

**Electronic Supplementary Information (ESI)**

**Construction of stable hydrogen-bonded organic framework  
for the photocatalytic reduction and removal of uranium**

Li Zhang,<sup>a\*</sup> Yu-Ting Luo,<sup>a</sup> Sai-Jin Xiao,<sup>b</sup> Jia-Qi Fan,<sup>a</sup> Quan-Gen Tan,<sup>a</sup> Chen Sun,<sup>a</sup>  
An-Min Song,<sup>a</sup> Ru-Ping Liang,<sup>a</sup> and Jian-Ding Qiu<sup>a,b\*</sup>

<sup>a</sup> School of Chemistry and Chemical Engineering, Nanchang University, Nanchang  
330031, China

<sup>b</sup> State Key Laboratory of Nuclear Resources and Environment, East China University  
of Technology (ECUT), Nanchang 330013, China

\* Corresponding author. Tel/Fax: +86-791-83969518. E-mail: zhangli8@ncu.edu.cn; jdqiu@ncu.edu.cn

## EXPERIMENT SECTION

**Materials.** 1,1,2,2-tetrakis(4-(1H-imidazol-1-yl)phenyl)ethene (TIPE) was purchased from Jilin Chinese Academy of Sciences-Yanshen Technology. N,N-dimethylformamide (DMF) was obtained from Energy Chemical. Ethanol, methanol and other nitrate salts were purchased from Sinopharm Chemical Reagent Co., Ltd. Water used in the experiment was prepared with a Millipore system (18.25 M $\Omega$ .cm).

**Instruments.** Fourier-transform infrared (FT-IR) spectra were recorded with a Bruker TENSOR 27 instrument. Powder X-ray diffraction (PXRD) data of the HOFs were collected on a Bruker AXS D8 Advance A25 Powder X-ray diffractometer (40 kV, 40 mA) using Cu K $\alpha$  ( $\lambda = 1.5406 \text{ \AA}$ ) radiation. The fluorescence (FL) spectra were recorded on a FL spectrophotometer (F-7000, Hitachi). X-ray photoelectron spectroscopy (XPS) spectra were performed on a Thermo VG Multilab 2000X with Al K $\alpha$  irradiation. The thermal properties of the HOFs were evaluated using a STA PT1600 Linseis thermogravimetric analysis (TGA) instrument over the temperature range of 30 to 800 °C under nitrogen atmosphere with a heating rate of 10 °C/min. Metal ion concentrations were determined using an iCAP Q inductively coupled plasma mass spectrometry (ICP-MS, Thermo Fisher Scientific, USA).

**Synthesis of HOF-T.** The TIPE (14.9 mg, 0.025 mmol) was mixed with 1 mL of DMF, 1mL of ethanol, 1mL of water and 60  $\mu$ L of HNO<sub>3</sub> in a 20 mL glass bottle. After being sealed, the glass bottle was placed in an oven at 110 °C for 3 days followed by 24 h of program cooling. Colorless acicular single crystals were collected after washing by water with a yield of 76%.

**Photoelectric performance test.** The Mott-Schottky plots were measured at the frequencies of 500, 1000, and 1500 Hz. The Mott-Schottky measurements were performed on a CHI 660B electrochemical workstation in 0.1 M Na<sub>2</sub>SO<sub>4</sub> electrolyte with Ag/AgCl electrode as the reference electrode and a Pt mesh as the counter electrode. PL decay spectra were measured at room temperature using FLS 1000 spectrometer (Edinburgh Instruments, UK). Photoelectrochemical measurements were carried out on CHI 660B electrochemical workstation, with a conventional three electrodes cell (a Indium-tin oxide (ITO) glasses as work electrode, a platinum mesh as the counter electrode and an Ag/AgCl electrode as reference electrode) at a particular voltage. The photocurrent responses were conducted with a CHI 660B workstation, with the working electrodes irradiated from the front side. The light was generated by a 300 W xenon lamp (PLS-SXE300D) with a light density of 1 kW m<sup>-2</sup>

at room temperature and the light wavelength from 320 nm to 780 nm.

**Calculation of the mean fluorescence lifetime.** The experimental data were fitted by the Exp Dec2 model:  $I(t) = I_0 + A_1 \exp(-t/t_1) + A_2 \exp(-t/t_2)$ , where  $A_1$  and  $A_2$  represent the amplifications,  $t_1$  and  $t_2$  represent the emission time, respectively. The mean fluorescence lifetime can be calculate according to formula:  $T = (A_1 t_1^2 + A_2 t_2^2) / (A_1 t_1 + A_2 t_2)$ .

**Stability test.** HOF-T was immersed in different pH solutions, respectively (pH 2-12). The mixture was then filtered and washed with ultra-pure water till the supernatant became neutral and dried under vacuum at 60 °C. Then PXRD patterns were obtained to investigate the stability.

**Isotherms for photocatalytic removal of uranium.** Considering that uranium exists mainly in the strong acidic environment and hydrolysis occurs in higher pH values, photoreduction experiments were carried out at pH 5.0. The catalyst (5 mg) was added to a 20 mL aqueous solution with different concentrations of U(VI) (25, 50, 100, 200, 300, 400, and 500 mg L<sup>-1</sup>) and 1.25% methanol. Then, they were placed under Xe light source and irradiated for 6 h. The treated solution was filtered through a 0.22 μm membrane filter, and the filtrate was analyzed by ICP-MS to determine the remaining U(VI) concentration. The removal capacity ( $q_e$ , mg g<sup>-1</sup>) at equilibrium is calculated by  $q_e = (C_0 - C_e) / m \times V$ , where  $V$  (L) is the volume of the treated solution,  $m$  (g) is the amount of used catalyst, and  $C_0$  and  $C_e$  (mg L<sup>-1</sup>) are the initial concentration and the final equilibrium concentration of U(VI), respectively. The experimental data were fitted by the Langmuir isotherm model. It can be described as:  $q_e = q_m b C_e / (1 + b C_e)$ , where  $b$  (L mg<sup>-1</sup>) represents the Langmuir constant,  $C_e$  (mg L<sup>-1</sup>) represents the equilibrium concentration of metal ions,  $q_m$  (mg g<sup>-1</sup>) represents the monolayer adsorption capacity,  $q_e$  (mg g<sup>-1</sup>) represent the equilibrium removal capacity

