 95%), 1, 4-diaminobenzene (Pa-1, 99%), $Eu(NO_3)_3 \cdot 6H_2O$ (99.5%) and $UO_2(NO_3)_2 \cdot 6H_2O$ (99.5%) were purchased from Macklin Bio-chemical Co., Ltd (Shanghai, China).

2. Kinetic models

The pseudo-first-order, pseudo-second-order and intraparticle diffusion models were calculated according to the Eq. (1, 2, 3).

$$\ln(Q_e - Q_t) = \ln Q_e - K_1 t \qquad \text{Eq. (1)}$$

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{t}{Q_e} \qquad \text{Eq. (2)}$$

$$Q_t = K_p t^{1/2} + C \qquad \text{Eq. (3)}$$

Where, Q_t (mg/g): the amounts of adsorption achieved equilibrium; C: the thickness of boundary layer; K_1 (min^{-1}), K_2 (g $min^{-1}mg^{-1}$) and K_p (g/mg· $min^{0.5}$): the rate constants of the pseudo-first, second-order and intraparticle diffusion, respectively.

3. Figures

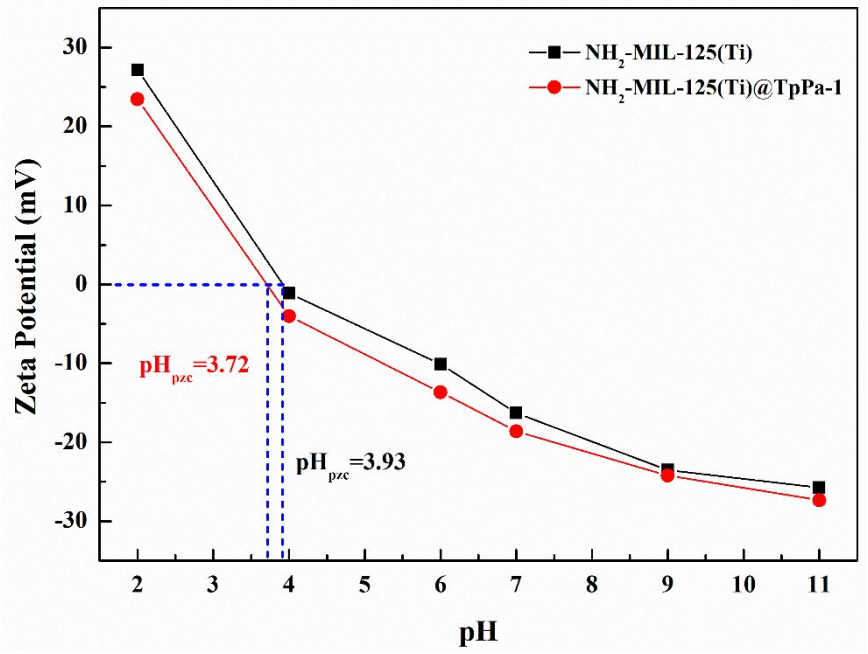

Figure S1 Zeta potential of NH_2-MIL-125(Ti) and NH_2-MIL-125(Ti-100)@TpPa-1.

