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Stable Zr-UiO-67 constructed through a polymeric network assisted post-synthetic modification strategy and its wettability modulation

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Experimental

1. Materials

Methanol anhydrous, *N*,*N*-dimethylformamide (DMF, 99.5%), hydrochloric acid (36-38%), dichloromethane (CH_2Cl_2, 99.5%), ethylene glycol ($C_2H_6O_2$, 99.5%), Sudan III and methylene blue (MB) were obtained from Cologne Chemical Co., Ltd. (Chengdu, China). 4,4'-biphenyldicarboxylic acid (bpdc, 97%) was obtained from Shanghai Macklin Biochemical Co., Ltd. Pentaerythritol tetra(3-mercaptopropionate) ($C_{17}H_{28}O_8S_4$, 95%) was bought from Saan Chemical Technology (Shanghai) Co., Ltd. Benzoic acid ($C_7H_6O_2$, 99%) was bought from Titan Scientific Co., Ltd. (Shanghai, China). Sodium hydroxide, sodium chloride, glycerol ($C_3H_8O_3$, 99.0%), cyclohexane (C_6H_{12}, 99.5%) and xylene (C_8H_{10}, 99%) were obtained from Chongqing Chuandong Chemical (Group) Co., Ltd. *o*-Dichlorobenzene ($C_6H_4Cl_2$, 98%), zirconium (IV) chloride (≥99.9%). 1*H*,1*H*,2*H*-perfluoro-1-decene ($C_{10}H_3F_{17}$, 98%), 1*H*,1*H*,2*H*-perfluoro-1-hexene ($C_6H_3F_9$, 97%) and 2-hydroxy-2-methyl propiophenone ($C_{10}H_{12}O_2$, 97%) were purchased from Aladdin Biochemical Technology Co., Ltd. (Shanghai, China).

2. Preparation of Zr-UiO-67

The preparation of Zr-UiO-67 was according to previous study [1] with some modification: $ZrCl_4$ (0.5 mmol), 4,4'-biphenyldicarboxylic acid (0.5 mmol) and benzoic acid (15 mmol) were added into DMF (20 mL) under 30 min of ultrasound, forming a milky solution. Then the milky solution was placed into a 50 mL PTFE reaction kettle for a reaction at 120 °C for 24 h. After cooling down to room temperature, the solution was washed with anhydrous methanol for three times and dried in a vacuum drying oven at 60 °C for 12 h to obtain the white Zr-UiO-67 powder.

3. Preparation of UiO-67-SH

Firstly, 1 mL pentaerythritol tetra(3-mercaptopropionate) (PTMP) and 0.1 g polyethylenimine (PEI) were transferred into a 250 mL beaker with 100 mL DMF. After stirring vigorously in water bath at 60 °C for 1 h, a stable and dispersed thiolfunctionalized crosslinking network solution was obtained. Then, 50 mg Zr-UiO-67 powder was added into 20 mL of the above crosslinking solution and stirred for 1 min to wrap the crosslinking network layer on the Zr-UiO-67. Finally, the sample was centrifugally washed with methanol for two times and dried in a vacuum drying oven at 60 °C for 12 h to obtain Zr-UiO-67-SH powder.

4. Preparation of Zr-UiO-67@F_x

The preparation of Zr-UiO-67@F_x was according to our previous work [2] with slight modification: A homogeneous reaction system was obtained by adding 50 mg UiO-67-SH and 1 mL 1*H*,1*H*,2*H*-perfluoro-1-hexene (or 1*H*,1*H*,2*H*-perfluoro-1-decene) into a 25 mL round-bottomed flask with magnetically stirring for 30 min. Then, 0.1 mL 2-hydroxy-2-methyl propiophenone as a catalyst was added into the solution and reacted for 3 h (or 1 h) under the irradiation of a xenon lamp. Finally, the sample was washed with anhydrous methanol for three times and dried in a vacuum drying oven at 60 °C for 12 h to obtain light yellow UiO-67-SH@F_9 (or UiO-67-SH@F_{17}) powder.

