Encapsulation of toxic liquid molecules and adsorption of water pollutants by a versatile pre-organized single crystalline coating material

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Materials and methods

1. Materials.

3,4-Dimethoxybenzyl alcohol (**G1**), 1,3-dimethoxybenzene (**G2**), 4-pyridinecarboxaldehyde (**G3**), cyclohexylbenzene (**G4**), eugenol (**G5**), 2-pyridinecarboxaldehyde (**G6**), benzyl alcohol (**G**7), 4-acetylpyridine (**G8**), 2,6-dimethylaniline (**G9**), methyl anthranilate (**G10**), 3-acetylpyridine (**G11**), 3-(aminomethyl)pyridine (**G12**) were purchased from Bide pharmaceutical Ltd (Shanghai, China). The unknown liquid (**Gx**) was stored in the lab of Pharmacy college, Jinan University.

2. Synthesis of ZrFMOF.

Synthesis of ZrFMOF was divided into three step: i) synthesis of tetraethyl 4,4',4'',4'''-(9,9'-spirobi[fluorene]-2,2',7,7'-tetrayl)tetrabenzoate (intermediate, **T2**); ii) synthesis of 4,4',4'',4'''-(9,9'-spirobi[fluorene]-2,2',7,7'-tetrayl)tetrabenzoic acid (ligand, **L**) and iii) synthesis of ZrMOF by solvothermal reaction of the ligand with $ZrOCl_2 \bullet 8H_2O$ in DEF / formic acid (3/1, v/v).

2a. Stability of PSCC.

3. Absorption of iodine.

We prepared a 0.3 mg/mL iodine in hexane. Then, ZrFMOF (3 mg) was added to iodine solution (4 mL), 0, 15, 60, 180 and 1080 min later, UV-Visible spectrophotometer was used to monitor the spectral changes. At 0, 180 and 1080 min, the photos showing color changes were taken.

4. Stability of ZrFMOF

For the air stability test, ZrFMOF was directly exposed to air on a coverslip.

For the solvent stability test, ZrFMOF (1.8 mg) was added in the solvents (0.5 mL). The system was sealed and kept static. 72 hours later, the solvents were removed by pipette. The final ZrFMOF was weighted and the solvent volume was measured. We found that the weight and solvent volume were unchanged.

5. Powder X-ray diffraction (PXRD).

PXRD of ZrFMOF in different solvents were performed on a Rigaku X-ray diffractometer miniflex600 with CuKα radiation (40kV, 15mA), scanning range 3°-50° and speed 5°/min.

6. Guest encapsulation.

Guest encapsulation was performed by a direct soaking procedure. Typically, for the preparation of ZrFMOF⊃G**1** (3,4-dimethoxybenzyl alcohol), the freshly prepared single crystals of ZrFMOF (2 mg) were soaked in 3,4-dimethoxybenzyl alcohol (200 μL) in a 2 mL vial. The vial was kept in 25 °C for 3 days. After soaking, one of the single crystals was selected for SCD analysis. For other guest encapsulation experiments (pure or mixture), see SI for details.

7. Single crystal X-ray diffraction.

All single-crystal X-ray measurements were performed on a Rigaku XtaLAB Pro diffractometer using CuKα (λ= 1.54056 Å) radiation. The diffraction data were collected in the ω-scanning mode (resolution 0.80-0.85Å). All crystal structures were solved by direct methods (SHELXTL-2014) and refined by full-matrix least-squares on F^2 using the Olex2 (version 1.5) software package. Due to high pore volumes, the solvent (diethylformamide) was extremely disordered, and could not be located for refinement. Thus, the residual electrons were squeezed by using the "solvent mask" function of Olex2 software. The numbers of masked solvent molecules were calculated based on the masked electrons. For these host-guest complexes, disorders were also found in the guest molecules, and thus proper restrains or constrains were applied.

8. Solution and solid-state NMR.

Both solution and solid-state NMR spectra were recorded on a Bruker Avance-400 NMR spectrometer. For the solution NMR of ZrFMOF complex, 10% D_2SO_4 was added to DMSO-d_6 to destroy the coordination of metal with ligand, and thus the sample could be totally dissolved.

9. Determination of unknown solution.

The freshly prepared single crystals of ZrFMOF (2 mg) were soaked in **Gx** (200 μL) in a 2 ml vial. After the soaking, one of the single crystals was used for SCD analysis. An aliquot (10 μL) of the unknown solution was added to $CDCl_3$, and ^{1}H-NMR spectrum was taken.

10. Thermogravimetric analysis (TGA).

To test the thermos-stability, TGA was performed on a Thermogravimetric Analyzer (TGA2, Mettler-Toledo). The temperature range was set at 50-800 °C with a speed of 10 °C/min.

11. Infrared spectroscopy.

Infrared spectroscopy (IR) was measured on a Shimadzu IRSpirit FTIR spectrophotometer. IR spectra (500-4000 cm^{-1}) were used to monitor the presence and disappearance of G**11** signal for the reusability study.

12. Adsorption on dyes in water.

Solutions of rhodamine B, congo red, methyl violet and methylene blue in water (0.3 mg/mL) were prepared. ZrFMOF (1 or 3 mg) was added to the solution. Photos were taken to indicate the color changes, and UV spectra were measured to monitor the absorbance changes of the solutions. The carbonyl bond signal in IR was used to indicate the adsorption of rhodamine B.

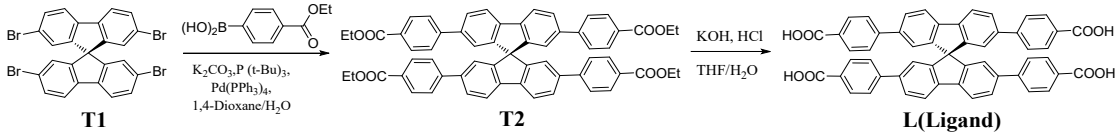
13. Adsorption of polyfluoroalkyl substances (PFAS).

Typical PFAS, i.e. PFOS and PFOA were dissolved in water, then ZrFMOF was added to the solution. After adsorption, the IR spectra for PFOS, ZrFMOF and ZrFMOF@PFOS, the solution ^{19}F-NMR spectrum for ZrFMOF@PFOS, and the in situ solid state ^{19}F-NMR spectrum for ZrFMOF@PFOA were measured.

14. Confocal laser scanning image.

The image was taken on a Zeiss LSM800 microscope with the excitation wavelength 481 nm and mission wavelength 565nm.

SI-1 Syntheses of intermediate, ligand and ZrFMOF



Scheme 1. synthesis of intermediate and ligand

(1) Synthesis of tetraethyl 4,4',4'',4'''-(9,9'-spirobi[fluorene]-2,2',7,7'-tetrayl)tetrabenzoate (**T2**)

2,2',7,7'-tetrabromo-9,9'-spirobi[fluorene] (**T1**) (1.5 g, 2.37 mmol), 4-(ethoxycarbonyl)phenylboronic acid (4.6 g, 23.74 mmol), and potassium carbonate (3.28 g, 23.74 mmol), P(*t*-Bu)$_3$ and were dissolved in 1,4-dioxane/distilled water (120 mL/20 mL). The resulting mixture was purged with nitrogen and refluxed at 90 ºC. When the temperature reached 90 ºC, tetrakis(triphenylphosphine)palladium (0.27 g, 0.24 mmol) was added. The reaction mixture was continued to stir at 90 ºC under nitrogen protection for 72 h. The crude product was subjected to column chromatography on silica gel (light petroleum ether/ethyl acetate=4:1) to afford **T2** (1.53 g, 70.83 %).

(2) Synthesis of 4,4',4'',4'''-(9,9'-spirobi[fluorene]-2,2',7,7'-tetrayl)tetrabenzoic acid (**L**)

4,4',4'',4'''-(9,9'-Spirobi[fluorene]-2,2',7,7'-tetrayl)tetramethylbenzoate (**T2**) (0.50g, 0.55 mmol) was dissolved in THF (20 mL). KOH (1M, 20 mL) was added and the resulting mixture was stirred (60 ºC for 12 h). When the resulting suspension was cooled to room temperature, it was acidified to pH = 7 using HCl (1M). Then, the organic solvent in the suspension was removed by evaporation completely. The suspension was filtered to obtain an ivory solid (**L**) (0.34 g, 77.58%).

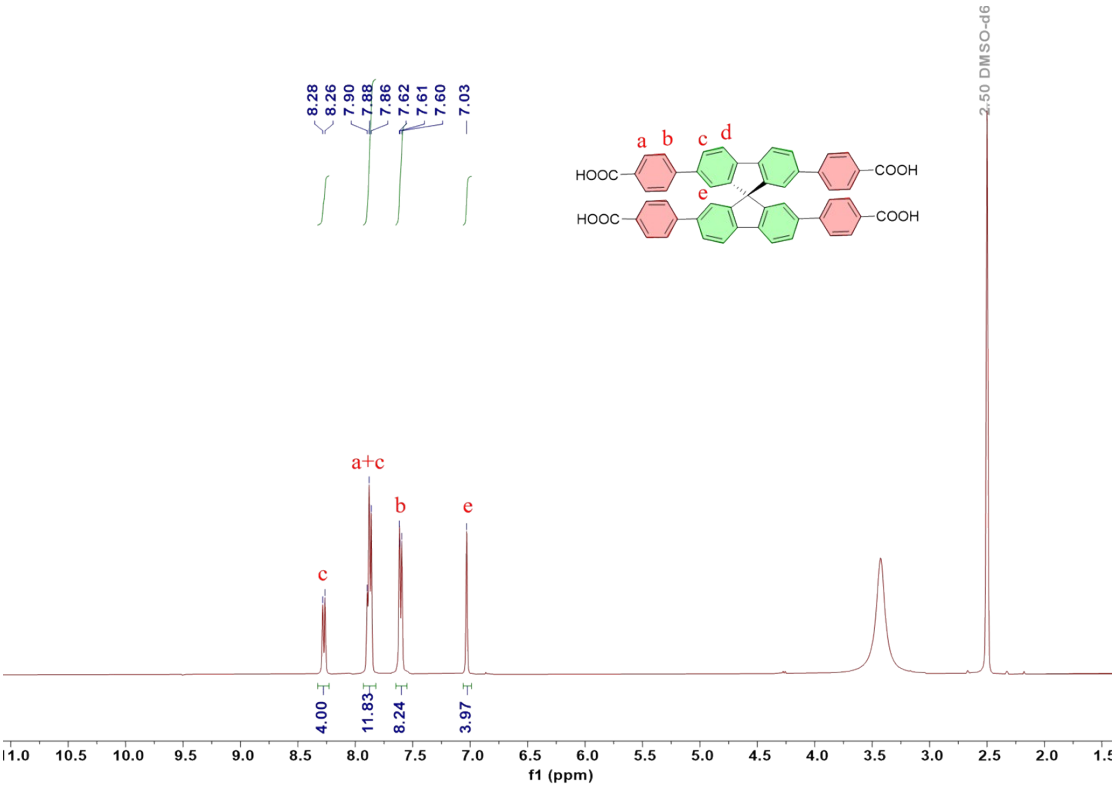


Fig. S1a ^{1}H-NMR spectrum of the ligand (**L**) (400 MHz, DMSO-d_6).

