Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information for:

A new post-synthetic polymerization strategy makes metal-organic frameworks more stable †

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Experimental Section

Materials: Free-base dopamine was synthesized according to our previous report.[1] Dopamine hydrochloride (99%), 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol (97%), zinc nitrate hexahydrate (reagent grade, 98%), 2-methylimidazole (99%), cyanuric chloride (99%), sodium hydroxide (reagent grade, =98%, pellets, anhydrous), terephthalic acid (98%), sodium hydride (dry, 95%) and styrene (ReagentPluse, contains 4-tert-butylcatechol as stabilizer, =99%) were provided by Sigma-Aldrich. Iron(III) chloride hexahydrate (97%) was bought from Alfa-Aesar. Copper(II) nitrate trihydrate (99.5%), 1,3,5-benzenetricarboxylic acid (98%), 5-aminoisophthalic acid (95%), cobalt(II) nitrate hexahydrate (99%, reagent), zirconium(IV) chloride (reactor grade, 99.5%, metals basis) were provided by ABCR GmbH. 2-Nitroimidazole was purchased from Fluorochem. 5-Chlorobenzimidazole, 1,3,5-trimethylbenzene (>97.0%) were supplied by TCI. 1,4-Dioxane (min. 99.5 %, extra pure) and triethylamine (min. 99.5 %, for synthesis) were purchased from Roth AG.

MOF synthesis:

Synthesis of HKUST-1: HKUST-1 crystals were synthesized following a procedure similar to those reported previously in the literature with some minor modifications.[2] 5.000 g of 1,3,5-benzenetricarboxylic acid and 10.400 g of copper(II) nitrate trihydrate were stirred 10 min in the solution of 85 mL of water, 85 mL of ethanol and 85 mL of N,N-dimethyl formaldehyde (DMF) in 1-L wide mouth glass jar. The jar was tightly capped and placed in oven for 20 h at 85 °C to yield small octahedral crystals. After decanting the hot mother liquor, the product was rinsed with DMF and dichloromethane (DCM) and dried.

Synthesis of Mg-MOF-74: Mg-MOF-74 was synthesized according to the literature while using the microwave to accelerate the synthetic process of Mg-MOF-74.[3] Typically, in a solution of 30 mL dimethylformamide, 2 mL ethanol, and 2 mL water were dissolved 0.299 g 2,5-dihydroxyterephthalic acid and 1.244 g $Mg(NO_3)_2 \cdot 6H_2O$ with sonication. The resulting stock solution was decanted into five 10 mL PTFE microwave reaction tubes. The reaction solution was then rapidly heated to 125 ^{o}C in 25 min (1200 W power) and was held at this temperature for 4 h. After cooling to room temperature, the solid products were collected by centrifugation and washed three times with methanol and dry for further use.

Synthesis of Cu-TDPAT: Cu-TDPAT crystals were synthesized following a procedure similar to those reported previously in the literature with some minor modifications.[4] H_6-TDPAT ligand was synthesized exactly as it has been reported in the literature.[4] 0.450 g of H_6-TDPAT, 2.640 g of $Cu(NO_3)_2{\cdot}3H_2O$, 30 mL of DMAc, 30 mL of DMSO, 13.5 mL of HBF_4, and 1.5 mL of water were mixed and stirred for 5 minutes in a 250 mL jar. This solution was located inside the 85 ^oC oven for 3 days. Then it was taken out of the oven. After decanting the hot mother liquor, the product was rinsed with DMAc and methanol and dried.

Synthesis of ZIF-8: ZIF-8 nanopolyhedrons were synthesized according to the previous report.[5] Typically, 1.172 g of zinc nitrate hexahydrate was dissolved into 20 mL of methanol to obtain a clear solution. Then 2.592 g of 2-methylimidazole was dissolved in 20 mL of methanol. The 2-methylimidazole solution was poured into the zinc ion solution under magnetic stirring. After stirring for 1.5 h, the resulting white precipitates were centrifuged and washed thoroughly with methanol four times and dry.

Synthesis of ZIF-67: The ZIF-67 nanocubes were prepared according to a previous report with minor modification.[6] In a typical experiment, 0.580 g of cobalt nitrate hexahydrate and 0.02 g of hexadecyl trimethyl ammonium bromide (CTAB) were dissolved into 20 mL of water to obtain a clear solution. Then 9.08 g of 2-methylimidazole was dissolved in 140 mL of water. Then the cobalt-containing solution was poured into the 2-methylimidazole solution under magnetic stirring. After stirring for 20 min, the resulting purple precipitates were centrifuged and washed thoroughly with ethanol three times and dried under vacuum at room temperature for 12 h.

Synthesis of UiO-66: UiO-66 was prepared by following the reported procedure for a large-scale synthesis.[7] Briefly, 1.398 g of $ZrCl_4$, 0.997 g of terephthalic acid, 400 mL DMF and 55 mL glacial acetic acid were loaded in 1 L microwave PTFE vessel and sonicated for 20 minutes, then the solution was heated to 120 ^oC with maximum power 1200 W for 3 h with nitrogen pressure 10 bar. After that, the resulting white precipitates were centrifuged and washed thoroughly with DMF three time followed by methanol three times and dried under vacuum at room temperature for 12 h.

Synthesis of Fe-BTC: We chose the previous steps for Fe-BTC synthesis as the reference and changed the components to simplify the synthetic process.[8] Simply, 9.72 g of iron(III) chloride hexahydrate, 3.36 g of 1,3,5-benzenetricarboxylic acid and 120 mL of distilled water were loaded in a 180 mL Teflon autoclave. The reaction mixture was heated to 130 °C for 72 hours. After cooling down to room temperature, the orange solid was filtered under vacuum and washed with water and methanol several times. The resulting orange powder was soxhleted with methanol for 24 hours. Then the sample was dried under vacuum overnight for further use.

Preparation of MOFs@PDA-SF composites:

Preparation of HKUST-1@PDA-SF: Typically, 300 mg of HKUST-1 was dispersed in 30 mL methanol under ultrasonic. Then, 75 mg free-base dopamine was added and the reaction was stirred under oxygen atmosphere. After 12 h, the HKUST-1@PDA composites were recovered through centrifuge and washed with methanol for three time and re-dispersed in 30 mL methanol. After adding 90 μL 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol and 90 μL triethylamine, the suspension was stirred for another 12 h. When the reaction time was reached, the products were washes with MeOH for 3 times and dry under vacuum for 6 h. Finally, the obtained materials were soxhleted using methanol overnight to wash the possible raw materials residual inside the MOF pores. The recovered sample was dried under vacuum at room temperature for further use.

Preparation of HKUST-1@PDA-SF-2: Typically, 300 mg of HKUST-1 was dispersed in 30 mL methanol under ultrasonic. Then, 38 mg free-base dopamine was added and the reaction was stirred under oxygen atmosphere. After 12 h, the HKUST-1@PDA composites were recovered through centrifuge and washed with methanol for three time and re-dispersed in 30 mL methanol. After adding 45 μL 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol and 45 μL triethylamine, the suspension was stirred for another 12 h. When the reaction time was reached, the products were washes with MeOH for 3 times and dry under vacuum for 6 h. Finally, the obtained materials were soxhleted using methanol for 24 h to wash the possible raw materials residual inside the MOF pores. The recovered sample was dried under vacuum at room temperature for further use.

Preparation of ZIF-67@PDA-SF: Typically, 200 mg of ZIF-67 was dispersed in 20 mL methanol under ultrasonic. Then, 50 mg free-base dopamine was added and the reaction was stirred under oxygen atmosphere. After 12 h, the ZIF-67@PDA composites were recovered through centrifuge and washed with methanol for three time and re-dispersed in 20 mL methanol. After adding 60 μL 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol and 60 μL triethylamine, the suspension was stirred for another 12 h. When the reaction time was reached, the products were washes with MeOH for 3 times and dry under vacuum for 6 h. Finally, the obtained materials were soxhleted using methanol overnight to wash the possible raw materials residual inside the MOF pores. The recovered sample was dried under vacuum at room temperature for further use.

Preparation of ZIF-67@PDA-SF-2: Typically, 200 mg of ZIF-67 was dispersed in 20 mL methanol under ultrasonic. Then, 25 mg free-base dopamine was added and the reaction was stirred under oxygen atmosphere. After 12 h, the ZIF-67@PDA composites were recovered through centrifuge and washed with methanol for three time and re-dispersed in 20 mL methanol. After adding 30 μL 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol and 30 μL triethylamine, the suspension was stirred for another 12 h. When the reaction time was reached, the products were washes with MeOH for 3 times and dry under vacuum for 6 h. Finally, the obtained materials were soxhleted using methanol for 24 h to wash the possible raw materials residual inside the MOF pores. The recovered sample was dried under vacuum at room temperature for further use.

Preparation of ZIF-8@PDA-SF: Typically, 100 mg of ZIF-8 was dispersed in 10 mL methanol under ultrasonic. Then, 25 mg free-base dopamine was added and the reaction was stirred under oxygen atmosphere. After 12 h, the ZIF-8@PDA composites were recovered through centrifuge and washed with methanol for three time and re-dispersed in 10 mL methanol. After adding 30 uL 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol and 30 uL triethylamine, the suspension was stirred for another 12 h. When the reaction time was reached, the products were washes with MeOH for 3 times and dry under vacuum for 6 h. Finally, the obtained materials were soxhleted using methanol overnight to wash the possible raw materials residual inside the MOF pores. The recovered sample was dried under vacuum at room temperature for further use.

Preparation of Fe-BTC@PDA-SF: Typically, 50 mg of Fe-BTC was dispersed in 5 mL methanol under ultrasonic. Then, 25 mg free-base dopamine was added and the reaction was stirred under oxygen atmosphere. After 12 h, the Fe-BTC@PDA composites were recovered through centrifuge and washed with methanol for three time and re-dispersed in 5 mL methanol. After adding 30 μL 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol and 30 μL triethylamine, the suspension was stirred for another 12 h. When the reaction time was reached, the products were washes with MeOH for 3 times and dry under vacuum for 6 h. Finally, the obtained materials were soxhleted using methanol overnight to wash the possible raw materials residual inside the MOF pores. The recovered sample was dried under vacuum at room temperature for further use.

Preparation of UiO-66@PDA-SF: Typically, 50 mg of UiO-66 was dispersed in 5 mL methanol under ultrasonic. Then, 50 mg free-base dopamine was added and the reaction was stirred under oxygen atmosphere. After 12 h, the UiO-66@PDA composites were recovered through centrifuge and washed with methanol for three time and re-dispersed in 5 mL methanol. After adding 60 μL 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol and 60 μL triethylamine, the suspension was stirred for another 12 h. When the reaction time was reached, the products were washes with MeOH for 3 times and dry under vacuum for 6 h. Finally, the obtained materials were soxhleted using methanol overnight to wash the possible raw materials residual inside the MOF pores. The recovered sample was dried under vacuum at room temperature for further use.

