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Supplemental Information

One-Step Synthesis of Superhydrophobic Zeolitic Imidazolate Framework F-ZIF-90 for Efficient Removal of Oil

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Experimental details:

Chemicals were used as received: Zinc nitrate hexahydrate (>99%, Aladdin), imidazolate-2-carboxyaldehyde (ICA, >99%, Alfa Aesar), Sodium formate (99.99%, Aladdin), methanol (>99.5 %, Sinopharm Chemical Reagent Co., Ltd), ethanol (>99.5%, Sinopharm Chemical Reagent Co., Ltd), 2,3,4,5,6-pentafluoroaniline (>98%, Aladdin), p-toluenesulfonic acid monohydrate (PTSA, 98%, Aladdin), dopamine (98%, Aladin), tris(hydroxymethyl) aminomethane (Tris–HCl, 99%, Aladin), oil red (Aladdin), methylene blue (Sinopharm Chemical Reagent Co., Ltd.), and doubly distilled water. Various kinds of oil (soybean oil, CCl_4, methylbenzene, acetone, diesel oil, gasoline, *n*-hexane and CH_2Cl_2) were bought from Aladdin. The self-priming pump (direct current diaphragm pump R385 with working voltage of 6-12 V), sponge and Teflon tubes (1 mm inner diameter and 3 mm outer diameter) were obtained from Crab Kingdom Diy Model Materials. Gasoline and diesel oil were purchased from local China Sinopec gas station. Crude oil was provided by China University of Petroleum (Ningbo).

Synthesis of fluorine-functionalized imidazole ligand: The fluorine-functionalized imidazolate-2-carboxyaldehyde (F-ICA) was prepared through amino condensation of 2,3,4,5,6-pentafluoroaniline with imidazolate-2-carboxyaldehyde (ICA) in ethanol by using p-toluenesulfonic acid (PTSA) as a catalyst. [1] Typically, 4 mmol imidazolate-2-carboxyaldehyde and 4 mmol 2,3,4,5,6-pentafluoroaniline was added into 10 ml ethanol in a round bottom flask, and then adding 0.0472 mmol of p-toluenesulfonic acid monohydrate. The reaction solution was heated under stirring and reflux at 80 ºC for 24 h. After removed the ethanol solvent, the crude product was column chromatographed over silica gel using using CH_2Cl_2/hexanes to give the product as white solid in ~98% yield based on imidazole-2-formaldehyde. ^{1}H NMR (400 MHz, DMSO-d_6): 8.58 (s, 1H), 7.02 (s, 2H). ^{19}F NMR (377 MHz, DMSO-d_6) δ -162.05– -162.23 (m, 2F), -166.13 – -166.56 (m,2F), -178.36 (s,1F).

Synthesis of superhydrophobic ZIF-90: The superhydrophobic ZIF-90 (hereafter called F-ZIF-90) was synthesized in a Teflon-lined autoclave by solvothermal synthesis method as reported previously. [2] A solid mixture of zinc nitrate hexahydrate (1.00 mmol), fluorine-functionalized imidazole-2-

formaldehyde (4.00 mmol), and sodium formate (1.00 mmol) was dissolved in 40 ml methanol by ultra sonic treatment. The as-prepared solution were placed in a Teflon-lined stainless steel autoclave, and heated at 85 ºC in an air-circulating oven for 24 h. Finally, the crystalline powder obtained was filtered and washed with methanol three times, and dried for 24 h at room temperature.

Computational construction of MOF crystal structures: Since it is hard to synthesis perfect large single F-ZIF-90 crystals, it is challenging to collect a serial of well enough diffraction data to solve its crystal structure by using single-crystal X-ray diffraction. However, the powder X-ray diffraction (PXRD) of F-ZIF-90 is very similar with ZIF-90's PXRD. Considering the PXRD of ZIF-90, we assume that F-ZIF-90 may be isostructual with ZIF-90. From the previous works, it is reported that ZIF-90 possesses SOD topology in which SOD corresponds to a cubic unit cell of *I43m* symmetry. Therefore we tried to use a reverse topological approach to build F-ZIF-90 structure by combination of computational construction and the structure parameter of existed ZIF-90 crystals.

Typically, we followed a reverse topological approach to computational construction of the F-ZIF-90 structure (Figure S1). The details are the following steps:

(1) The ZIF-90 structure of SOD topology which corresponds to an *I43m* symmetry with the 24-coordinated sites located at [0.5, 0.25, 0] (Figure S1a), used as a topological template to guide the placements of the F-ZIF-90 by using the Crystal Builder module of Materials Studio.[3] (2) replace the 24-coordinated vertexes with Zn^{2+} ions (Figure S1b); (3) build and optimize the fragment of F-ICA (fluorine-functionalized imidazolate-2-carboxyaldehyde) linker to form F-ICA^{2-} fragment; (4) place the F-ICA^{2-} fragment into the suitable positions of the unit cell to construct the preliminary model (Figure S1c) to obtain the preliminary structure of F-ZIF-90; and (5) optimize the preliminary structure of F-ZIF-90 by molecular simulation with Forcite module implemented in Materials Studio software (Figure S1d).[4] The Universal force field (UFF) was used to describe the bonded and non-bonded interactions, but the potential parameter of the Zn^{2+} ion was assigned according to the UFF4MOF force field. Finally, to verify the credibility of F-ZIF-90 model, we calculated the PXRD pattern of computational model of F-ZIF-90. When compared with experimental PXRD pattern, our simulated PXRD pattern was in good agreement

with the experimental PXRD data of F-ZIF-90, indicating the computationally generated structure is credible. Similar method using computationally building to work out the structures of MOF crystals has been widely adopted previously. [3-8]