5. Characterization

PXRD patterns of MOFs were obtained using a Bruker D8 ADVANCE X-ray diffractometer at this test condition 40 kV and 40 mA. Thermogravimetric analysis (TGA) was conducted on a Netzsch DTG-60H system in nitrogen condition and at a heating rate of 10 °C/min from 25 to 1000 °C. The morphology was observed on a Hitachi SU8010 scanning electron microscope and a Tecnai F30 transmission electron microscopy. Distribution of different elements was also analyzed through the Tecnai F30 transmission electron microscopy. Fourier transform infrared spectroscopy (FTIR) spectra were measured on a NicoletTM iSTM 10 spectrometer. The liquid-state ^{1}H nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance-400 (400 MHz) spectrometer. The static contact angle was investigated by dripping a 5 μL droplet on the flat MOF surface that was impacted by a glass slide, using a Defnuo ZR-SDJ-QH6 contact angle analyzer.

6. Stability testing of the MOFs

At room temperature, a small amount of the MOF powder was added into a vial containing pH=1, pH=12 or 20% NaCl aqueous solution for a period of time. After that, the sample was taken out, washed and dried for PXRD characterization to analyze the change of crystallinity. Stability of the samples was obtained by comparing the PXRD spectra before and after the test.

7. Liquid separation applications of MOFs

7.1 Preparation of the liquid mixture

Dichloromethane and water were dyed red and blue with a small amount of Sudan III and methylene blue, respectively. Layered dichloromethane/water mixture was obtained by mixing 20 mL dichloromethane with 20 mL water. Dichloromethane/ethylene glycol incompatible organic liquid mixture was prepared by mixing 20 mL dichloromethane with 20 mL glycol. Because the density of dichloromethane is larger than water and ethylene glycol, dichloromethane is in the bottom layer.

7.2 Preparation of liquid emulsion

0.5 mL deionized water was added into 50 mL organic solvent (*o*-dichlorobenzene, cyclohexane and xylene) and stirred vigorously for 1 h, obtaining milky water-in-*o*-dichlorobenzene, water-in-cyclohexane and water-in-xylene emulsions.

7.3 Liquid separation process

A homemade separation device was used for the liquid separation. For the separation of layered liquids, the cotton was filled in the narrow head of the syringe as the support, and MOFs powder is placed on the support as the separation layer to get a simple separator. The dichloromethane/water or dichloromethane/ethylene glycol mixture was slowly poured into the upper part of the syringe. The separation was proceeded under gravity. For the separation of liquid emulsion, a micro-filtration filter head and a cotton layer were needed as the supporting layer. A compacted MOFs layer is placed on top of the cotton layer. The separation was driven by a certain extra pressure.

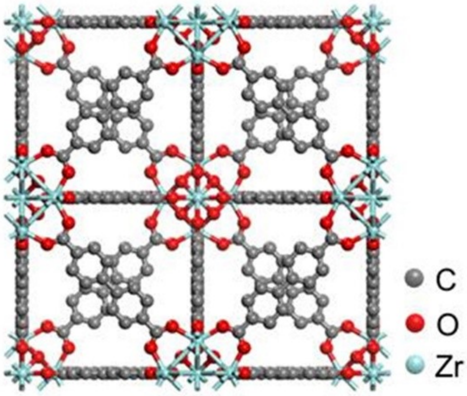


Fig. S1 The chemical structure of Zr-UiO-67.

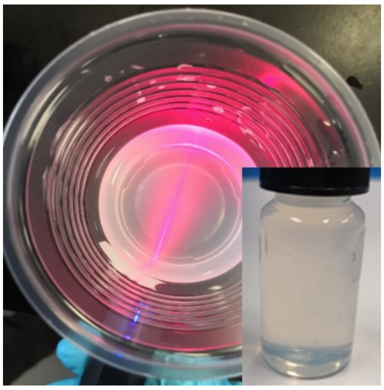


Fig. S2 The PEI@PTMP crosslinking network solution with a Tyndall effect.