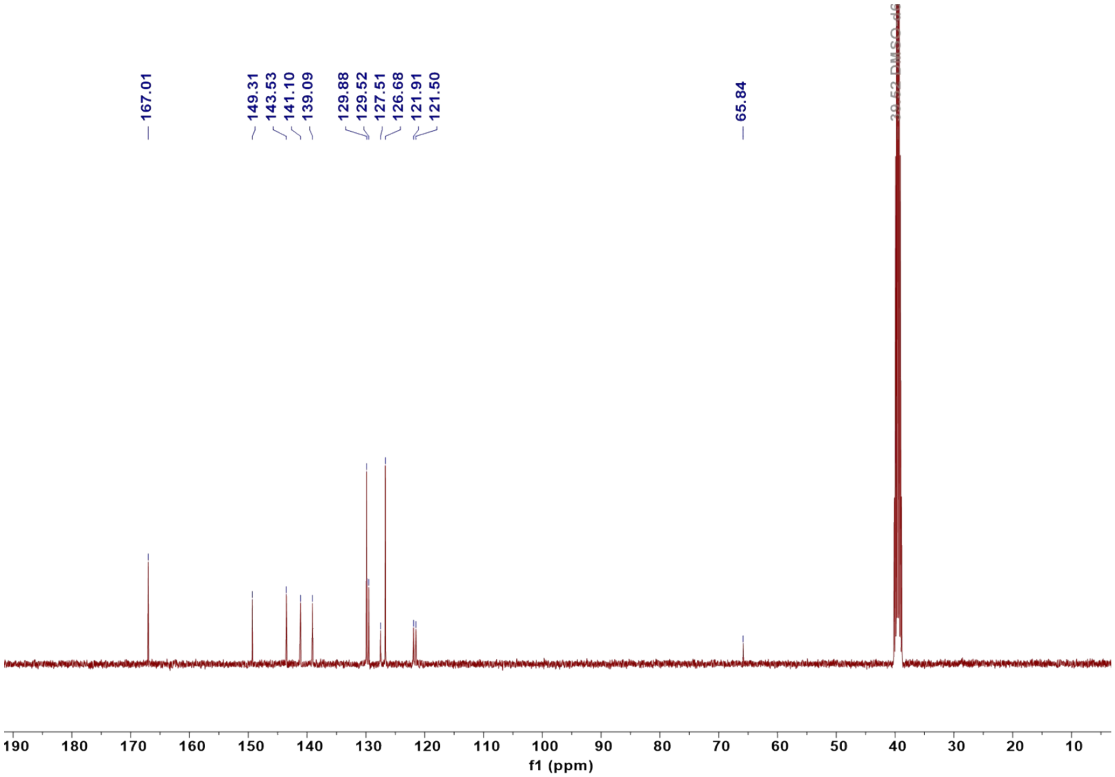


Fig. S1b ^{1}H-NMR spectrum of the ligand (**L**) (400 MHz, DMSO-d_6).

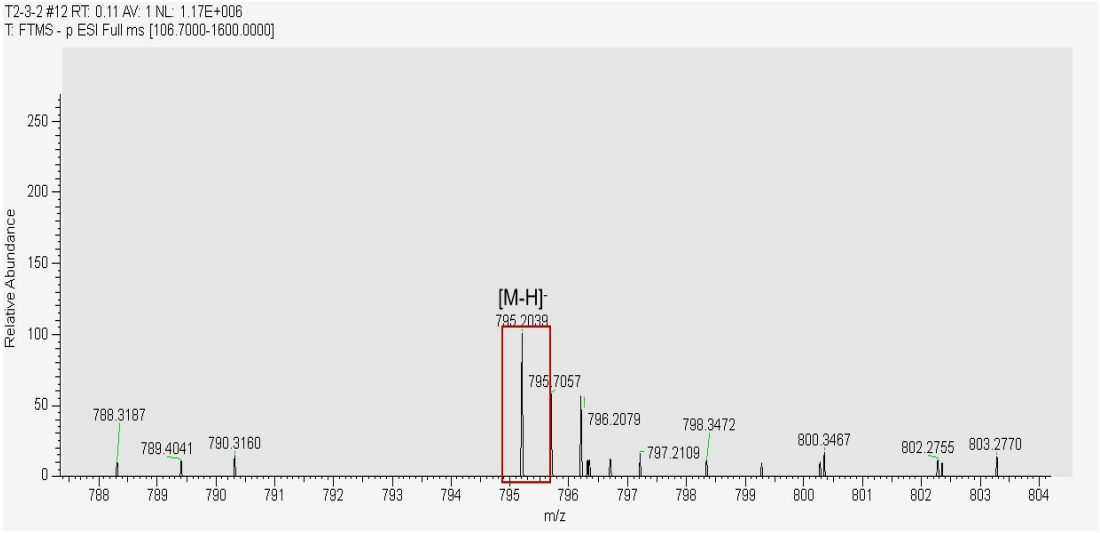


Fig. S1c HRESI-MS of the ligand showing the molecular ion: $[M-H]^{+}$=795.2039

(3) Synthesis of ZrFMOF in two different containers

4,4',4'',4'''-(9,9'-Spirobi[fluorene]-2,2',7,7'-tetrayl)tetrabenzoic acid (**L**) (3.50 mg, 0.75 mmol) was dissolved in DEF/formic acid (3/1, v/v) (0.80 mL), and the solution was sonicated for 10 min. $ZrOCl_2 \cdot 8H_2O$ (10.00 mg, 3.10 mmol) was separately dissolved in DEF/formic acid (3/1, v/v) (0.80 mL) and the solution was sonicated for 10 mins. The first solution was poured into the second solution, and the mixture was sonicated for 1 min. Then, the mixture was transferred to a PTFE reactor (25 mL) or a HPLC vial (2 mL). The milky solution was kept in 120 ºC oven for 24h. After cooling down to room temperatures, twin or polycrystals in the PTFE reactor and single crystals in the HPLC vial were obtained. The crystals were rinsed with fresh DEF three times per day for three days.

Due to the instability in air, the BET area of ZrFMOF was not measured. However, the large pore is consistent with the color changes when ZrFMOF (3 mg) was added to iodine solution (0.3 mg/mL in hexane, 1 mL). The purple color was changed to colorless in 12 hours, indicating that ZrFMOF could adsorb iodine (around 100%) (Fig. S1d).

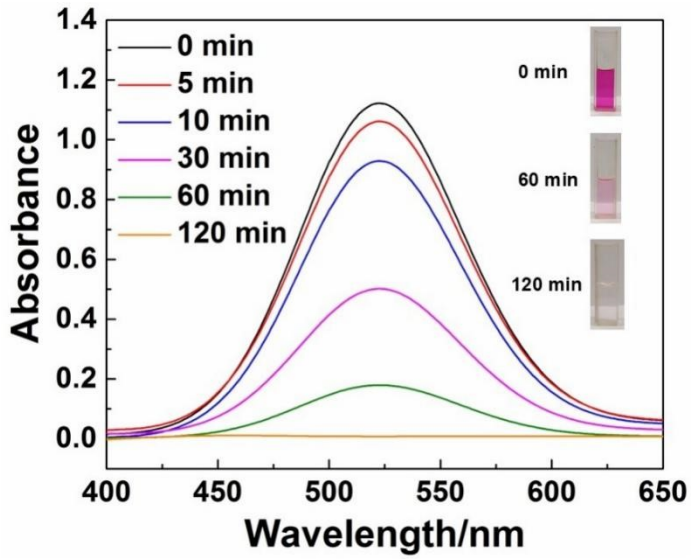


Fig. S1d Adsorption of iodine by ZrFMOF

SI-2 Comparison of ZrFMOF from DEF and DMF

All the reaction conditions were the same except for the reaction solvents. One batch of ZrFMOF was synthesized in DEF/formic acid, and another batch of ZrFMOF was synthesized in DMF/formic acid.

(1) Morphology

The crystals size from DEF/formic acid was much larger than those from DMF/formic acid (Fig. S2a)

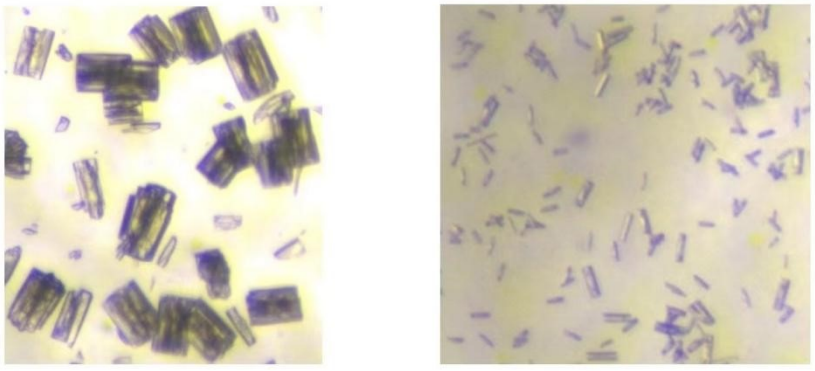


Fig. S2a The picture of (a) ZrFMOF(DEF) and (b) ZrFMOF(DMF).

(2) Adsorption efficiency

The same amounts of Rhodamine B and ZrFMOF were used. The absorbance at 1020 min of ZrFMOF (DEF) was much lower than that of ZrFMOF (DMF), indicating

that the former had high adsorption efficiency (Fig. S2b).

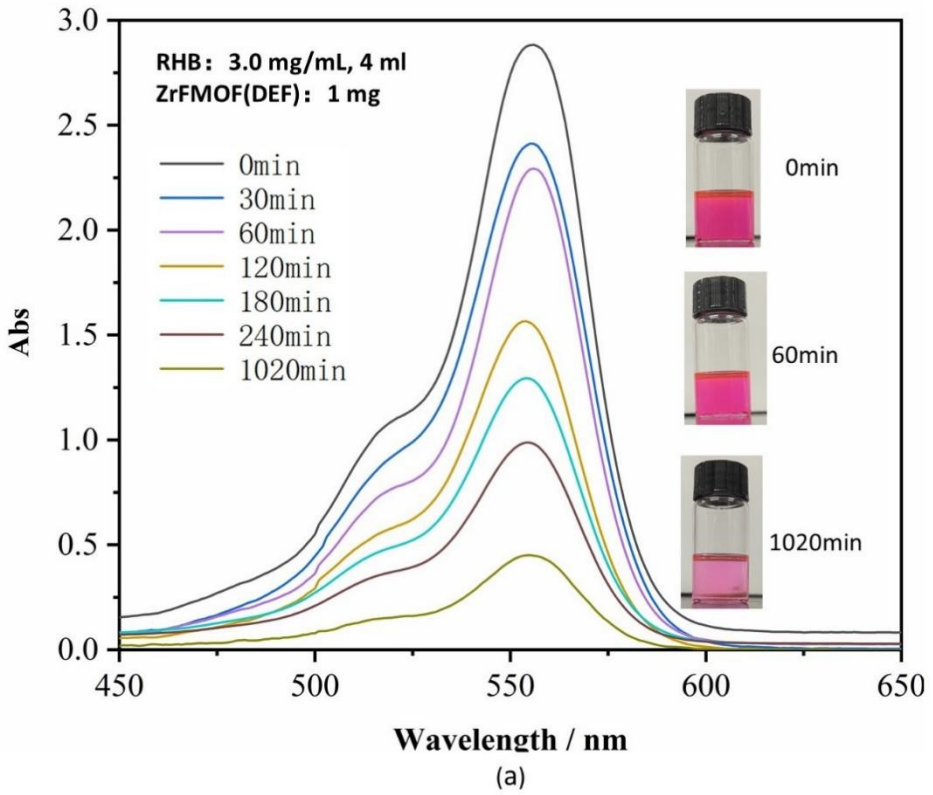


Fig. S2b Adsorption of rhodamine (0.3 mg/mL) by ZrFMOF (1 mg). The absorbance was decreased with the time.

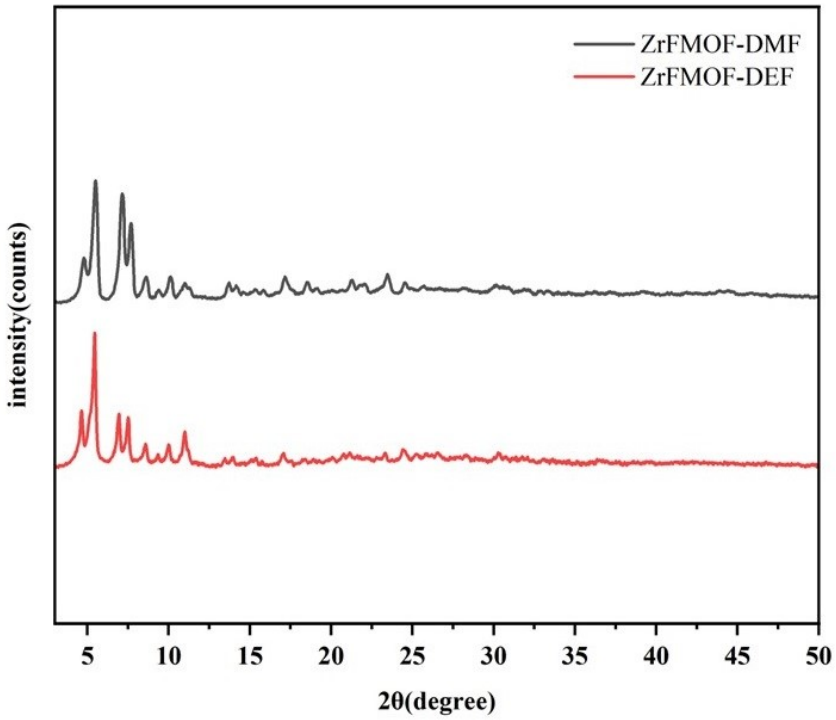


Fig. S2c Comparison of PXRD patterns of ZrFMOF from DEF and DMF solvents

SI-3 Thermogravimetric analysis of the ZrFMOF (TGA)

TGA was performed on a Thermogravimetric Analyzer (TGA2, Mettler-Toledo). The temperature range was set at 50-800 °C with a speed of 10 °C/min. The TGA analysis was finished in 75 min. During this time, ZrFMOF was still stable (Fig. S4B).

