Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Zr-based MOFs integrated with chromophoric ruthenium complex for specific and reversible Hg^{2+} sensing

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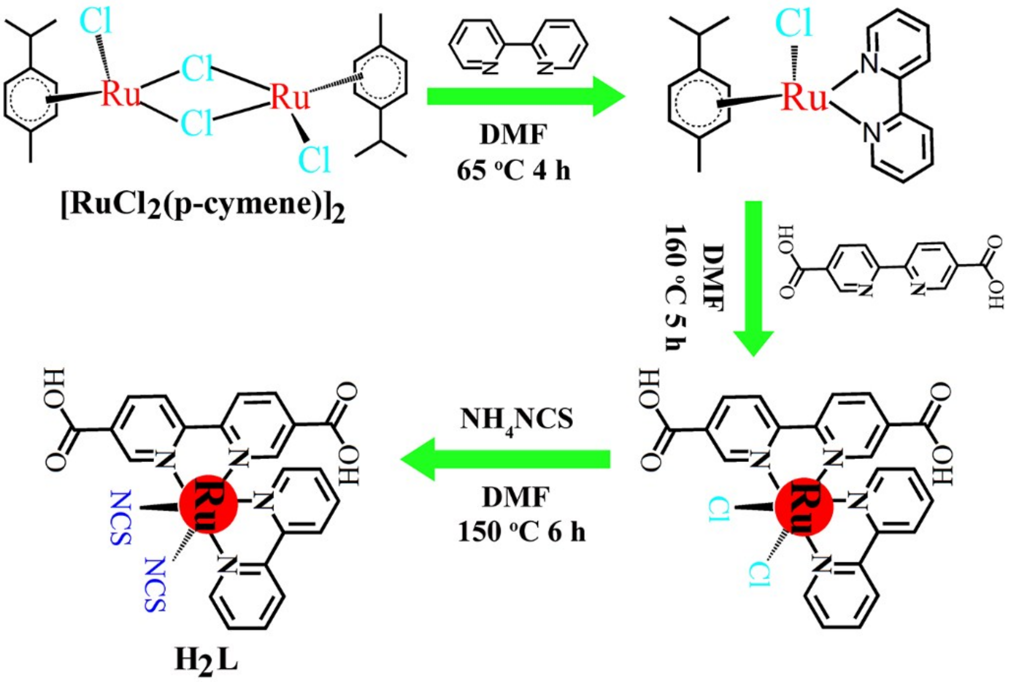
Experiment section

1. Chemicals and materials.

2,2’-bipyridine-5,5’-dicarboxy (H_2bpydc), 2,2'-bipyridine (bpy), [$RuCl_2$(p-cymene)]$_2$ were obtained from TCI (Shanghai) Development Co., Ltd. NH_4NCS, $Hg(NO_3)_2$ (1 mg mL^{-1}, 2%-5% HNO_3), tetrabutylammonium hydroxide (10% in methanol) and HEPES (4-(2-hydroxyethyl)piperazine-1-ethanesulfonic acid) were purchased from J&K Scientific Ltd, China. Other chemicals were obtained from Sinopharm Chemical Reagent Co., Ltd, China. All reagents were of analytical grade and used as received without additional purification. The stock solution of the chromophoric probe was prepared by dispersing 30 mg doped UiO-67 in 100 mL CH_3OH/H_2O (80/20, v/v, 20 mM HEPES, pH 7.4) solutions under ultrasonic condition for 20 min. Then, it was stored in a refrigerator at 5 ^oC under dark condition for further use. The stock solutions of Hg^{2+} (300 μM) were also prepared by dissolving $Hg(NO_3)_2$ in CH_3OH/H_2O (80/20, v/v, 20 mM HEPES, pH 7.4) mixture solutions.