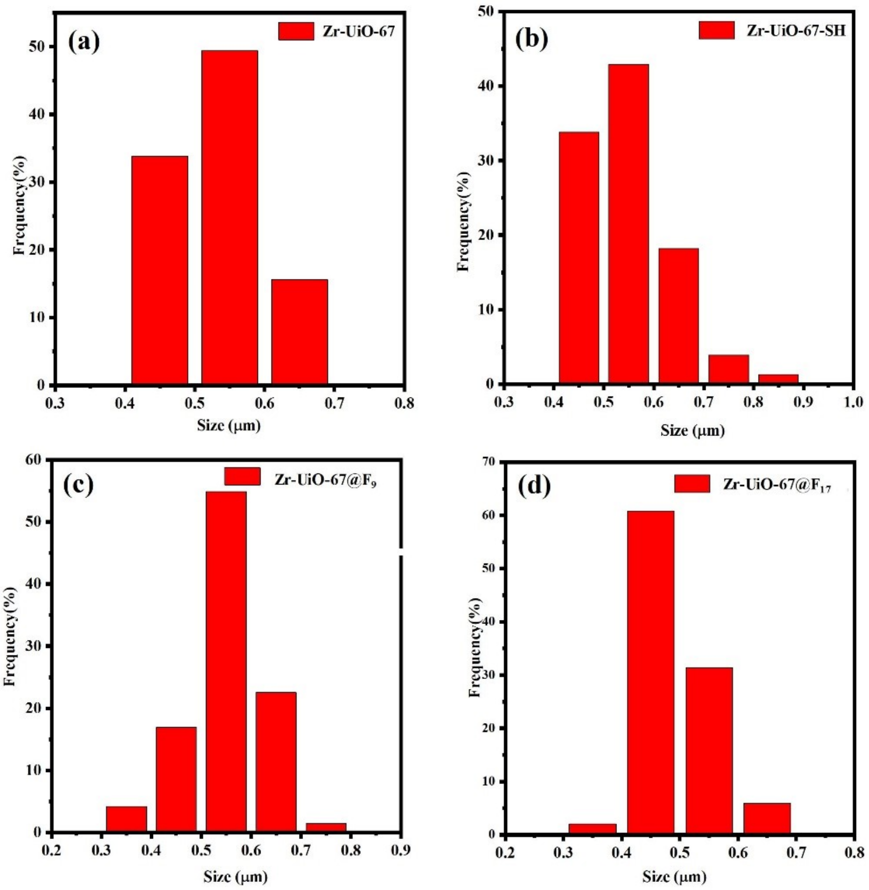


Fig. S3 Size distribution of the MOFs: (a) Zr-UiO-67, (b) Zr-UiO-67-SH, (c) Zr-UiO-67@F_9 and (d) Zr-UiO-67@F_{17}.