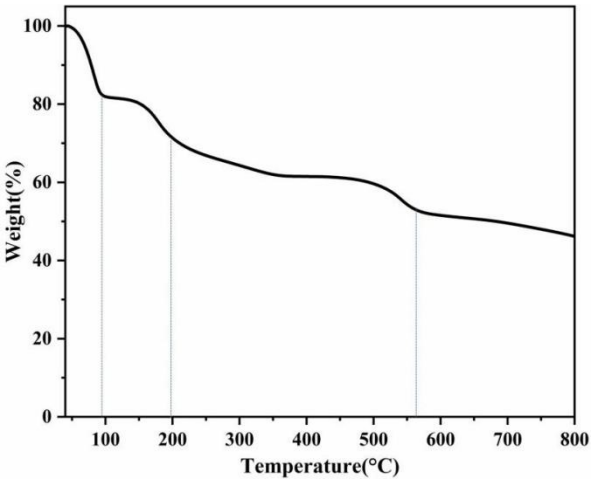


Fig. S3 Thermogravimetric analysis of ZrFMOF.

SI-4 Stability of the ZrFMOF

Powder X-ray diffraction patterns of ZrFMOF in different solvents were performed

on a Rigaku X-ray diffractometer miniflex600 with CuKα radiation (40kV, 15mA), scanning range 3°-50° and speed 5°/min (Fig. S4A).

ZrFMOF synthesized from DEF solvent was exposed to air for 12, 24, 48 and 72h, then the PXRD patterns of these four samples were measure (Fig. S4B). We could see that diffraction peaks disappeared with the times, indicating the instability in air.

ZrFMOF synthesized from DEF solvent was sealed for 12, 24, 48 and 72h, then the PXRD patterns of these four samples were measure (Fig. S4C). We could see that most diffraction peaks were kept.

Motivated by the literature[1], ZrFMOF was exchanged to more volatile solvent. ZrFMOF synthesized from DEF solvent was exchanged to acetone, then exposed to air for 12, 24, 48 and 72h. The PXRD patterns of these four samples were measure (Fig. S4D). We could see that most diffraction peaks disappeared (even faster than DEF).

ZrFMOF (synthesized from DEF solvent) which was exposed to air for 72 hours was subjected to single crystal X-ray diffraction (Fig. S4E); however, the resolution was very low, and no cell parameter could be calculated.

ZrFMOF (synthesized from DEF solvent) which was exchanged to acetone, and then exposed to air for 72 hours. The final sample was subjected to single crystal X-ray diffraction (Fig. S4F); however, the resolution was very low, and no cell parameter could be calculated.

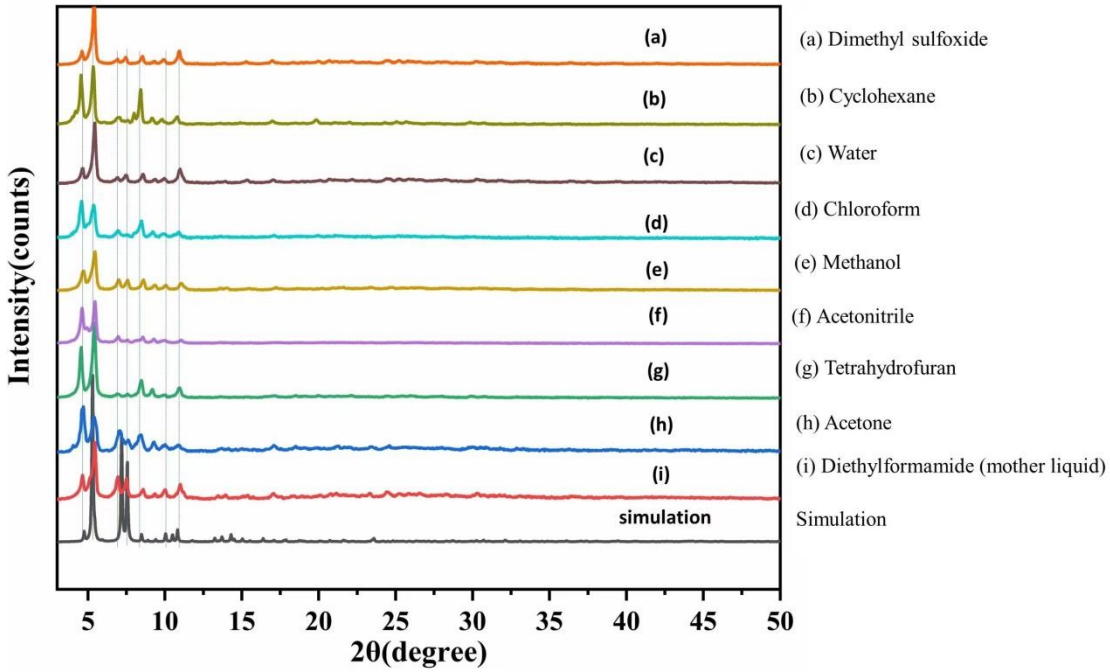


Fig. S4A Powder X-ray diffraction patterns of ZrFMOF in different solvents

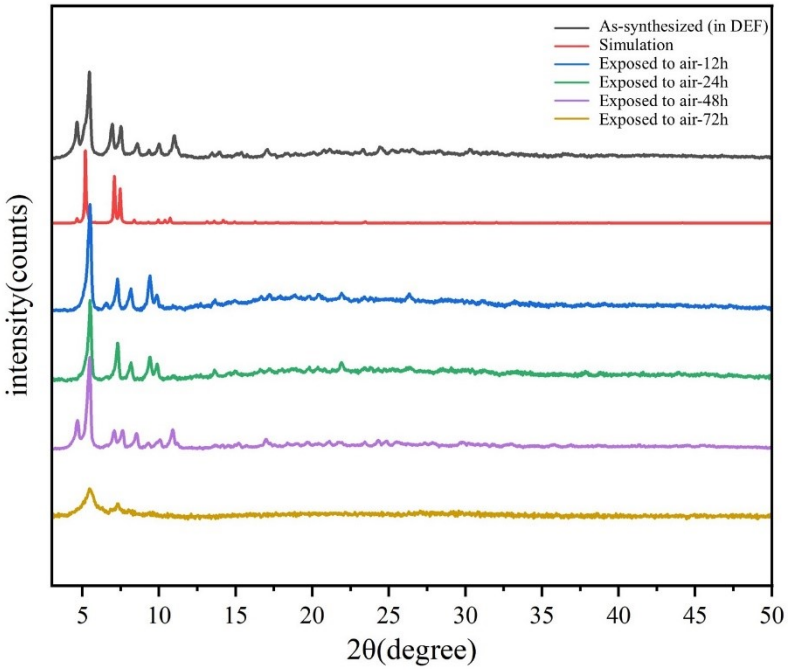


Fig. S4B PXRD patterns of ZrFMOF (synthesized from DEF solvent) which were exposed to air for 12, 24, 48 and 72h.

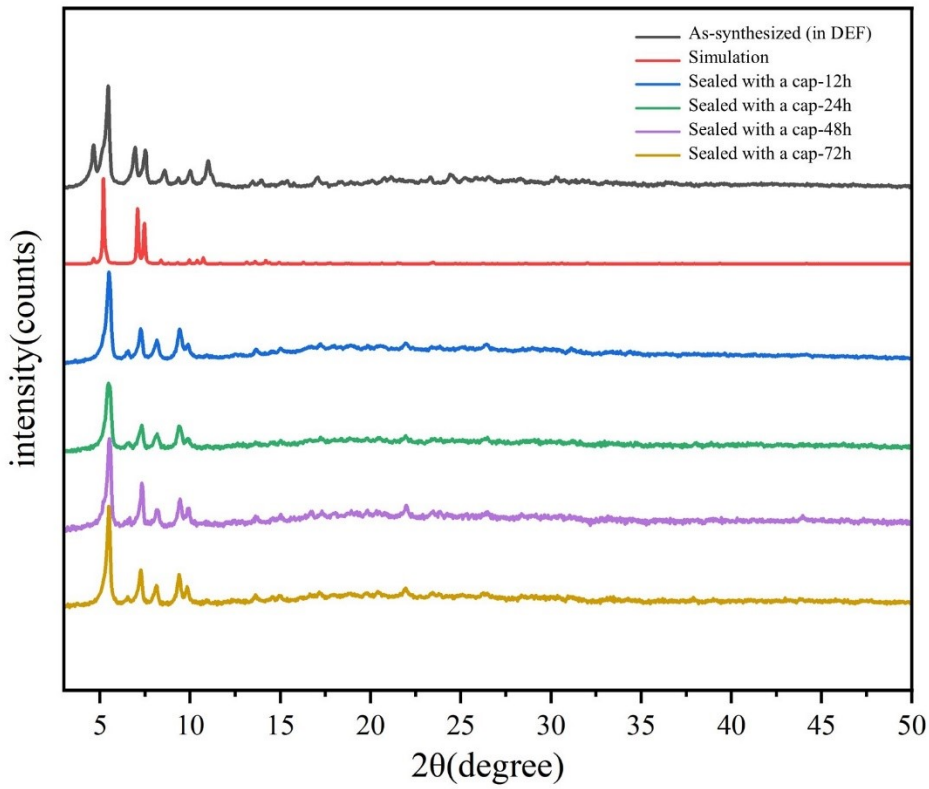


Fig. S4C PXRD patterns of ZrFMOF (synthesized from DEF solvent) which were sealed with a cap for 12, 24, 48 and 72h.

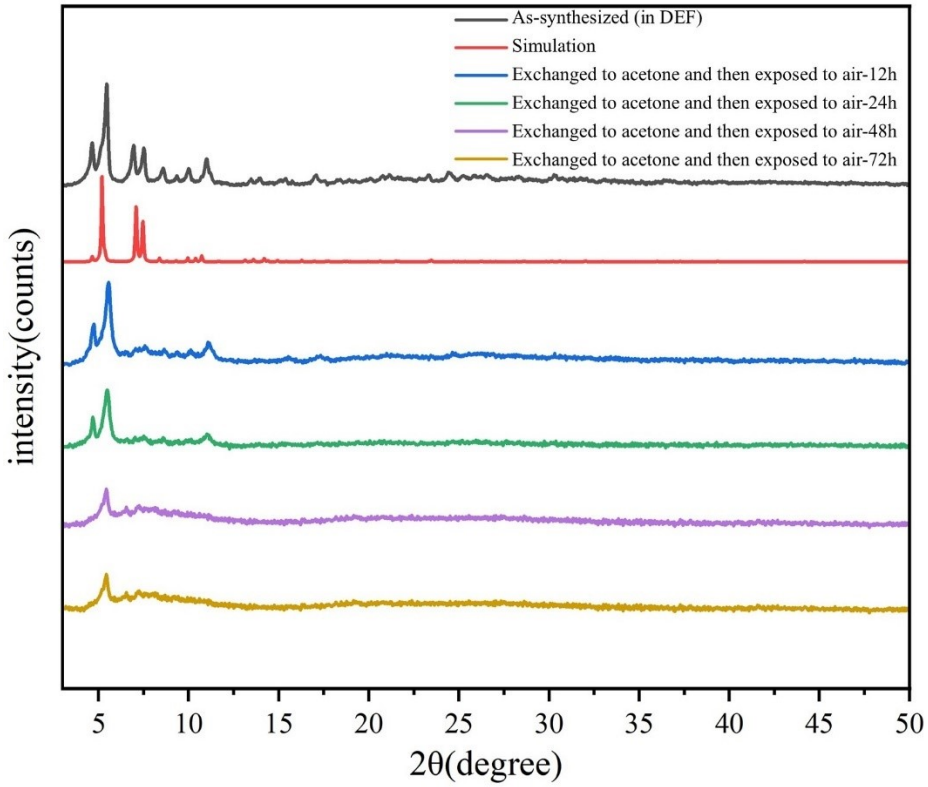


Fig. S4D PXRD patterns of ZrFMOF (synthesized from DEF solvent) which were exchanged to acetone, and then exposed to air for 12, 24, 48 and 72h.