Preparation of PDA@sponge: A commercially available macroporous sponge was cleaned by water and acetone several times, followed by drying at 100 °C overnight and cutting into small cubes (approximately 1 × 1 × 1 cm^3). The PDA@sponge was prepared according to a published procedure with slight modification. [32,33] Dopamine (2 mg mL^{-1}) was dissolved in 10 mM Tris–HCl (pH 8.5) in an open watch glass (diameter: 180 mm). And then the cleaned-sponge was added to contact the dopamine solution (50 mL). The solution was stirred for 24 h at 25 °C, leading to a polydopamine layer being deposited on the inner surface macroporous sponge. Then the PDA@sponge was washed with de-ionized water several times and dried in air at 50 °C overnight.

Preparation of F-ZIF-90@PDA@sponge: A mixture of zinc nitrate hexahydrate (1.00 mmol), fluorine-functionalized imidazole-2-formaldehyde (4.00 mmol), sodium formate (1.00 mmol), and 40 ml methanol was placed in a 50 ml Teflon-capped autoclave and sonicated to obtain a homogeneous solution by ultra sonic treatment. The as-prepared PDA@sponge was put into the solution, and the autoclave was then sealed and heated at 85 ºC for 24 h. After cooling down to room temperature the F-ZIF-90@PDA@sponge was washed with methanol three times, and dried at room temperature for 24 h.

Characterization of F-ZIF-90 and F-ZIF-90@PDA@sponge: The morphology of the ZIF-90 and F-ZIF-90 were characterized by field emission scanning electron microscopy (FESEM). FESEM micrographs were taken on an S-4800 (Hitachi) with a cold field emission gun operating at 4 kV and 10 μA. The phase purity and crystallinity of the ZIF-90 and F-ZIF-90 were confirmed by X-ray diffraction (XRD). The XRD patterns were recorded at room temperature under ambient conditions with Bruker D8 ADVANCE X-ray diffractometer with CuKa radiation at 40 kV and 40 mA. FT-IR spectra of ZIF-90 crystals and F-ZIF-90 crystals were obtained by using Bruker TENSOR27 Impact spectrometer. Nuclear magnetic resonance (NMR) spectra were obtained at ambient temperature using a Bruker 400 MHz instrument (NMR Switzerland Bruker 400 MHz AVANCE III). The signals are presented relative to TMS

as 0 ppm, and DMSO was used for solvent. Thermal stability test was carried by TGA analyizer. Thermogravimetric analyses (TGA) were carried out using a Mettler Toledo TGA/STDA 851e. Samples (10 mg) placed in 70 μL alumina pans were heated in a nitrogen flow from 0 to 900 ºC at a heating rate of 5 ºC/min. BET surface area measurements were collected at 77 K using nitrogen on an automatic volumetric adsorption apparatus (Micrometrics ASAP 2020). Prior to measurements, the samples were heated at 150 °C for 16 h under vacuum. After adsorption, the samples were regenerated by degassing under vacuum at room temperature for a few hours. The water contact angle (CA) was measured with a Dataphysics OCA20 contact-angle system at room temperature under ambient conditions. Water droplets (about 2 μL) were dropped carefully onto the membrane surface. The contact angle value for each sample was obtained by measuring four different positions of the same sample and averaging them to get the final contact angle value.

Absorption of oils or organics solvents by using the F-ZIF-90@PDA@Sponge: Different types of oil or organic solvents with different densities, including soybean oil, CCl_4, methylbenzene, acetone, diesel oil, gasoline, *n*-hexane and CH_2Cl_2, were used in this study. Typically, a piece of superhydrophobic F-ZIF-90@PDA@sponge was immersed to a kind of oil or organic solvent until it was completely filled with the oil or organic solvents. Subsequently, the superhydrophobic F-ZIF-90@PDA@sponge saturated with the oil or organic solvent was taken out for weight measurement. The weight of the superhydrophobic F-ZIF-90@PDA@sponge (*one piece*) before and after absorption was recorded for calculating the weight gain, as illustrated as following equation.

$$Weight_{gain}(\%) = \frac{M_{after} - M_{before}}{M_{before}} \times 100\%$$

where M_{after} was the weight of the F-ZIF-90@PDA@sponge after adsorption (mg), and M_{before} was the weight of the F-ZIF-90@PDA@sponge before adsorption (mg).

Fabrication of the oil collection apparatus: One end of a Teflon tube was inserted into the F-ZIF-90@PDA@sponge sorbent, and the other end was connected to the inlet of the self-priming pump that

was driven by a 1.8 W (6 V × 0.3 A) power supply. Then, the outlet of the self-priming pump was connected to another Teflon tube that was introduced to the collection tank.

