Protocol

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Publisher’s note: Undertaking any experimental protocol requires adherence to local institutional guidelines for laboratory safety and ethics.
Protocol

Synthesis of Zr metal–organic frameworks (MOFs) to remove Fe$^{3+}$ from water

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SUMMARY

Although a trace amount of Fe$^{3+}$ is essential for human physiological function, excessive amounts are lethal. Here, we present a protocol for removing Fe$^{3+}$ from water through highly crystalline and stable thiol-functionalized Zr metal-organic frameworks (Zr-MOFs). We provide details of the MOFs synthesis and post-functionalization procedures, and include key performance data of the Zr-MOFs for removing Fe$^{3+}$, which were collected from the inductively coupled plasma-optical emission spectrometer (ICP-OES) and inductively coupled plasma mass spectrometer (ICP-MS).

For complete details on the use and execution of this protocol, please refer to Yuan et al. (2022).

BEFORE YOU BEGIN

Iron is one of the essential nutrients which maintains various human physiological functions. However, an excess amount of Fe$^{3+}$ can induce various biological disorders. Specifically, 20–60 mg L$^{-1}$ Fe$^{3+}$ can damage DNA and cellular components, leading to hemochromatosis, liver cirrhosis, diabetes, and heart disease (Hartmann et al., 2013; Khatri et al., 2017). A concentration of Fe$^{3+} > 200$ mg L$^{-1}$ induces severe Fe$^{3+}$ poisoning, leading to death. Therefore, it is crucial to exploit technology that can purify the Fe$^{3+}$ contaminated water to a drinkable level (< 0.3 mg L$^{-1}$) (WHO World Health Organization, 2003). Compared with water purification methods such as ion exchange, precipitation, electrodialysis, coagulation, and flocculation, adsorption is the most promising feature high removal efficiency, improved recyclability, and cost-effectiveness (Duan et al., 2018; Gabarrón et al., 2016; Nemati et al., 2017; Sun et al., 2018). Therefore, plenty of research interests focus on the synthesis of novel adsorbent. MOFs have the merits of high specific surface area and facile tunable structure, ensuring high removal efficiency for toxic heavy metal ions. Hence, MOFs are prominent for water purification compared with traditional activated carbon and zeolites (Hui et al., 2005; Wang et al., 2009). However, the aqueous stability restricts the application of the MOFs. One solution to improve the stability is synthesizing MOFs from a hard Lewis acid, a hard Lewis base pair, or a soft Lewis acid, and a soft Lewis base pair (Feng et al., 2018; Huang et al., 2020; Yuan et al., 2018a, 2018b). The Zr-based UiO-66 type MOFs have demonstrated high stability in various environments but low water purification efficiency. Therefore, in this protocol, we synthesize UiO-66 type MOFs from the Zr cluster and 2,5-dichloroterephthalic acid (H$_2$BDC-Cl$_2$) under solvothermal conditions and then further post-functionalize with 1,2-Ethanedithiol (EDT) (Scheme 1) to introduce the thiol chelation groups to boost the Fe$^{3+}$ removal efficiency. Further knowledge of solvothermal synthesis and post-functionalization procedures can be found in the literature (Yuan et al., 2022).
Preparation of stock solution

Timing: 30 min

1. Slowly add 113.44 mL 65% HNO₃ to 2000 mL of deionized water under vigorous stirring to obtain 5% HNO₃.

\[ \text{CRITICAL: Nitric acid is a corrosive chemical; thus, it should be handled in the fume hood. Also, the nitric acid solution should be stored in a glass container, tightly closed and well-ventilated at room temperature.} \]

2. Weight 101 mg lead (II) nitrate, 163.1 mg iron (III) nitrate nonahydrate, 133.1 mg cadmium nitrate tetrahydrate, 174.5 mg magnesium nitrate hexahydrate, 126.5 mg copper (II) nitrate hemihydrate, and 160.2 mg zinc nitrate hexahydrate to 100 mL 5% HNO₃ separately to obtain 1000 ppm Pb²⁺, Fe³⁺, Cd²⁺, Mg²⁺, Cu²⁺, Zn²⁺ stock solution.