Preparation of Cu-TDPAT@PDA-SF: Typically, 100 mg of Cu-TDPAT was dispersed in 10 mL methanol under ultrasonic. Then, 6.3 mg free-base dopamine was added and the reaction was stirred under oxygen atmosphere. After 12 h, the Cu-TDPAT@PDA composites were recovered through centrifuge and washed with methanol for three time and re-dispersed in 10 mL methanol. After adding 7.5 μL 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol and 7.5 μL triethylamine, the suspension was stirred for another 12 h. When the reaction time was reached, the products were washes with MeOH for 3 times and dry under vacuum for 6 h. Finally, the obtained materials were soxhleted using methanol overnight to wash the possible raw materials residual inside the MOF pores. The recovered sample was dried under vacuum at room temperature for further use.

Preparation of Mg-MOF-74@PDA-SF with contact angle ~ 100^o: Typically, 100 mg of Mg-MOF-74 was dispersed in 10 mL methanol under ultrasonic. Then, 25 mg free-base dopamine was added and the reaction was stirred under oxygen atmosphere. After 12 h, the Mg-MOF-74@PDA composites were recovered through centrifuge and washed with methanol for three time and re-dispersed in 10 mL methanol. After adding 30 μL 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol and 30 μL triethylamine, the suspension was stirred for another 12 h. When the reaction time was reached, the products were washes with MeOH for 3 times and dry under vacuum for 6 h. Finally, the obtained materials were soxhleted using methanol to wash the possible raw materials residual inside the MOF pores. The recovered sample was dried under vacuum at room temperature for further use.

Preparation of Mg-MOF-74@PDA-SF with contact angle ~ 130°: Typically, 50 mg of Mg-MOF-74 was dispersed in 5 mL methanol under ultrasonic. Then, 25 mg free-base dopamine was added and the reaction was stirred under oxygen atmosphere. After 12 h, the Mg-MOF-74@PDA composites were recovered through centrifuge and washed with methanol for three time and re-dispersed in 5 mL methanol. After adding 30 μL 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol and 30 μL triethylamine, the suspension was stirred for another 12 h. When the reaction time was reached, the products were washes with MeOH for 3 times and dry under vacuum for 6 h. Finally, the obtained materials were soxhleted using methanol to wash the possible raw materials residual inside the MOF pores. The recovered sample was dried under vacuum at room temperature for further use.

Preparation of Mg-MOF-74@PDA-SF with contact angle ~ 138°: Typically, 50 mg of Mg-MOF-74 was dispersed in 5 mL methanol under ultrasonic. Then, 50 mg free-base dopamine was added and the reaction was stirred under oxygen atmosphere. After 12 h, the Mg-MOF-74@PDA composites were recovered through centrifuge and washed with methanol for three time and re-dispersed in 5 mL methanol. After adding 60 μL 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol and 60 μL triethylamine, the suspension was stirred for another 12 h. When the reaction time was reached, the products were washes with MeOH for 3 times and dry under vacuum for 6 h. Finally, the obtained materials were soxhleted using methanol to wash the possible raw materials residual inside the MOF pores. The recovered sample was dried under vacuum at room temperature for further use.

General procedure for water stability test: 9.0 mg of composites were dispersed in water under ultrasonic. Then the system was kept static until the desired time was reached. After the test, the sample was recovered and dried under vacuum for further characterizations.

General procedure for base stability test: 9.0 mg of MOFs or MOF composites were dispersed in the NaOH solution (pH=11, 12 or 13) or H_2SO_4 solution (pH=0, 1 or 2) under ultrasonic. Then the system was kept static until the desired time was reached. After the test, the sample was rinsed with water to remove the residual base on the sample surface. The recovered sample was dried under vacuum for further characterizations.

Oil/water separation experiment: Here, dichloromethane, hexane, toluene and gasoline were chosen as the representative of oil. To make it more distinguishable between the oil phase and water phase, the water phase was dyed with methylene blue dye. The oil-water separation experiment was conducted on a home-made setup. Typically, a small piece of gauze was put on the bottom of a syringe, on which was placed with HKUST-1@PDA-SF, and then another piece of gauze was put on the sample to generate a simple filter. Since the organic compounds including hexane, toluene and gasoline are lighter than water, they will remain on water and there is thus no contact with the sample. So the device was placed slantways to ensure the contact of the tested oil with the material. Hexane, toluene or gasoline quickly passed through the hydrophobic material and fell into the vial beneath it. And to the end, the device was straightened and water will contact with the material completely. The water could not penetrate the hydrophobic material layer. For dichloromethane/water separation, the dichloromethane is heavier than water thus laid at the bottom of water. The dichloromethane passed through the filter very fast while the water remained in the syringe and could not permeate through the material. For HKUST-1 test, the procedure was the same with hydrophobic HKUST-1@PDA-SF except the hydrophilic HKUST-1 was used.

Characterizations: X-ray diffraction (XRD) patterns were performed on a Bruker D8 diffractometer with Cu Kα radiation (λ= 1.5418 Å) at 40 kV and 40 mA. The morphology and microstructures of the samples were characterized by scanning electron microscopy (FEI Teneo SEM) and transmission electron microscopy (FEI Tecnai G2 Spirit Twin). Scanning electron microscopy (SEM) analysis was performed on a FEI Teneo at an accelerating voltage of 1.00 kV and using a beam current of 100 pA. SEM images were acquired with an in-column (Trinity) detector. SEM energy dispersive X-ray (EDX) spectra were acquired using an XFlash silicon drift detector from Bruker. The electron beam condition was optimized for the SEM-EDX measurements with an accelerating voltage of 20 kV and a beam current of 1.6 nA. Conventional bright-field transmission electron microscopy (BF-TEM) images were acquired with a FEI Tecnai G2 Spirit Twin at an accelerating voltage of 120 kV. High-angle annular dark-field images and EDX elemental maps were acquired with a FEI Osiris in scanning TEM (STEM) mode at an accelerating voltage of 200 kV. This microscope is equipped with a high brightness X-FEG gun and silicon drift Super-X EDX detectors. XPS measurement was performed using a Physical Instruments AG PHI VersaProbe II scanning XPS microprobe. Analysis was performed using a monochromatic Al Kα X-ray source of 24.8 W power with a beam size of 100 μm. Nitrogen adsorption-desorption isotherms were obtained on a BELSORP-max instrument at 77 K. For N_2 adsorption-desorption measurement, the samples were activated at 125 ^{o}C for 12 h. The surface area of the materials was measured by the Brunauer-Emmett-Teller (BET) method. Water contact angle was tested on MXC906 Easy

Drop instrument with drop volumn:10 uL, flow rate: 285 uL/min. The IR data was obtained on PerkinElmer Frontier Spectrometer in ATR mode. In-situ IR data were collected in transmission mode on a self-supported wafer of sample using a custom-built infrared cell at 150 K.

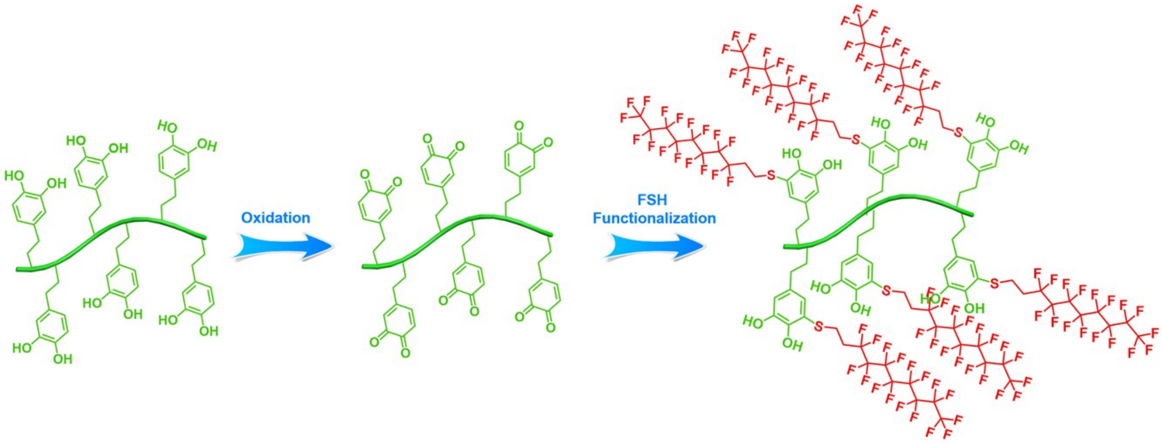


Fig. S1 Michael-type addition reaction: schematic of the oxidation of dopamine and the irreversible chemical reaction between the PDA and *1H,1H,2H,2H*-perfluorodecanethiol (FSH).

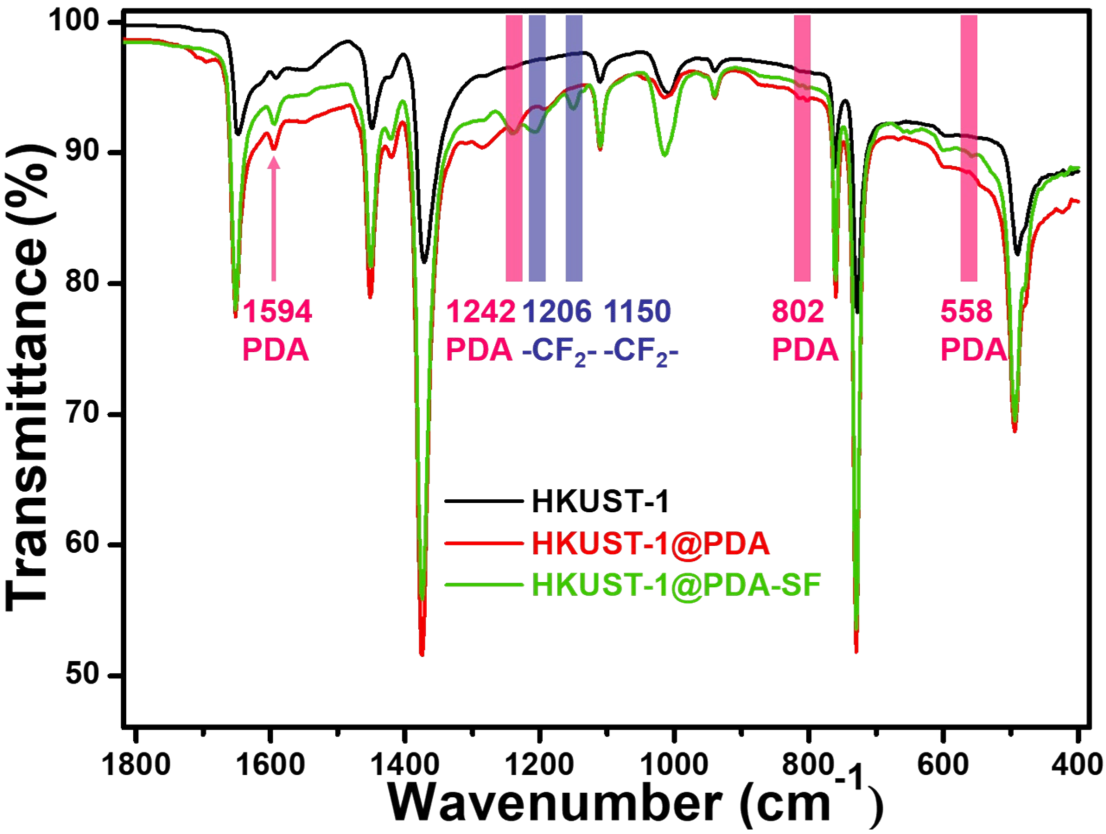


Fig. S2 Fourier transform infrared spectra (FT-IR) of the prepared HKUST-1, HKUST-1@PDA and HKUST-1@PDA-SF sample. The characteristic peaks of PDA located at 558, 802, 1242 and 1594 cm^{-1}, revealing the existence of PDA species in the HKUST-1@PDA and HKUST-1@PDA-SF sample. Also, the vibrational bands at 1150 and 1206 cm^{-1} ascribed to the symmetric and asymmetric CF_2 stretches respectively could be observed clearly in the HKUST-1@PDA-SF sample, which also confirmed the presence of -SF functional molecules in the fluorination sample HKUST-1@PDA-SF.