Reference

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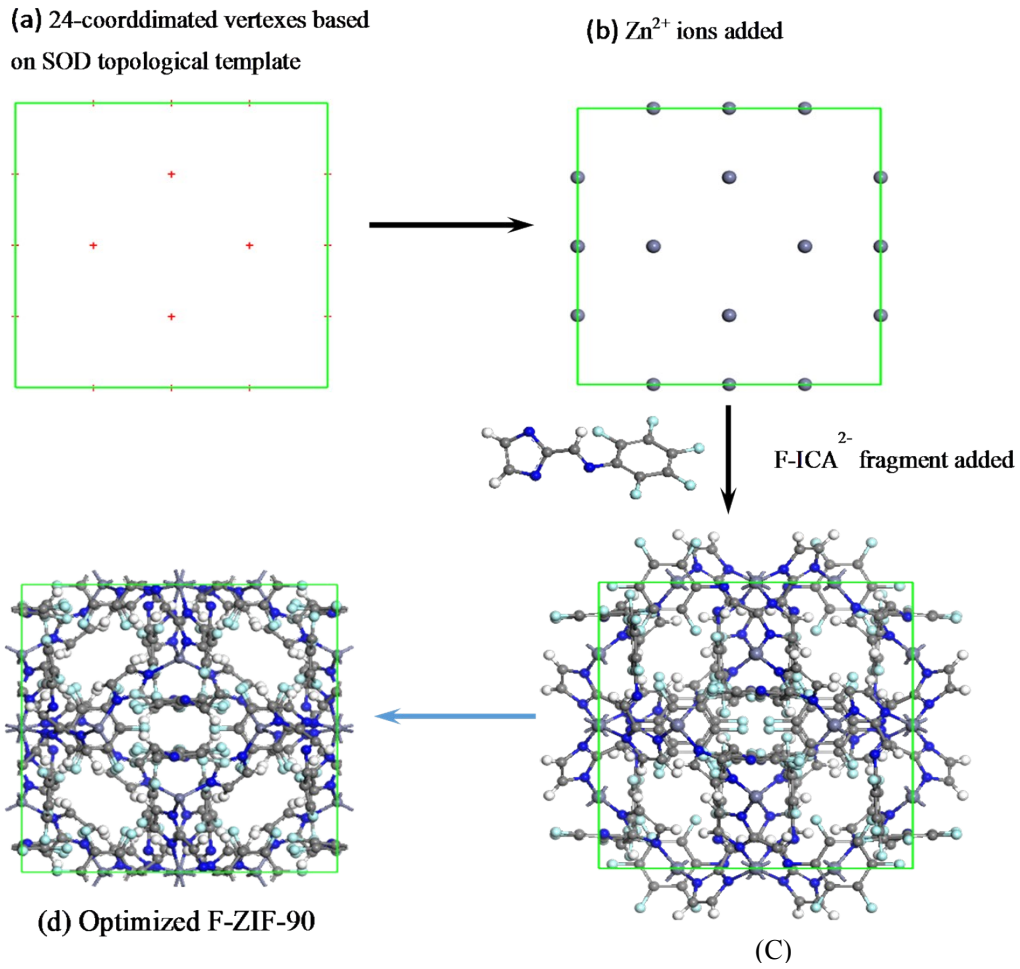

Figure S1. Scheme of of the building of the F-ZIF-90 structure.

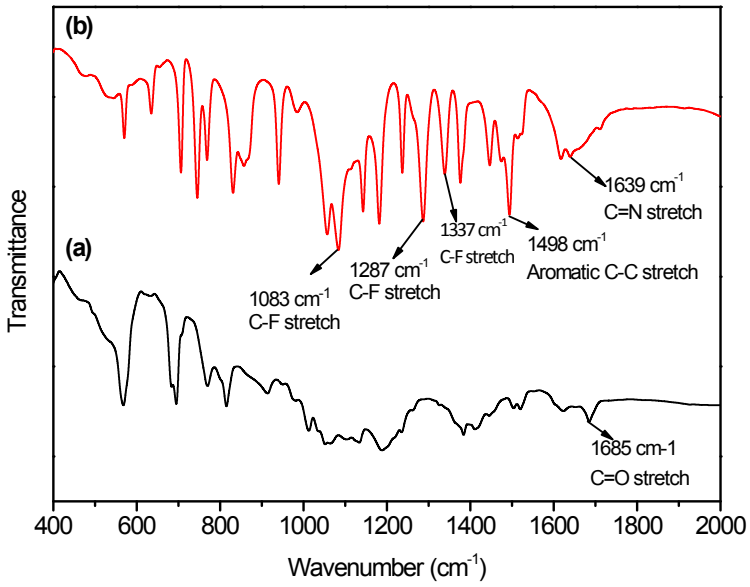

Figure S2. FT-IR spectra of the imidazole-2-formaldehyde (ICA, a), and fluorine-functionalized imidazole-2-formaldehyde (F-ICA, b).