**Uranium removal kinetics.** The catalyst (5 mg) was added to 20 mL of 100 mg L<sup>-1</sup> U(VI) solution containing 1.25% methanol at pH 5.0. Then the mixture was vigorously stirred for different time under the light irradiation. The treated solution was filtered through a 0.22 μm membrane filter, and the filtrate was collected and analyzed by ICP-MS to determine the remaining U(VI) content. The experimental data was fitted using Pseudo-second-order kinetic model. It can be expressed as follows:  $t/q_t = 1/(k_2 q_e^2) + t/q_e$ , where  $q_t$  and  $q_e$  (mg g<sup>-1</sup>) represent the removal amount at time and at equilibrium  $t$  (min), respectively,  $k_2$  (g mg<sup>-1</sup> min<sup>-1</sup>) represents the Pseudo-second-order rate constant of adsorption. The percentage removal of uranium

concentration was calculated as follows:  $R\% = (C_0 - C_e)/C_0 \times 100\%$ ,  $C_0$  and  $C_e$  ( $\text{mg L}^{-1}$ ) are the initial concentration and the final equilibrium concentration of U(VI), respectively.

**Optimum photocatalytic conditions.** Uranium extraction at different pH values: The catalyst (5 mg) was added to 20 mL of  $100 \text{ mg L}^{-1}$  U(VI) solution containing 1.25% methanol at different pH values. Uranium extraction with different scavengers: The catalyst (5 mg) was added to 20 mL of  $100 \text{ mg L}^{-1}$  U(VI) solution containing different scavengers at pH 5.0. The mixtures were illuminated by Xe lamp for 4 h, filtered through a  $0.22 \mu\text{m}$  membrane filter, and the filtrate was collected and analyzed by ICP-MS to determine the remaining U(VI) content. The removal capacity ( $q$ ,  $\text{mg g}^{-1}$ ) was calculated by  $q = (C_0 - C_e)/m \times V$ , where  $V$  (L) is the volume of the treated solution,  $m$  (g) is the amount of used catalyst, and  $C_0$  and  $C_e$  ( $\text{mg L}^{-1}$ ) are the initial concentration and the final equilibrium concentration of U (VI), respectively.

**Selectivity.** The ions stock solutions were prepared by dissolving the corresponding nitrate salts or sodium salts of  $\text{Mg}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Ca}^{2+}$ ,  $\text{VO}_4^{3-}$ ,  $\text{Cr}^{3+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Y}^{3+}$ ,  $\text{La}^{3+}$ ,  $\text{Ce}^{3+}$ ,  $\text{Pr}^{3+}$ ,  $\text{Nd}^{3+}$ ,  $\text{Sm}^{3+}$ ,  $\text{Eu}^{3+}$ ,  $\text{Gd}^{3+}$ ,  $\text{Tb}^{3+}$ ,  $\text{Dy}^{3+}$ ,  $\text{Ho}^{3+}$ ,  $\text{Er}^{3+}$ ,  $\text{Tm}^{3+}$ , and  $\text{Lu}^{3+}$  in ultrapure water. U(VI) with the concentration of  $50 \text{ mg L}^{-1}$  and other metal ions 4 times higher than U(VI) were used to carry out the adsorption experiment. The removal capacity ( $q$ ,  $\text{mg g}^{-1}$ ) was calculated by  $q = (C_0 - C_e)/m \times V$ , where  $V$  (L) is the volume of the treated solution,  $m$  (g) is the amount of used catalyst, and  $C_0$  and  $C_e$  ( $\text{mg L}^{-1}$ ) are the initial concentration and the final equilibrium concentration of different ions, respectively.

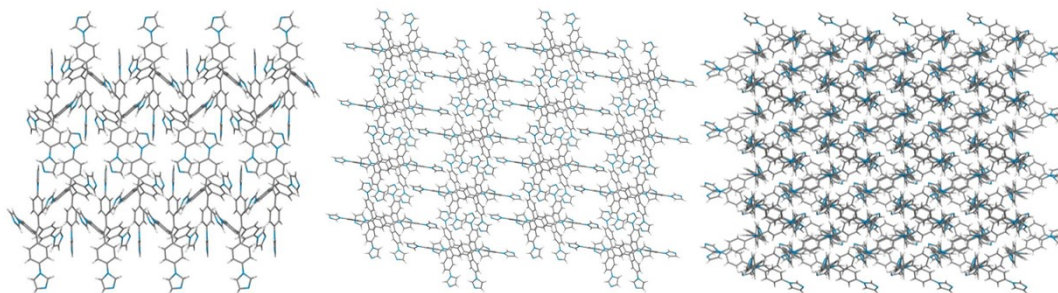
**Recyclability test.** After a photocatalytic process, the solid powder was filtered. The materials were then placed in a solution of 100 mL  $\text{Na}_2\text{CO}_3$  (1 M) and shaken for 24 h. Then the suspension was filtered and washed with 0.01 M  $\text{HNO}_3$  and ultra-pure water until the supernatant became neutral. After drying under vacuum, the obtained material was used in the next photocatalytic experiment.