3. Add 1 mL 1000 ppm Pb²⁺, Fe³⁺, Cd²⁺, Mg²⁺, Cu²⁺, Zn²⁺ As (V) (AsO₄³⁻), Cd²⁺, and Cr (VI) (Cr₂O₇²⁻) stock solution to 99 mL 5% HNO₃ separately to obtain 10 ppm Pb²⁺, Fe³⁺, Cd²⁺, Mg²⁺, Cu²⁺, Zn²⁺ As (V) (AsO₄³⁻), Cd²⁺, and Cr (VI) (Cr₂O₇²⁻) stock solution. The stock solution should be stored in a glass container, tightly closed, and well ventilated at room temperature.

KEY RESOURCES TABLE

| REAGENT or RESOURCE | SOURCE | IDENTIFIER |
|---------------------|--------|------------|
| Chemicals, peptides, and recombinant proteins | Sigma-Aldrich | CAS: 13520-92-8 |
| Zirconyl chloride octahydrate (98%) | Sigma-Aldrich | CAS: 13520-92-8 |
| 2,5-dichloroterephthalic acid (H₂DCTP, 98%) | Energy Chemical | CAS: 13799-90-1 |

(Continued on next page)
**Continued**

### REAGENT or RESOURCE | SOURCE | IDENTIFIER
--- | --- | ---
1,2-Ethanedithiol (EDT, ≥98%) | Sigma-Aldrich | CAS: 540-63-6
Potassium carbonate (≥99.0%) | Sigma-Aldrich | CAS: 584-08-7
Lead (II) nitrate (≥99.0%) | Sigma-Aldrich | CAS: 10099-74-8
Iron (III) nitrate nonahydrate (≥98%) | Sigma-Aldrich | CAS: 7782-61-8
Cadmium nitrate tetrahydrate (99%) | Sigma-Aldrich | CAS: 10022-68-1
Magnesium nitrate hexahydrate (99%) | Sigma-Aldrich | CAS: 13446-18-9
Copper (II) nitrate hemi(pentahydrate) (98%) | Sigma-Aldrich | CAS: 19004-19-4
Zinc nitrate hexahydrate (98%) | Sigma-Aldrich | CAS: 10196-18-6
Potassium iodide (≥99.0%) | Sigma-Aldrich | CAS: 7681-11-0
1000 ppm chromium stock solution | High-Purity Standards Inc. | SKU: 100012-1
1000 ppm arsenic stock solution | High-Purity Standards Inc. | SKU: 10003-1
Acetone (min. 99.5%) | RCI Labscan | CAS: 67-64-1
**Other**
Screw-capped glass jar | Synthware Co., Ltd | N/A
Sonicator | Branson Co., Ltd | N/A
Oven | Shanghai Yiheng Co., Ltd (Shanghai, China) | N/A
Stir plate | Heidolph Co., Ltd | P/N: 505-30000-00
Centrifuge | Centurion Scientific Co., Ltd | K3
Hot plate | Heidolph Co., Ltd | P/N: 505-30000-00
Schlenk line | Synthware Co., Ltd | N/A
Inductively coupled plasma mass spectrometer (ICP-MS) | Agilent Co., Ltd | 7800
Thermo gravimetric analyzer | PerkinElmer Co., Ltd | UNIX/7GA7
Inductively coupled plasma–optical emission spectrometer (ICP-OES) | PerkinElmer Co., Ltd | 7300DV
Fourier-transform infrared spectrometer (FTIR) | Thermo Fisher Scientific Co., Ltd | Nicolet IS50
JSM-7100F field emission scanning electron microscope | JEOL (Europe) BV Co., Ltd | JSM-7100F
Analytical x-ray diffractometer | Malvern Panalytical Co., Ltd | X’pert Pro
JSX-3201Z (JEOL) X-ray fluorescence spectrometer | JEOL Co., Ltd | JSX-3201Z
400 MHz Bruker NMR spectrometer | Bruker | N/A
Gas chromatography-mass spectrometer | Thermo Fisher Scientific Co., Ltd | N/A
Surface area and pore size distribution analyzer | Microtrac Co., Ltd | BELSORP MINI X

> **CRITICAL:** 1,2-Ethanedithiol has a strong and unpleasant odor; handle it inside the fume hood.