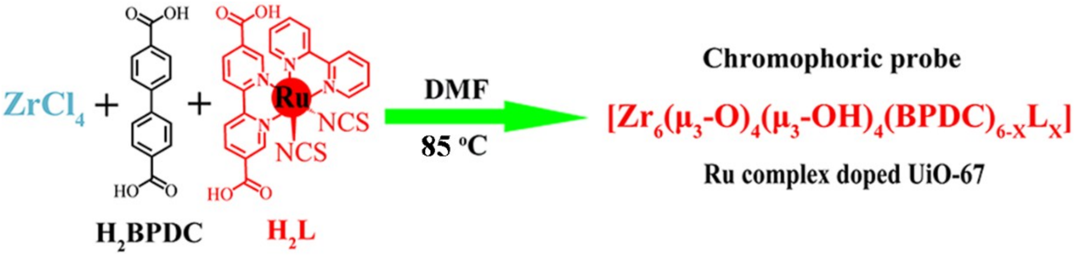
2. Synthesis of Ru(H_2bpydc)(bpy)$(NCS)_2$.

The ligand of Ru(H_2bpydc)(bpy)$(NCS)_2$ was prepared by a well-reported one-pot synthesis strategy with slight modification.[1,2] Specifically, [$RuCl_2$(p-cymene)]$_2$ (0.153 g, 0.25 mmol) was dissolved in DMF (50 mL), and following with bpy (0.078 g, 0.5 mmol) addition into this solution. The reaction mixture was heated to 65 ^oC under nitrogen and kept at this temperature for 4 h with constant stirring. After this period, H_2bpydc (0.122 g, 0.5 mmol) was added to the above solution and refluxed at 160 ^oC for 5 h. Then, excess of NH_4NCS (0.76 g, 10 mmol) was further added to the reaction mixture and continued refluxing for another 6 h at 150 ^oC. The reaction flask was cooled down to room temperature and the filtrate was obtained by filtering the solution through a G4 sintered glass crucible. The solvent was removed by using a rotary-evaporator under vacuum. The resulting solid was washed with water to remove excessive NH_4NCS and the insoluble product was collected on a G4 sintered glass crucible by suction filtration. The dark purple solid was further washed with distilled water and diethyl ether for several times. The crude complex was dissolved in a basic methanolic solution and purified on a Sephadex LH-20 column using methanol as an eluent. After collecting the target band (purple) and evaporating the solvent, the resultant solid was re-dissolved in water. $Ru(H_2bpydc)(bpy)(NCS)_2$ was produced as a precipitate after treating with 0.02 M HNO_3. The final obtained sample was washed with a large amount of water and dried under vacuum.



Scheme S1. Schematic illustration for the synthesis process of $Ru(H_2bpydc)(bpy)(NCS)_2$ ligand.

3. Synthesis of UiO-67 with chromophoric ruthenium complex (RuUiO-67).



Scheme S2. Schematic illustration for the synthesis process of RuUiO-67 MOFs.

46.6 mg (0.20 mmol) of $ZrCl_4$ and 3.45 mL of acetic acid were ultrasonically dissolved in 12.5 mL of DMF for 10 min. Meanwhile, another part of solutions was separately prepared by dissolving (0.01 mmol, 6.13 mg; 0.02 mmol, 12.26 mg; 0.03 mmol, 18.39 mg; 0.04 mmol, 24.52 mg) of Ru(H_2bpydc)(bpy)$(NCS)_2$, (0.19 mmol, 46.02 mg; 0.18 mmol, 43.60 mg; 0.17 mmol, 41.18 mg; 0.16 mmol, 38.76 mg) of H_2bpdc, and 289 μL of triethylamine were dissolved in 12.5 mL of DMF, respectively. The above two solutions were mixed in a vial, then capped and put in an oven at 85 °C for 24 h. The resulting RuUiO-67 was repeatedly washed with DMF for three times. Then, the as-made RuUiO-67 MOFs were immersed in 40 mL DMF at 60 °C for 12 h (2×6 h) to remove the free H_2bpdc and Ru(H_2bpydc)(bpy)$(NCS)_2$. Subsequently, the trapped DMF was replaced with acetone (6×40 mL) at 60 °C for 3d. Finally, the mixtures were centrifuged, and the acetone was removed by decanting. Finally, the volatile acetone was removed at 60 °C for 24 h *in vacuo* to obtain the activated RuUiO-67 MOFs for sensing use. The Ru-complex content in the RuUiO-67 was determined by ICP-OES.