### Theoretical calculation

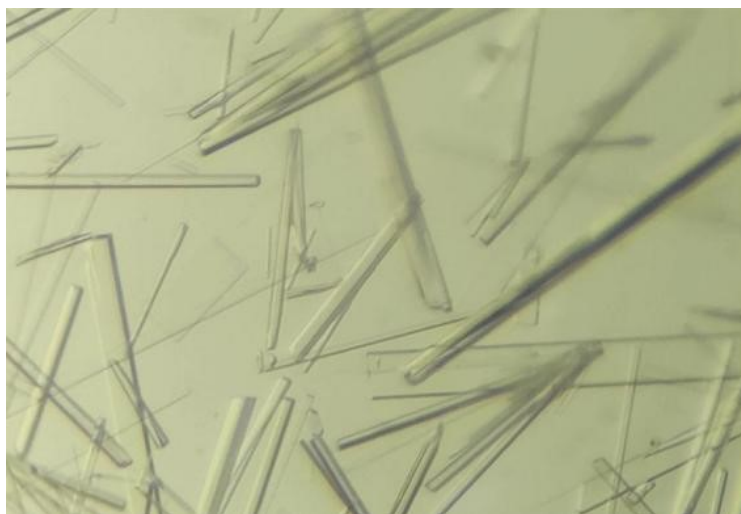
The ground state geometry is optimized using DFT. All calculations are performed with the Gaussian 16 package (Rev. A.03) using the hybrid B3LYP functional and the 6-311G(d)/SDD basis set.

**Table S1.** Crystal data of as-synthesized HOF-T

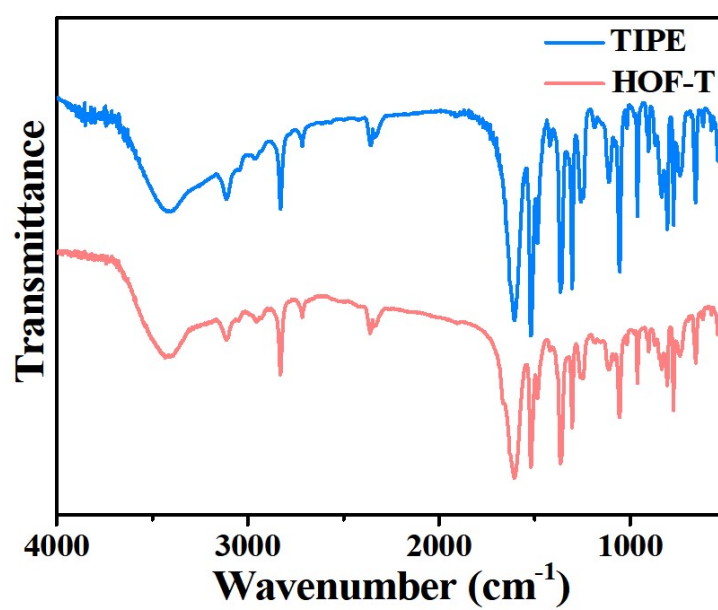
CCDC deposition number	2257677
Empirical formula	$C_{38}H_{28}N_8$
$M/g \cdot mol^{-1}$	596.68
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/n$
$a / \text{\AA}$	11.5521(2)
$b / \text{\AA}$	9.4107(2)
$c / \text{\AA}$	32.5260(6)
$\alpha / ^\circ$	90
$\beta / ^\circ$	95.722(2)
$\gamma / ^\circ$	90
Volume/ $\text{\AA}^3$	3518.39(12)
$Z$	4
$\rho_{calc}/cm^3$	1.126
$\mu/mm^{-1}$	0.548
$F(000)$	1248(0)
Crystal size/ $mm^3$	$0.2 \times 0.08 \times 0.05$
Radiation	Cu $K\alpha$ ( $\lambda = 1.54184$ )
$2\theta$ range for data collection/ $^\circ$	5.462 to 149.926
Index ranges	$-14 \leq h \leq 12, -11 \leq k \leq 11, -40 \leq l \leq 40$
Reflections collected	24093
Independent reflections	6993 [ $R_{int} = 0.0397, R_{sigma} = 0.0384$ ]
Data/restraints/parameters	6993/0/416
Goodness-of-fit on $F^2$	1.080
Final R indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0610, wR_2 = 0.1818$
Final R indexes [all data]	$R_1 = 0.0740, wR_2 = 0.1956$
Largest diff. peak/hole / $e \text{\AA}^{-3}$	0.47/-0.40



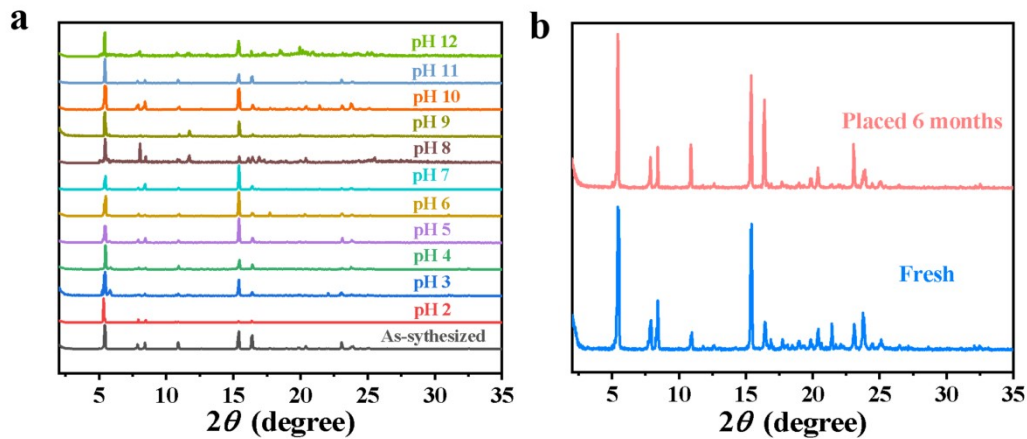
**Fig. S1** Packing diagrams of HOF-T along the a axis, b axis, and c axis (from left to right).



