Electronic Supplementary Information

A Zr/Ti-based bimetallic AO-UiO-66 framework for effective uptake of radioactive iodine

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General procedures

The crystal structures of the target materials were characterized using a Rigaku Ultima IV Xray diffractometer (Rigaku Corporation, Japan) operated at 40 kV and 40 mA with a scanning angle range of 5-40° and a step size of 0.15°/s. The morphologies of the samples were examined using a scanning electron microscope (SEM, S4800, Hitachi, Japan). Specific surface area and pore size distribution were determined using an ASAP 2020M instrument (Micromeritics Instruments, USA). Thermal stability was evaluated using a Pyris 1 TGA thermogravimetric analyzer (PerkinElmer, USA). Characteristic functional groups and molecular structures were identified using a Spectrum Two FTIR spectrometer (PerkinElmer, USA) within the wavenumber range of 400-2000 cm⁻¹. The chemical states and elemental compositions were analyzed using a Thermo Scientific K-Alpha Xray photoelectron spectrometer (Thermo Fisher Scientific, UK). UV-visible diffuse reflectance spectra were recorded using a UV-3600 UV-visible near-infrared spectrophotometer (Shimadzu, Japan). The concentration of the I₂ solution was measured using an HB-7 UV spectrophotometer (Beijing Haotianhui Instrument Co., China).

Experimental procedures



Scheme S1. Synthetic scheme of H₂L ligand.

Synthesis of 2,5-dihydroxyterephthalate (S1)

2,5-dihydroxyterephthalic acid (DTHA) (1.005 g, 5 mmol), absolute ethanol (50 mL) and a star bar were added into a 150 mL two-necked flask charged with a condenser. And then, 1 mL of concentrated sulfuric acid were added into the mixture drop by drop with stirring. The reaction mixture was stirred and refluxed with stirring at 90 °C for 48 h. After the reaction was completed, the solution was cooled to room temperature and a large amount of DI water was added into the mixture. Yellow-green crystals S1 (1.1753g, 91% yield) were obtained by suction filtration and washed with plenty of water and dried in oven under 80 °C. ¹H NMR (400 MHz, CDCl₃) δ 10.14 (s, 2H, ArOH), 7.48 (s, 2H, ArCH), 4.40-4.44 (m, 4H, CH₂), 1.41-1.44 (m, 6H, CH₃). ¹³C NMR (100 MHz,

Synthesis of Ethyl 2,5-bis (allyloxy) terephthalate (S2)

S1 (0.5120 g, 2 mmol) was added into a 150 mL two-neck flask charged with a magnetic stirring bar and a condenser. The flask was evacuated and purged with nitrogen for three times, and about 45 mL of N₂ bubbled acetone was added to the flask under an atmosphere of N₂. Then K₂CO₃ (1.22 g, 8.7 mmol) and KI (0.071 g, 4.2 mmol) were added into the mixture under N₂ atmosphere, finally, a solution of allyl bromide (0.73 g, 6 mmol) in acetone (5 mL) was injected under N₂ protection. The resultant reaction mixture was stirred for 24 h at room temperature, the solid were removed by filtration when the reaction was completed, and the filtrate was collected and distilled through rotary evaporator. S2 (yellow-brown solid, 0.6740 g) was obtained after the purification by column chromatography. ¹H NMR (400 MHz, CDCl₃) δ 7.38 (s, 2H, ArCH), 6.02-6.08 (m, 2H, CH), 5.47-5.49 (m, 2H, CH), 5.28-5.30 (m, 2H, CH), 5.59 (m, 4H, CH₂), 4.36-4.40 (m, 4H, CH₂), 1.38-1.40 (m, 6H, CH₃). ¹³C NMR (100 MHz, CDCl₃) δ 165.67, 151.49, 132.72, 124.87, 117.65, 117.28, 70.52, 61.44, 14.30.