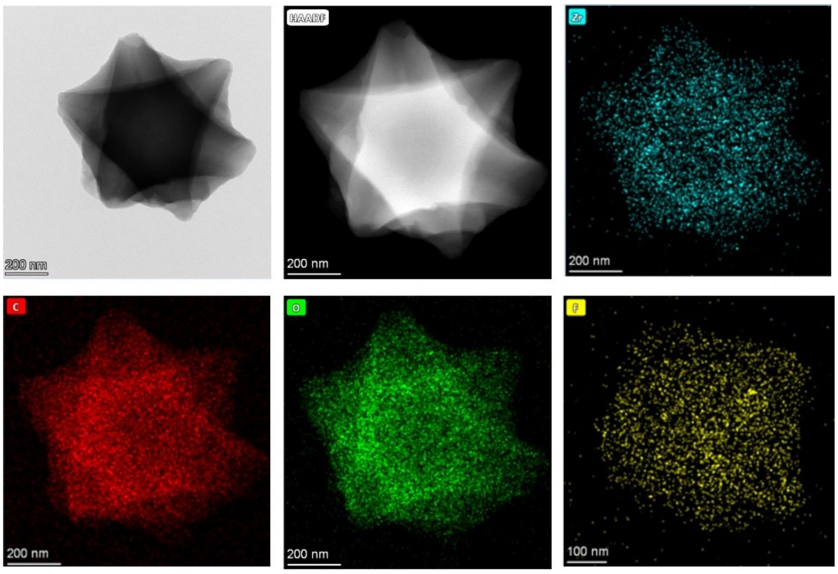


Fig. S4 TEM image of Zr-UiO-67@F_{17} and corresponding elemental mapping of Zr, C, O, and F.

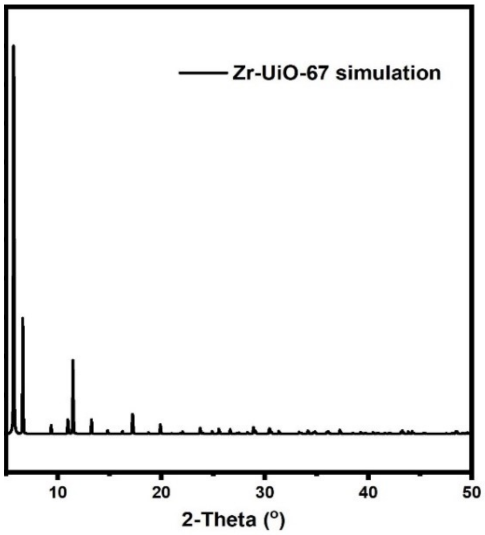


Fig. S5 The simulated XRD pattern of Zr-UiO-67.

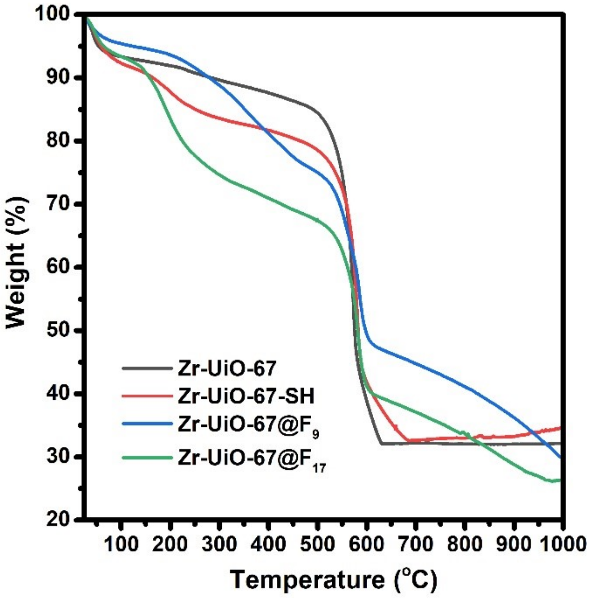


Fig. S6 TGA curves of the MOFs.