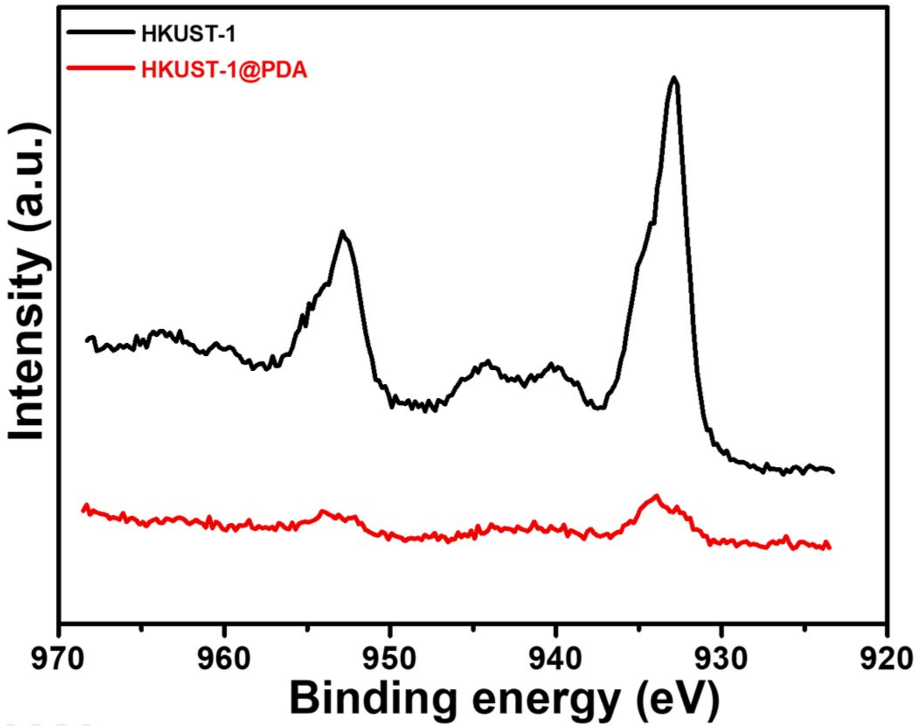


Fig. S3 High resolution XPS Cu 2p spectra of HKUST-1 and HKUST-1@PDA sample.

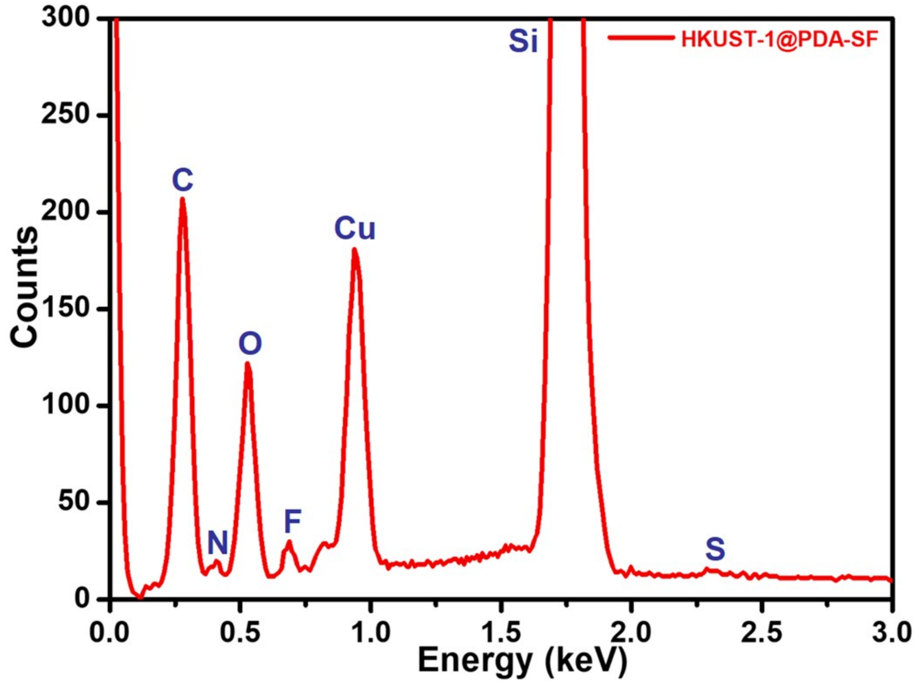


Fig. S4 EDX spectrum of HKUST-1@PDA-SF confirmed the presence of Cu, C, O, N, F and S elements in the composite. The Si element signal was from the silicon wafer support.

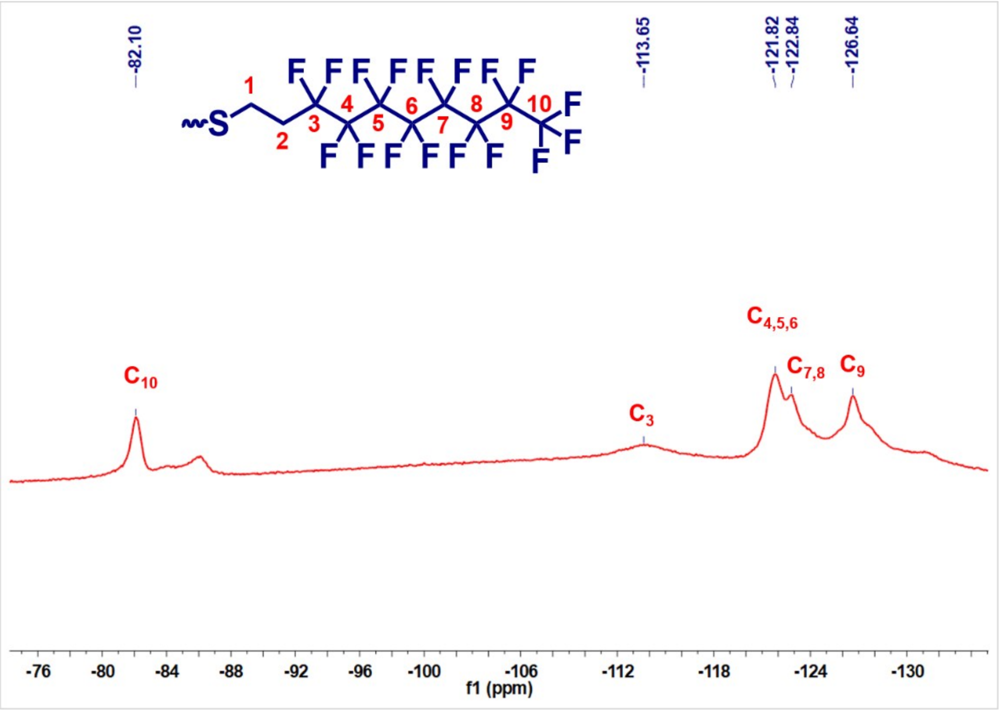


Fig. S5 Solid-state ^{19}F MAS NMR spectrum of HKUST-1@PDA-SF.

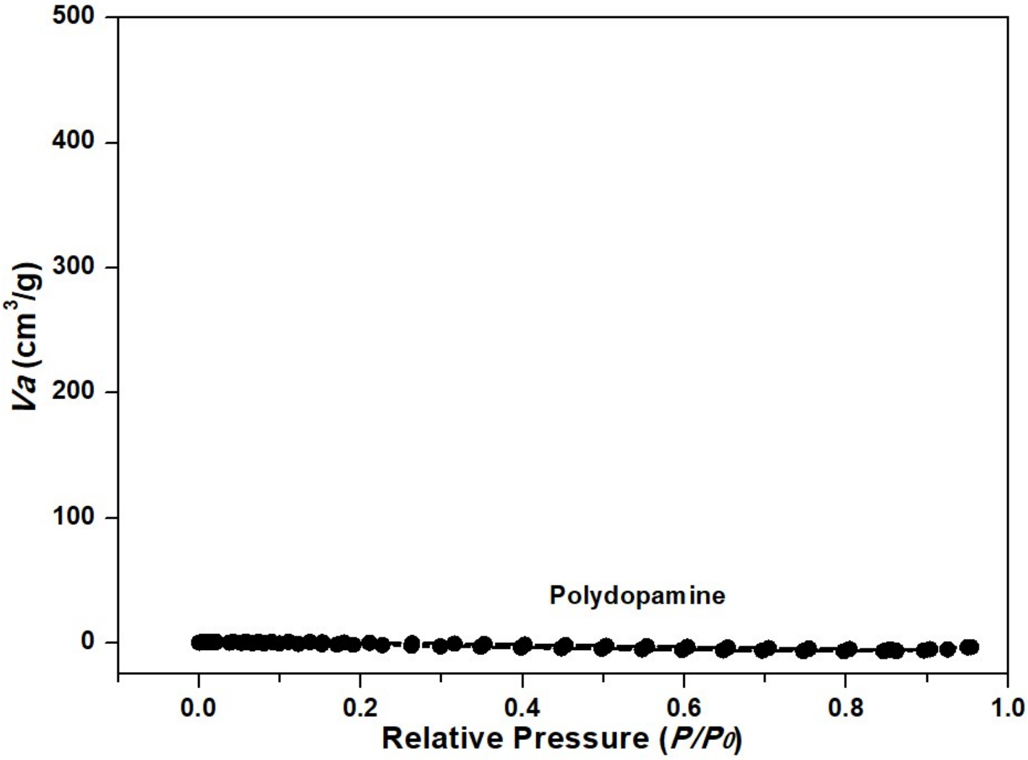


Fig. S6 N_2 adsorption-desorption isotherms of as-synthesized polydopamine. Surface area: 4 m^2/g.