Synthesis of 2,5-bis (allyloxy)terephthalic acid (H₂L)

S2 (0.6680 g, 2 mmol) was added into a 100 mL two-necked flask charged with a stir bar and a condenser, NaOH aqueous solution (3 M, 25 mL, bubbled with N₂) and methanol (15 mL, bubbled with N₂) were added into the flask under N₂ protection. The reaction mixture was then stirred at 70 °C for 24 h. The mixture was cooled down to room temperature and 30 mL of DI water was added into the flask under N₂, HCl (36 wt%) was then added dropwise with stirring until the pH of the solution was lower than 2.0. A yellow solid product was formed and collected by filtration and washed with plenty of DI water. The ligand H₂L (0.4884 g, 87.8%) was obtained after dried in an oven at 60 °C under vacuum. ¹H NMR (400 MHz, DMSO-d₆) δ 13.02 (s, 2H, COOH), 7.30 (s, 2H, ArCH), 5.97-6.04 (m, 2H, CH), 5.41-5.45 (m, 2H, CH), 5.22-5.25 (m, 2H, CH), 4.68 (m, 4H, CH₂). ¹³C NMR (100 MHz, DMSO-d₆) δ 167.19, 150.50, 133.91, 125.78, 117.41, 116.26, 69.81.

Iodine adsorption kinetics in cyclohexane

The absorbance value of the original solution was normalized to 100%. The removal efficiency (R) of iodine were calculated as follows:

$$R = \frac{(C_0 - C_t)}{C_0} \times 100\%$$
 (1)

where C₀ and C_t represent the initial concentration and concentration at time, respectively. Sorption kinetics of iodine in AO-UiO-66-ZrTi11 were fitted to a Pseudo-first-order and pseudo-second-order kinetics model, respectively:

$$ln\left(q_e - q_t\right) = lnq_e - k_1 t \tag{2}$$

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e} \tag{3}$$

where q_t , q_e represent the amounts of adsorbate at certain time t or at equilibrium time, h is the initial adsorption rate, $h = k_2 q_e^2$, and k_1 and k_2 is the rate constant (see Table S1).

Iodine adsorption isotherm

The linear equation of the Langmuir isotherm model is expressed as follow:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \tag{4}$$

Where q_m is the maximum sorption capacity corresponding to complete monolayer coverage (mg g⁻¹) and K_L is a constant indirectly related to sorption capacity and energy of sorption (L mg⁻¹), 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 linear equation of Freundlich isotherm model can be expressed by:

$$lnq_e = lnK_F + \frac{1}{n}lnC_e \tag{5}$$

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 lnq_e against lnC_e , and the values of K_F and n were calculated from the slope and intercept of the straight line (see Table S2).

Additional Figures



Fig. S1 PXRD patterns (A) of AO-UiO-66 (a), AO-UiO-66-ZrTi31 (b), AO-UiO-66-ZrTi11 (c), AO-UiO-66-ZrTi13, (d) and Ti-MOFs (e). XPS survey spectra (B) of AO-UiO-66-ZrTi31 (a), AO-UiO-66-ZrTi11 (b), AO-UiO-66-ZrTi13 (c).



Fig. S2 N_2 sorption isotherms of AO-UiO-66-ZrTi11 (a) and AO-UiO-66 (b).



Fig. S3 TGA curves of AO-UiO-66-ZrTi11 (a) and AO-UiO-66 (b).



Fig. S4 (A) Trend plots of AO-UiO-66-ZrTi11 (a), AO-UiO-66-ZrTi31 (b) and AO-UiO-66 (c) and photographs of (B) AO-UiO-66-ZrTi11, (C) AO-UiO-66-ZrTi31 and (D) AO-UiO-66 for the adsorption of I_2 in cyclohexane solution.



Fig. S5 Adsorption capacity (a) and removal efficiency (b) of I_2 in cyclohexane solution with different dosages of AO-UiO66-ZrTi11.



Fig.S6 Comparison of the iodine uptake in cyclohexane solution by different MOF adsorbents.



Fig. S7 (A) UV-Vis spectra of iodine in ethanol. (B) Desorption kinetic curve of I₂@AO-UiO-66-ZrTi11 in ethanol solution. (C) pseudo-first-order kinetics fitting curve. (D) pseudo-secondorder kinetics fitting curve.



Fig. S8 (A) Removal efficiency of I_2 in cyclohexane solution in cycle experiment. (B) The PXRD pattern of retrieved AO-UiO-66-ZrTi11 after the I_2 desorption of $I_2@AO$ -UiO-66-ZrTi11.

Additional tables

Simple	Content W (%)		
	Zr	Ti	
AO-UiO-66	23.5	-	
AO-UiO-66-ZrTi31	19.35	2.1	
AO-UiO-66-ZrTi11	12.05	6.89	

 Table S1 ICP date of AO-UiO-66-ZrTi11.