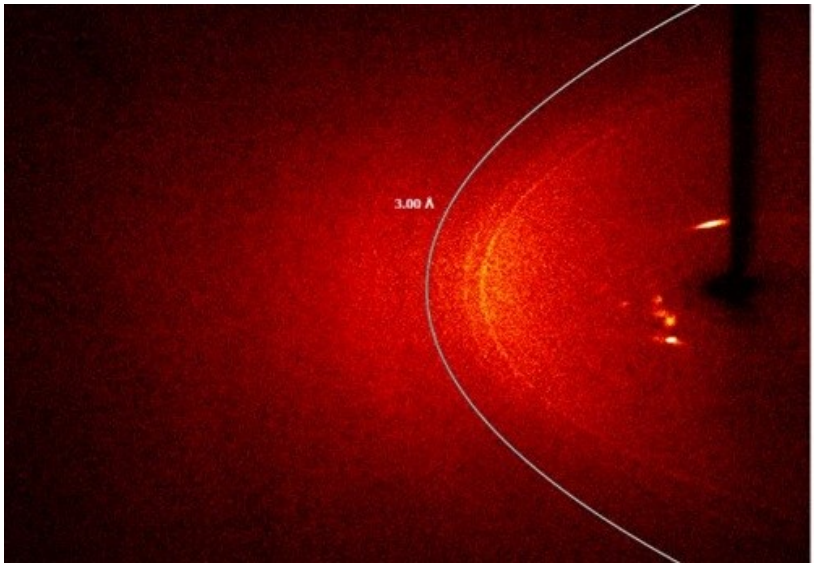


Fig. S4E Single crystal X-ray diffraction image of ZrFMOF (synthesized from DEF solvent) which was exposed to air for 72 hours.

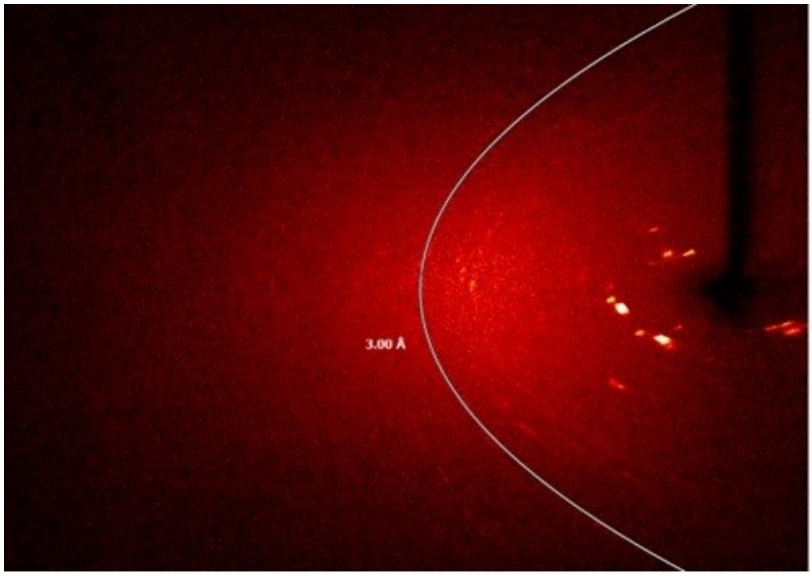


Fig. S4F Single crystal X-ray diffraction image of ZrFMOF (synthesized from DEF solvent) which was exchanged to acetone, and then exposed to air for 72 hours.

SI-5 Guest encapsulation by ZrFMOF

ZrFMOF ⊃ G**1** (3,4-dimethoxybenzyl alcohol). The freshly prepared single crystals of ZrFMOF (2 mg) were soaked in 3,4-dimethoxybenzyl alcohol (200 μL) in a 2 mL vial. The vial was kept in 25 °C for 3 days. After the reaction, one of the single crystals was used for SXRD analysis.

ZrFMOF ⊃ G**2** (1,3-dimethoxybenzene). The freshly prepared single crystals of ZrFMOF (2 mg) were soaked in 1,3-dimethoxybenzene (200 μL) in a 2 mL vial. The vial was kept in 25 °C for 3 days. After the reaction, one of the single crystals was used for SXRD analysis.

ZrFMOF ⊃ G**3** (4-pyridinecarboxaldehyde). The freshly prepared single crystals of ZrFMOF (2 mg) were soaked in 4-pyridinecarboxaldehyde (200 μL) in a 2 mL vial. The vial was kept in 25 °C for 3 days. After the reaction, one of the single crystals was used for SXRD analysis.

ZrFMOF ⊃ G**4** (cyclohexylbenzene). The freshly prepared single crystals of ZrFMOF (2 mg) were soaked in cyclohexylbenzene (200 μL) in a 2 mL vial. The vial was kept in 25 °C for 3 days. After the reaction, one of the single crystals was used for SXRD analysis.

ZrFMOF ⊃ G**5** (eugenol). The freshly prepared single crystals of ZrFMOF (2 mg) were soaked in eugenol (200 μL) in a 2 mL vial. The vial was kept in 25 °C for 3 days.

After the reaction, one of the single crystals was used for SXRD analysis.

ZrFMOF ⊃ G**6** (2-pyridinecarboxaldehyde). The freshly prepared single crystals of ZrFMOF (2 mg) were soaked in 2-pyridinecarboxaldehyde (200 μL) in a 2 mL vial. The vial was kept in 25 °C for 3 days. After the reaction, one of the single crystals was used for SXRD analysis.

ZrFMOF ⊃ G**7** (benzyl alcohol). The freshly prepared single crystals of ZrFMOF (2 mg) were soaked in benzyl alcohol (200 μL) in a 2 mL vial. The vial was kept in 25 °C for 3 days. After the reaction, one of the single crystals was used for SXRD analysis.

ZrFMOF ⊃ G**8** (4-acetylpyridine). The freshly prepared single crystals of ZrFMOF (2 mg) were soaked in 4-acetylpyridine (200 μL) in a 2 mL vial. The vial was kept in 25 °C for 3 days. After the reaction, one of the single crystals was used for SXRD analysis.

ZrFMOF ⊃ G**9** (2,6-dimethylaniline). The freshly prepared single crystals of ZrFMOF (2 mg) were soaked in 2,6-dimethylaniline (200 μL) in a 2 mL vial. The vial was kept in 25 °C for 3 days. After the reaction, one of the single crystals was used for SXRD analysis.

ZrFMOF ⊃ G**10** (methyl anthranilate). The freshly prepared single crystals of ZrFMOF (2 mg) were soaked in methyl anthranilate (200 μL) in a 2 mL vial. The vial was kept in 25 °C for 3 days. After the reaction, one of the single crystals was used for SXRD analysis.

ZrFMOF ⊃ G**11** (3-acetylpyridine). The freshly prepared single crystals of ZrFMOF (2 mg) were soaked in 3-acetylpyridine (200 μL) in a 2 mL vial. The vial was kept in 25 °C for 3 days. After the reaction, one of the single crystals was used for SXRD analysis.

ZrFMOF ⊃ G**12** (3-(aminomethyl)pyridine). The freshly prepared single crystals of ZrFMOF (2 mg) were soaked in 3-(aminomethyl)pyridine (200 μL) in a 2 mL vial. The vial was kept in 25 °C for 3 days. After the reaction, one of the single crystals was used for SXRD analysis.

ZrFMOF ⊃ G**x** (3-Aminopyridine). The freshly prepared single crystals of ZrFMOF (2 mg) were soaked in 3-Aminopyridine (200 μL) in a 2 mL vial. The vial was kept in 25 °C for 3 days. After the reaction, one of the single crystals was used for SXRD analysis.

ZrFMOF ⊃G**1**&G**8** (3,4-dimethoxybenzyl alcohol + 4-acetylpyridine). The freshly prepared single crystals of ZrFMOF (2 mg) were soaked in [3,4-dimethoxybenzyl alcohol (100 uL) and 4-acetylpyridine (100 μL)] in a 2 mL vial. The vial was kept in 25 °C for 3 days. After the reaction, one of the single crystals was used for SXRD analysis.

ZrFMOF ⊃G**8**&G**10** (4-acetylpyridine + methyl anthranilate). The freshly prepared single crystals of ZrFMOF (2 mg) were soaked in [4-acetylpyridine (100 μL) and methyl anthranilate (100 μL)] in a 2 mL vial. The vial was kept in 25 °C for 3 days. After the reaction, one of the single crystals was used for SXRD analysis.

SI-6 ^{1}H-NMR of the ZrFMOF ⊃ Guest complexes

NMR spectra were obtained on a Bruker Avance-400 NMR spectrometer. ZrFMOF ⊃ Guests could not be directly dissolved in the deuterated solvents. So, suitable acid was used. The ^{1}H-NMR of the ZrFMOF ⊃ Guests were measured in a 10% D_2SO_4/DMSO-d_6 solution and heat at 70℃.

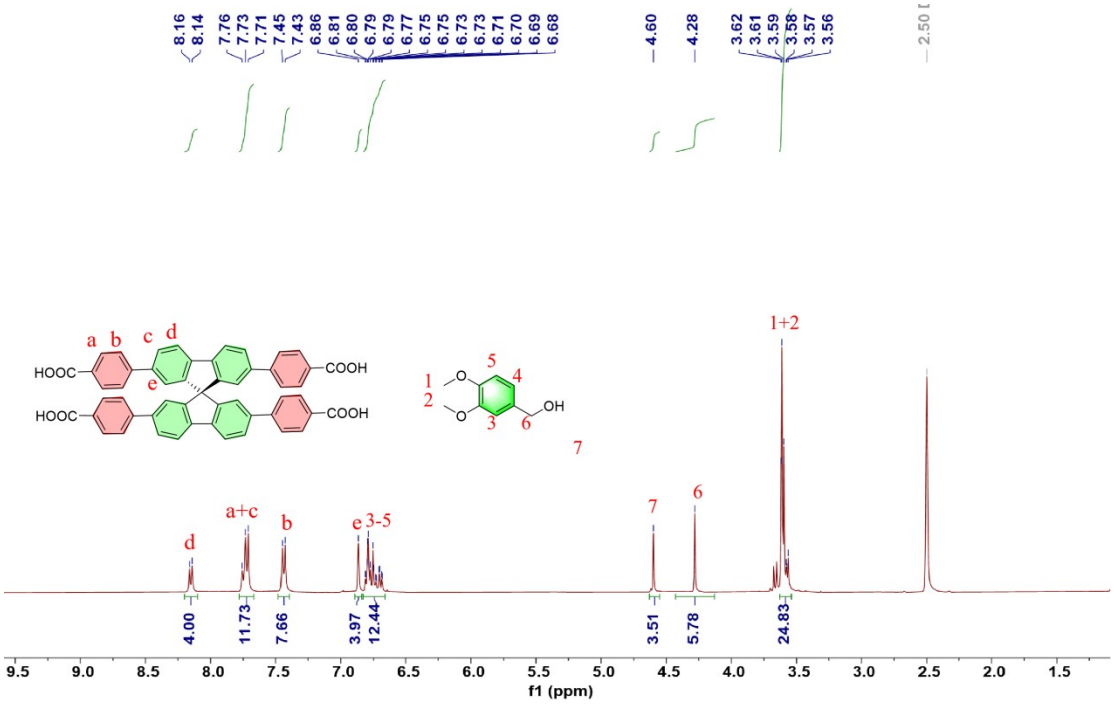


Fig. S6a ^{1}H NMR spectrum of digested ZrFMOF ⊃ G**1** in DMSO-d_6.

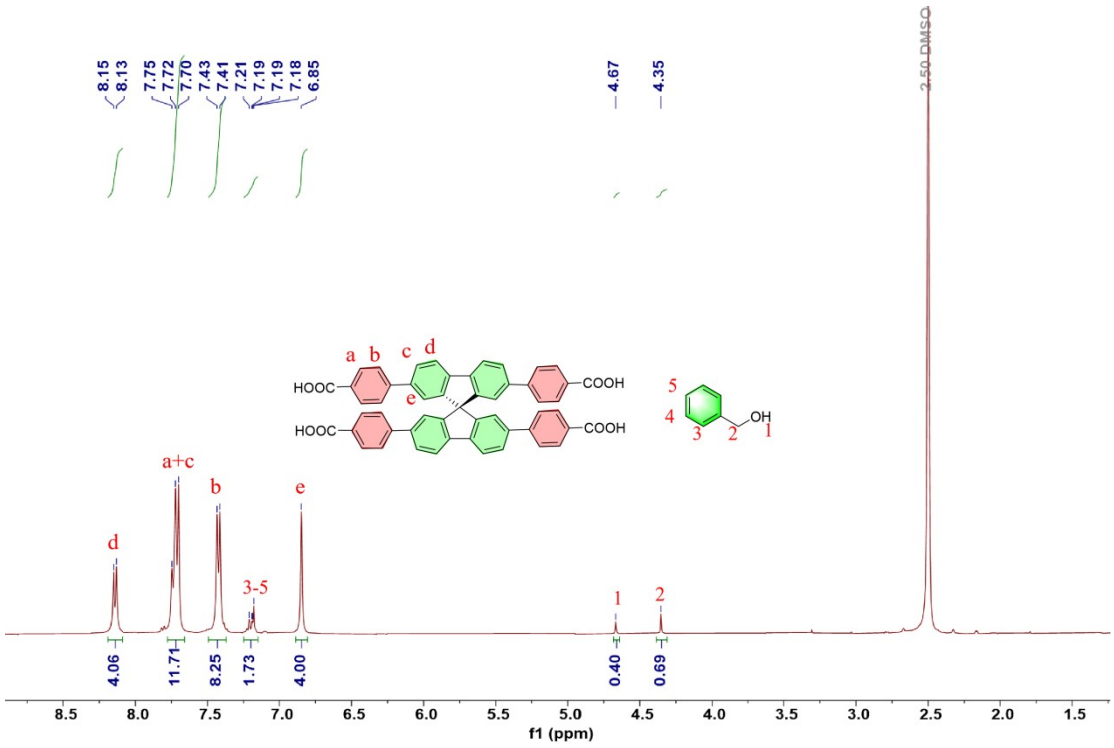


Fig. S6b ^{1}H NMR spectrum of digested ZrFMOF ⊃ G**7** in DMSO-d_6.