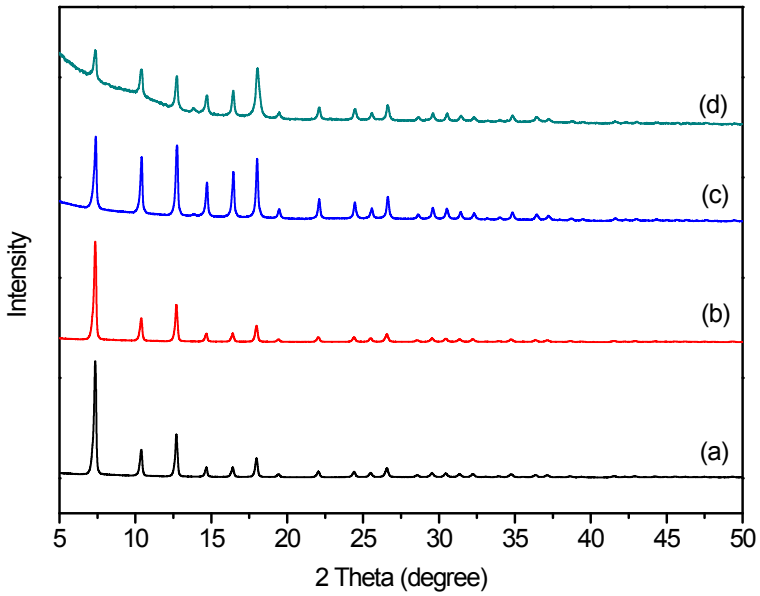

Figure S3. XRD patterns of the F-ZIF-90 samples which were refluxed in water at 100 °C for different time: (a) as-synthesized F-ZIF-90, (b) 1 day, (c) 3 days, (a) 5 days.

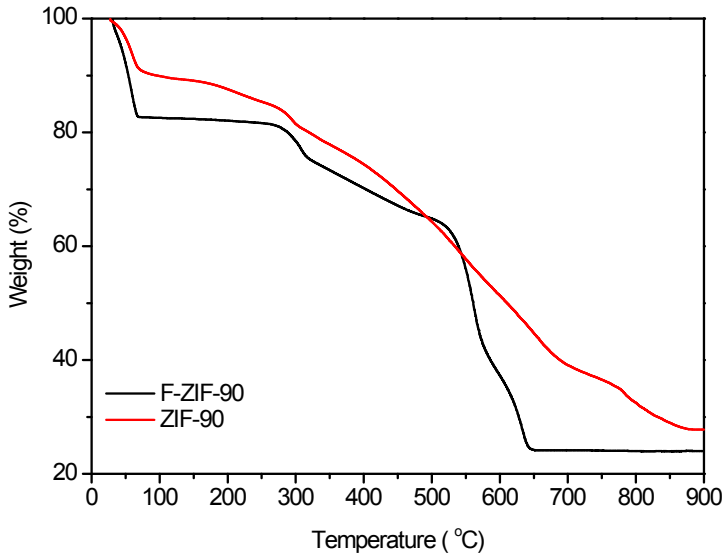

Figure S4. Thermogravimetric (TG) analysis for the as-synthesized ZIF-90 and superhydrophobic F-ZIF-90. The initial weight loss 30-60 ºC is due to methanol trapped within the pores.

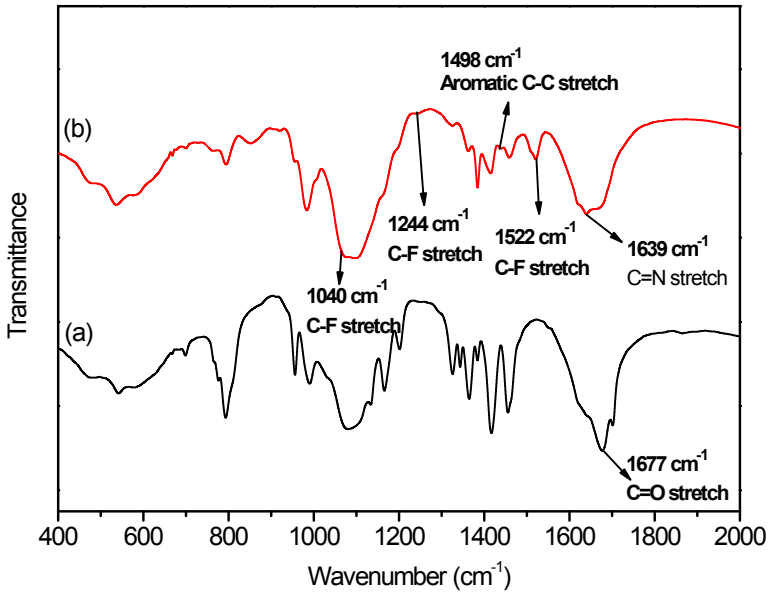

Figure S5. FT-IR spectrums of the ZIF-90 (a) and F-ZIF-90 (b).

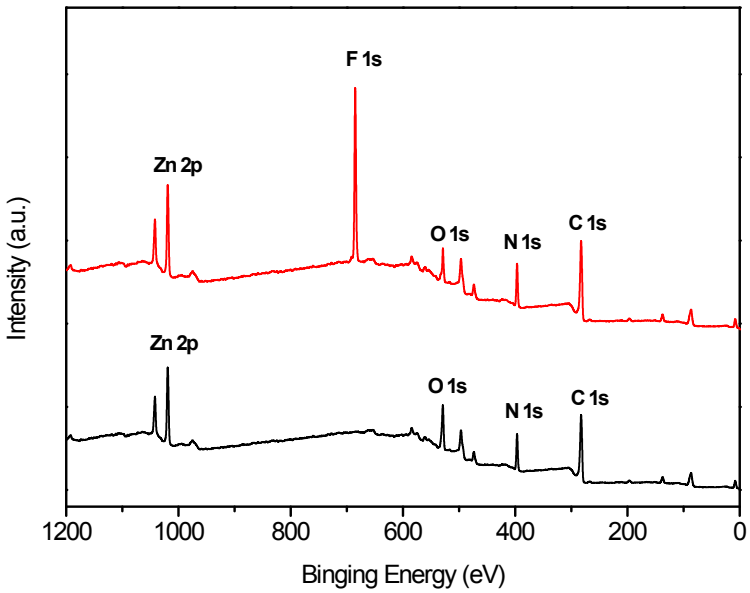

Figure S6. XPS spectra of the ZIF-90 and F-ZIF-90.