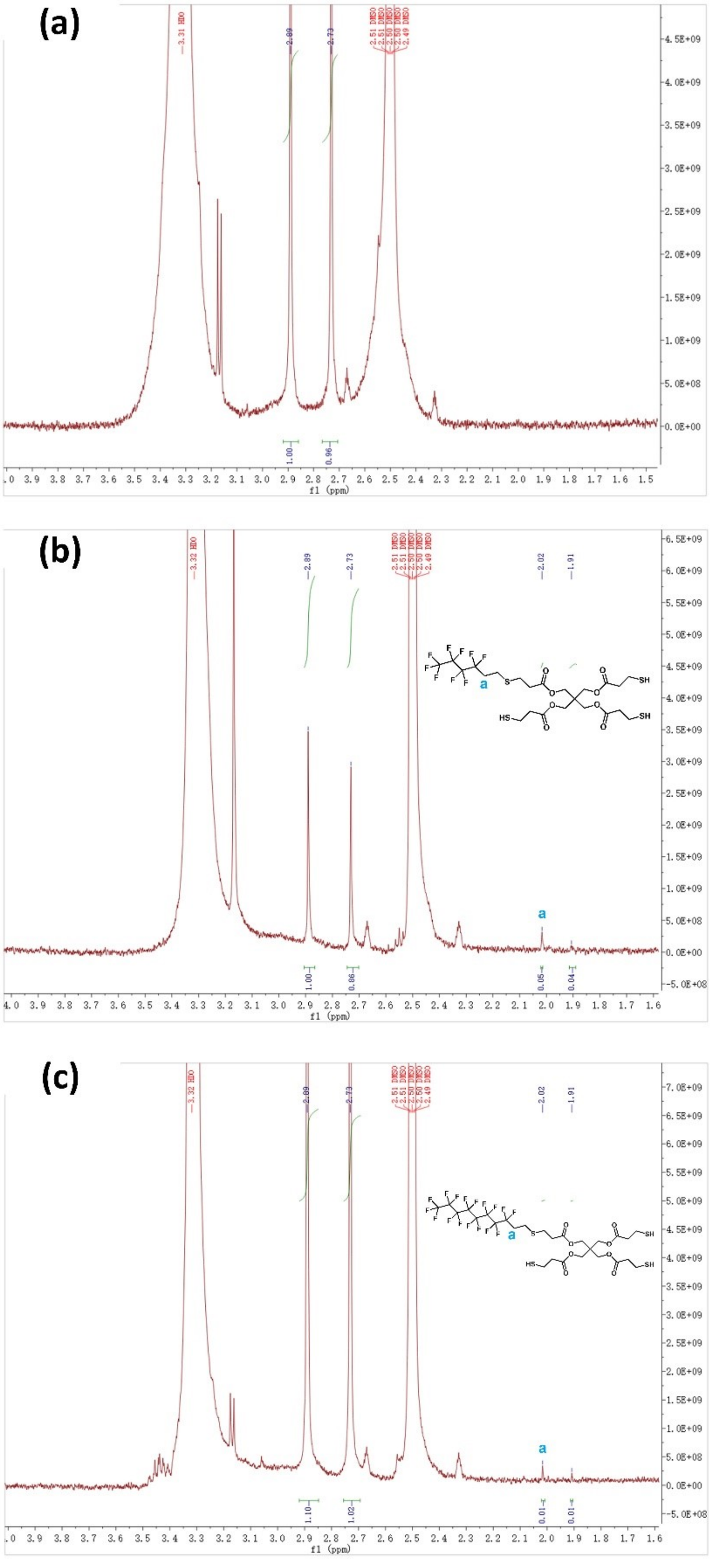


Fig. S7 ^{1}H NMR spectra of (a) Zr-UiO-67-SH, (b) Zr-UiO-67@F_9 and (c) Zr-UiO-67@F_{17}.