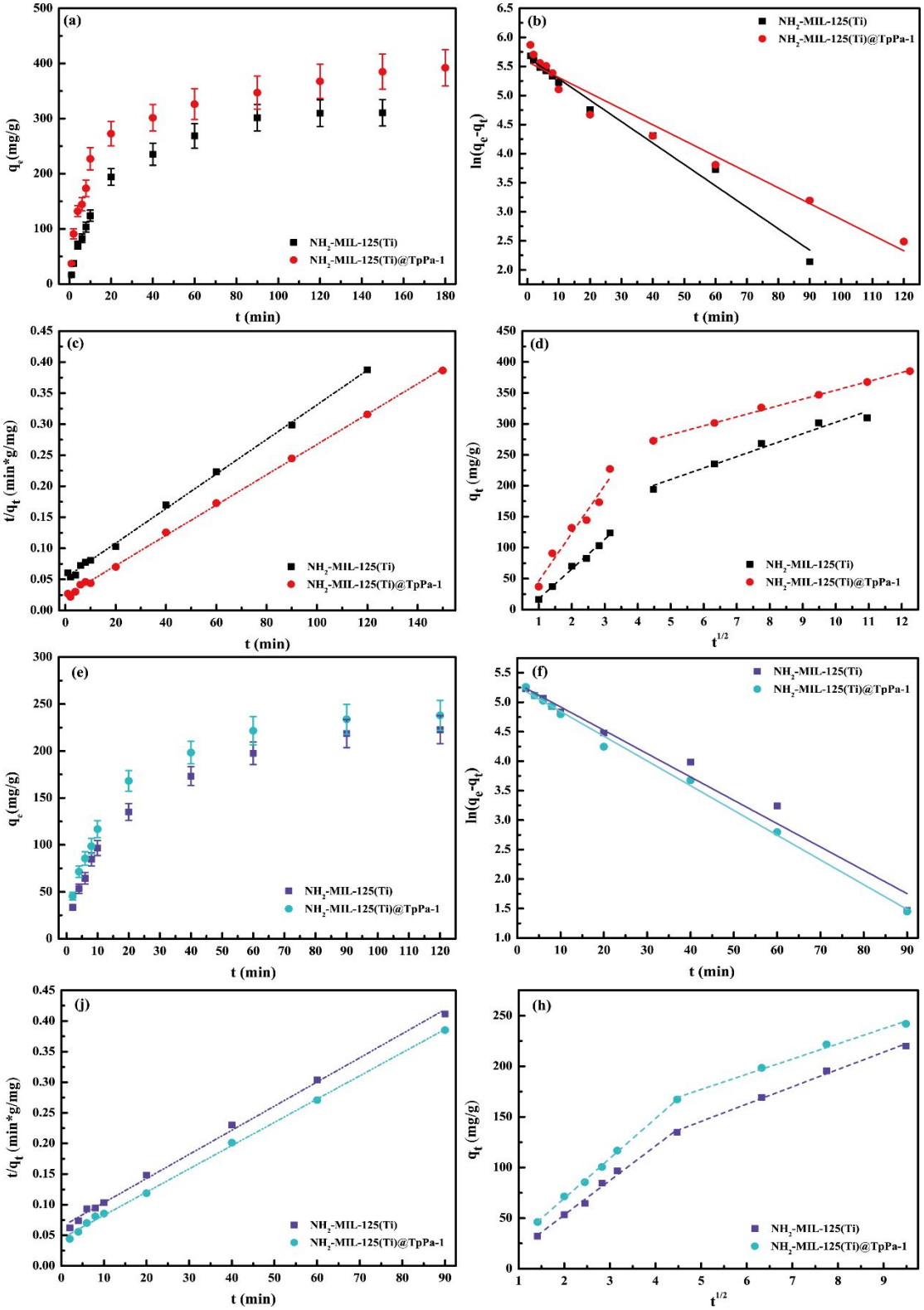

Figure S2 (a) Effect of contact time on UO_2^{2+} adsorption onto NH2-MIL-125(Ti) and NH2-MIL-125(Ti)@TpPa-1; (b) the pseudo-first-order model--UO_2^{2+}; (c) the pseudo-second-order model--UO_2^{2+}; (d) intraparticle diffusion model--UO_2^{2+}; (e) Effect of contact time on Eu^{3+} adsorption onto NH2-MIL-125(Ti) and NH2-MIL-125(Ti)@TpPa-1; (f) the pseudo-first-order model--Eu^{3+}; (j) the pseudo-second-order model--Eu^{3+}; (h) intraparticle diffusion model--Eu^{3+}.