**Alternatives:** We use the screw-capped glass jar for MOFs synthesis in this protocol. However, alternative tools such as autoclaves can also be used.

**Optional:** The resources listed above were only based on our experience. The chemicals and resources obtained from reliable commercial sources are feasible.

### STEP-BY-STEP METHOD DETAILS

#### MOFs synthesis

**Timing:** 48 h

The initial step for the synthesis of UiO-66-S is the UiO-66-Cl synthesis. We synthesize UiO-66-Cl via a solvothermal method; the details are listed below (**Figure 1**).
1. Weigh 13.2 mg (0.041 mmol) Zirconyl chloride octahydrate and 9.6 mg (0.041 mmol) 2,5-dichloroterephthalic acid to a screw-capped glass jar.
2. Add 4.1 mL DMF and 0.82 mL formic acid to the jar.
3. Sonicate the mixture for 30 min until the solid is fully dissolved.
4. Put the jar in the oven and heat at 120°C for 48 h.
5. After cooling down to room temperature, collect the white-colored octahedral crystal, UiO-66-Cl, by centrifugation (Yield: 84%, based on Zr).

**Activation of MOFs**

**Timing:** 6 days

After the MOFs synthesis, remove the unreacted starting materials. In addition, replace the high boiling point solvent, DMF, inside the pore of MOFs with a low boiling point solvent that can be easily removed.

6. Immerse the as-synthesized UiO-66-Cl in 10 mL DMF and stir for three days, during which replace the DMF three times per day by centrifugation.
7. Immerse the as-synthesized UiO-66-Cl in 10 mL of anhydrous acetone and stir for three days, during which replace the anhydrous acetone three times per day by centrifugation.
8. Then dry the sample under vacuum at 100°C overnight to obtain the activated UiO-66-Cl.

**Post-functionalization of UiO-66-Cl to UiO-66-S**

**Timing:** 48 h

Use deprotonation reaction to post-functionalize the UiO-66-Cl to UiO-66-S, in which nucleophilic 1,2-Ethanedithiol easily replaces the chlorides.

9. Add 1.175 g UiO-66-Cl, 1.68 mL 1,2-Ethanedithiol, 2.764 g K₂CO₃, and 58.1 mg potassium iodide (KI) to a 50 mL reaction vial.
10. Change to the atmosphere in the reaction vial to nitrogen by Schlenk line.
11. Add 20 mL DMF to the reaction vial under a nitrogen atmosphere.
12. Heat the mixture to 85°C and keep at different times (24 h, 48 h, 72 h, 96 h, and 120 h).
13. After cooling down to room temperature, collect the product by centrifugation.
14. Wash the product with 20 mL H₂O six times.
15. Immerse the as-synthesized UiO-66-S in 10 mL DMF and stir for three days, during which replace the DMF three times per day by centrifugation.
16. Immerse the as-synthesized UiO-66-S in 10 mL of anhydrous acetone and stir for three days, during which replace the anhydrous acetone three times per day by centrifugation.
17. Then dry the sample under vacuum at 100 °C overnight to obtain the activated UiO-66-S.

Characterizations of MOFs

- Timing: 24 h

After the synthesis of UiO-66-Cl and UiO-66-S, use scanning electron microscopy (SEM), powder X-ray diffraction (PXRD), surface area, thermogravimetric analysis (TGA), and Fourier-transform infrared spectroscopy (FTIR) characterizations to characterize the synthesized MOFs (Figure 2). (Area et al., 1996; Mohammadinezhad and Akhlaghinia, 2019; Yuan et al., 2022).

Stability of MOFs

- Timing: 35 days

Immerse the UiO-66-S and UiO-66-Cl in water (pH = 6.8), 0.1 mol L⁻¹ HCl, and 0.01 mol L⁻¹ NaOH aqueous solutions at room temperature for different times to investigate the stability of the MOFs (Figure 3), which demonstrate their high chemical stability (Yuan et al., 2022).