4. Characterization and measurements.

Powder X-ray diffraction (XRD) patterns were carried out on Bruker D8 Advance diffractometer using Cu Kα (λ = 0.15406 nm) radiation (40 kV, 40 mA) from 5º to 50º with a scan speed of 6º $\min^{-1}$. FTIR spectra were determined on a Nicolet 6700 spectroscopy with a resolution of 4 cm^{-1} using the KBr method and UV-vis absorption spectra were recorded on a Shimadzu UV-vis 3100 spectroscopy. Gas sorption analysis was performed on a Tristar surface area and porosity analysis instrument. A liquid nitrogen bath (77 K) and ultra-high purity grade nitrogen were used for the nitrogen sorption experiment. All samples were degassed at 120 ºC for 12 h before measurements. The specific surface areas were determined by the Brunauer-Emmett-Teller (BET) method using adsorption data. The amounts of Ru in the RuUiO-67 were analyzed by an ICP-OES spectroscope (Optima 7000 DV, Perkin Elmer). Hitachi S-4800 (Japan) field emission scanning electron microscope (FESEM) was utilized to characterize the morphologies of the samples.

5. Colorimetric detection of Hg^{2+}.

RuUiO-67 nanoparticles were dispersed in CH_3OH/H_2O (80/20, v/v, 20 mM HEPES, pH 7.4) solutions to prepare the probe suspension (0.3 mg mL^{-1}). Then, various concentrations of Hg^{2+} (0, 7.2, 12, 16.8, and 21.6 μM) ions were added to the RuUiO-67 probe suspension and mixed for 150 s. The UV-vis spectra of current system were recorded with the adsorption wavelength in the range from 350 to 800 nm, and photographic images were taken by a digital camera.

To estimate the kinetics response, 0, 15, and 30 μM of Hg^{2+} were added to 2.5 mL RuUiO-67 (0.3 mg mL^{-1}) suspension, respectively. The absorption intensity of the resultant mixture was recorded at wavelength of 435 nm for different time intervals from 0 to 600 s.

To investigate the effect of possible co-existent cations, the standard solutions containing Cr^{3+}, Cu^{2+}, Zn^{2+}, NH_4^+, Mg^{2+}, Pb^{2+}, Fe^{3+}, Al^{3+} (10 mM) were added to the sensing system. The concentrations of interfering species were set as 360 μM, while the concentration of Hg^{2+} was preset as 90 μM. The final volumes of the prepared batches of solutions were kept at 1.0 mL. After incubation at room temperature for 150 s, the photographic images were simultaneously taken by digital camera for the direct naked eye observation.

6. Spectrophotometric detection limit for Hg^{2+}.

To evaluate the spectrophotometric detection for Hg^{2+}, Then, Hg^{2+} standard solutions were added to the RuUiO-67 suspension. The final Hg^{2+} concentrations were in the range from 0 to 13.2 μM, and the final volumes of the prepared batches of suspension were kept constant at 2.5 mL. After the reaction reached full equilibrium for *ca.* 150 s, the changes in the absorbance of the RuUiO-67 suspension were collected at wavelength of 540 nm versus the concentrations of Hg^{2+}.

7. Reversibility for Hg^{2+} sensing.

The reversible and repetitive transformations between Hg-RuUiO-67 and free MOFs were investigated upon the alternate addition of Hg^{2+} and I^- ions. Specifically, 40 μM KI (2 eqv. to a Hg^{2+} concentration of 20 μM) was added to the probe suspensions for 20 min to regenerate absorption spectra, and then the absorption spectra were measured. The reversibility of color change was directly observed by the naked eye and recorded with a digital camera. The reversible interconversion of Hg-RuUiO-67/RuUiO-67 was repeated for six cycles.