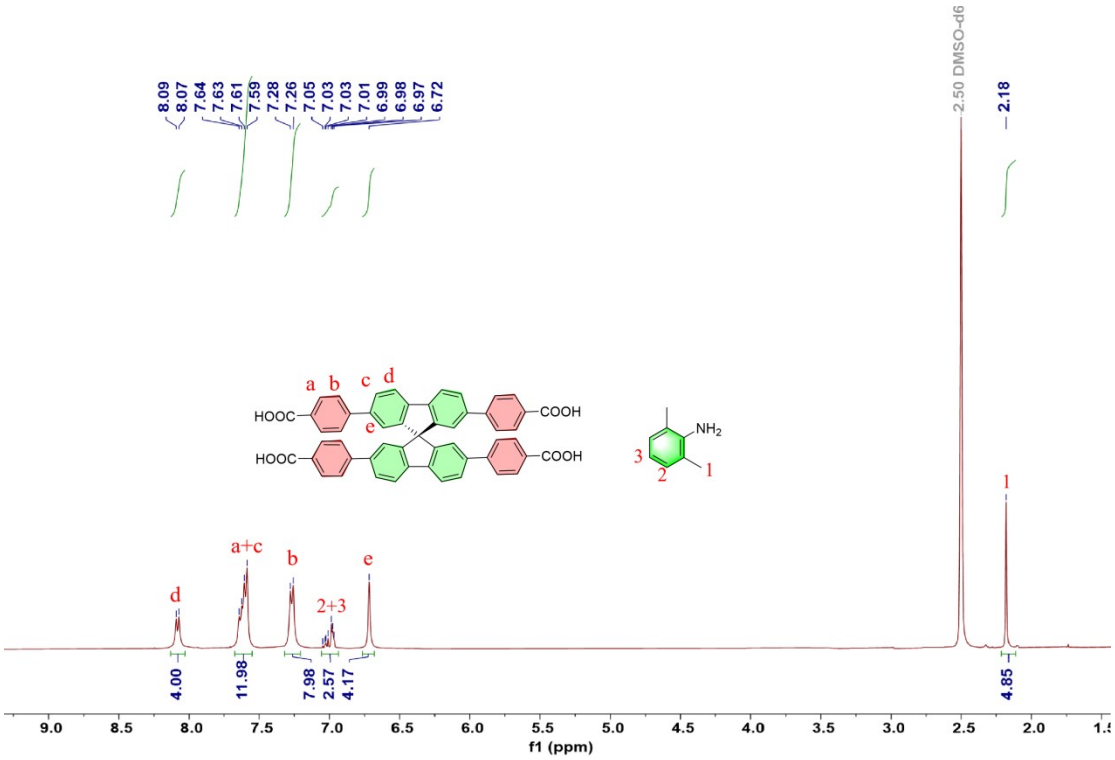


Fig. S6c ^{1}H NMR spectrum of digested ZrFMOF ⊃ G**9** in DMSO-d_6.

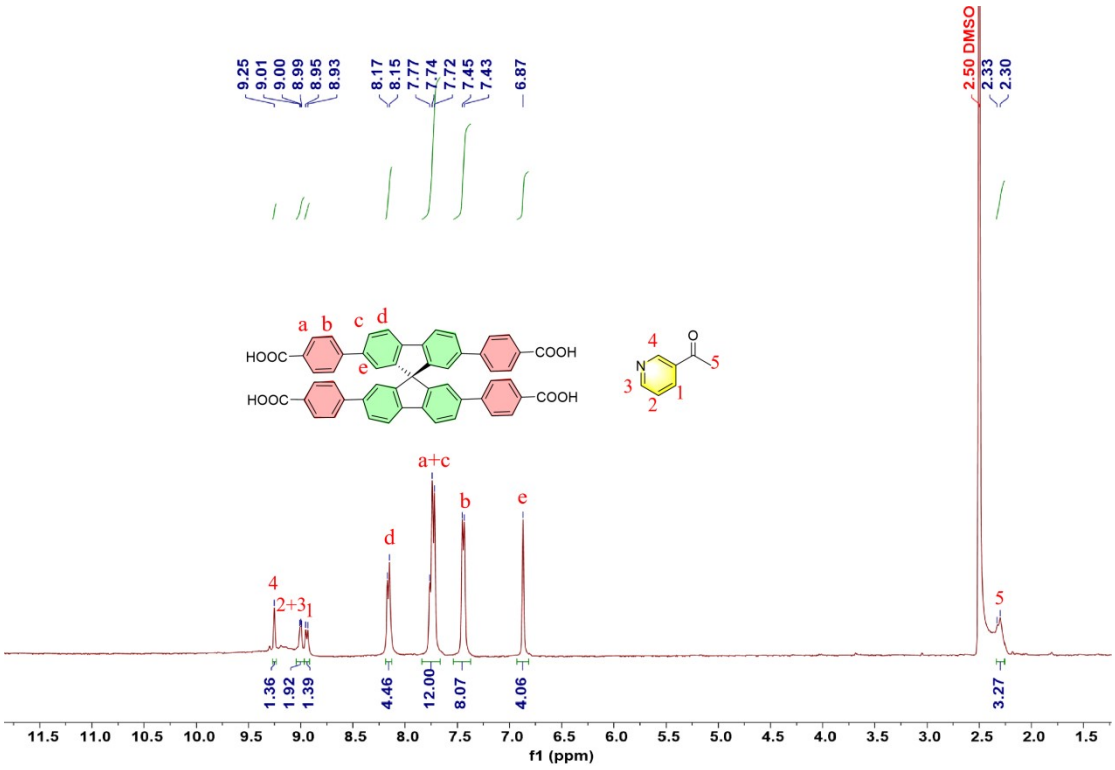


Fig. S6d ^{1}H NMR spectrum of digested ZrFMOF ⊃ G**11** in DMSO-d_6.

SI-7 Reusability of ZrFMOF and absorption on other liquid molecules

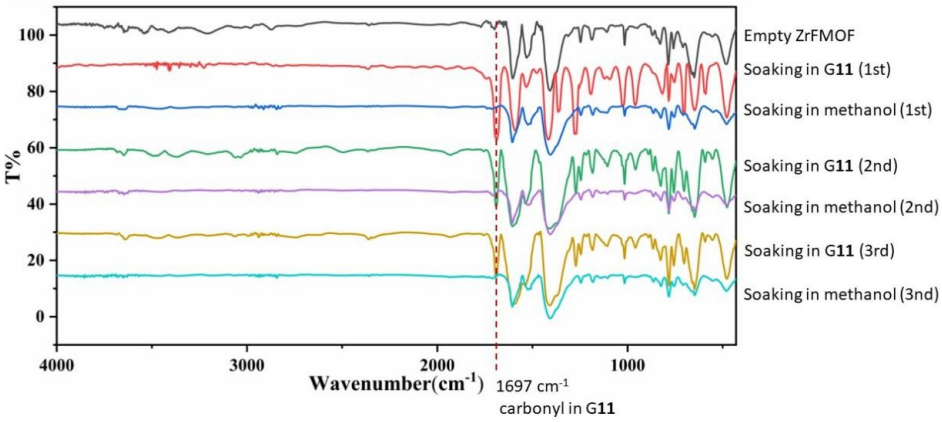
Infrared spectroscopy (IR) was measured on a Shimadzu IRSpirit FTIR spectrophotometer. IR spectra (500-4000 cm^{-1}) were used to monitor the presence and disappearance of G**11** signal for the reusability study (Fig. S7a).

Beside the qualitative analysis by IR spectra, we further used UV spectra for quantitative analysis. The adsorb and desorb processes were monitored by UV absorbance, and we could calculate the average adsorption performance was 96.8% with a small standard error of 3.0% (Fig. S7b).

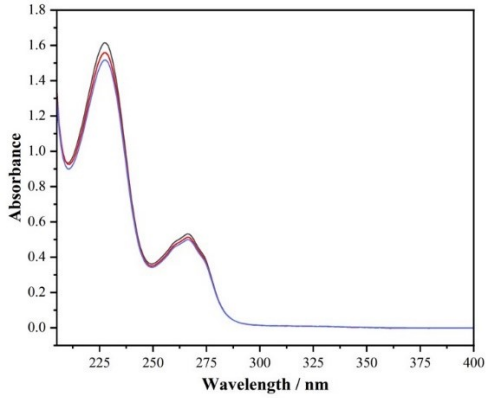
We used ZrFMOF to encapsulate G**8**. 12 hours later, we could clearly observe the carbonyl group in ZrFMOF⊃G**8** complex in the IR spectrum. Then the complex was soaked in fresh methanol. 12 hours later, carbonyl group signal disappeared indicating the release of G**8**. We also used acetone to desorb and found that acetone showed similar desorb potency as methanol (Fig. S7c).

We used ZrFMOF to encapsulate 2-acetylpyridine and 4-pyridinecarboxaldehye. 12 hours later, we could clearly observe the carbonyl group of these two compounds in the IR spectrum (Fig. S7d).

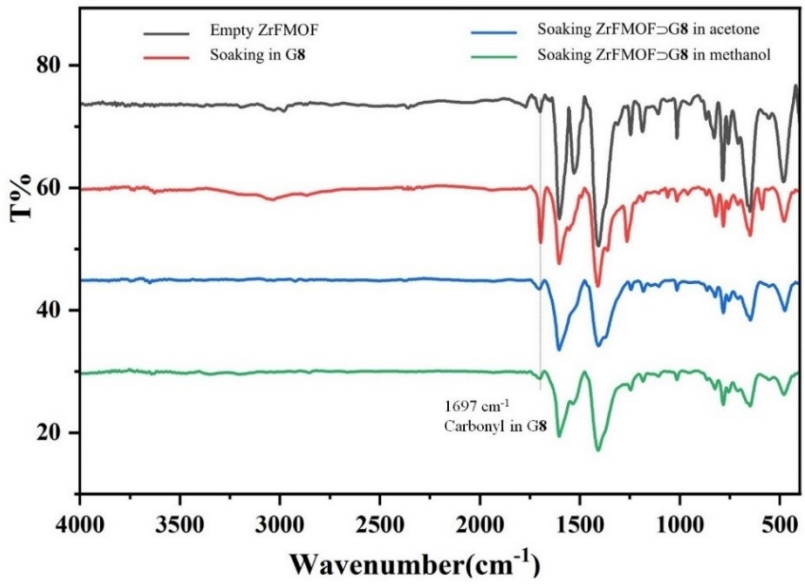
(a)



(b)



(c)



(d)

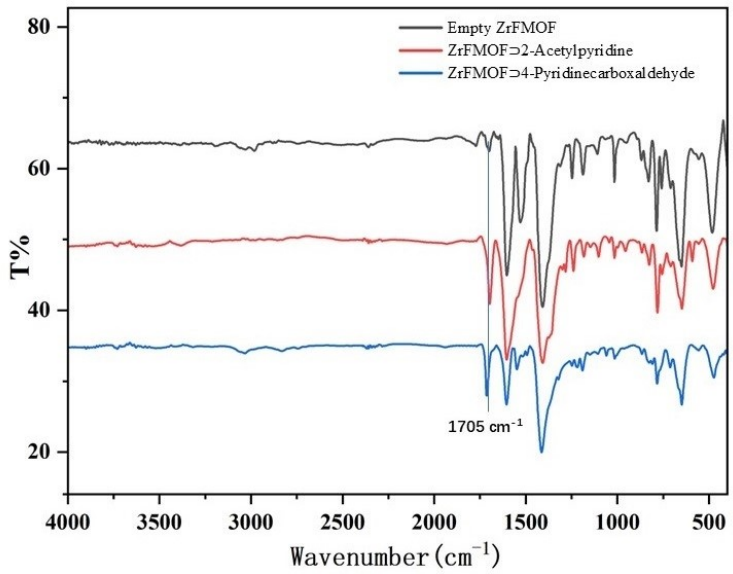


Fig. S7 (a) IR spectrum was used to monitor the presence and disappearance of G**11** signal. (b) Quantitative analysis of G**11** by UV absorbances (three cycles). (c) IR

spectrum showing the presence and desorb of G**8** by methanol and acetone. (d) IR spectrum showing the adsorption of 2-acetylpyridine and 4-pyridinecarboxyaldehyde by ZrFMOF.