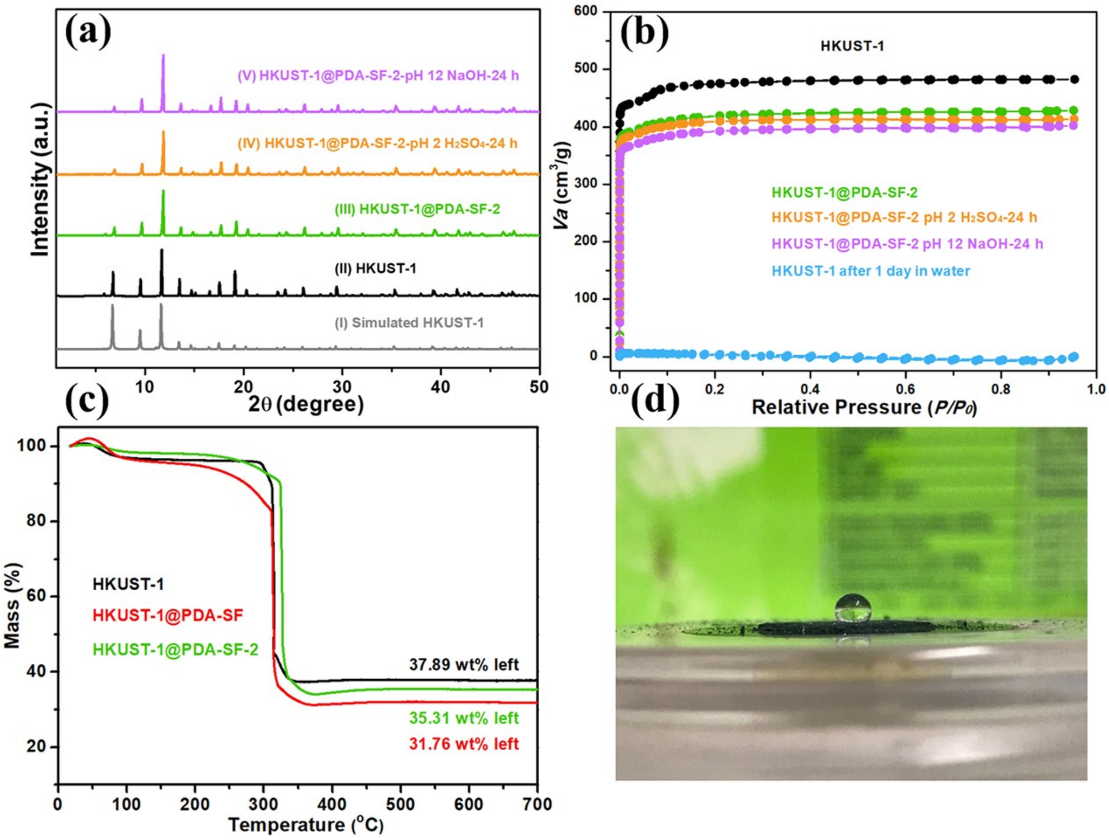


Fig. S7 XRD patterns (a), N_2 adsorption-desorption isotherms (b) and thermogravimetric analysis (c) of the unmodified HKUST-1 and the corresponding modified samples containing 6.2 wt % PDA-SF. Image (d) is the digital photo of the HKUST-1@PDA-SF-2, the volume of water drop is 10 μL. The surface areas of samples are: as-synthesized HKUST-1 (black, 1843 m^2/g), HKUST-1@PDA-SF-2 (green, 1600 m^2/g), HKUST-1@PDA-SF-2 after exposure to pH = 2 H_2SO_4 aqueous solution for 24 h (orange, 1586 m^2/g) and pH = 12 NaOH aqueous solution for 24 h (orange, 1571 m^2/g). The polymer loading of HKUST-1@PDA-SF-2 and HKUST-1@PDA-SF are (1-35.31/37.89)*100% = 6.8 wt% and (1-31.76/37.89)*100% = 16.2 wt%, respectively.

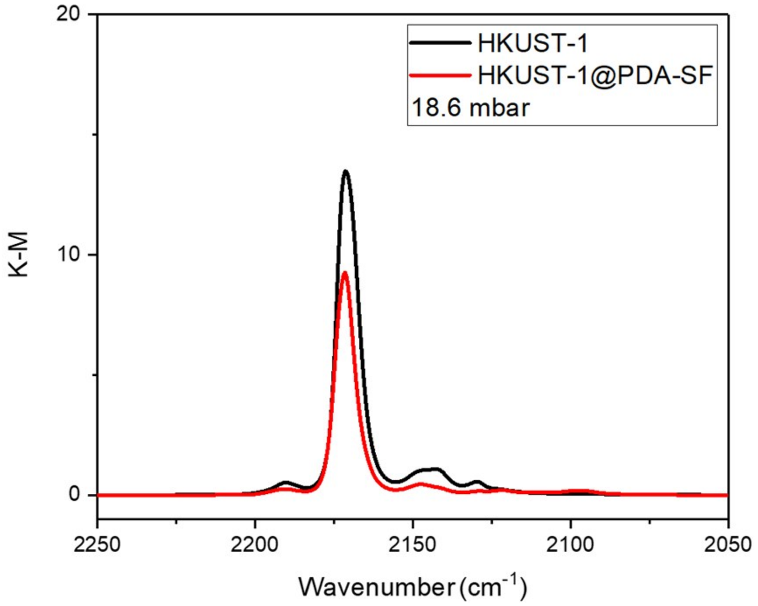


Fig. S8 In situ DRIFTs spectra of HKUST-1 and HKUST-1@PDA-SF (CO pressure: 18.6 mbar).

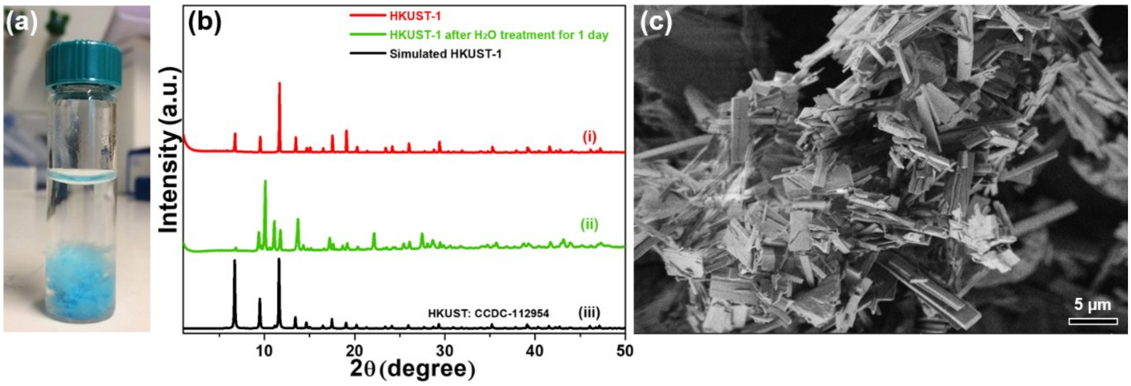


Fig. S9 Digital photo of HKUST-1 after exposed to H_2O for 1 day (a). XRD pattern of the prepared HKUST-1 (b-i), HKUST-1 after exposed to H_2O for 1 day (b-ii) and the simulated HKUST-1 (b-iii). SEM image of the HKUST-1 after exposed to H_2O for 1 day (c).

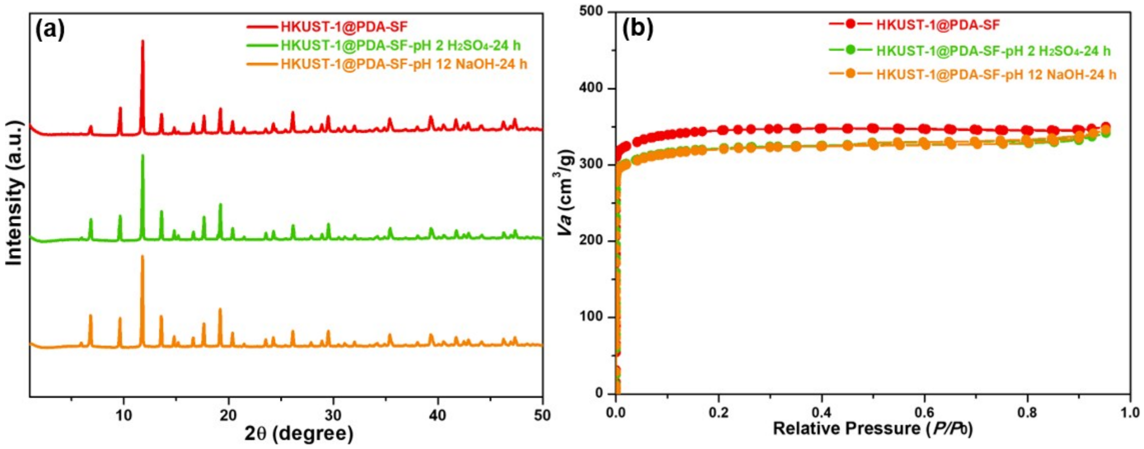


Fig. S10 (a) XRD patterns of HKUST-1@PDA-SF (red), HKUST-1@PDA-SF after exposure to H_2SO_4 aqueous solution (pH = 2) for 24 h (green) and NaOH aqueous solution (pH = 12) for 24 h (orange). (b) N_2 isotherm at 77 K of HKUST-1@PDA-SF (red), HKUST-1@PDA-SF after exposure to H_2SO_4 aqueous solution (pH = 2) for 24 h (green) and NaOH aqueous solution (pH = 12) for 24 h (orange). The surface areas of samples are: HKUST-1@PDA-SF (red, 1286 m^2/g), HKUST-1@PDA-SF after exposure to H_2SO_4 aqueous solution (green, 1247 m^2/g), HKUST-1@PDA-SF after exposure to NaOH aqueous solution (orange, 1242 m^2/g).