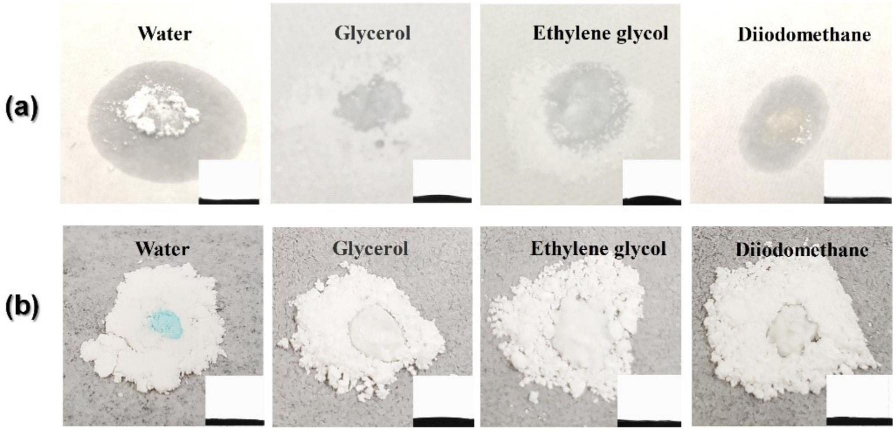


Fig. S8 Wetting state of different liquid droplets on (a) Zr-UiO-67 and (b) Zr-UiO-67-SH.

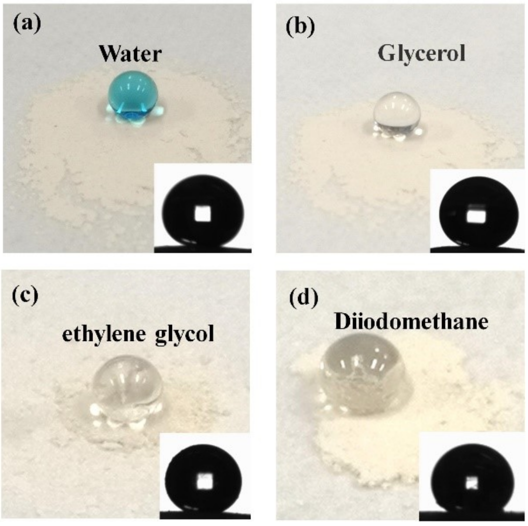


Fig. S9 Wetting state of different liquid droplets on Zr-UiO-67@F_{17}: (a) water, (b) glycerol, (c) ethylene glycol, and (d) diiodomethane.

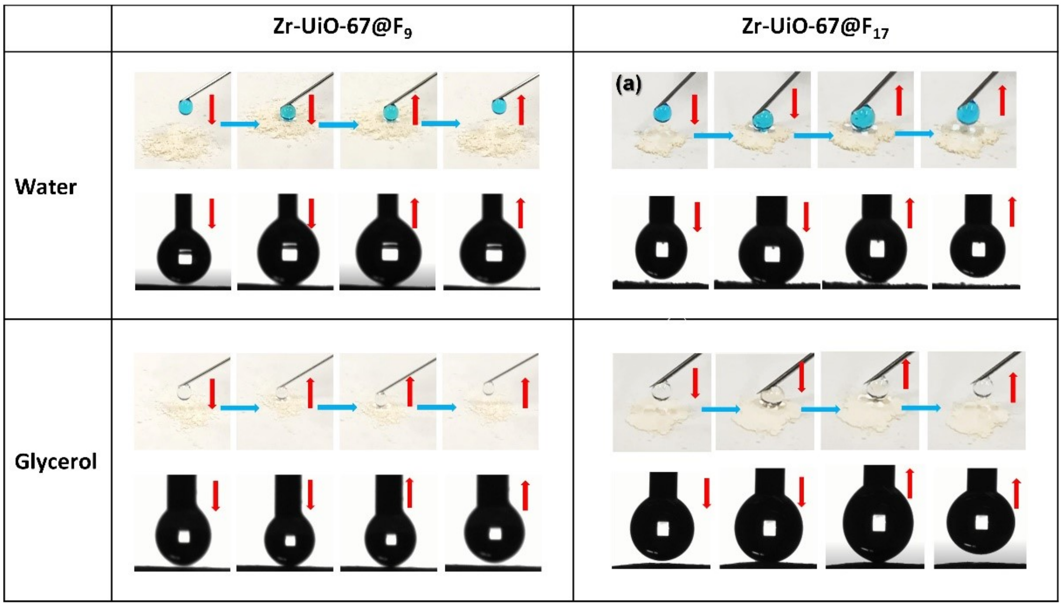


Fig. S10 Continuous photographs show the repellence of Zr-UiO-67@F_9 and Zr-UiO-67@F_{17} for water and glycerol droplets.