Optimization of post-functionalization

- Timing: 120 h

Optimize the sulfur content in the UiO-66-S by changing the reaction time of the post-functionalization. The crystallinity is maintained during the post-functionalization process (Figure 4) (Yuan et al., 2022).

Post-functionalization – digested NMR

- Timing: 2 h

Analyze the sulfur content in the UiO-66-S by the Nuclear Magnetic Resonance (NMR) spectrum of digested UiO-66-S (Figure 5). Comparing with the ¹H NMR spectrum of digested UiO-66-Cl, UiO-66-S shows three new peaks at δ 0.98–1.02 ppm, 3.4–3.44 ppm, and 7.09 ppm. After post-functionalization, dithiol replaces part of the Cl, resulting in the upshift of aromatic proton resonance, making a new resonance peak at 7.09 ppm. The peaks at 0.98–1.02 ppm correspond to the proton of methyl in CH₃CH₂SH, and the peaks at 3.40–3.44 ppm are the proton of -CH₂CH₂- and methylene of CH₂CH₂SH. The conversion efficiency of post-functionalization is about 43.67%. The gas chromatography-mass spectrometry results show that CH₃CH₂SH exists in the digested UiO-66-S, which results from the cleaved C-S bond (Yuan et al., 2022).

18. Add 30.64 mg NH₄F to the mixture of 0.4 mL DMSO-d₆ and 0.2 mL D₂O to obtain the deuterated stock solution.
19. Add 10 mg UiO-66-S to the deuterated stock solution and sonicate until fully dissolved.
20. Measure the NMR spectrum by the Bruker 400 MHz NMR.
21. After the NMR measurement, remove the solvent of the mixture, add the chloroform to the residual, and then filtration. The gas chromatography-mass spectrometry was conducted for the filtrate.

**Ion adsorption – Uptake tests**

- **Timing:** 24 h

Use the stock solution with different concentrations (100 ppm, 200 ppm, 400 ppm, 500 ppm, 600 ppm, 800 ppm, 1000 ppm) to determine the adsorption capacity of the synthesized MOFs; details are listed below.

22. Add 10 mL Fe³⁺ stock solution with different concentrations (100 ppm, 200 ppm, 400 ppm, 500 ppm, 600 ppm, 800 ppm, 1000 ppm) to 7 batches of 20 mL glass vial.

23. Add 10 mg of as-synthesized MOFs (UiO-66-Cl or UiO-66-S) to every stock solution vial.

24. Stir the mixture for 24 h.

25. Filter the solution through a syringe filter and use the inductively coupled plasma-optical emission spectroscopy (ICP-OES) to measure the Fe³⁺ concentration in the filtrate.

26. Before running the ICP-OES test, prepare three standard stock solutions, 5% HNO₃, 500 ppm, and 1000 ppm Fe³⁺ stock solution, for calibration.

27. If the correlation coefficients (R²) values of the calibration curve are larger than 0.9999, measure the Fe³⁺ concentration of the filtrate by ICP-OES (Figure 6A).
Ion adsorption – Kinetic tests

© Timing: 24 h

In this protocol, we show the synthesized MOFs for heavy metal ion removal and investigate their adsorption performance, including uptake, kinetics, selectivity, and recyclability. We use the same amount of MOFs to remove the metal ions at different times to investigate the adsorption kinetics. Details are listed below.

28. Add 10 ppm Fe³⁺ stock solution to 10 batches of 20 mL glass vial, 10 mL for each vial.
29. Add 10 mg of as-synthesized MOFs (UiO-66-Cl or UiO-66-S) to every stock solution vial.
30. Stir the mixture for 20 min, 40 min, 60 min, 90 min, 2 h, 2.5 h, 3 h, 4 h, 6 h, and 8 h, respectively.
31. Filter the solution through a syringe filter and use the ICP-MS to measure the Fe³⁺ concentration in the filtrate (see Figure 7 for Fe³⁺ adsorption kinetics measurements of UiO-66-S, Methods Video S1 for UiO-66-S removing 500 ppm Fe³⁺ stock solution from 0 to 240 min, related to step 30).
32. Before running the ICP-MS test, prepare the standard stock solution, 5% HNO₃, 2.5 ppm, 5 ppm, 7.5 ppm, and 10 ppm Fe³⁺ stock solution, for calibration.
33. If the R² values of the calibration curve are larger than 0.9999, measure the Fe³⁺ concentration of the filtrate by ICP-MS (Figure 6B).