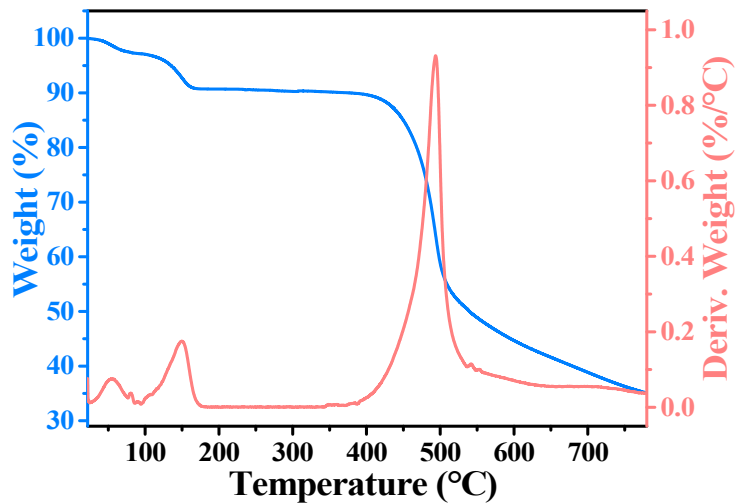
**Fig. S2** Light microscopy of HOF-T.



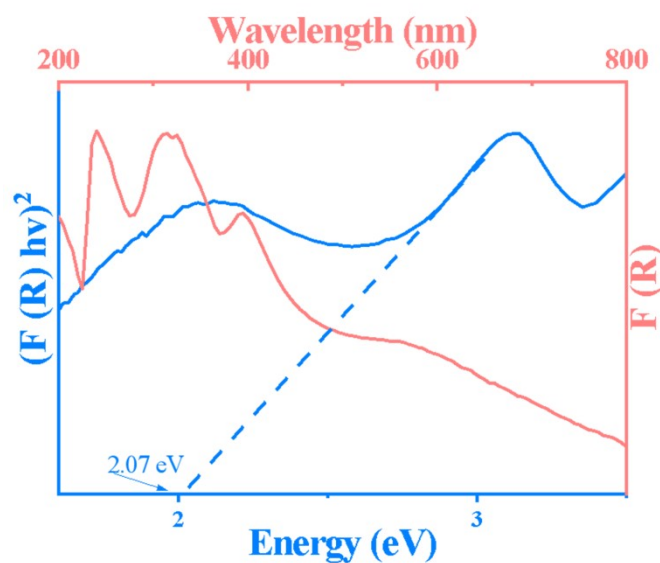
**Fig. S3** The FT-IR spectra of TIPE and HOF-T.



**Fig. S4** (a) PXRD patterns of HOF-T at different pH values. (b) PXRD patterns of the as-synthesized HOF-T and the HOF-T after being placed in air for six months.



**Fig. S5** TGA analysis of HOF-T.



**Fig. S6** The UV/Vis diffuse reflectance spectrum of HOF-T and the band gap determined from the Kubelka-Munk function of HOF-T.

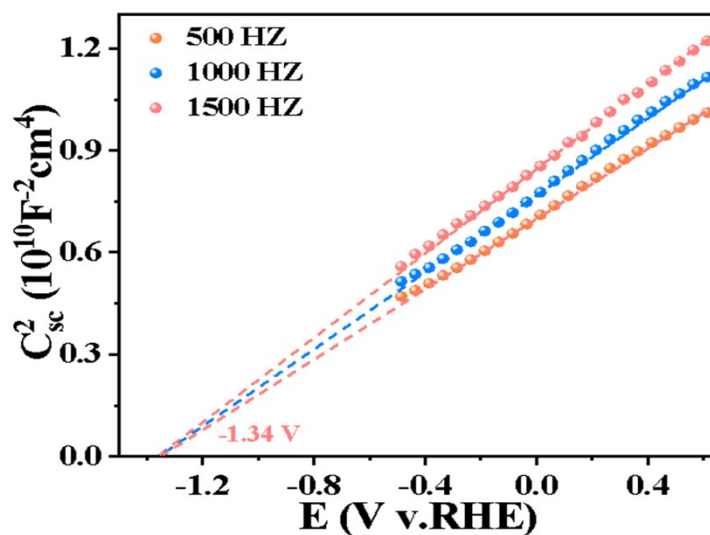


Fig. S7 Mott-Schottky plots of HOF-T.

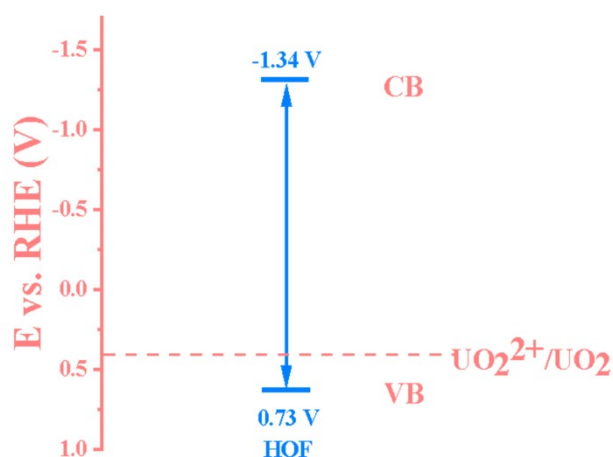


Fig. S8 Band alignment of HOF-T.