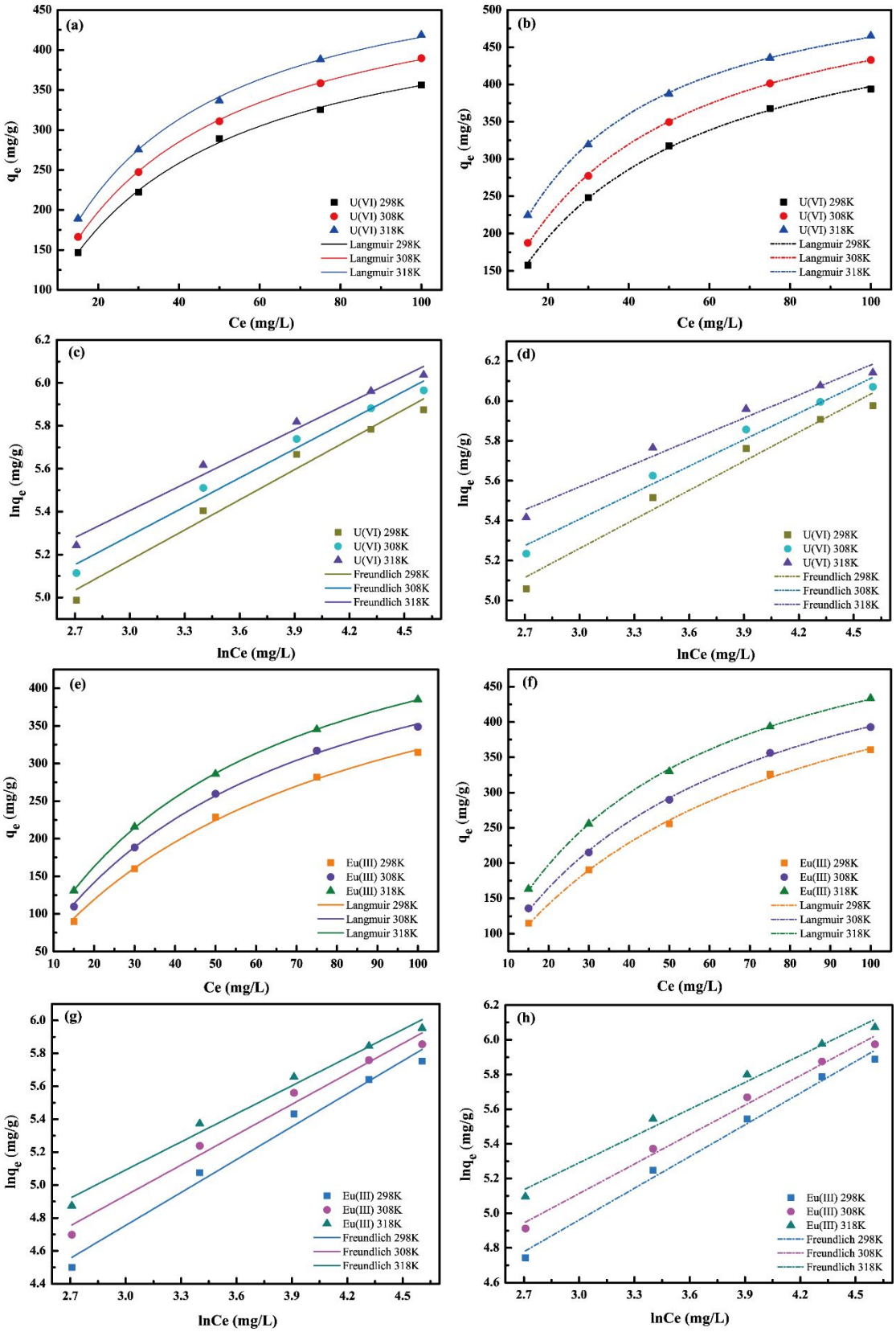

Figure S3 Fitting curves for UO_2^{2+} adsorption onto NH_2-MIL-125(Ti) and NH_2-MIL-125(Ti)@TpPa-1 using Langmuir model (a-b) and Freundlich model (c-d). Fitting curves for Eu^{3+} adsorption onto NH_2-MIL-125(Ti) and NH_2-MIL-125(Ti)@TpPa-1 using Langmuir model (e-f) and Freundlich model (j-h).