Table S2 Kinetic fitting parameters of the pseudo-first-order model and the pseudo-second-ordermodel for iodine adsorption by AO-UiO-66-ZrTi11.

pseudo-first-order kinetics fitti				pseudo-second-order kinetics fittings		
Sample	q _e	k ₁	R ²	q_{e}	k ₂	R ²
	(mg g⁻¹)	(min⁻¹)		(mg g ⁻¹)	(g mg ⁻¹ min ⁻¹)	
AO-UiO-66-ZrTi11	184.07	0.13492	0.901	384.62	0.0043	0.999

Table S3 Fitting results of the sorption isotherm according to the Langmuir and Freundlich equations.

	Langmuir adsorption isotherm			Freundlich adsorption isother		
Sample	q _m	KL	D ²	K _F	2	D ²
	(mg g⁻¹)	(L mg⁻¹)	ĸ	(mg g ⁻¹)(L mg ⁻¹) ^{1/n}	п	ĸ
AO-UiO-66-ZrTi11	1133	0.0103	0.998	298	5.73	0.995

Table S4 Comparison of adsorption capacity of I_2 in cyclohexane solution by different MOF adsorbents at room temperature.

Matarial	I ₂ conc. in cyclohexane	Adsorbent dosage	Deferences
	(mg g ⁻¹)	(g L⁻¹)	References
ZBPU-I ₂	1260.7	-	1
UiO-66-PYDC	1250	0.6	2
AO-UiO-66-ZrTi11	1084.4	1	This work
ZBPU-I	896.3	-	1
FJI-H39	884.96	2	3
FJI-H40	719.42	2	3
ZBPU	329.25	-	1
Th-BPYDC	312.18	2	4
Th-SINAP-10	292.4	-	5
CAU-1	290	-	6
MIL-101(Cr)-SO₃Ag	244.2	1	7
Th-UiO-66-(NH ₂) ₂	241.5	2.5	8
Th-UiO-67	196.7	2	4
Mn–Ni-MOF-74	163	1	9
MOF-5	115	5	10
Th-UiO-66-Cl	107.5	2.5	8
Mn–Co-MOF-74	54.23	1	9
Mn–Zn-MOF-74	42.23	1	9

A de sub susta	Temp.	adsorption capacity	Adsorption time	References
Adsorbents	(°C)	(g g ⁻¹)	(h)	
HIAM-4014	80	2.680	5	11
AO-UiO-66-ZrTi11	80	2.463	4.7	This work
HBS-W8	-	2.320	84	12
MOF-808	80	2.180	72	13
NH ₂ -MIL-101-on-NH ₂ -UiO-66	80	1.930	4	14
HBS-W9	-	1.920	84	12
MIL-125	-	1.900	120	15
MIL-125-NH ₂	-	1.600	120	15
NU-1000	80	1.450	72	13
Zn/Cd@JLUN-4	80	1.400	-	16
UiO-66-NH-T.D	75	1.330	2.5	17
CAU-1(AI)-NH ₂	-	1.300	72	18
Th-SINAP-17	75	1.255	-	19
UiO-66-NH-B.D	75	1.170	2.5	17
CZ-3	75	1.150	5	20
Ln-MOF	75	1.138	60	21
Th-SINAP-19	75	1.002	-	19
Th-UiO-66-(NH ₂) ₂	75	0.969	9	8
MOF-303	80	0.956	12	22
MOF-867	80	0.880	72	13
UiO-66	80	0.660	72	13
Zn-MOF	70	0.660	30	23
Th-SINAP-16	75	0.552	-	19
UiO-67	80	0.530	72	13

 Table S5 Comparison of capture performance for iodine vapor by different MOF adsorbents.

Table S6 Kinetic fitting parameters of the pseudo-first-order model and the pseudo-second-ordermodel for iodine desorption by AO-UiO-66-ZrTi11.

	pseudo-first-order	kinetics fittings	pseudo-second-order kinetics fittings		
Sample	k ₁	R ²	k ₂	R ²	
	(min⁻¹)		(g mg⁻¹ min⁻¹)		
AO-UiO-66-ZrTi11	0.07683	0.993	0.05407	0.995	

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