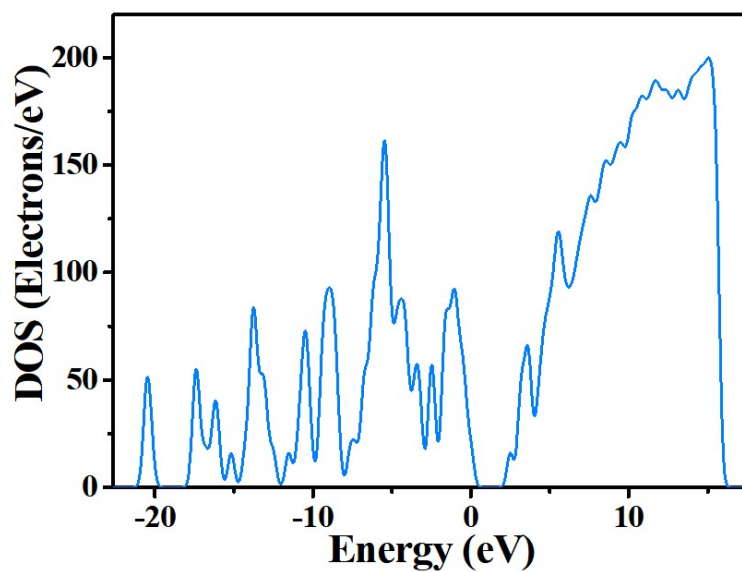
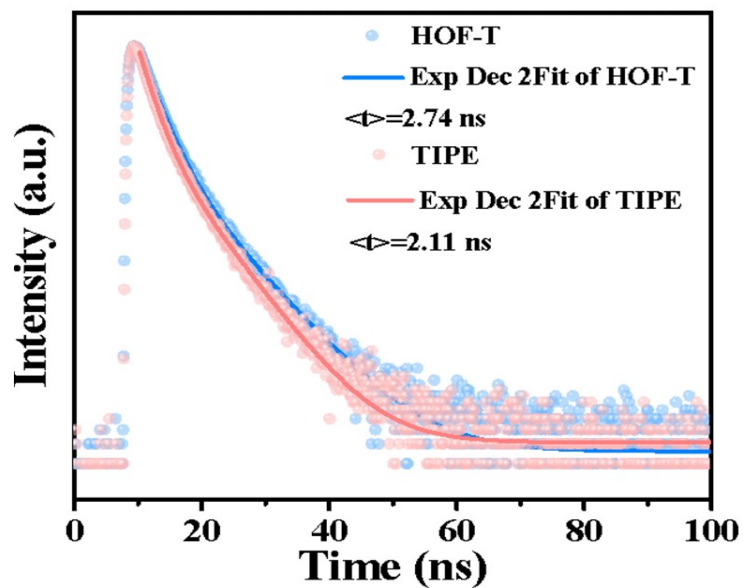


Fig. S9 Calculated density of electronic states for HOF-T.

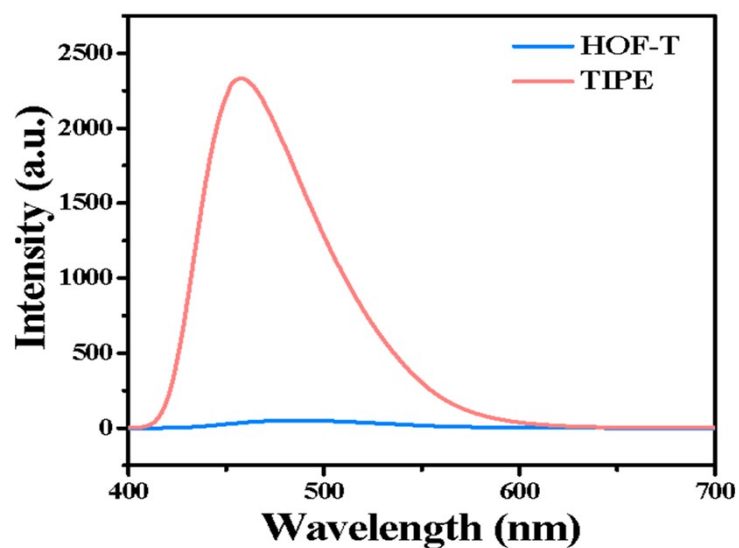




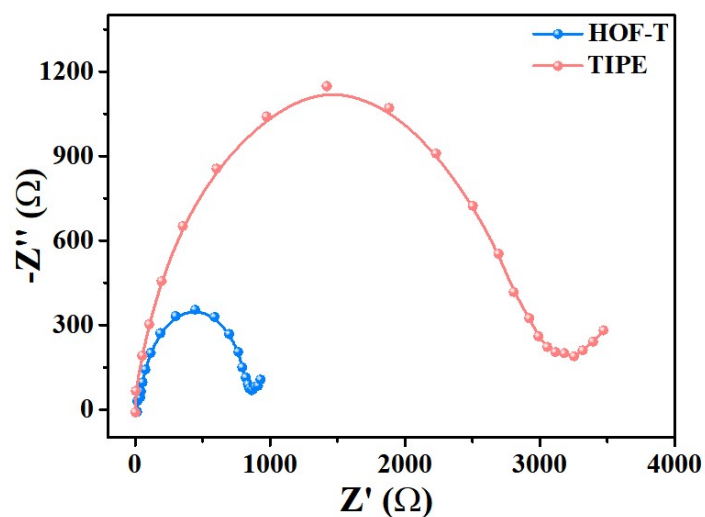
**Fig. S10** PL decay curves of HOF-T and TIPE.