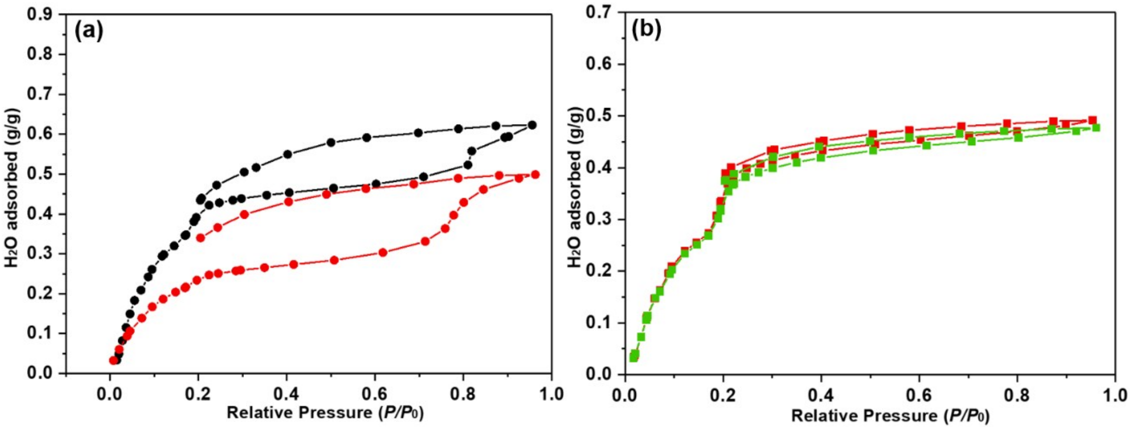


Fig. S11 (a) Water vapor adsorption and desorption at 298 K for HKUST-1 for the first run (black), HKUST-1 for second run (red). (b) Water vapor adsorption and desorption at 298 K for HKUST-1@PDA-SF for the first run (red squares) and the second run (green squares). The recovered samples were activated at 125 ^oC for 12 h under dynamic vacuum before each measurement.

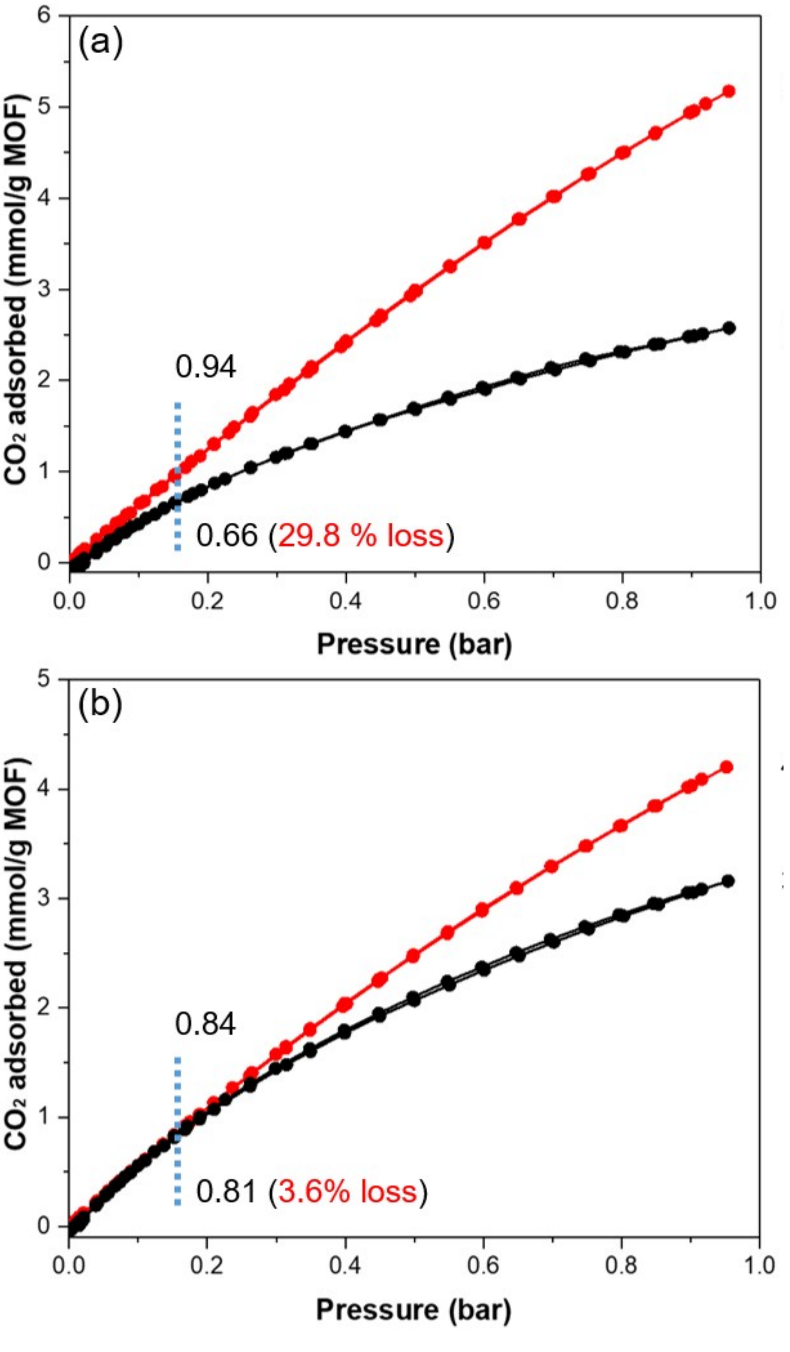
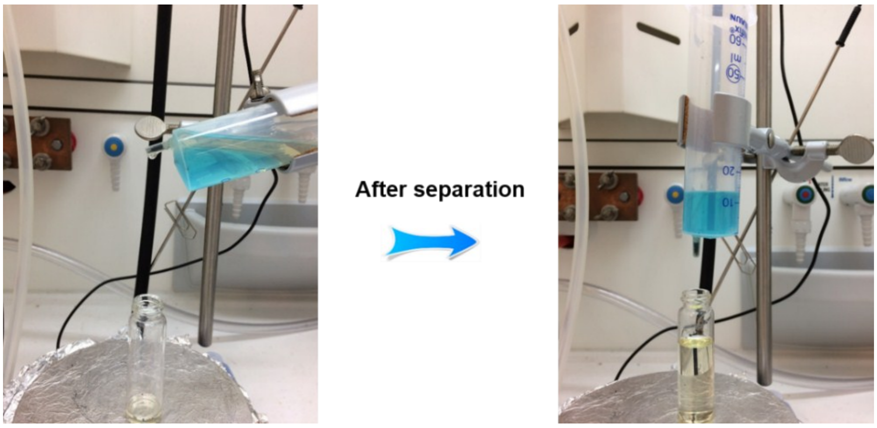


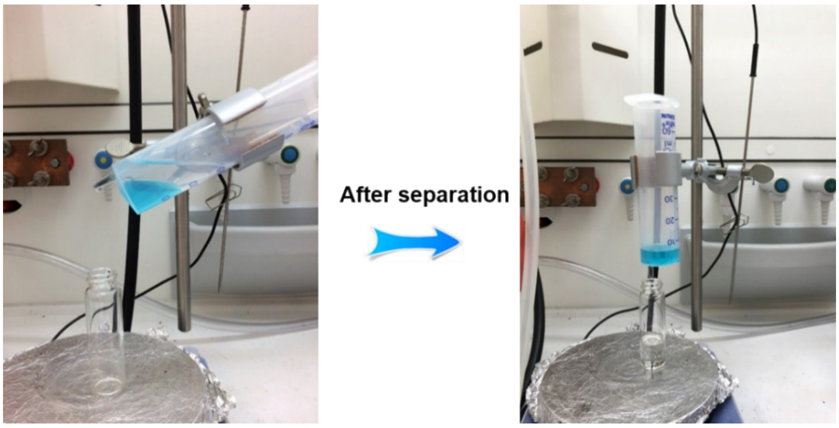
Fig. S12 (a) CO_2 adsorption at 298 K for activated HKUST-1 (red), air exposed HKUST-1 (black), (b) activated HKUST-1@PDA-SF (red), air exposed HKUST-1@PDA-SF (black). For the air exposed samples, the materials were exposed to air with 34% relative humidity for 3 minutes and then CO_2 adsorption isotherms were collected without reactivation.

(a) HKUST-1 for gasoline/water separation (left) and chloroform/water separation (right). It can be seen that both water and oil phases can pass through the HKUST-1 layer because HKUST-1 is not water- or oil-repellant.

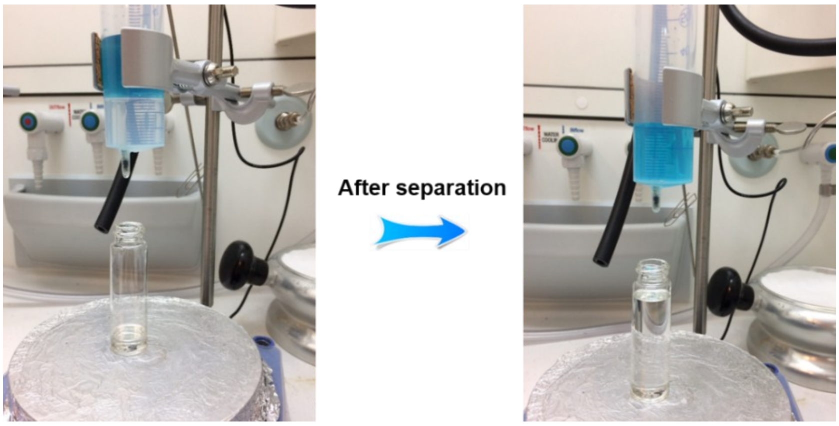


(b) HKUST-1@PDA-SF for gasoline/water separation.

HKUST-1@PDA-SF for toluene/water separation.



HKUST-1@PDA-SF for hexane/water separation.



HKUST-1@PDA-SF for chloroform/water separation.

Fig. S13 To make it more distinguishable between the oil phase and water phase, the water phase was dyed with methylene blue dye. HKUST-1 could not realize the oil/water separation (a), while the hydrophobic HKUST-1@PDA-SF could stop the water permeation (b).

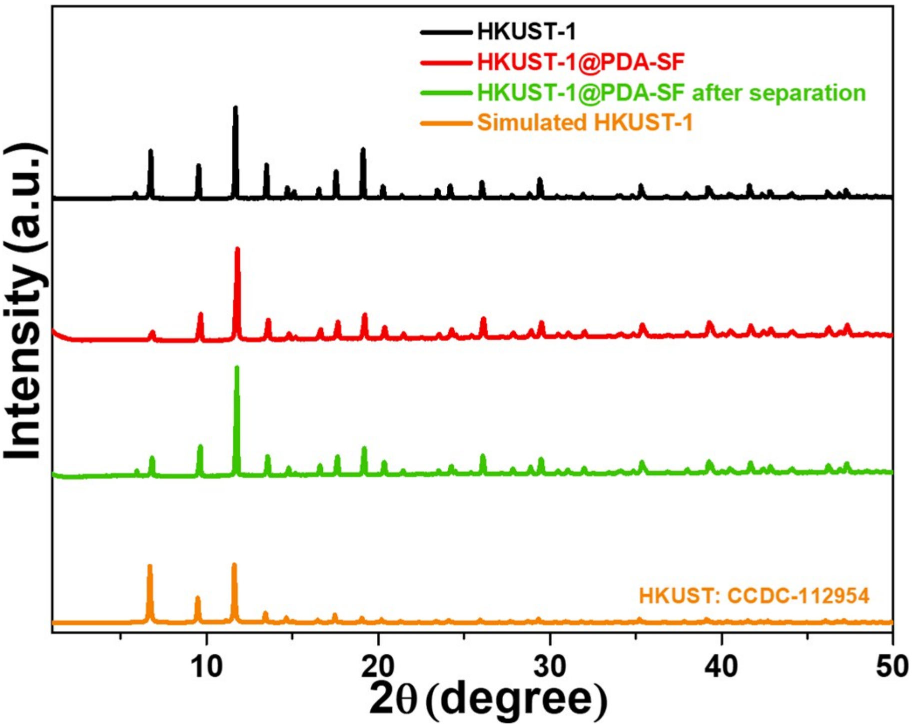


Fig. S14 XRD patterns of the HKUST-1@PDA-SF after oil/water separation experiment.