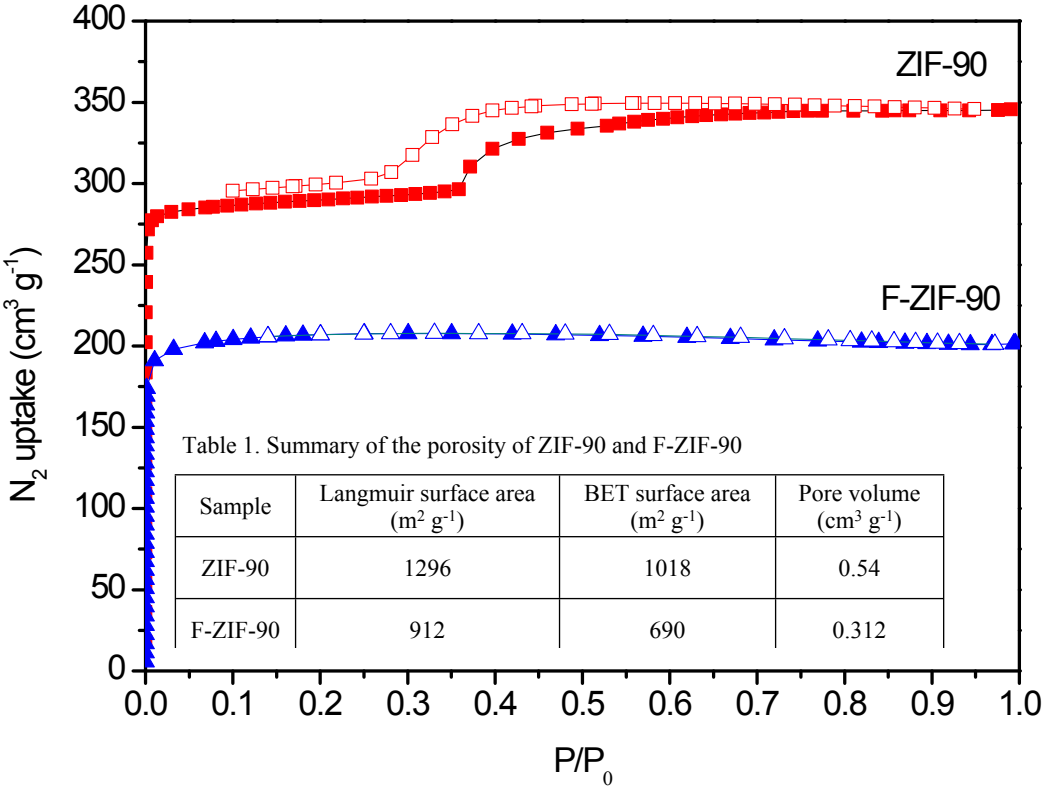

Table 1. Summary of the porosity of ZIF-90 and F-ZIF-90

Sample	Langmuir surface area (m^2 g^{-1})	BET surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})
ZIF-90	1296	1018	0.54
F-ZIF-90	912	690	0.312

Figure S7. N_2 isotherms for the ZIF-90 and F-ZIF-90 measured at 77 K. Filled and open circles represent adsorption and desorption branch, respectively. The inset show the porosity of ZIF-90 and F-ZIF-90.

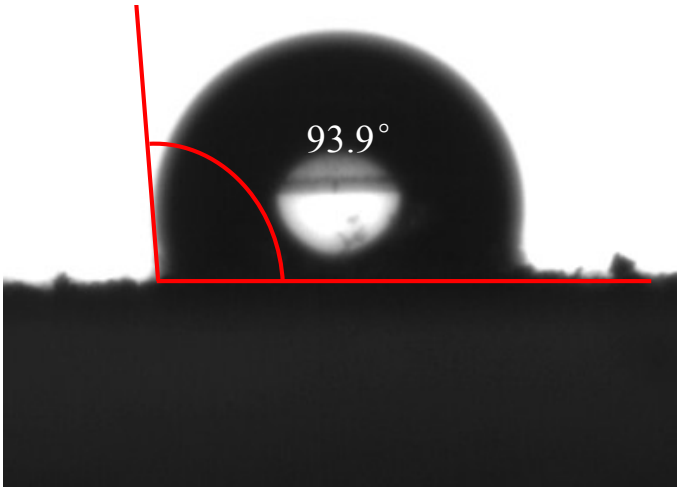

Fig. S8. Measurement of water contact angle (CA) for the ZIF-90 (C. Liu, et al., Chemical Communications, 2016, 52, 3400-3402).