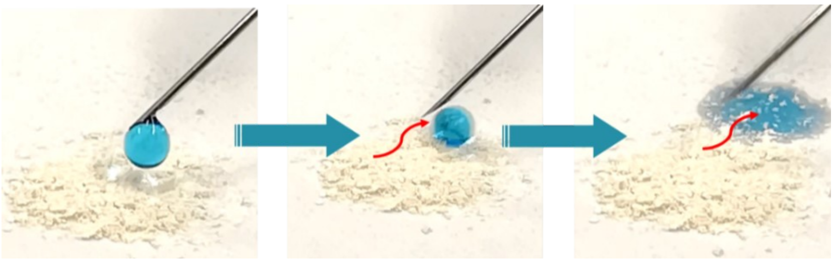


Fig. S11 Dynamic processes of a water droplet sliding on the Zr-UiO-67@F_9 surface.

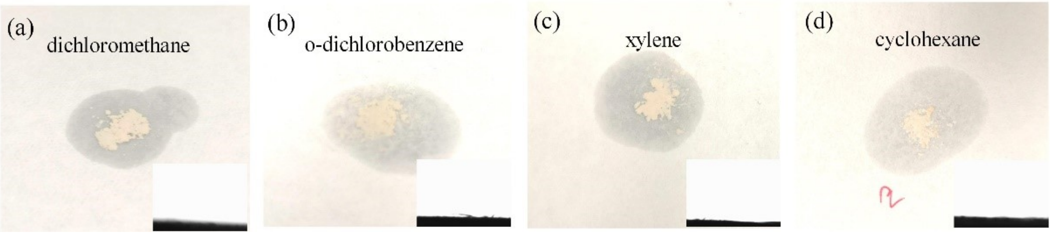
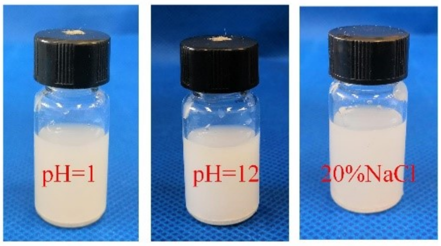
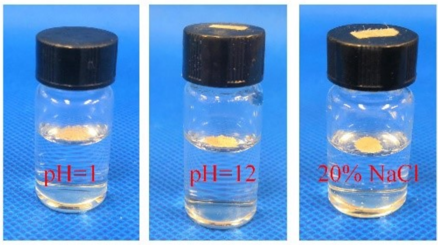


Fig. S12 Wetting state of different organic droplets on Zr-UiO-67@F_9: (a) dichloromethane, (b) *o*-dichlorobenzene, (c) xylene, and (d) cyclohexane.

(a) Zr-UiO-67



(b) Zr-UiO-67@F_9



(c) Zr-UiO-67@F_{17}

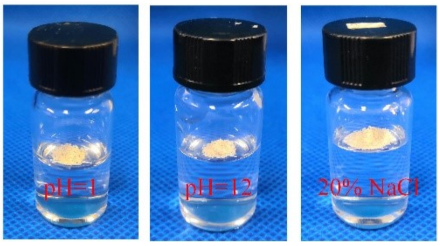


Fig. S13 Digital images of (a) Zr-UiO-67, (b) Zr-UiO-67@F_9 and (c) Zr-UiO-67@F_{17} in different harsh solutions.