**Table S2** A1, A2, t1, t2, k1, k2, tau1, tau2 and R-Square value of HOF-T and TIPE.

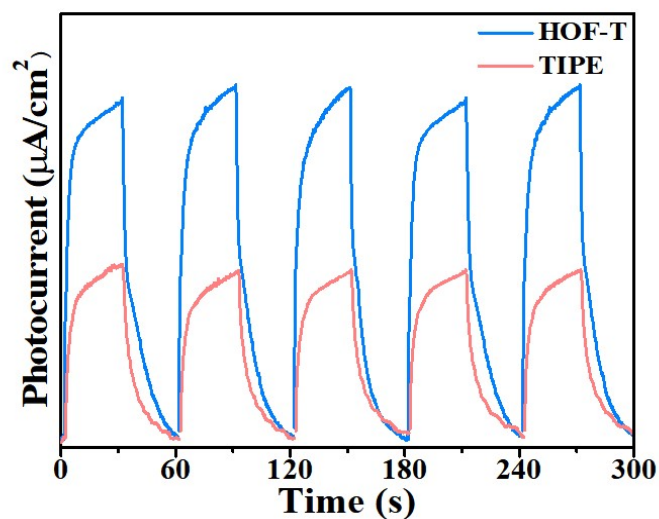
Samples	A1	t1	A2	t2	k1	k2	tau1	tau2	R-Square
HOF-T	424874	2.57	6095	7.1	0.38929	0.14092	1.78054	4.9187	0.999
TIPE	10900	5.83	115079	2.0	0.17124	0.49805	4.04784	1.39173	0.999



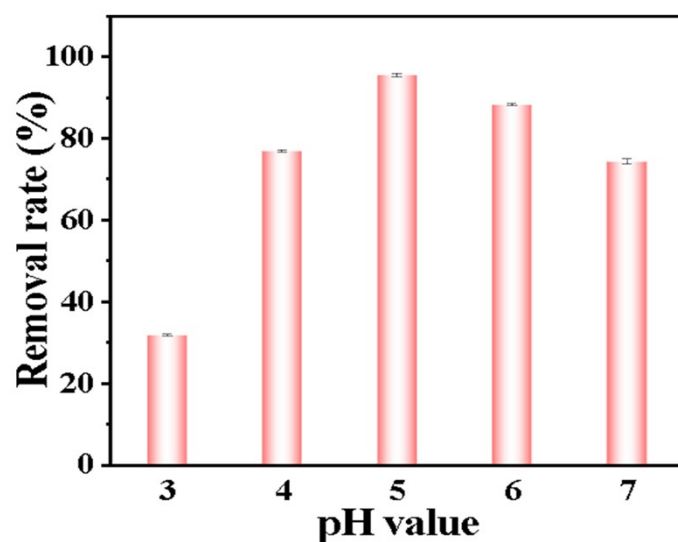
**Fig. S11** FL emission of HOF-T and TIPE.



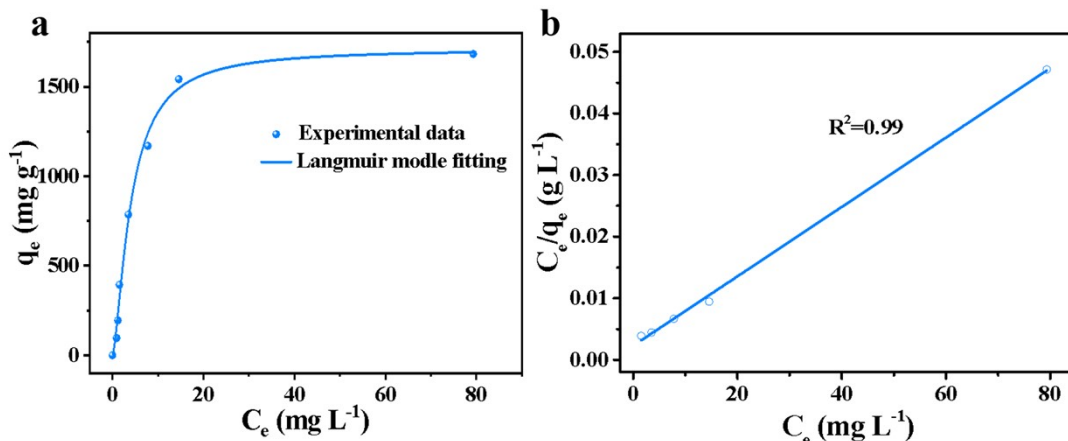
**Fig. S12** EIS curve of HOF-T and TIPE.



**Fig. S13** Transient photocurrent response of HOF-T and TIPE.



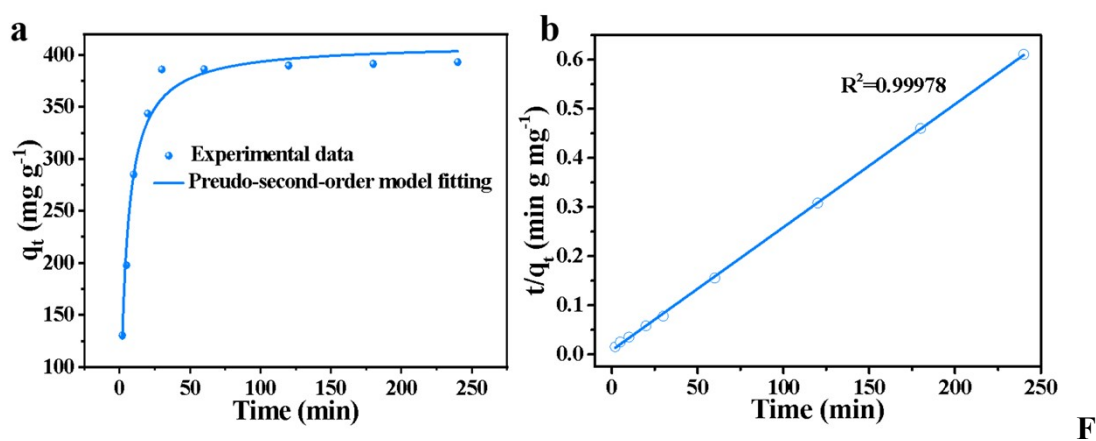
**Fig. S14** Removal rate of U(VI) by HOF-T under different pH conditions ( $C_0 = 100 \text{ mg L}^{-1}$ ,  $m_{\text{catal}}/V_{\text{sol}} = 250 \text{ mg L}^{-1}$ ).



**Fig. S15** (a) Removal isotherm of U(VI) by HOF-T under light condition and the solid line displays the Langmuir model fitting results. (b) The Langmuir model kinetic plot.