SI-8 Adsorption of dyes by ZrFMOF

Solutions of rhodamine B, congo red, methyl violet and methylene blue in water (0.3 mg/mL) were prepared. ZrFMOF (3 mg) was added to the solution (1 mL). The UV spectra were taken to monitor the adsorption changes of the dyes, and photos were taken in some point. The results of rhodamine B were shown in the main text; while the adsorptions of congo red, methyl violet and methylene blue by ZrFMOF were shown in Fig. S8.

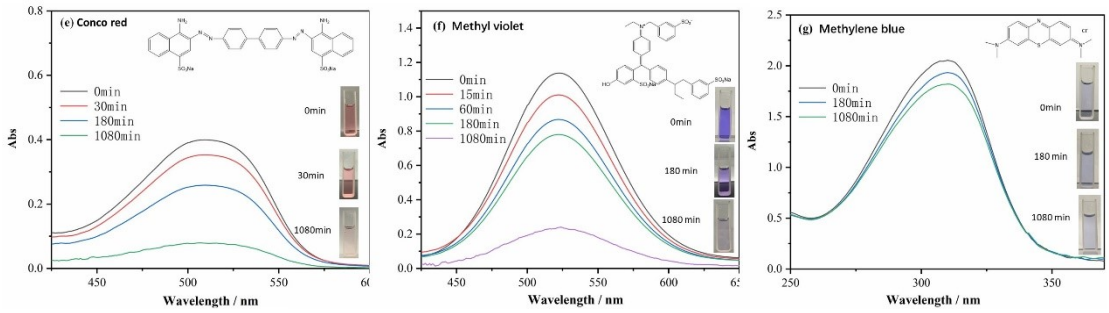


Fig. S8 Adsorption of dyes by ZrFMOF. (e) Congo red, (f) methyl violet and (g) methylene blue

SI-9 Adsorption of perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) and other anion groups by ZrFMOF

(1) Absorption of ZrFMOF on PFOS

PFOS and PFOA were dissolved in D_2O (1.25 mg/mL) in a test tube, then ZrFMOF (4 mg) was added to the water solution (1 mL). After adsorption, the IR spectra for PFOS, ZrFMOF and ZrFMOF@PFOS (Fig. S9a), and the solution ^{19}F-NMR spectrum for ZrFMOF@PFOS (Fig. S9b).

(2) Quantitative measurement of the absorption capacity of ZrFMOF on PFOA

ZrFMOF (2 mg) was added into PFOA (2.5mg/mL in D_2O). After 8 hours, internal standard (trifluroethanol, 1μL) was added, and solution ^{19}F-NMR was measured. Through integration of the peak area, ZrFMOF (2 mg) was found to adsorb PFOA (2.47 mg). So, the adsorption capacity of ZrFMOF on PFOA was 1.23 mg/mg (Fig. S9c). The morphologies of ZrFMOF before and after adsorption of PFOA were taken (Fig. S9d).

(3) Absorption of ZrFMOF on PFOA in the presence of ions or organic compounds.

PFOA was dissolved in D_2O (2.0 mg/mL) in a test tube, then ZrFMOF (2 mg), ZrFMOF (2mg) + NaCl (10mg), ZrFMOF (2mg) + KCl (10mg), ZrFMOF (2 mg) + $ZnCl_2$ (10mg) or ZrFMOF (2 mg) + urea (10 mg) was added to the water solution (1 mL). After adsorption or 8 hours, the ^{19}F-NMR spectra were taken (Fig. S9e).

(4) Measurement of solid-state NMR

^{19}F magic-angle spinning (MAS) NMR spectra were obtained on a Bruker Avance 400 spectrometer operating at a Larmor frequency of 400.13 MHz for 1H. The temperature was maintained at 20°C for the duration of each experiment. Samples were spun at a MAS rate of 25000 kHz and standard 1D MAS NMR spectra were obtained.

(5) Chemical shift calculations

DFT calculations of ^{19}F chemical shifts were performed using CASTEP with the GGA PBE functional[2,3] and core–valence interactions were described by ultrasoft pseudopotentials.[2,3] Calculations were performed using a planewave energy cut-off of 50 Ry (680 eV) and due to the large cell size, a single *k*-point at the fractional coordinate (0.25, 0.25, 0.25) in reciprocal space for integration over the Brillouin zone. The outcome of the calculations included the isotropic ^{19}F magnetic shielding values, shielding anisotropy and asymmetry parameter. Calculations were performed on isolated molecules confined within a pseudo-triclinic (*P*1) unit cell of dimensions 25 x 15 x 15 Å, set up as the simulation box, using the software CrystalMaker®. The atomic positions were expressed as fractional coordinates in this unit cell. The molecular geometry within the simulation box was optimised within the CASTEP environment. All atomic positions were allowed to vary and the Grimme G06 semi-empirical dispersion correction scheme was used.[1] Typical optimisation times were 24-36 hours.

(6) Simulations of ^{19}F MAS NMR spectra

Simulations were performed in the SIMPSON software environment, taking as input parameters the ^{19}F Larmor frequency (376 MHz), MAS frequency (25 kHz), calculated ^{19}F isotropic chemical shifts (d_{iso}), chemical shift anisotropy ($d_{zz} - d_{iso}$) and asymmetry parameter h, and ^{19}F-^{19}F dipolar couplings greater than 4000 Hz.

As shown in Figure 10d, the top two simulated spectra are for all *trans*

conformations of the CF_2 groups and differ only in the geometry of the COOH group. The bottom simulated spectrum is for a geometry in which all the CF_2 groups deviated from the *trans* conformation by up to 30°.

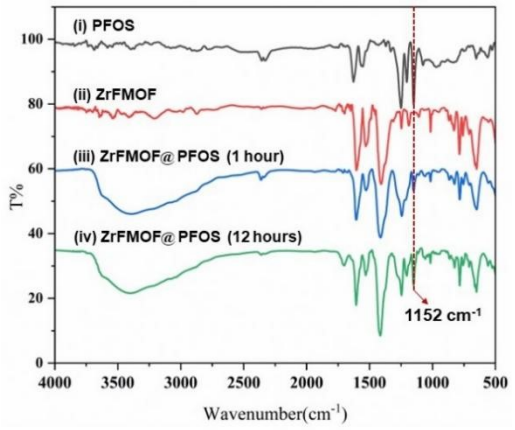
(7) Besides the -COOH or -SO_3H groups, we also tested -MnO_4^{2-}, -$Cr_2O_7^-$ and -$B(OH)_2$ and found that these anionic groups could also be adsorbed (Fig. S9f, Fig. S9g and Fig. S9h).

ZrFMOF (2 mg) was added to the KCr_2O_7 solution (0.1 mg/mL, 4 mL), the UV spectrum (320-420 nm) after 0, 30 min, 1 hour, 2 hours and 12 hours were measured (Fig. S9f).

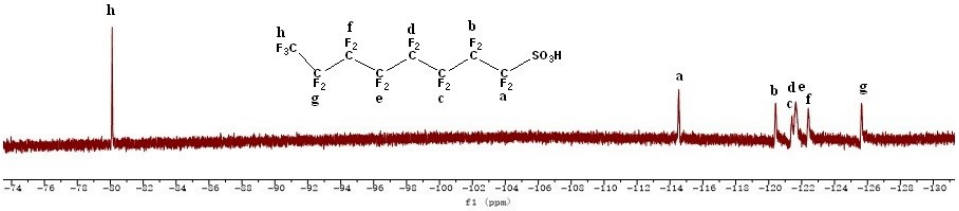
ZrFMOF (2 mg) was added to the $KMnO_4$ solution (0.05 mg/mL, 4 mL), the UV spectrum (490-600 nm) after 0, 30 min, 1 hour, 2 hours and 12 hours were measured, (Fig. S9g).

ZrFMOF (2 mg) was added to the 4-cyanophenylboronic acid solution (0.2 mg/mL, 4 mL), the UV spectrum (255-310 nm) after 0, 10 min, 30 min, 1 hour and 2 hours were measured (Fig. S9g).

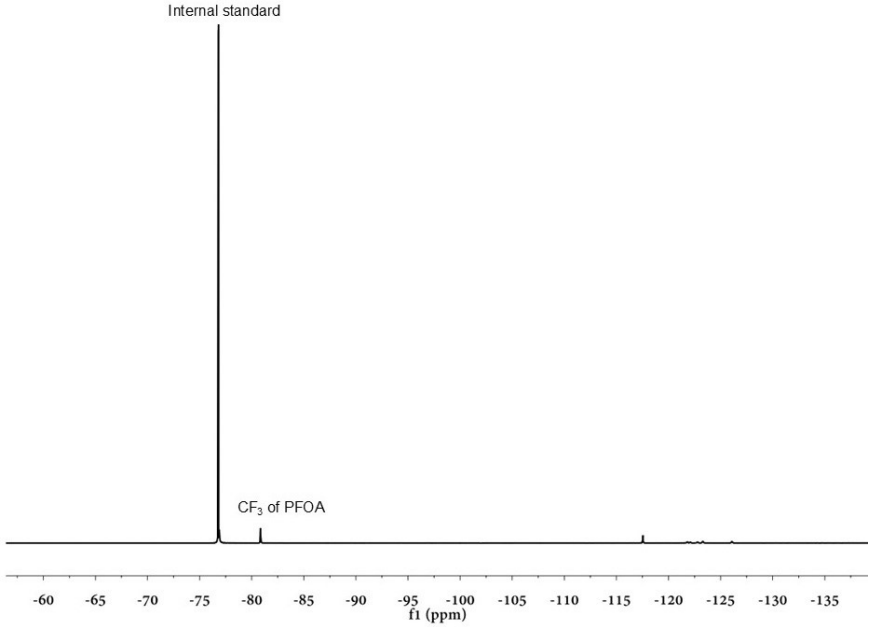
(a)



(b) Solution NMR (^{19}F-NMR) of ZrFMOF@PFOS

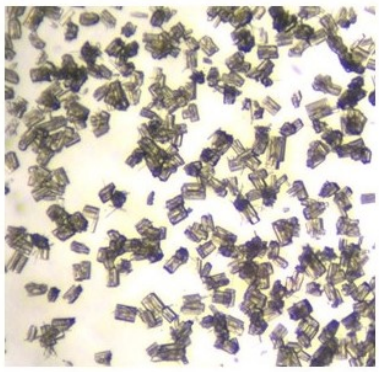


(c) Quantitative measurement of the absorption capacity of ZrFMOF on PFOA

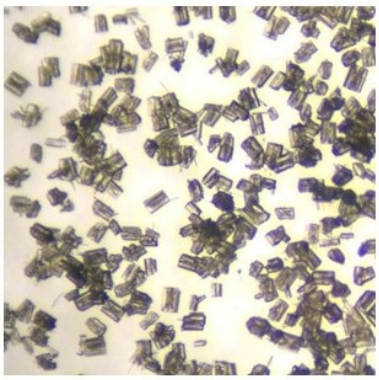


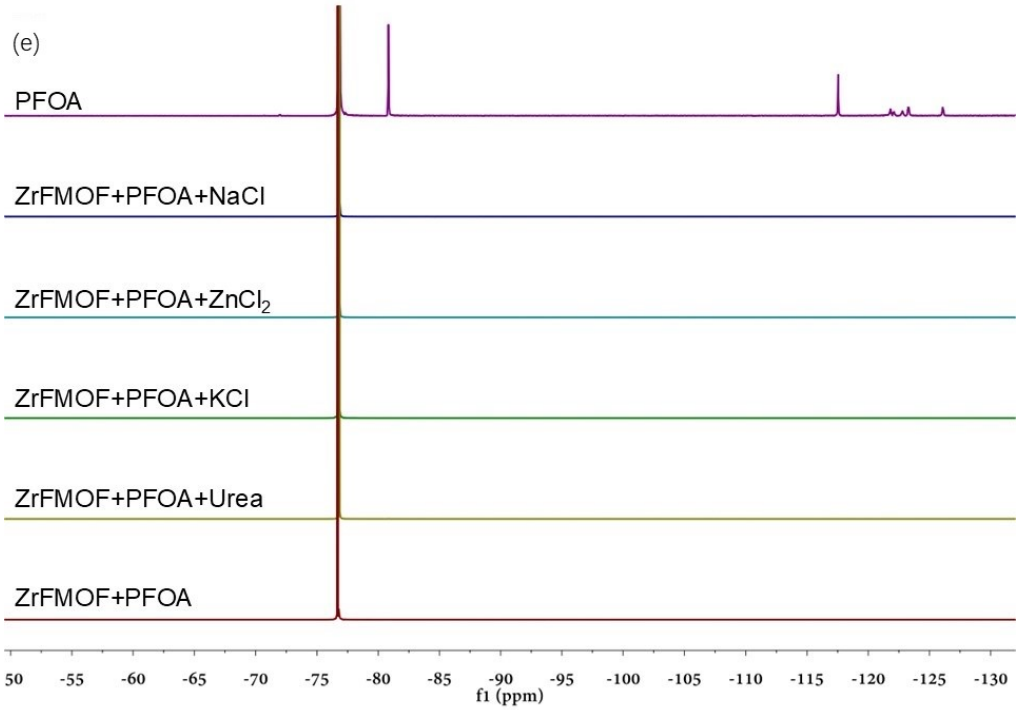
(d)