The resulting particles of RuUiO-67 were collected by centrifugation and washed three times with water. Then, XRD and N_2 adsorption techniques were used to determine the change of structural integrity.

References

1. M. K. Nazeeruddin, S. M. Zakeeruddin, J. J. Lagref, P. Liska, P. Comte, C. Barolo, G. Viscardi, K. Schenk and M. Graetzel, *Coord. Chem. Rev.*, 2004, **248**, 1317.
2. E. Hodson and S. J. Simpson, *Polyhedron*, 2004, **23**, 2695.

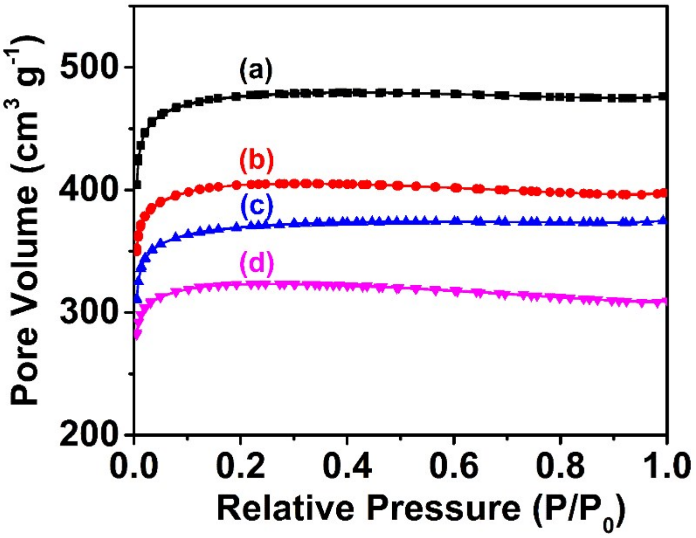


Fig. S1 N_2 adsorption-desorption isotherms of RuUiO-67 MOFs synthesized at different H_2L/H_2bpdc molar ratios of (a) 1:19, (b) 1:9, (c) 1:5.66, and (d) 1:4 in the initial reactants.

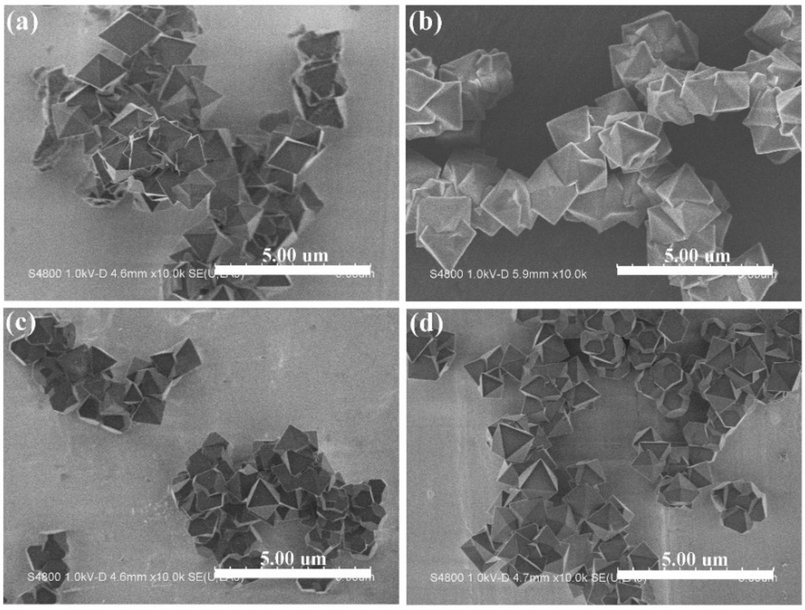


Fig. S2 FESEM images of RuUiO-67 MOFs synthesized at various H_2L/H_2bpdc molar ratios of (a) 1:19, (b) 1:9, (c) 1:5.66, and (d) 1:4 in the initial reactants.