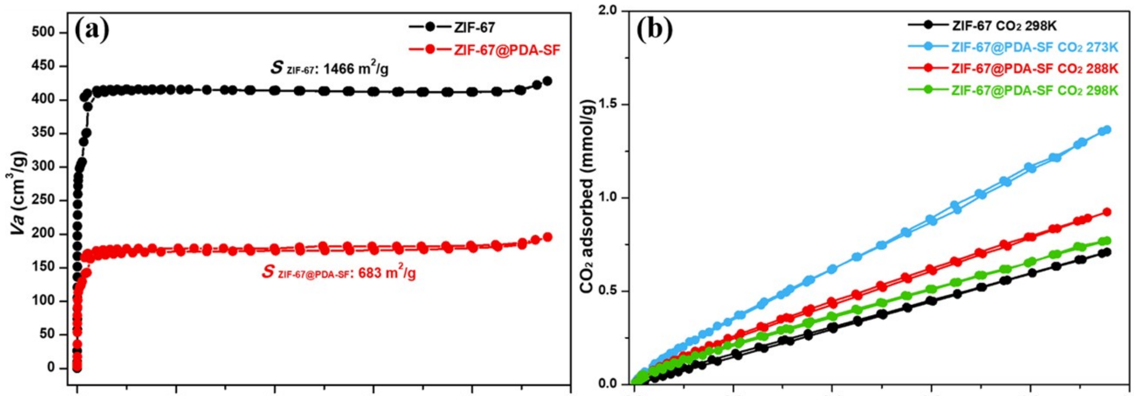


Fig. S15 N_2 adsorption-desorption isotherms (a) and the CO_2 adsorption isotherms (b) of the synthesized ZIF-67 nanocubes and the modified ZIF-67@PDA-SF.

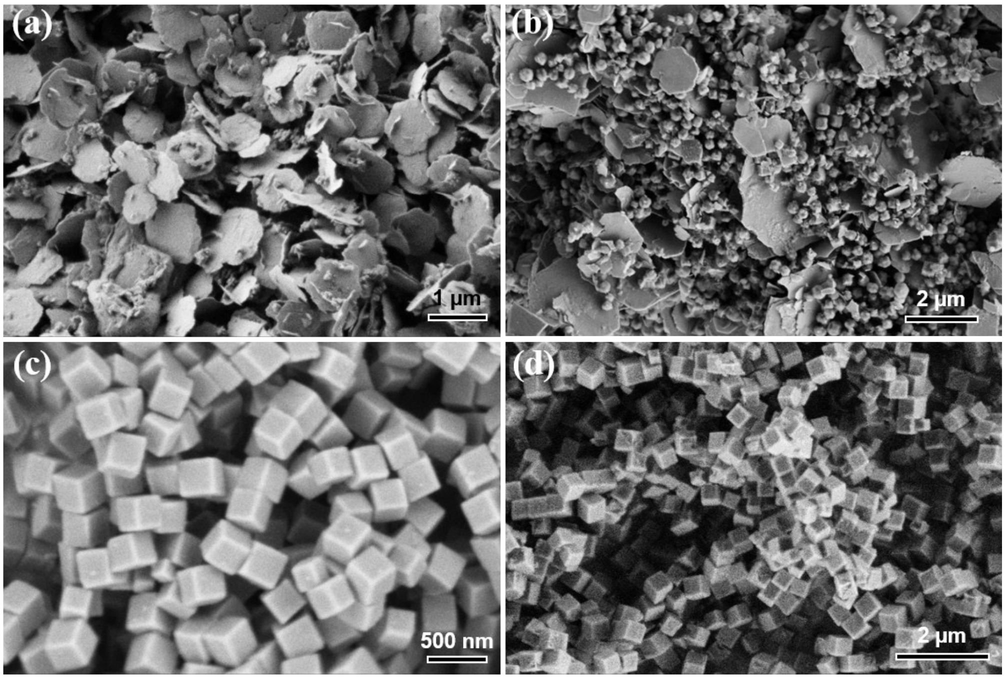


Fig. S16 SEM images of the recovered ZIF-67 after exposure to pH = 13 NaOH aqueous solution (a) and pH = 3 H_2SO_4 aqueous solution (b) for 24 h; SEM images of the recovered ZIF-67@PDA-SF samples after exposure to pH = 13 NaOH aqueous solution (c) and pH = 3 H_2SO_4 aqueous solution (d) for 24 h.

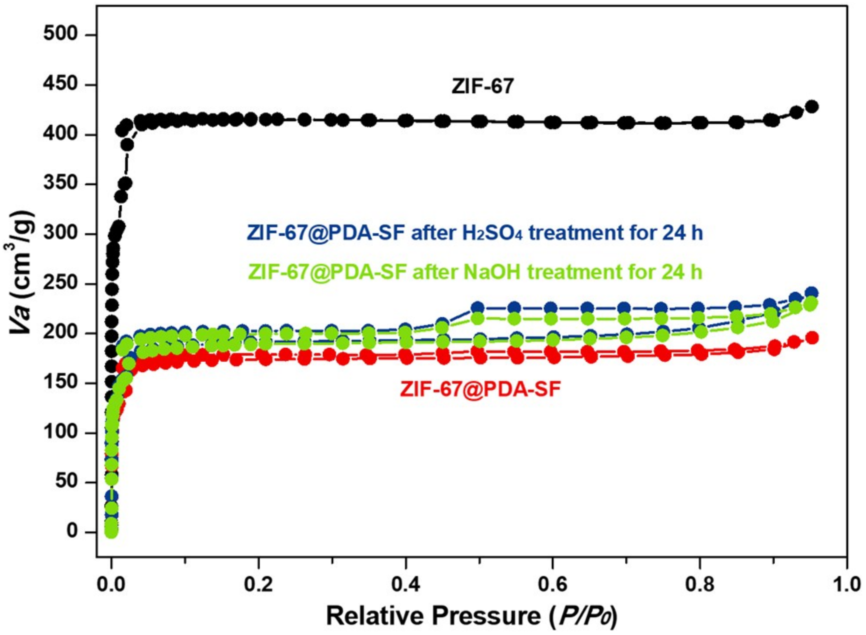


Fig. S17 N_2 adsorption-desorption isotherms of as-synthesized ZIF-67 (black, BET surface area: 1466 m^2/g), ZIF-67@PDA-SF (red, BET surface area: 683 m^2/g) and ZIF-67@PDA-SF after exposed to H_2SO_4 (pH=3, green, BET surface area: 729 m^2/g)/NaOH (pH=13, BET surface area: 738 m^2/g) solution for 24 h.

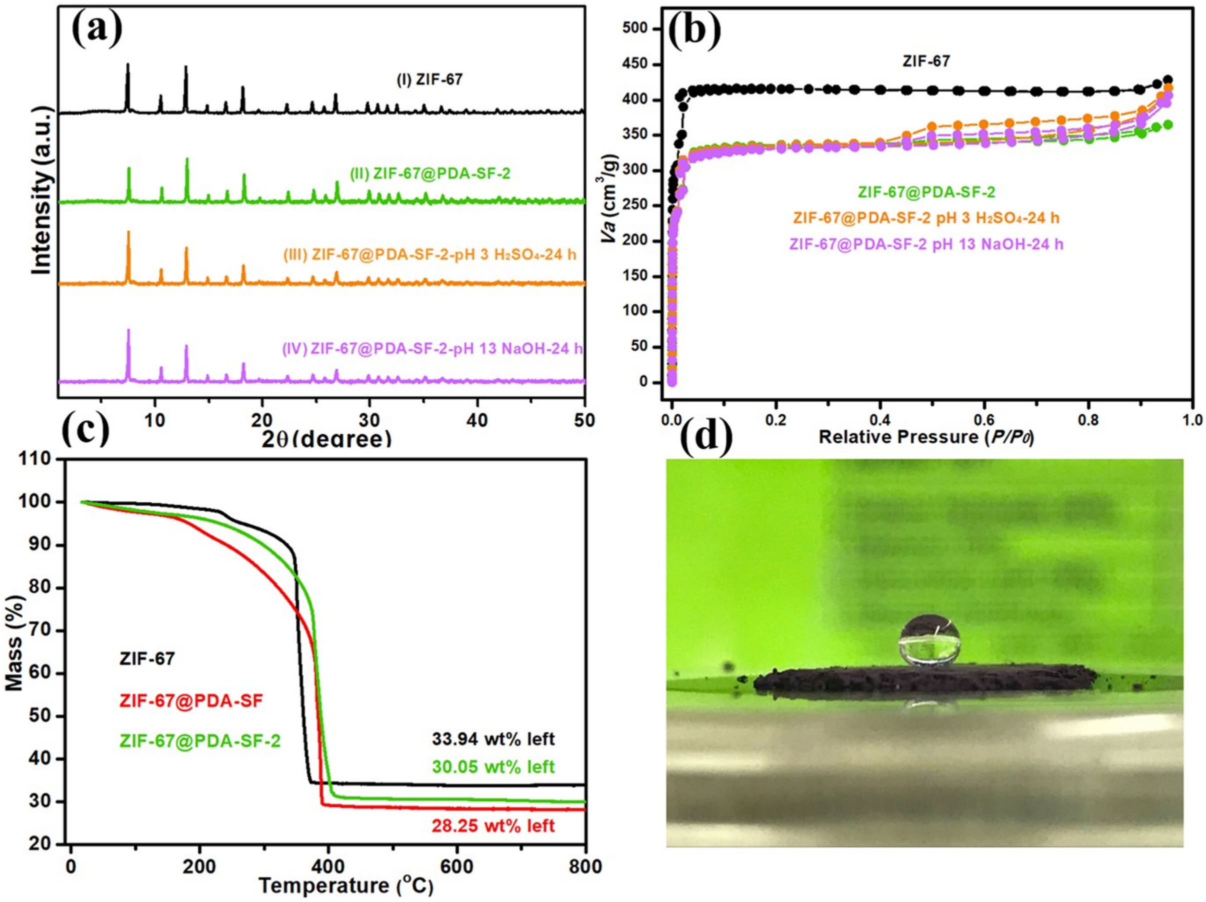


Fig. S18 XRD patterns (a), N_2 adsorption-desorption isotherms (b) and thermogravimetric analysis (c) of the unmodified ZIF-67 and the corresponding modified samples. Image (d) is the digital photo of the ZIF-67@PDA-SF-2, the volume of water drop is 10 µL. The surface areas of samples are: as-synthesized ZIF-67 (black, 1466 m^2/g), ZIF-67@PDA-SF-2 (green, 1312 m^2/g), ZIF-67@PDA-SF-2 after exposure to pH = 3 H_2SO_4 aqueous solution for 24 h (orange, 1303 m^2/g) and pH = 13 NaOH aqueous solution for 24 h (purple, 1293 m^2/g). The polymer loading of ZIF-67@PDA-SF-2 and ZIF-67@PDA-SF and are (1-30.05/33.94)*100% = 11.5 wt% and (1-28.25/33.94)*100% = 16.8 wt%, respectively.