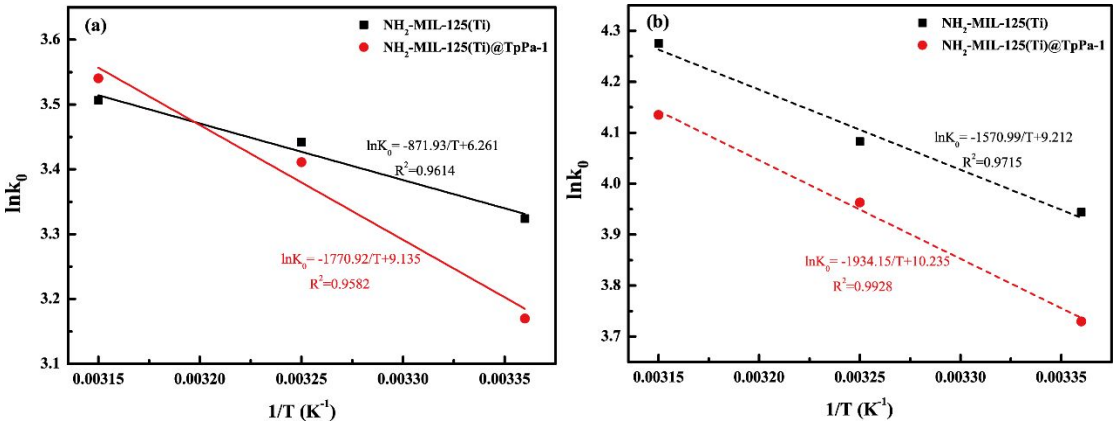

Figure S4 The linear plots of $\ln K_0$ of UO_2^{2+} and Eu^{3+} ions versus 1/T at three different temperatures (T=298-318 K). (a) UO_2^{2+}; (b) Eu^{3+}.