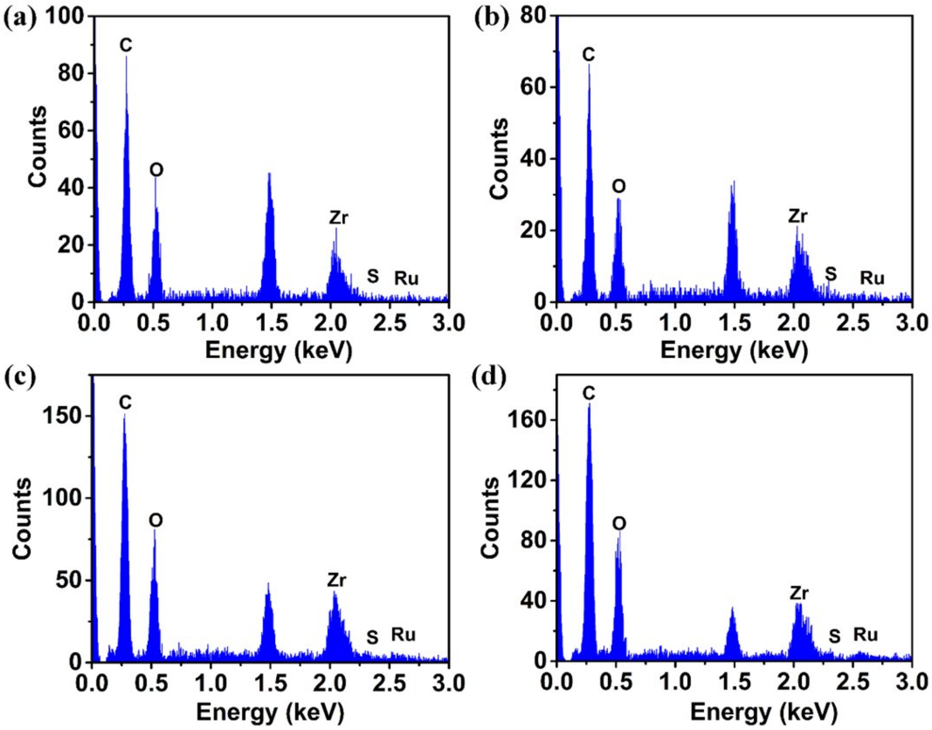


Fig. S3 EDS spectra for (a) RuUiO-67-0.05, (b) RuUiO-67-0.10, (c) RuUiO-67-0.15, and (d) RuUiO-67-0.20.

Table S1. The content of Ru element in RuUiO-67 MOFs calculated by EDS measurements.

Samples	Element	Weight %	Atom %
RuUiO-67-0.05	Ru Kα	0.28	0.05
RuUiO-67-0.10	Ru Kα	0.61	0.11
RuUiO-67-0.15	Ru Kα	0.76	0.14
RuUiO-67-0.20	Ru Kα	0.84	0.18

Table S2. CHN analysis for H_2L, RuUiO-67-0.05, RuUiO-67-0.10, RuUiO-67-0.15, and RuUiO-67-0.20.

Samples	C (wt %)	N (wt %)	H (wt %)
H_2L	50.84	11.25	4.99
RuUiO-67-0.05	45.03	2.25	3.04
RuUiO-67-0.10	45.47	2.98	3.39
RuUiO-67-0.15	40.39	3.66	3.63
RuUiO-67-0.20	43.11	4.06	3.73