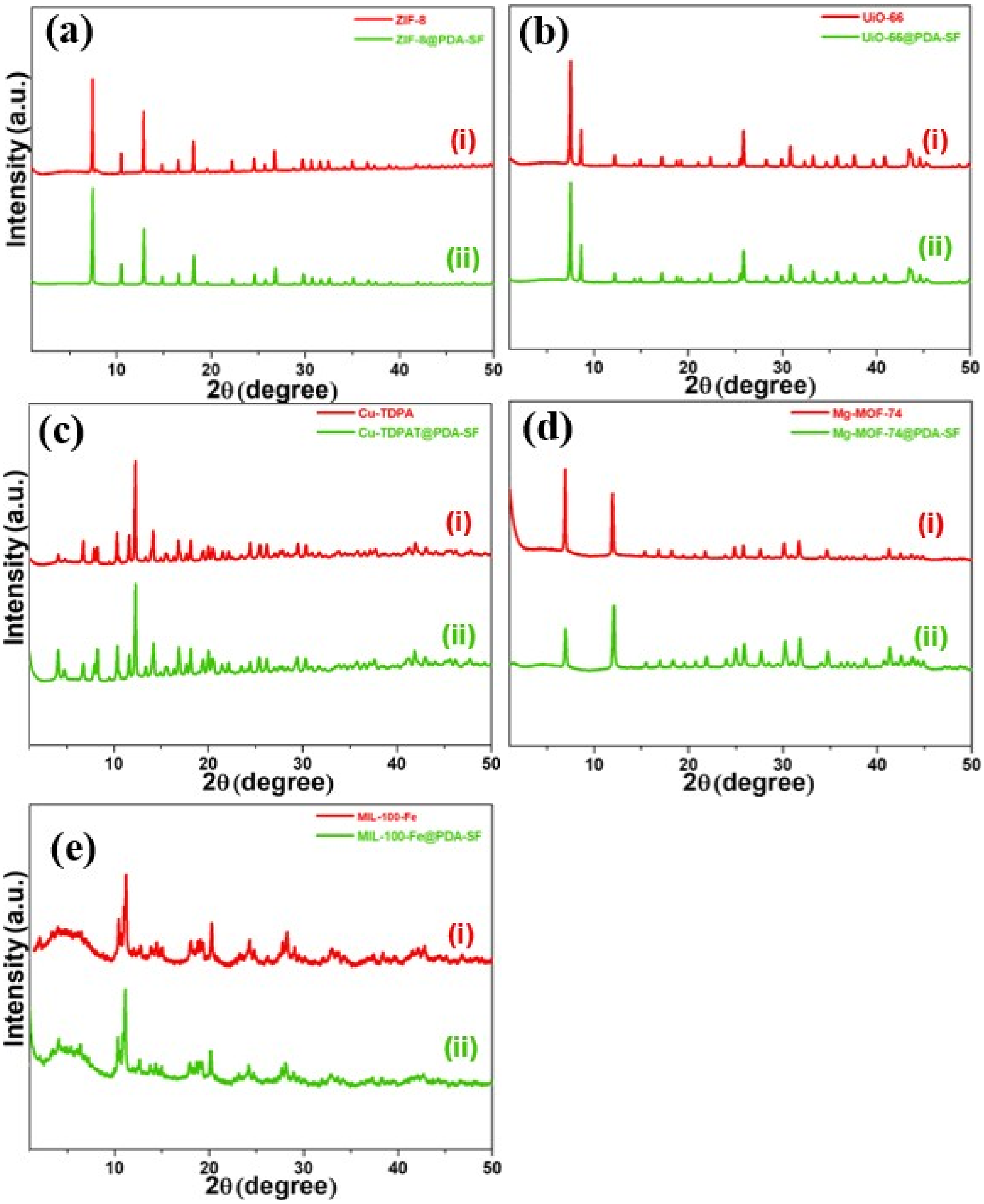


Fig. S19 XRD patterns of the ZIF-8 (a-i), UiO-66 (b-i), Cu-TDPAT (c-i), Mg-MOF-74 (d-i), MIL-100-Fe (e-i) and the corresponding XRD patterns of ZIF-8@PDA-SF (a-ii), UiO-66@PDA-SF (b-ii), Cu-TDPAT@PDA-SF (c-ii), Mg-MOF-74@PDA-SF (d-ii), MIL-100-Fe@PDA-SF (e-ii).

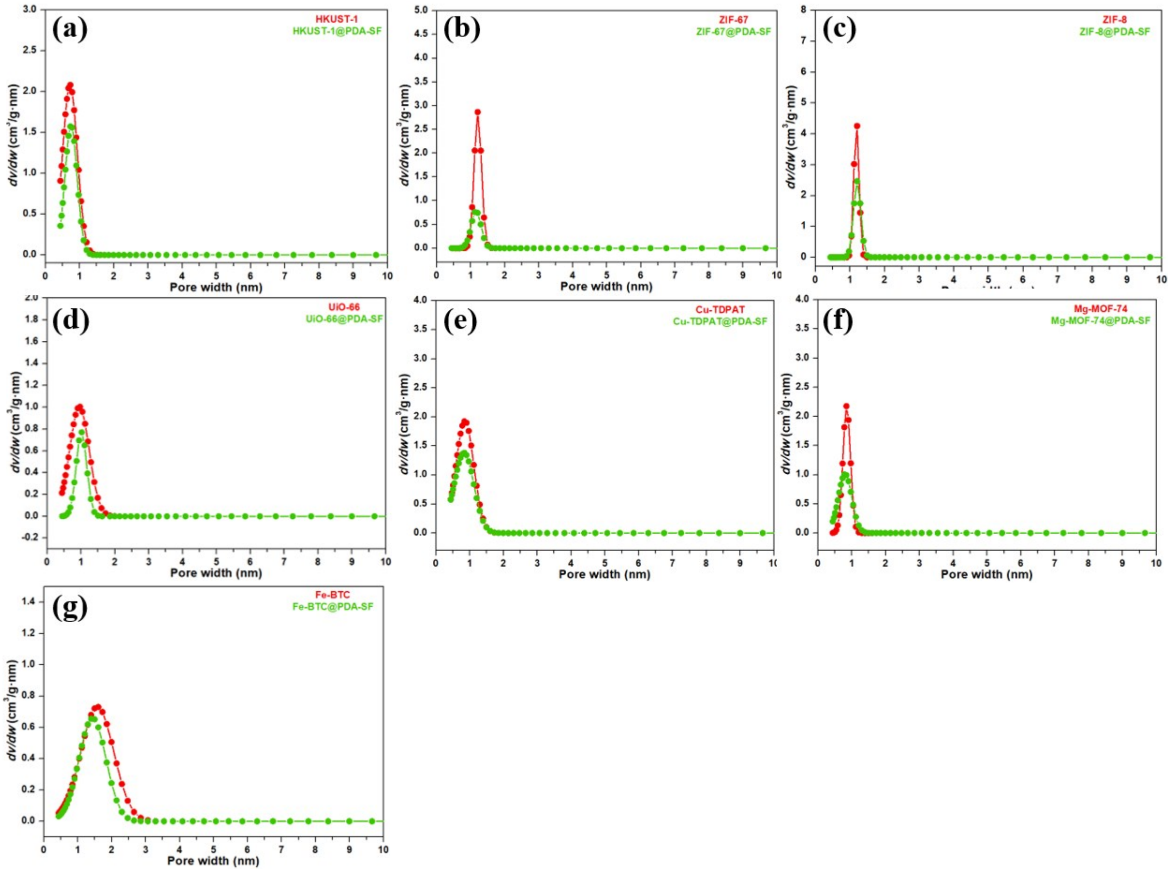
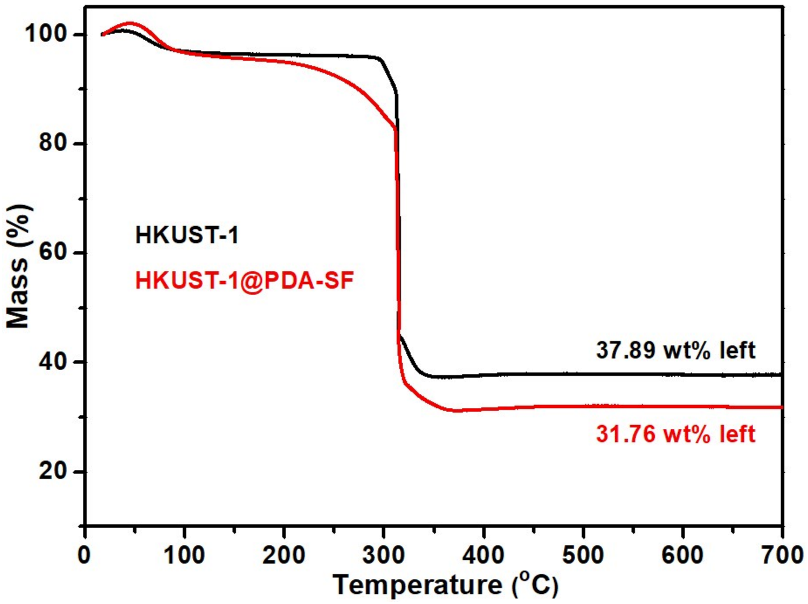
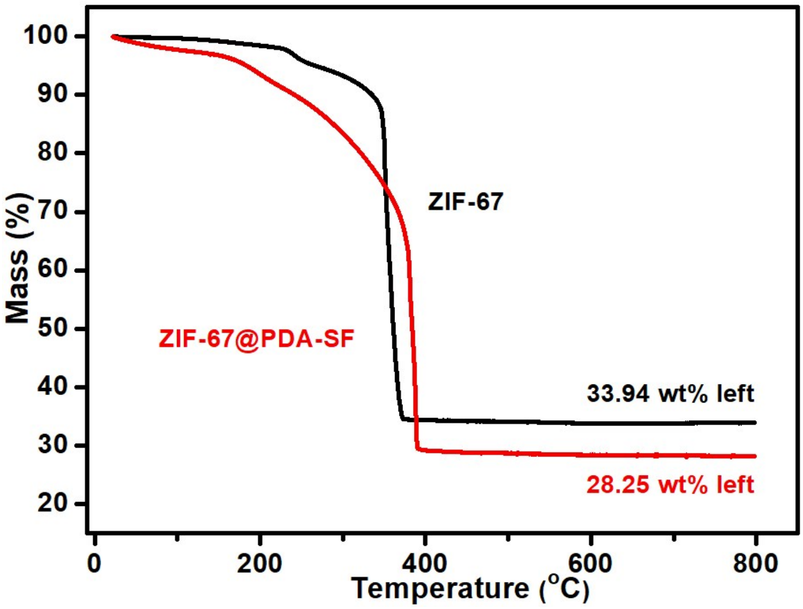