**Table S3.** Parameters of the Langmuir isotherms for the removal of uranium on catalysts.

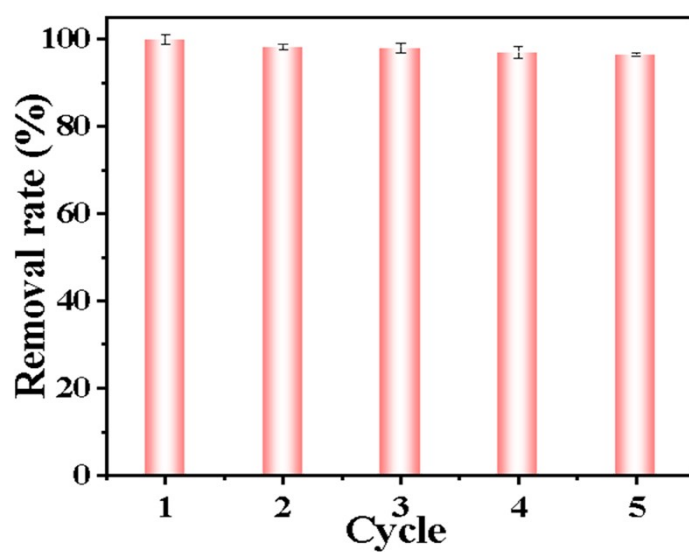
catalyst	Langmuir Model		
	$Q_{exp}$ (mg g <sup>-1</sup> )	$Q_{max, fitted}$ (mg g <sup>-1</sup> )	$b$ (L mg <sup>-1</sup> )
<b>HOF-T</b>	1682.7	1711.87	0.12117



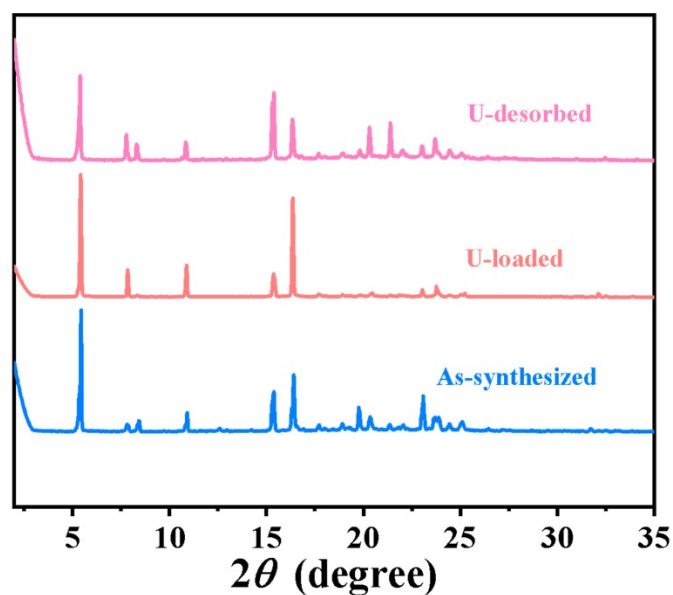
**Fig. S16** (a) Removal kinetics of U(VI) by HOF-T under light condition and the solid line displays the pseudo-second-order fitting results. (b) The pseudo-second-order kinetic plot.

**Table S4** Parameters of the Pseudo-second-order kinetics for the adsorption of U(VI) on HOF-T.

catalyst	Pseudo-second-order kinetics		
	$q_{e,expt}$ (mg g <sup>-1</sup> )	$q_{e,calc}$ (mg g <sup>-1</sup> )	$k_2$ (g·mg <sup>-1</sup> ·min <sup>-1</sup> )
HOF-T	393.01	410.88	5.45257E-4



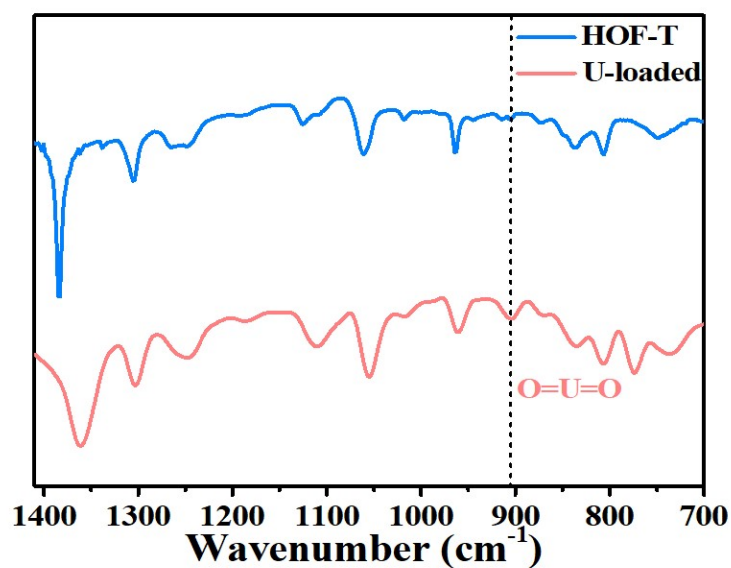
**Fig. S17** Cyclic performance of U(VI) removal using regenerated HOF-T (pH 5,  $C_0 = 100 \text{ mg L}^{-1}$ ,  $m_{\text{catal}}/V_{\text{sol}} = 250 \text{ mg L}^{-1}$ ).