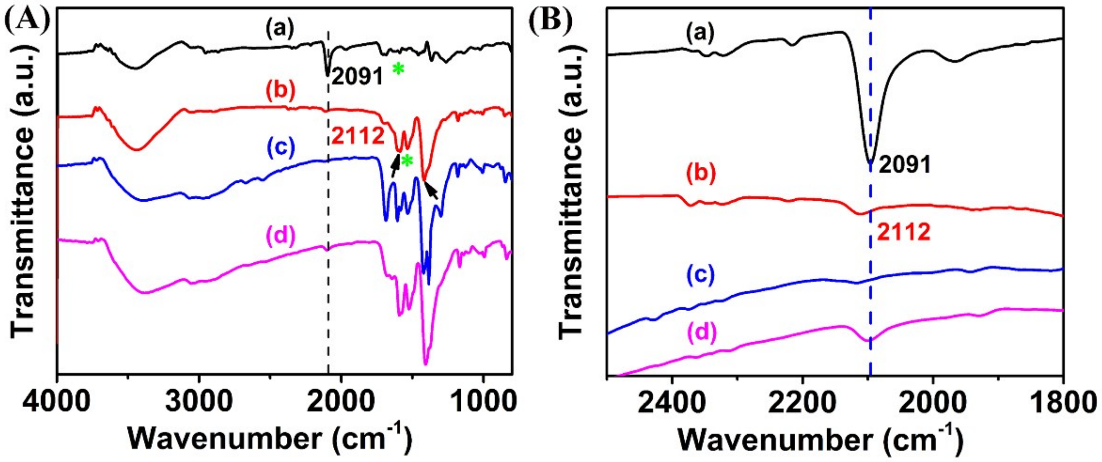


Fig. S4 (A) FT-IR spectra of (a) free Ru(H_2bpydc)(bpy)$(NCS)_2$ ligand, (b) activated RuUiO-67 and (c) RuUiO-67 treated with $Hg(NO_3)_2$. (d) is the spectrum of (c) after its further treated with KI. (B) is the corresponding magnified FT-IR picture.

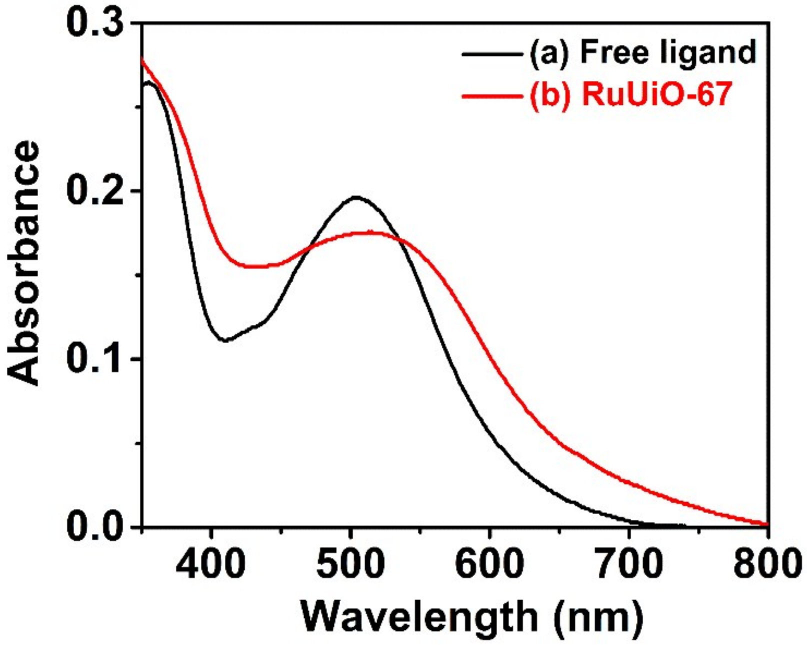


Fig. S5 UV-vis spectra of (a) free H_2L ligand and (b) RuUiO-67 suspension (0.3 mg mL^{-1}) in CH_3OH/H_2O (80/20, v/v, 20 mM HEPES, pH 7.4) solutions.