Ion adsorption – Selectivity tests

© Timing: 24 h

We use the stock solution containing multiple metal ions to test the MOF’s selectivity toward the ions.

34. Add 10 mg of as-synthesized MOFs (UiO-66-Cl or UiO-66-S) to a 20 mL glass vial.
35. Add 10 mL aqueous mixed solution (1.25 mL each 1000 ppm Fe³⁺, As (V) (AsO₄³⁻), Cd²⁺, Cr (VI) (Cr₂O₇²⁻), Pb²⁺, Mg²⁺, Cu²⁺, Zn²⁺ stock solution) to the vial.
36. Stir the mixture for 24 h.
37. Filter the solution through a syringe filter and use the ICP-OES to measure the ion concentration in the filtrate.

Figure 4. Optimization of UiO-66-S MOFs
(A) The sulfur content of UiO-66-S under different post-functionalization times was measured by X-ray fluorescence (XRF).
(B) PXRD pattern of the UiO-66-S with different post-functionalization times. Reproduced with permission (Yuan et al., 2022); Copyright, 2022 Elsevier Inc.
Figure 5. Digested NMR

(A) $^1$H NMR spectra of the digested UiO-66-S.

(B) Stacked $^1$H NMR spectra of the digested UiO-66-S, digested UiO-66-Cl, and 1,2-Ethanedithiol.

(C) Gas chromatography-mass spectrometry (GC-MS) of digested UiO-66-S.

(D) Proposed UiO-66-S digested in 0.4 mL DMSO and 0.2 mL NH$_4$F in H$_2$O stock solution (4.14 M). Reproduced with permission (Yuan et al., 2022); Copyright, 2022 Elsevier Inc.
38. Before running the ICP-OES test, prepare three standard stock solutions, 5% HNO₃, 60 ppm, 125 ppm mix ion stock solution (Fe³⁺, As (V) (AsO₄³⁻), Cd²⁺, Cr (VI) (Cr₂O₇²⁻), Pb²⁺, Mg²⁺, Cu²⁺, Zn²⁺) for calibration.

39. If the R² values of all the calibration curves are larger than 0.9999, measure the Fe³⁺ concentration of the filtrate by ICP-OES (Figure 6C).

**Ion adsorption – Recyclability tests**

© Timing: 198 h

After ion adsorption, we collect the MOFs powder to desorb the ion, which is used for another round of ion adsorption—repeating the adsorption/desorption cycles to analyze the recyclability of the MOFs.

40. Add 10 mg as-synthesized UiO-66-S to a 20 mL glass vial.
41. Mix 10 mL Fe³⁺ stock solution (10 ppm) with the MOFs.
42. Stir the mixture for 24 h.
43. Collect the filtrate by centrifuge, and measure the Fe³⁺ concentration by the ICP-MS.
44. Immerse the residual UiO-66-S in 10 mL citric acid (10 mM) for 9 h to desorption.
45. Wash the residual UiO-66-S with distilled water and anhydrous acetone and dry it in a vacuum oven overnight.
46. Use the regenerated UiO-66-S to measure the recyclability by repeating the adsorption/desorption process.
47. Before running the ICP-MS test, prepare the standard stock solution, 5% HNO₃, 2.5 ppm, 5 ppm, 7.5 ppm, and 10 ppm Fe³⁺ stock solution for calibration.

48. If the R² value of the calibration curve is larger than 0.9999, measure the Fe³⁺ concentration of the filtrate by ICP-MS (Figure 6D).