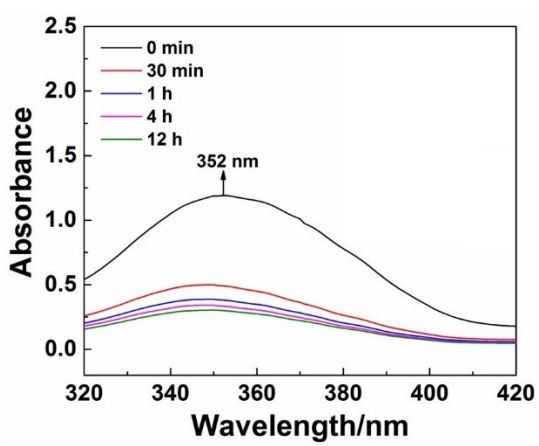
Before adsorption



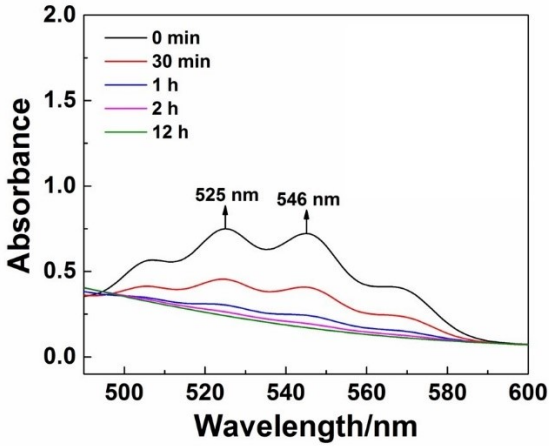
After adsorption of PFOA



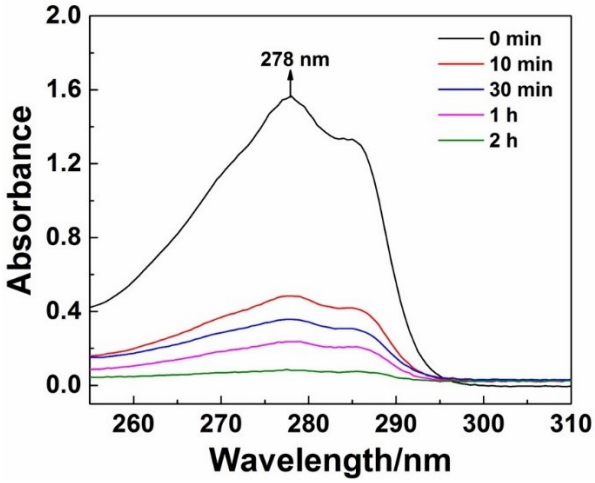

(e)
PFOA
ZrFMOF+PFOA+NaCl
ZrFMOF+PFOA+ZnCl2
ZrFMOF+PFOA+KCl
ZrFMOF+PFOA+Urea
ZrFMOF+PFOA
50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130
f1 (ppm)


0 min
30 min
1 h
4 h
12 h
352 nm
Absorbance
Wavelength/nm

(f)


0 min
30 min
1 h
2 h
12 h
525 nm
546 nm
Absorbance
Wavelength/nm

(g)


0 min
10 min
30 min
1 h
2 h
278 nm
Absorbance
Wavelength/nm

(h)

Fig. S9 Adsorption of perfluorooctane sulfonic acid (PFOS), perfluorooctanoic acid (PFOA) and other anion groups by ZrFMOF. IR of ZrFMOF⊃PFOS (a); solution ^{19}F-NMR spectrum (b, DMSO-d_6 containing 10% H_2SO_4) of ZrFMOF⊃PFOS (perfluorooctane sulfonic acid); quantitative measurement of the absorption capacity of ZrFMOF on PFOA by ^{19}F-NMR (c); pictures showing the morphologies of ZrFMOF before and after adsorption of PFOA (d); ^{19}F-NMR spectrum showing the influence of ions and organic compound on the adsorption of PFOA by ZrFMOF (e); UV spectrum of the K_2MnO_4 solutions after the addition of ZrFMOF at different time (f); UV spectrum of the KCr_2O_7 solutions after the addition of ZrFMOF at different time (g) and UV spectrum of the 4-cyanophenylboronic acid solutions after the addition of ZrFMOF at different time (h).

Table S1 Stability (morphology) of ZrFMOF in different solvents

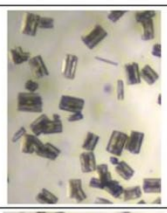
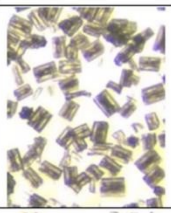
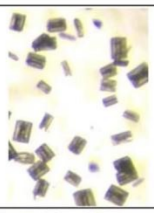
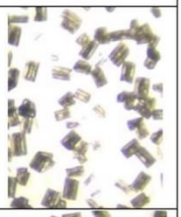
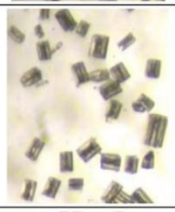
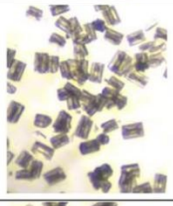
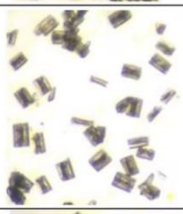
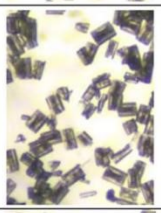
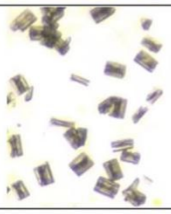
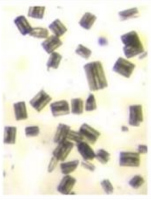
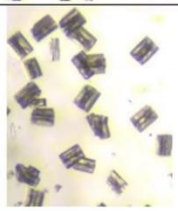
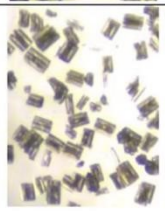
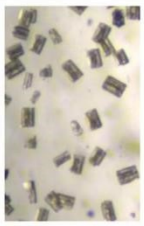
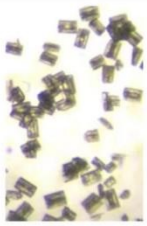
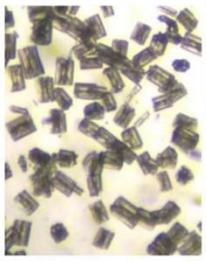
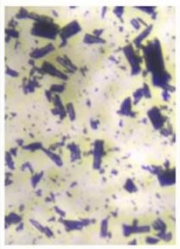
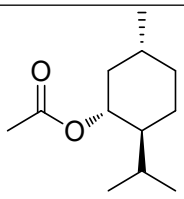
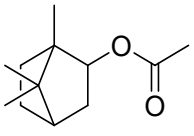
Solvent	0 h	72 h	Solvent	0 h	72 h
DMSO			Methanol		
Acetonitrile			Chloroform		
Acetone			Tetrahydrofuran		
Cyclohexane			Water		
Air					

Table S2 The guest volume and three-dimensional values

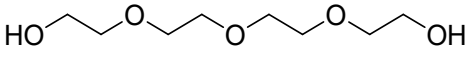
Guest	Length (Å)	Width (Å)	Height (Å)	Volume (Å^3)	Standard Deviation (Å^3)
G**1**	7.9	11.1	4.3	377.1	3.6
G**2**	9.5	8.0	4.2	319.2	2.9
G**3**	7.9	6.9	3.4	185.3	2.1
G**4**	7.0	6.7	11.6	543.0	2.4
G**5**	12.4	7.3	4.3	389.2	5.5
G**6**	8.6	6.6	3.4	193.0	3.3
G**7**	7.1	9.4	4.2	280.3	4.4
G**8**	8.7	6.7	4.2	244.8	2.6
G**9**	9.2	8.0	4.2	309.1	5.7
G10	10.4	7.7	4.2	336.3	3.9
G11	6.7	9.4	4.2	264.5	4.3
G12	6.6	9.3	4.8	294.6	1.8
G**x**	6.7	7.9	3.4	180.0	3.7
(1*R*)-(-)-menthyl acetate	10.8	8.5	6.7	615.1	2.1
isobornyl acetate	7.6	10.5	7.7	614.5	3.7
tetraethylene glycol	18.1	4.6	4.2	349.7	1.2



(1*R*)-(-)-Menthyl acetate



Isobornyl acetate



Tetraethylene glycol

Table S3 Crystal data and refinement details of ZrFMOF ⊃ Guests

Items	ZrFMOF	ZrFMOF ⊃ G1	ZrFMOF ⊃ G2	ZrFMOF⊃ G3	ZrFMOF ⊃ G4	ZrFMOF ⊃ G5
Formula	$C_{27}H_{18}O_9Zr_2$	$C_{27}H_{18}O_9Zr_2$ 1*0.5($C_9H_{12}O_3$)	$C_{27}H_{18}O_9Zr_2$ 1*0.5($C_8H_{10}O_2$)	$C_{27}H_{18}O_9Zr_2$ 1*0.5(C_6H_5NO)	$C_{27}H_{18}O_9Zr_2$ 1*0.5($C_{12}H_{16}$)	$C_{27}H_{18}O_9Zr_2$ 1*0.3($C_{10}H_{12}O_2$)
Mw [gmol−1]	668.87	752.97	737.95	722.43	1366.75	743.60
System	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic
Space group	Cccm	Cccm	Cccm	Cccm	Cccm	Cccm
a(Å)	19.0405(10)	18.9944(9)	22.8364(11)	19.4439(11)	19.2754(2)	22.3775(3)
b(Å)	37.8444(16)	37.2177(10)	37.7706(16)	37.9177(9)	38.2023(4)	37.2623(2)
c(Å)	33.2803(14)	33.8899(8)	31.0109(8)	32.9874(8)	32.7080(3)	31.8466(2)
α(°)	90	90	90	90	90	90
β(°)	90	90	90	90	90	90
γ(°)	90	90	90	90	90	90
V(Å)	23981.0(19)	23957.7(14)	26748.3(18)	24320.6(16)	24085.0(4)	26554.9(4)
Z	8	8	8	8	8	8
Rint	0.0939	0.0676	0.0809	0.1068	0.0466	0.0384
GOOF	1.016	1.016	0.921	0.983	1.084	1.074
Temp. (K)	100.00(3)	100.00(2)	99.97(13)	99.96(17)	100.00(3)	99.98(11)
R1 [I >2σ(I)]	0.0760	0.0614	0.0708	0.0919	0.0571	0.0671
wR2(all data)	0.2244	0.1917	0.1699	0.2722	0.1849	0.2230
F(000)	4816.0	9568.0	5408.0	5272.0	8263.0	9486.0
CCDC No.	2365295	2365280	2365281	2365282	2365283	2365284