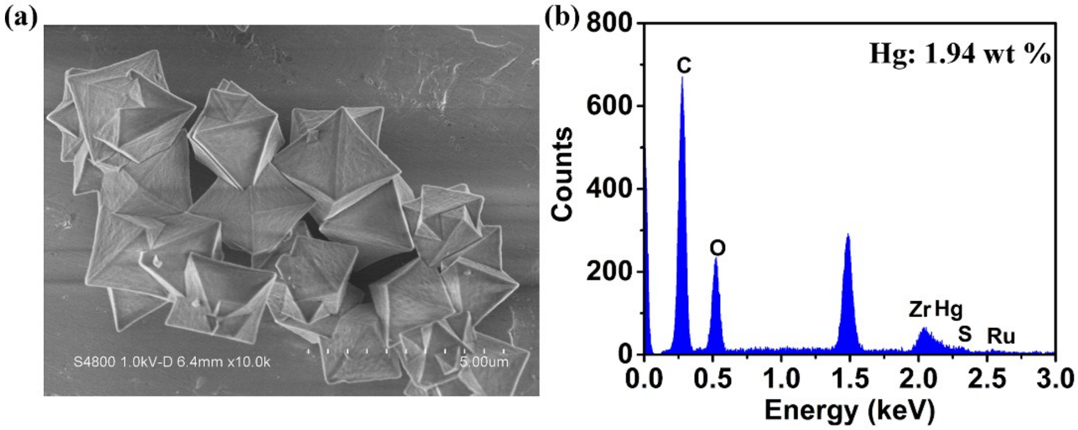


Fig. S6 (a) FESEM image and (b) the corresponding EDS spectrum of Hg-RuUiO-67 MOFs.

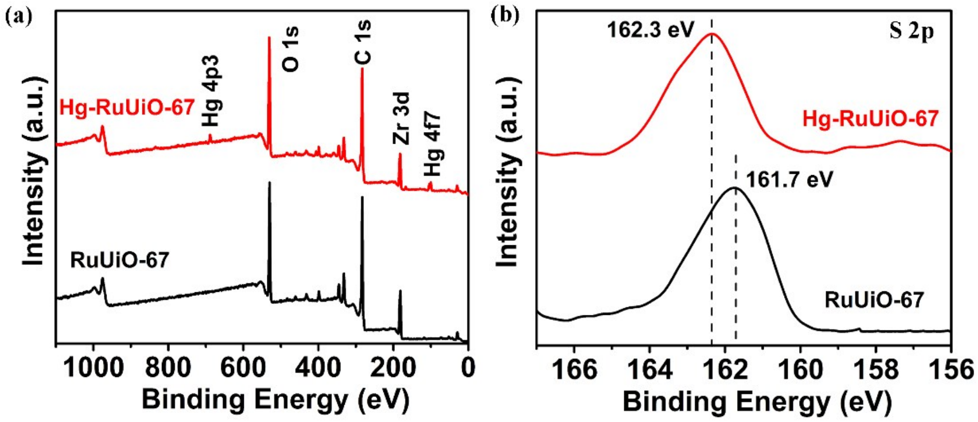


Fig. S7 (a) Wide scan XPS survey spectra for RuUiO-67 (black) and Hg-RuUiO-67 (red), and (b) the corresponding magnified S 2p XPS spectra of RuUiO-67 (black) and Hg-UiO-67 (red).