**Adsorption process analysis**

**Timing:** 24 h

49. Calculate the adsorption amount of Fe³⁺ using Equation 1,

\[
q_e = \frac{(C_0 - C_e) V}{m} \quad \text{(Equation 1)}
\]

where \(q_e\) (in mg g⁻¹) is the amount of Fe³⁺ adsorption at equilibrium, \(C_0\) (in mg L⁻¹) is the initial concentration of the used stock solution, and \(C_e\) (in mg L⁻¹) is the measured concentration of the filtrate by the ICP-OES or ICP-MS. \(V\) (in L) is the volume of the solution used for measurement, and \(m\) (in mg) is the corresponding weight of the MOFs.

50. Use the Langmuir isotherm model and Freundlich isotherm model to analyze the adsorption process according to Equations 2 and 3. Treating the data collected from the uptake tests by the below two equations (Yao et al., 2022).

\[
\frac{C_e}{q_e} = \frac{C_0}{q_{\text{max}}} + \frac{1}{q_{\text{max}}b} \quad \text{(Equation 2)}
\]

\[
\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad \text{(Equation 3)}
\]

where \(q_{\text{max}}\) is the maximum adsorption capacity. \(b\) and \(K_f\) are Langmuir constant and Freundlich constant, respectively. \(n\) is dimensionless exponent of Freundlich equation. Setting \(C_e\) as x-axis, \(C_0/q_e\) as y-axis.
as y-axis, using excel to linear fit the data collected from the uptake tests. According to Equation 2, the slope and intercept of the fitted curve correspond to the $1/q_{\text{max}}$ and $1/(q_{\text{max}}b)$, respectively. Then the maximum adsorption capacity was obtained.

51. Set $\ln(C_a)$ as an x-axis, $\ln(q_a)$ as a y-axis, using excel to linear fit the data collected from the uptake tests. According to Equation 3, the slope and intercept of the fitted curve correspond to the $1/n$ and $\ln(K_f)$, respectively.

52. Compare the $R^2$ values obtained from the fitted results of Equations 2 and 3. The Langmuir model describes the adsorption process of Fe$^{3+}$ better (Figures 8A and 8B), indicating that the Fe$^{3+}$ is adsorbed on the monolayer surface of MOFs and the adsorption process is uniform chemical adsorption.

53. Use the pseudo-first-order kinetic model and pseudo-second-order kinetic model to analyze the adsorption kinetics according to Equations 4 and 5, respectively.

\[
\log(q_a - q_t) = \log(q_a) - \frac{k_1}{2.303}t
\]  

(Equation 4)

\[
\frac{t}{q_t} = \frac{1}{k_2q_e^*} + \frac{t}{q_a}
\]  

(Equation 5)

where $q_t$ and $q_a$ (in mg g$^{-1}$) are the amounts of Fe$^{3+}$ adsorbed at time $t$ and at equilibrium, respectively. $k_1$ (in min$^{-1}$) and $k_2$ (in g mg$^{-1}$ h$^{-1}$) are the rate constant of pseudo-first-order and pseudo-second-order kinetic model.
pseudo-second-order adsorption, respectively. Setting t as x-axis, \( \log(q_e-q_t) \) as y-axis, using excel to linear fit the data collected from the kinetics tests. According to Equation 4, the slope and intercept of the fitted curve correspond to the \(-k_1/2.303 \) and \( \log(q_e) \), respectively. Then the rate constant \( k_1 \) was obtained.

54. Set \( t \) as an x-axis, \( t/q_t \) as a y-axis, using excel to linear fit the data collected from the kinetics tests. According to the Equation 5, the slope and intercept of the fitted curve correspond to the \( 1/q_e \) and \( 1/(k_2 q_e^2) \), respectively. Then the rate constant \( k_2 \) was obtained.

55. Compare the \( R^2 \) values obtained from the fitted results of Equations 4 and 5. The Fe\(^{3+}\) adsorption matches well with the pseudo-second-order reaction model, which indicates the rate-limiting factor in the Fe\(^{3+}\) adsorption process depends on chemisorption. The rate constant \( k \) for UiO-66-S and UiO-66-Cl was calculated to be 1.07 and 0.124 g mg\(^{-1}\) h\(^{-1}\), respectively (Figures 8C and 8D).