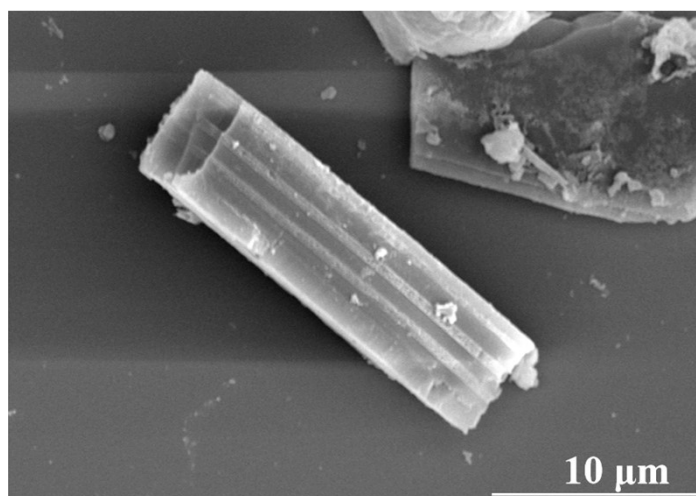
**Fig. S18** PXRD patterns of HOF-T, U-loaded HOF-T and U-desorbed HOF-T.

**Table S5** The concentrations of major cations in the rare earth tailings wastewater before and after photocatalytic treatment (150-fold dilution).

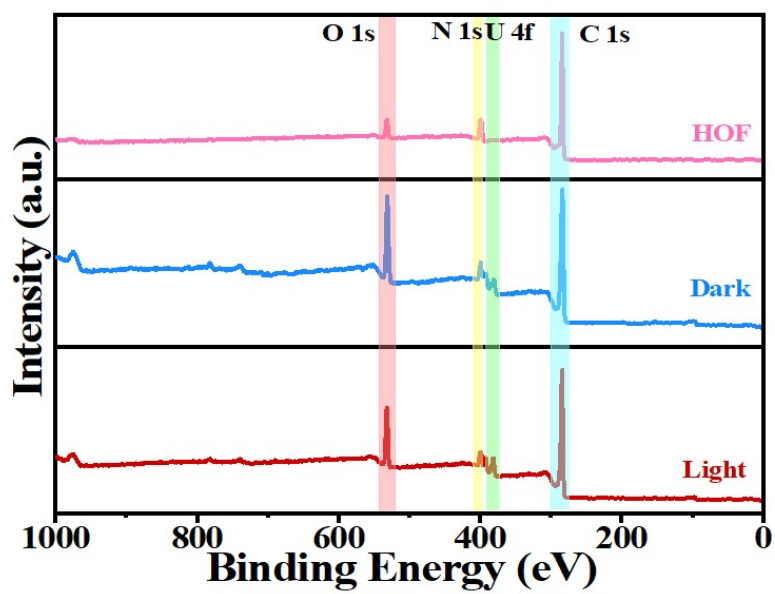
Cation species	Concentration ( $\mu\text{g L}^{-1}$ )	
	Before	After
$\text{UO}_2^{2+}$	66.81	1.87
$\text{Na}^+$	40702.97	40536.31
$\text{Mg}^{2+}$	2310.64	2236.96
$\text{Al}^{3+}$	4278.50	4235.65
$\text{K}^+$	5908.38	5846.43
$\text{Ca}^{2+}$	11834.81	11569.72
$\text{Zn}^{2+}$	153.00	150.76
$\text{Y}^{3+}$	659.93	621.45
$\text{La}^{3+}$	246.65	245.94
$\text{Pr}^{3+}$	108.57	101.05
$\text{Pm}^{3+}$	347.56	335.23
$\text{Nd}^{3+}$	348.18	336.25
$\text{Sm}^{3+}$	121.82	115.53
$\text{Gd}^{3+}$	164.32	154.07
$\text{Tb}^{3+}$	34.12	32.28
$\text{Dy}^{3+}$	38.28	35.36
$\text{Ho}^{3+}$	49.49	43.22
$\text{Er}^{3+}$	125.57	116.90



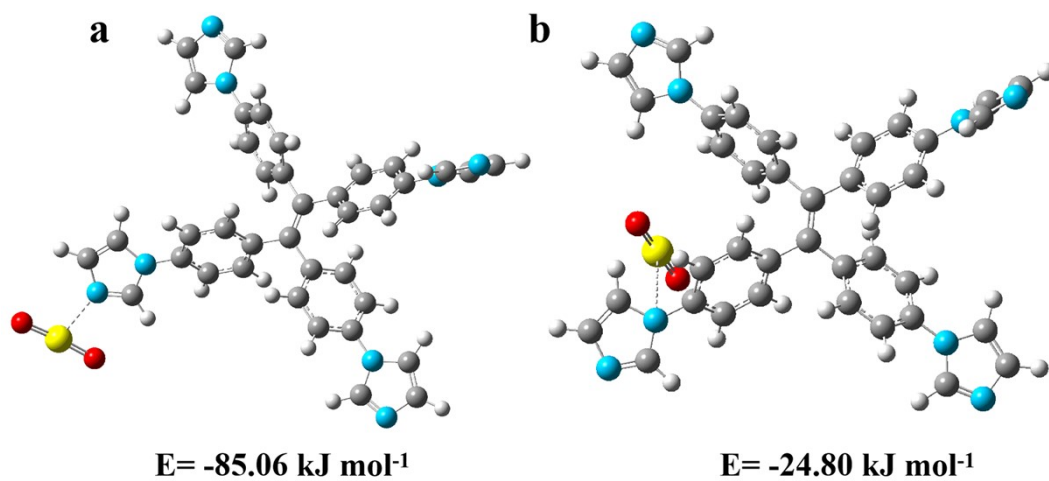
**Fig. S19** FT-IR spectra of HOF-T before and after photocatalysis of U.



**Fig. S20** SEM of HOF-T after photocatalysis of U.



**Fig. S21** The XPS survey spectra of HOF-T before and after U(VI) treatment in dark and light conditions.



**Fig. S22** The binding energy of  $\text{UO}_2^{2+}$  at different binding sites (Color Code: uranium, yellow; carbon, gray; nitrogen, blue; oxygen, red).