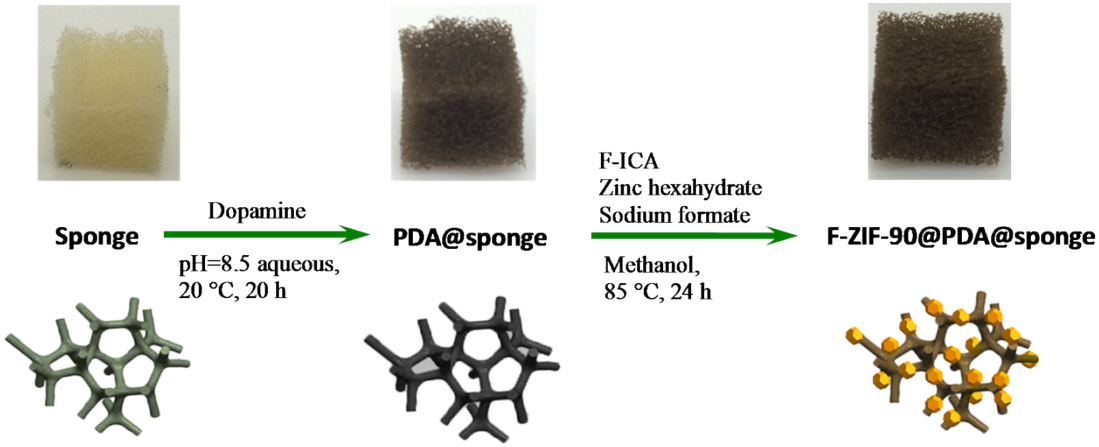

Figure S9. Scheme of the synthesis of F-ZIF-90@PDA@sponge. The photographs clear show a significant color change of the macroscopic sponge, PDA@sponge and F-ZIF-90@PDA@sponge.

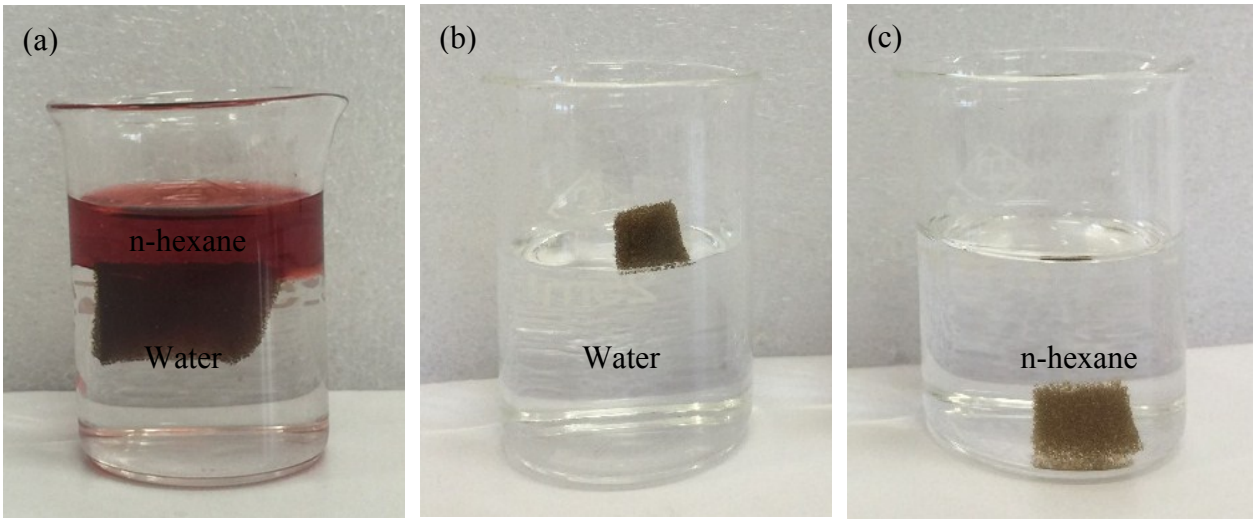

Figure S10. Proof of superhydrophobicity of the F-ZIF-90@PDA@sponge: showing the PDA@sponge sinks in water due to its hydrophilicity (a), the F-ZIF-90@PDA@sponge floats on the water surface (b), but sinks to the bottom in n-hexane immediately (c).

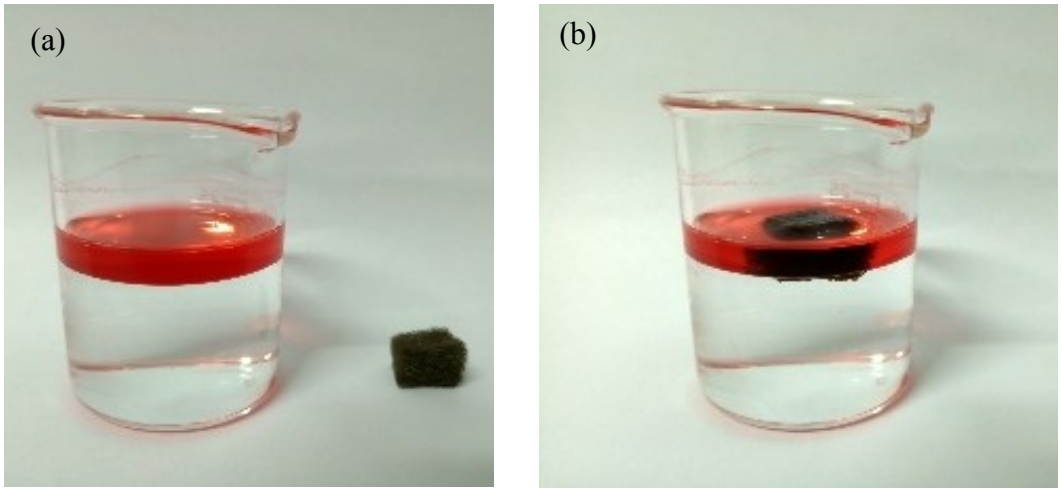

Figure S11. Proof of low n-hexane adsorption selectivity of ZIF-90@PDA@sponge: photograph of n-hexane-water mixture before (a) and after (b) puting ZIF-90@PDA@sponge in it.