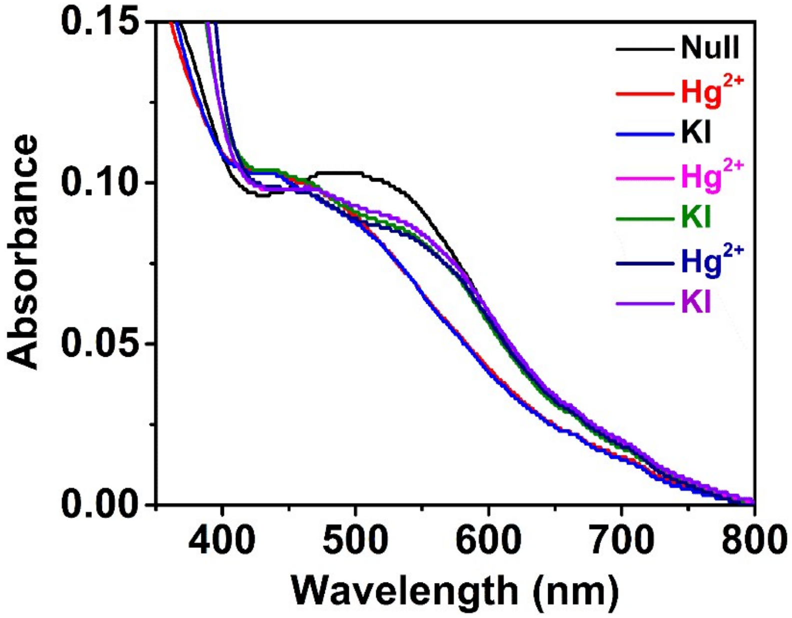


Fig. S8 UV-vis spectra of RuUiO-67 suspension in CH_3OH/H_2O (80/20, V/V, 20 mM HEPES, pH 7.4) upon the alternate addition of Hg^{2+}/KI.

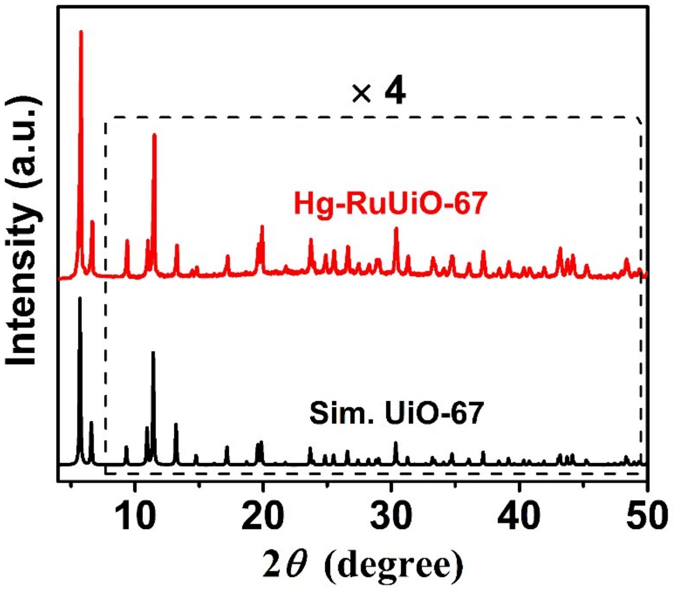


Fig. S9 PXRD patterns of simulated UiO-67 (black) and RuUiO-67 treated with Hg^{2+} (red).

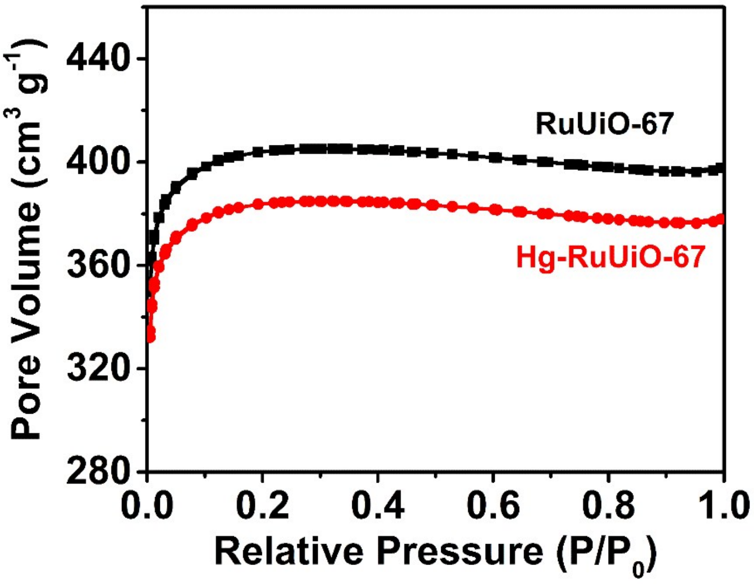


Fig. S10 N_2 adsorption-desorption isotherms of RuUiO-67 MOFs before (black) and after (red) treating with Hg^{2+} (red).

Table S3. Pore structure parameters for RuUiO-67 before and after treating with Hg^{2+}.

Samples	S_{BET} (m^2/g)	V_P (cm^3/ g^{-1})
RuUiO-67	1293	0.62
Hg-RuUiO-67	1181	0.54