**EXPECTED OUTCOMES**

This protocol provides the procedure for MOFs synthesis and post-functionalization. The synthesized MOFs show high crystallinity and stability, which are stable in water (pH = 6.8) at room temperature for 35 days, demonstrating their feasibility for water purification application. The synthesized MOFs show Brunauer–Emmett–Teller (BET) surface area of 446 and 275 m\(^2\) g\(^{-1}\) for UiO-66-Cl and UiO-66-S, respectively. Under practical operating temperatures, i.e., < 200°C, UiO-66-S shows improved thermal stability. In addition, the synthesized MOFs have been stable for more than a week under acidic conditions (0.1 mol L\(^{-1}\) HCl). Optimizing the reaction condition of post-functionalization, the maximum 52.13% of Cl was replaced by 1,2-Ethanedithiol after 48 h of reaction time, which shows the highest adsorption capacity.

UiO-66-S can remove Fe\(^{3+}\) with the highest adsorption capacity (481 mg g\(^{-1}\)) and fastest kinetics (1.07 g mg\(^{-1}\) h\(^{-1}\)) for water purification application. In addition, the UiO-66-S shows high selectivity toward Fe\(^{3+}\). The removal efficiency of UiO-66-S remained at over 89% after six cycles demonstrating its high recyclability.

**LIMITATIONS**

Various conditions, including acidic, basic, and neutral, are common for the practical application of water purification. The synthesized MOFs in this protocol are stable in acidic and neutral conditions. However, it can only be stable in the basic condition (0.01 mol L\(^{-1}\) NaOH) for two days. Therefore, the synthesized MOFs are limited to extremely basic conditions. The reason is the coordination of the hydroxides with Zr\(^{4+}\). This limitation can be improved by hydrophobic surface treatment, insertion of stabilizing pillars, and composite construction. See the reference for more detailed information (Ding et al., 2019).

**TROUBLESHOOTING**

**Problem 1**
The synthesized MOFs show low crystallinity (steps 1–4 in “MOFs synthesis”).

**Potential solution**
Add modulators to the reaction solution, such as formic acid, acetic acid, and trifluoroacetic acid. The modulator could coordinate with the metal cluster and slow down the reaction leading to improved crystallinity.

**Problem 2**
The stock solution is used in the adsorption process (step 18 in “ion adsorption – uptake tests”).
Potential solution
Iron can be easily precipitated by a hydrolytic mechanism. Therefore, the matrix used to prepare the stock solution must be acidic to ensure the existing iron is in an ion state. The potential solution for the stock solution preparation should be 5% HNO₃, which is clarified in the “before you begin” section.

Problem 3
The results obtained from ICP-MS were not good enough (step 31 in “ion adsorption – kinetic tests”).

Potential solution
Prepare the stock solution more accurately. The 10 ppm stock solution should be diluted from the 1000 ppm stock solution. In addition, the R² values of the calibration curve should be larger than 0.9999, and then conduct the ICP-MS measurement.

Problem 4
Incomplete removal of unreacted starting material and DMF molecules (steps 6–8 in “activation of MOFs”).

Potential solution
Replace the DMF and acetone in steps 6–8 more frequently. Alternatively, wash the MOFs by Soxhlet extraction with methanol and acetone as a solution, each solution for three days.

Problem 5
Low conversion efficiency of the post-functionalization (steps 9–17 in “post-functionalization of UiO-66-Cl to UiO-66-S”).

Potential solution
Use anhydrous DMF as a solvent and set up the reaction under the inert gas atmosphere. The 1,2-Ethanedithiol (EDT) is air-sensitive and should be stored under inert gas.

RESOURCE AVAILABILITY
Lead contact
Further information and requests for resources and reagents should be directed to and will be fulfilled by the lead contact, Yoonseob Kim (yoonseobkim@ust.hk).

Materials availability
This study did not generate any new unique reagents.

Data and code availability
Data and code would be made available upon request.

SUPPLEMENTAL INFORMATION
Supplemental information can be found online at https://doi.org/10.1016/j.xpro.2022.101477.

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AUTHOR CONTRIBUTIONS
Y.K. conceived and supervised the project. Y.Y. designed and performed all the experiments and data analysis.
DECLARATION OF INTERESTS

The authors declare no competing interests.

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