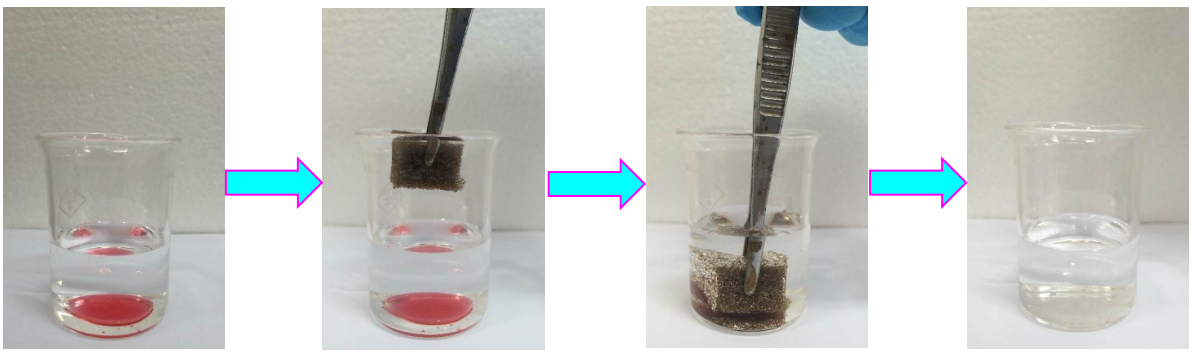

Figure S12. Photographs of the removal of CCl_4 from water by using F-ZIF-90@PDA@sponge.

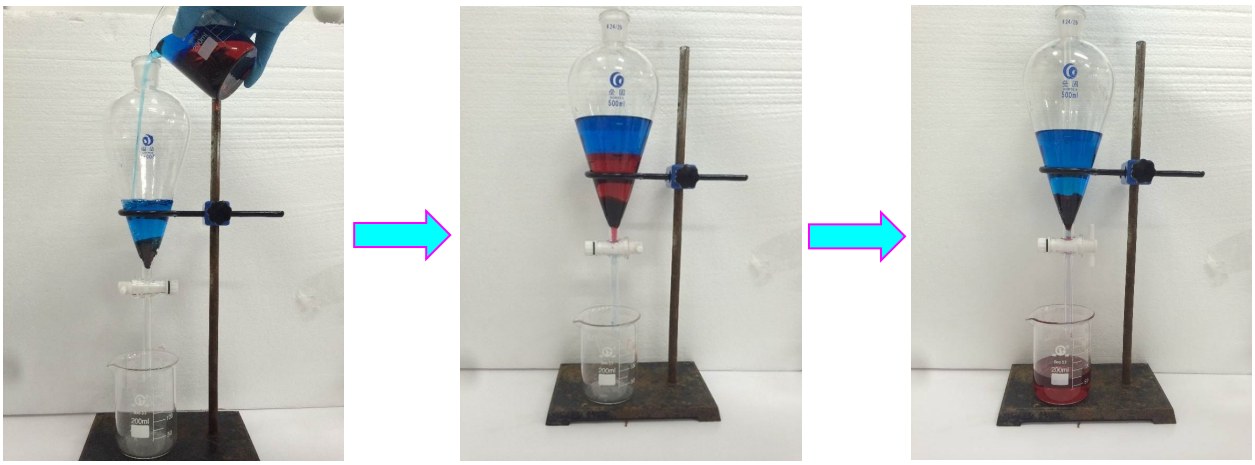

Figure S13. Photographs of the separation of CCl_4 from water by using F-ZIF-90@PDA@sponge.

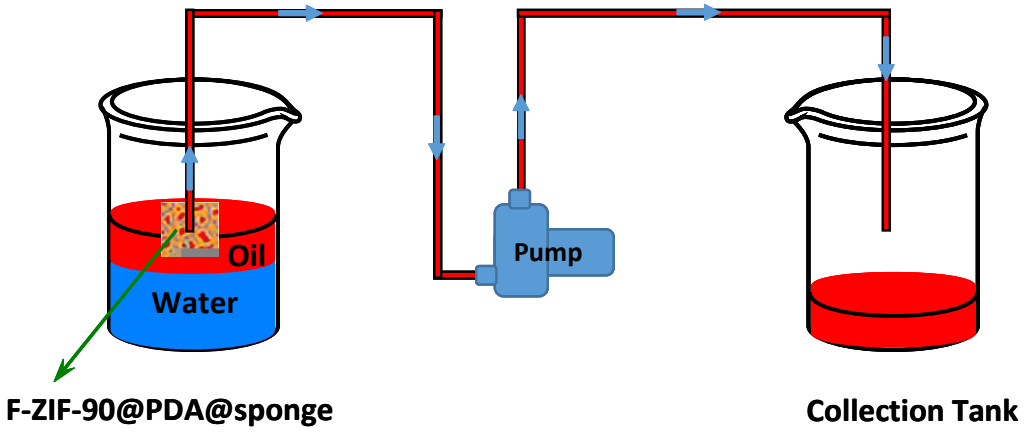

Figure S14. Scheme of the experimental apparatus for continue collection of oil on the surface of water into the recovery vessel. The oil and the water are colored blue and red respectively. Purple arrows indicate flow direction.