Items	ZrFMOF ⊃ G6	ZrFMOF ⊃ G7	ZrFMOF ⊃ G8	ZrFMOF ⊃ G9	ZrFMOF ⊃ G10
Formula	$C_{27}H_{18}O_9Zr_2$ 1*0.5(C_6H_5NO)	$C_{27}H_{18}O_9Zr_2$ 1*0.5(C_7H8O)	$C_{27}H_{18}O_9Zr_2$ 1*1(C_7H_7NO)	$C_{27}H_{18}O_9Zr_2$ 1*0.5($C_8H_{11}N$)	$C_{27}H_{18}O_9Zr_2$ 2*0.5($C_8H_9O_2N$)
Mw [gmol−1]	1412.66	722.43	810.01	729.46	820.03
System	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic
Space group	Cccm	Cccm	Cccm	Cccm	Cccm
a(Å)	21.6496(9)	22.2314(17)	21.1899(6)	23.5292(10)	23.1592(6)
b(Å)	37.8092(6)	36.9241(14)	37.5303(4)	37.2735(12)	37.0815(6)
c(Å)	31.7775(8)	32.4312(19)	32.4114(4)	31.0881(8)	31.6487(6)
α(°)	90	90	90	90	90
β(°)	90	90	90	90	90
γ(°)	90	90	90	90	90
V(Å)	26011.6(13)	26622(3)	25775.6(8)	27264.8(16)	27179.2(10)
Z	8	8	8	8	8
Rint	0.0713	0.0974	0.0531	0.0764	0.0812
GOOF	1.094	1.016	1.052	1.003	1.083
Temp. (K)	100.00(10)	99.90(2)	99.90(2)	100.00(11)	99.90(2)
R1 [I >2σ(I)]	0.1066	0.1006	0.0759	0.0848	0.0943
wR2(all data)	0.3269	0.3141	0.2416	0.2592	0.2872
F(000)	5264.0	9172.0	8976.0	9488.0	8729.0
CCDC No.	2365285	2365288	2365286	2365287	2365291

Items	ZrFMOF ⊃ G11	ZrFMOF⊃ G12	ZrFMOF ⊃ Gx	ZrFMOF⊃ 1&G8	ZrFMOF⊃G8&G10
Formula	$C_{27}H_{18}O_9Zr_2$ 2*0.5(C_7H_7NO) 1*0.3(C_7H_7NO)	$C_{27}H_{18}O_9Zr_2$ 2*0.5($C_6H_8N_2$)	$C_{27}H_{18}O_9Zr_2$ 1*1($C_5H_6N_2$) 1*0.5(C_5H_6N)	$C_{27}H_{18}O_9Zr_2$ 1*0.5($C_9H_{12}O_3$)1*1(C_7H_7NO)	$C_{27}H_{18}O_9Zr_2$ 1*0.5(C_7H_7NO) 1*0.5($C_8H_9O_2N$)
Mw [gmol−1]	951.53	777.01	810.04	874.08	805.02
System	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic
Space group	Cccm	Cccm	Cccm	Cccm	Cccm
a(Å)	18.9051(4)	19.7517(3)	19.4928(4)	20.251(2)	22.1551(12)
b(Å)	37.6655(4)	37.5759(3)	37.3531(4)	37.6068(17)	37.5903(9)
c(Å)	33.4943(3)	33.2955(3)	33.5842(4)	32.8102(16)	31.7670(10)
α(°)	90	90	90	90	90
β(°)	90	90	90	90	90
γ(°)	90	90	90	90	90
V(Å)	23850.3(6)	24711.5(5)	24453.2(6)	24988(3)	26456.1(18)
Z	8	8	8	8	8
Rint	0.0414	0.0354	0.0417	0.1461	0.1260
GOOF	1.098	1.064	1.091	0.922	1.009
Temp (K)	100.00(2)	100.01(10)	100.01(11)	100.0(3)	99.9(5)
R1 [I >2σ(I)]	0.0715	0.0685	0.0789	0.0986	0.1141
wR2(all data)	0.2445	0.2257	0.2478	0.3003	0.3386
F(000)	7861.0	9768.0	9980.0	6584.0	6000.0
CCDC No.	2365290	2365289	2365294	2365292	2365293

Table S4. C-H···π intermolecular interactions in ZrFMOF ⊃ Guests

Host-Guest	X-H···Cg	H···Cg(Å)	X-H···Cg(°)	X···Cg(Å)
ZrFMOF⊃G**1**	None			

Host-Guest	X-H···Cg	H···Cg(Å)	X-H···Cg(°)	X···Cg(Å)
ZrFMOF⊃G**2**	C4-H4···Cg1	2.80(0)	149	3.64(0)

Symmetry codes: x, y, 1-z; Cg1 is the centroid of C2, C3, C4, C5, C6, C7.

Host-Guest	X-H···Cg	H···Cg(Å)	X-H···Cg(°)	X···Cg(Å)
ZrFMOF⊃G**3**	None			

Host-Guest	X-H···Cg	H···Cg(Å)	X-H···Cg(°)	X···Cg(Å)
ZrFMOF ⊃G**4**	C11-H11···Cg1a	3.23(1)	145	4.05(0)
	C1-H1B···Cg2b	2.77(0)	154	3.68(0)

Symmetry codes: [a]1/2-x, 1/2-y, -z; [b]1/2-x, 1/2-y, z;Cg1 is the centroid of C20,C21,C22,C23,C24,C25;Cg2 is the centroid of C20, C21, C22, C23, C24, C25.

Host-Guest	X-H···Cg	H···Cg(Å)	X-H···Cg(°)	X···Cg(Å)
ZrFMOF⊃G**5**	C5-H5···Cg1	2.65(1)	171	3.60(1)

Symmetry codes: x, y, z; Cg1 is the centroid of C31, C32, C33, C34, C35, C36.

Host-Guest	X-H···Cg	H···Cg(Å)	X-H···Cg(°)	X···Cg(Å)
ZrFMOF⊃G**6**	C4-H4···Cg1	2.47(0)	161	3.39(2)

Symmetry codes: x, y, z; Cg1 is the centroid of C27, C28, C29, C30, C31, C32.

Host-Guest	X-H···Cg	H···Cg(Å)	X-H···Cg(°)	X···Cg(Å)
ZrFMOF⊃G**7**	C29-H29···Cg1	3.17(1)	127	3.82(1)

Symmetry codes: x, y, z; Cg1 is the centroid of C2, C3, C4, C5, C6, C7.

Host-Guest	X-H···Cg	H···Cg(Å)	X-H···Cg(°)	X···Cg(Å)
ZrFMOF⊃G**8**	None			

Host-Guest	X-H···Cg	H···Cg(Å)	X-H···Cg(°)	X···Cg(Å)
ZrFMOF⊃G**9**	C5-H5···Cg1	3.19(1)	140	3.97(3)

Symmetry codes: x, y, z; Cg1 is the centroid of C16, C17, C18, C19, C20, C21.

Host-Guest	X-H···Cg	H···Cg(Å)	X-H···Cg(°)	X···Cg(Å)
ZrFMOF⊃G**10**	C22-H22···Cg1a	3.25(1)	147	4.08(1)
	C14-H14···Cg2b	2.93(0)	140	3.72(2)

Symmetry codes: [a]x, y, 1-z; [b]x, y, z; Cg1a is the centroid of C3, C4, C5, C6, C7, C8; Cg2b is the centroid of C18, C19, C20, C21, C22, C23,

Host-Guest	X-H···Cg	H···Cg(Å)	X-H···Cg(°)	X···Cg(Å)
ZrFMOF⊃G**11**	C1-H1···Cg1a	2.82(0)	170	3.76(2)
	C2-H2···Cg2b	2.48(1)	162	3.40(1)

Symmetry codes: [a]x, y, z; [b]1-x, y, 3/2-z; Cg1a is the centroid of C36, C37, C38, C39, C40, C41; [b]1-x, y, 3/2-z; Cg2b is the centroid of C42, C43, C44, C45, C46, C47.

Host-Guest	X-H···Cg	H···Cg(Å)	X-H···Cg(°)	X···Cg(Å)
ZrFMOF⊃G**12**	C32-H32···Cg1a	2.77(1)	171	3.71(2)
	C38-H38···Cg2b	3.16(0)	139	3.88(1)

Symmetry codes: [a]1-x, y, 1/2+z; [b]1-x, y, 1/2+z; Cg1a is the centroid of C8, C9, C10, C11, C12, C13; Cg2b is the centroid of C15, C16, C17, C18, C19, C20.

Host-Guest	X-H···Cg	H···Cg(Å)	X-H···Cg(°)	X···Cg(Å)
ZrFMOF⊃G**x**	C10-H10···Cg1a	2.31(1)	167	3.26(1)
	C16-H16···Cg2b	3.02(0)	140	3.80(1)

Symmetry codes: [a]1-x, 1-y, 1-z; b1-x, 1-y, 1-z; Cg1a is the centroid of C31, C32, C33, C34, C35, C36; Cg2b is the centroid of C1, C2, C3, C4, C5, N2.

Host-Guest	X-H···Cg	H···Cg(Å)	X-H···Cg(°)	X···Cg(Å)
ZrFMOF ⊃ G**8**&G**10**	C55-H55A···Cg1a	2.78(0)	132	3.49(1)

Symmetry codes: [a]-1/2+x, -1/2+y, z; Cg1a is the centroid of C2, C3, C4, C5, C6, C7.

Table S5. Geometric parameters of the hydrogen bonds in ZrFMOF⊃guests

Host-Guest	Interactions	D−H(Å)	H···A(Å)	D···A(Å)	D-H···A (deg)	Symmetry code
ZrFMOF ⊃G**1**	C31-H31···O3	0.95	3.22(3)	3.80(3)	122	x, y, z
	C16-H16···O1	0.95	2.60(1)	3.47(1)	152	x, y, z
	C15-H15···O2	0.95	2.80(1)	3.64(1)	149	x, y, z
ZrFMOF ⊃G**2**	C19-H19···O14	0.95	2.44(2)	3.60(2)	170	x, y, 1-z
ZrFMOF ⊃G**3**	C4-H4···O3	0.95	2.74(2)	3.51(2)	151	x, y, z
ZrFMOF ⊃G**4**	None					
ZrFMOF ⊃G**5**	C4-H4···O6	0.95	3.45(0)	4.29(1)	149	x, y, z
ZrFMOF ⊃G**6**	C32-H32···N1	0.95	2.88(2)	3.44(2)	118	x, y, z
ZrFMOF ⊃G**7**	None					
ZrFMOF⊃G**8**	C33-H33···O1	0.95	2.77(2)	3.31(2)	117	x, y, z
	O9-H9A···N20	0.87	1.90(1)	2.61(1)	137	x, y, z
ZrFMOF ⊃G**9**	N1-H1B···O8	0.88	2.53(1)	3.25(3)	140	x, y, z
ZrFMOF ⊃G**10**	C39-H39···O10	0.95	2.65(2)	3.56(2)	159	x, y, 1-z
	N18-H18A···O3	0.88	2.52(1)	3.21(2)	136	x, y, z
	C20-H20···O12	0.95	2.41(2)	3.33(2)	165	x, y, z
ZrFMOF ⊃G**11**	C5-H5···O4	0.95	1.62(2)	2.50(2)	154	x, y, z
ZrFMOF ⊃G**12**	N3-H3B···O8	0.95	2.80(0)	3.49(2)	136	x, y, 1-z
	N1-H1D···O1	0.95	2.71(0)	2.78(2)	84	x, y, z
ZrFMOF ⊃ G**x**	N3-H3B···O8	0.88	2.86(4)	3.42(1)	122	x, y, z
	N1-H1A···N1	0.88	2.28(1)	2.67(2)	106	1-x,1-y, 1-z
ZrFMOF⊃G**1**&G**8**	C25-H25···O9	0.93	2.66(3)	3.53(3)	157	x, -1+y, 1-z
	C26-H26···O10	0.93	2.57(3)	3.39(4)	147	x, -1+y, 1-z
	C17-H17···O28	0.93	3.12(3)	3.82(3)	134	1-x, -1+y, -1/2+z
	C32-H32···O3	0.93	2.67(1)	3.27(3)	121	1-x, -1+y, -1/2+z
	O3-H3A···N28	0.88	1.70(2)	2.52(2)	153	1-x, -1+y, -1/2+z
ZrFMOF⊃G**8**&G**10**	O7-H7A···N2	0.87	2.02(1)	2.55(1)	119	-1/2+x, -1/2+y, z
	C25-H25···O11	0.93	2.74(0)	3.60(1)	153	1/2-x,-1/2+y,-1/2+z
	C6-H6···O10	0.93	2.93(1)	3.63(1)	133	1/2-x,-1/2+y,-1/2+z

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