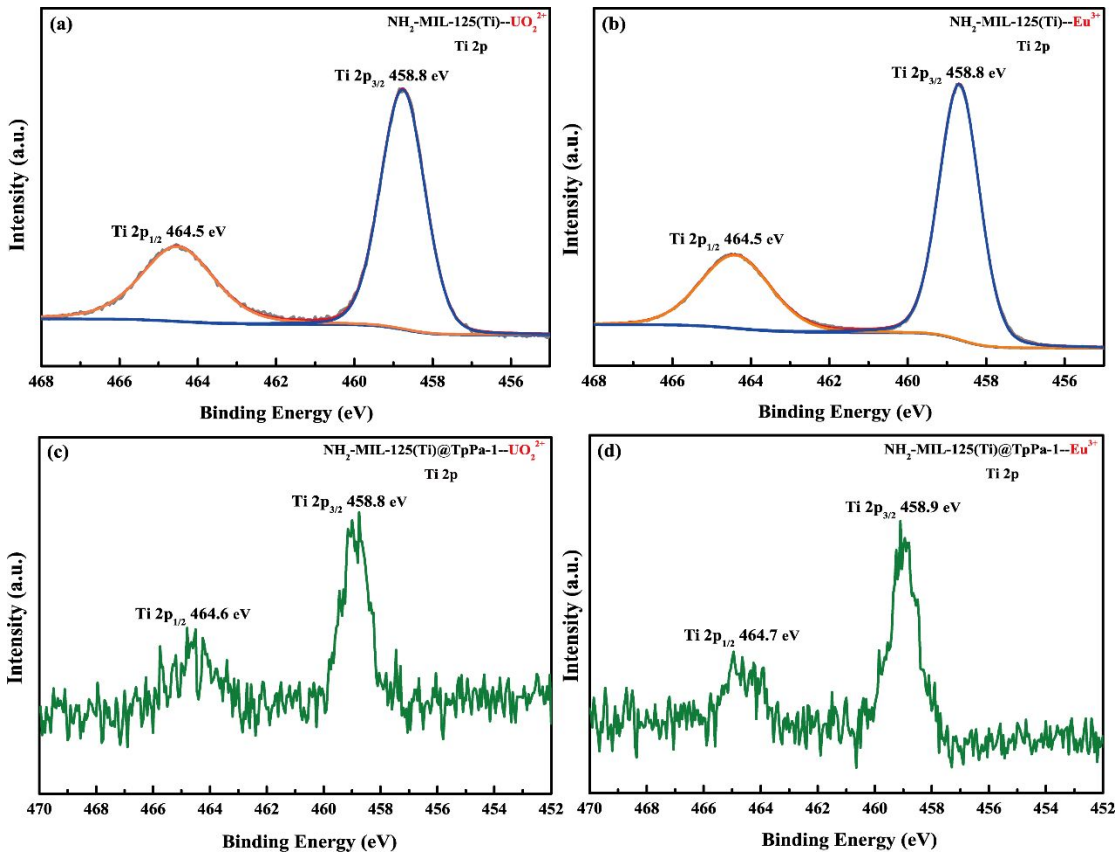

Figure S5 (a) Ti 2p for NH_2-MIL-125(Ti) after UO_2^{2+} adsorption; (b) Ti 2p for NH_2-MIL-125(Ti) after Eu^{3+} adsorption; (a) Ti 2p for NH_2-MIL-125(Ti)@TpPa-1 after UO_2^{2+} adsorption; (b) Ti 2p for NH_2-MIL-125(Ti) @TpPa-1 after Eu^{3+} adsorption.

Table S1 Kinetic model parameters for the adsorption of UO_2^{2+} and Eu^{3+} ions.

Adsorbents/ Adsorbates		Pseudo-first-order			Pseudo-second-order			Intra-particle-diffusion		
		K_1	Q_e	R^2	K_2	Q_e	R^2	K_p	C	R^2
NH_2-MIL-125(Ti)	**UO_2^{2+}**	0.0369	287.15	0.9826	1.5×10^{-4}	357.14	0.9982	48.15	-30.87	0.9916
								18.51	117.57	0.9598
	Eu^{3+}	0.0396	203.96	0.9764	2.4×10^{-4}	253.81	0.9968	34.05	-14.92	0.9906
								17.09	60.12	0.9934
NH_2-MIL-125(Ti)@TpPa-1	**UO_2^{2+}**	0.0271	265.60	0.9634	2.6×10^{-4}	409.83	0.9991	77.32	-31.43	0.9483
								14.35	210.79	0.9962
	Eu^{3+}	0.0420	193.64	0.9954	3.2×10^{-4}	263.16	0.9983	39.43	-9.25	0.9984
								15.04	101.94	0.9890

Table S2 Isotherm parameters for the adsorption of UO_2^{2+} and Eu^{3+} ions.

Adsorbents/ Adsorbates		T (K)	Langmuir model			Freundlich model		
			Q_{max} (mg/g)	K_L (L/mg)	R^2	K_F ($mg^{1-1/n} \cdot g^{-1} \cdot L^{-1/n}$)	$1/n$	R^2
NH_2-MIL-125(Ti)	**UO_2^{2+}**	298	474.50	0.030	0.9983	43.38	0.468	0.9709
		308	511.08	0.032	0.9994	51.42	0.449	0.9792
		318	532.29	0.036	0.9984	63.43	0.419	0.9794
	Eu^{3+}	298	548.02	0.014	0.9978	15.80	0.666	0.9785
		308	561.63	0.017	0.9983	21.98	0.615	0.9767
		318	583.19	0.019	0.9999	29.67	0.569	0.9818
NH_2-MIL-125(Ti)@TpPa-1	**UO_2^{2+}**	298	536.73	0.029	0.9987	44.79	0.486	0.9646
		308	565.34	0.033	0.9997	59.15	0.443	0.9768
		318	572.88	0.042	0.9996	83.10	0.384	0.9725
	Eu^{3+}	298	593.97	0.016	0.9980	22.87	0.609	0.9887
		308	603.50	0.019	0.9990	30.57	0.566	0.9883
		318	614.58	0.024	0.9995	42.10	0.516	0.9831

9 Thermodynamic parameters for the adsorption of UO_2^{2+} and Eu^{3+} ions.

Adsorbents/Adsorbates		T(K)	$-\Delta G^0$ (kJ/mol)	ΔS^0 (J/(mol·K))	ΔH^0 (J/mol)
NH_2-MIL-125(Ti)	**UO_2^{2+}**	298	14.64	52.05	871.93
		308	15.16		
		318	15.68		
	Eu^{3+}	298	21.25	76.59	1570.99
		308	22.02		
		318	22.78		
NH_2-MIL-125(Ti)@TpPa-1	**UO_2^{2+}**	298	20.86	75.95	1770.92
		308	21.62		
		318	22.38		
	Eu^{3+}	298	23.42	85.09	1934.15
		308	24.27		
		318	25.12		