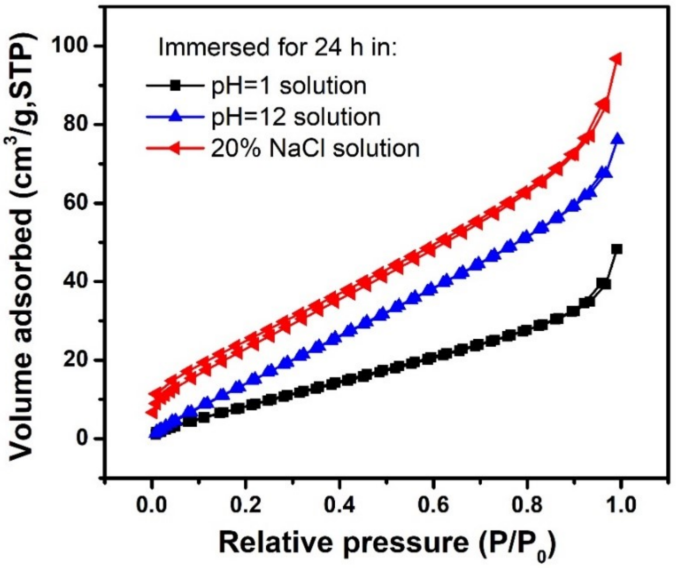


Fig. S14 Nitrogen adsorption-desorption isotherms of Zr-UiO-67@F_9 after immersed in different chemical solutions for 24 h.

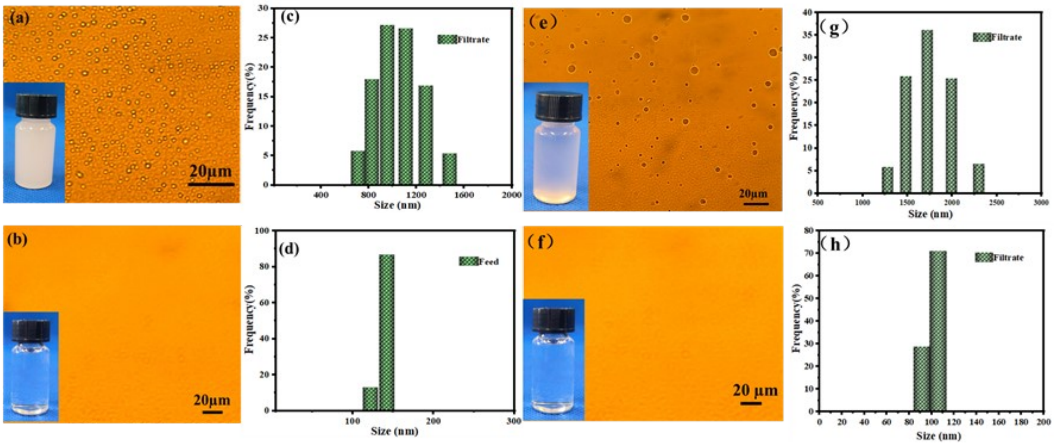


Fig. S15 Separation of two water-in-oil emulsions by Zr-UiO-67@F_9: Optical image of water-in-*o*-dichlorenzene emulsion before (a) and after (b) filtration. Particle size distribution of water droplets in water-in-*o*-dichlorenzene emulsion before (c) and after (d) filtration; Optical image of water-in-cyclohexane emulsion before (e) and after (f) filtration. Particle size distribution of water droplets in water-in-cyclohexane emulsion before (g) and after (h) filtration.

Video S1. Dynamic water and glycerol repelling on the Zr-UiO-67@F_9.

Video S2. Water sliding on the Zr-UiO-67@F_9.

Video S3. Separation of dichloromethane/water and dichloromethane/ethylene glycol mixtures by the Zr-UiO-67@F_9.

References

[1] Wang K., Huang H., Zhou X., et al., Highly chemically stable MOFs with trifluoromethyl groups: Effect of position of trifluoromethyl groups on chemical stability. *Inorg. Chem.*, **2019**, *58*, 5725-5732.

[2] Du J., Chen L., Zeng X., et al., Hard-and-soft integration strategy for preparation of exceptionally Stable Zr(Hf)-UiO-66 via thiol-ene click chemistry. *ACS Appl. Mater. Interfaces*, **2020**, *12*, 28576-28585.