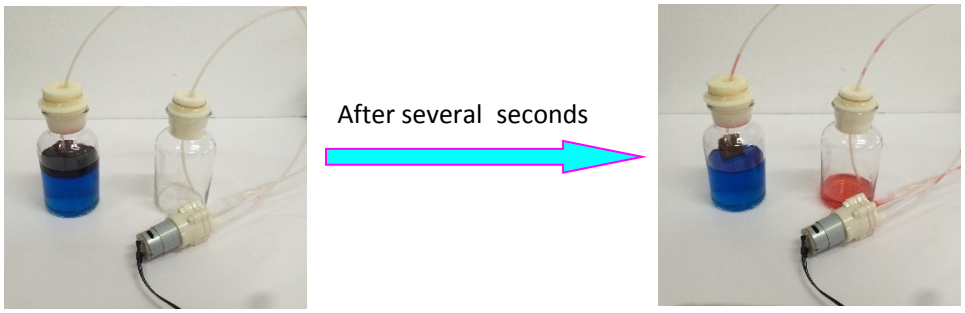

Figure S15. Photograph of in-situ and continuous collection of n-hexane from a water surface by usingthe F-ZIF-90@PDA@sponge.

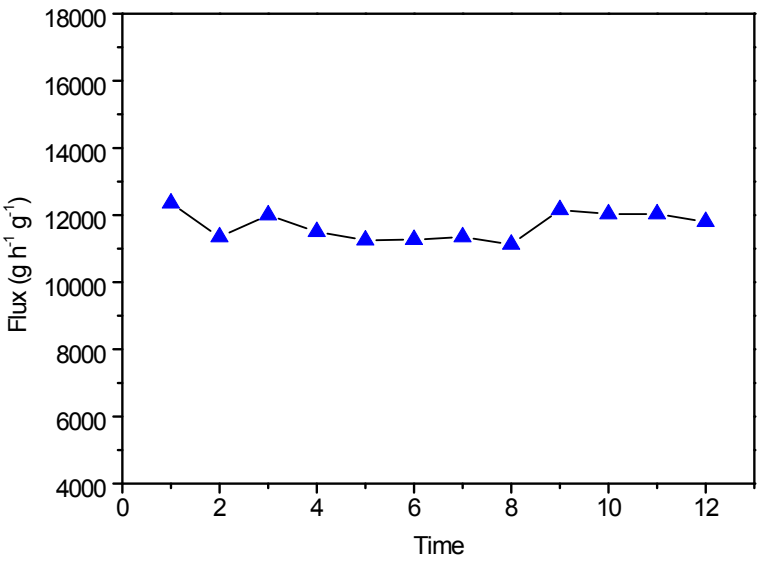

Figure S16. Long-term continuous operation ability was demonstrated by 10 h of continuous separation and recovery of n-hexane from water without a noticeable decrease in efficiency：a plot of the flux of oil (n-hexane) versus time with such a system. The voltage and current for direct current diaphragm pump R385 is 9.0 V and 0.3 A respectively, and the inner diameter of tube is 1.0 mm (outer: 3.0 mm). The volumes of the oil and water are 50ml and 150 ml in a 250 ml jars.

Table S1. Comparisons of the absorption capacities of F-ZIF-90 with various porous materials

Materials	CA [°]	Absorption substance	Absorption capacities	Ref.
UHMOF-100	176	Hexadecane, CCl_4, biodiesel, crude oil, toluene	2 ~ 4 ($g \cdot g^{-1}$)	1
HCMP-1	167	Methanol, ethanol, acetone, DMF, THF, DMSO, benzene, toluene, ethylbenzene, 1, 2-dichlorobenzene, chloroform, nitrobenzene, phenol, hexane, octane, decane, dodecane, pump-oil, vegetable oil.	700 ~1500 wt%	2
HCMP-2	157		600 ~2300 wt%	
Sponge@HFGO@ZIF-8	162	Etroleum ether, silicone oil, chloroform, coconut oil, deca octane oil, veg oil	1.5 ~ 6 times	3
ZIF-8/CN foam	135	Pentane, petroleum ether, hexane, isopropyl ether, decane, ethanol, acetone, methanol, pump oil, propanol, toluene, THF, NMP, ethylene glycol, 1, 2-dichlormethane, chloroform	55 ~136 ($g \cdot g^{-1}$)	4
USTC-6	132	Deesel oil, gasoline, soybean oil, light petroleum, hexane, bromobenze, DMF, THF, acetone, CCl_4, methylbenzene	1500 - 4000 wt%	5
OPA-UiO-66-SO_3H	162	Toluene, acetone, DMF, $CHCl_3$, methanol	150 ~ 350 wt%	6
F-ZIF-90	159.1	Hexane, gasoline, diesel oil, soybean oil, toluene, $CHCl_3$, CCl_4	1600 - 4800 wt%	This work

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