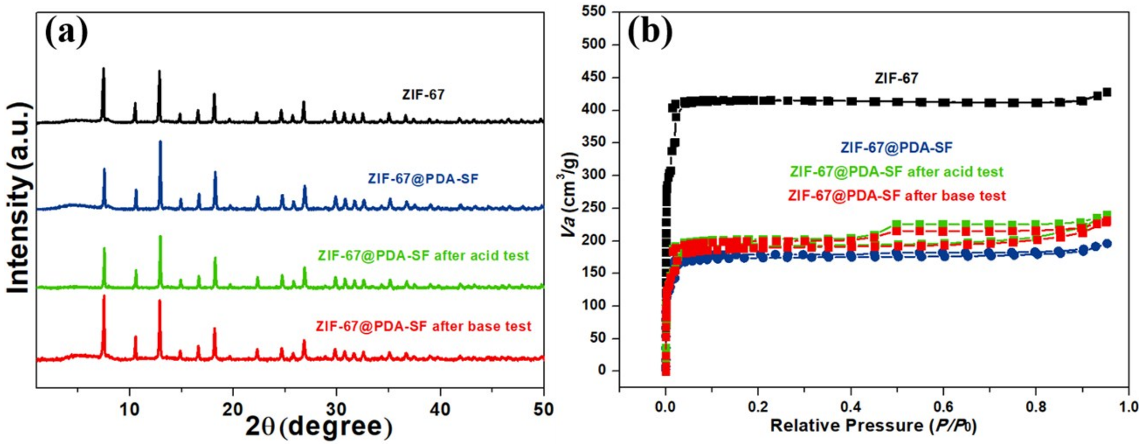
Fig. S20 Pore size distribution of the HKUST-1 (a, red), ZIF-67 (b, red), ZIF-8 (c, red), UiO-66 (d, red), Cu-TDPAT (e, red), Mg-MOF-74 (f, red), MIL-100-Fe (g, red) and the corresponding PDA-SF modified samples (green).



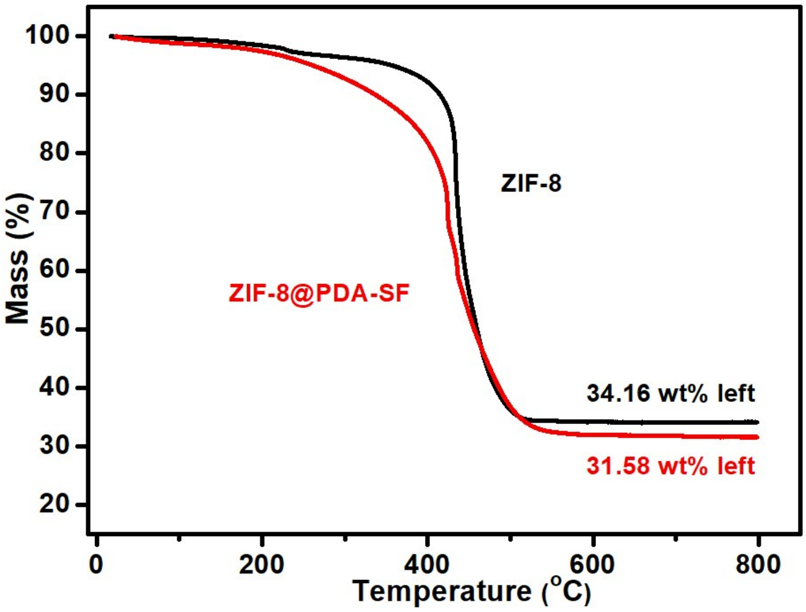
Thermogravimetric analysis of HKUST-1 and HKUST-1@PDA-SF revealed the HKUST-1@PDA-SF composite with polymer loading: (1-31.76/37.89)*100% = 16.2 wt%.



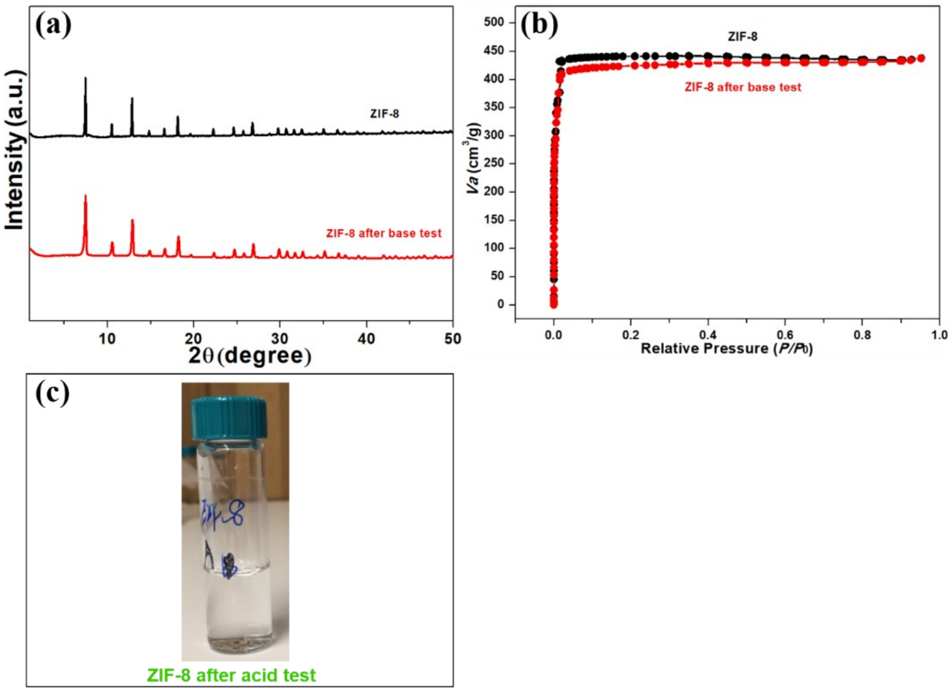
Thermogravimetric analysis of ZIF-67 and ZIF-67@PDA-SF revealed the ZIF-67@PDA-SF composite with polymer loading: (1-28.25/33.94)*100% = 16.8 wt%.



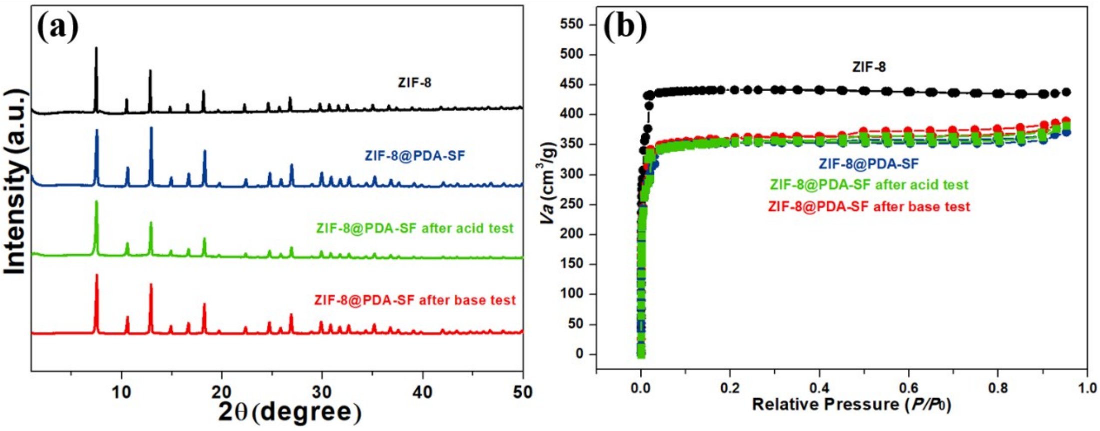
ZIF-67@PDA-SF under H_2SO_4 (pH=3)/NaOH (pH=13) condition for 24 h, is stable. XRD patterns (a) of ZIF-67 and the corresponding modified sample ZIF-67@PDA-SF after acid-base test. N_2 adsorption-desorption isotherms (b) of the unmodified ZIF-67, the modified sample ZIF-67@PDA-SF and ZIF-67@PDA-SF after stability test. The surface areas of samples are: ZIF-67 (black, 1466 m^2/g), ZIF-67@PDA-SF (navy, 683 m^2/g), ZIF-67@PDA-SF after acid test (green, 729 m^2/g) and ZIF-67@PDA-SF after base test (red, 738 m^2/g).



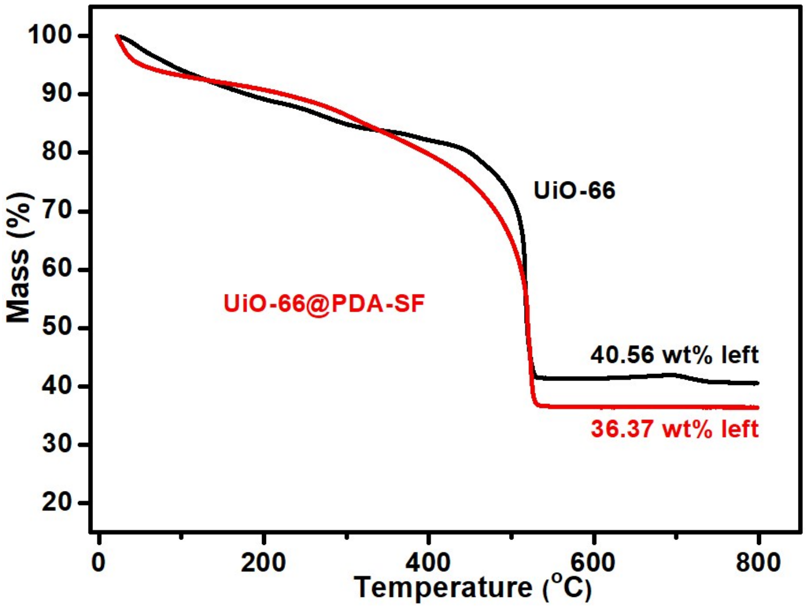
Thermogravimetric analysis of ZIF-8 and ZIF-8@PDA-SF revealed the ZIF-8@PDA-SF composite with polymer loading: (1-31.58/34.16)*100% = 7.6 wt%.



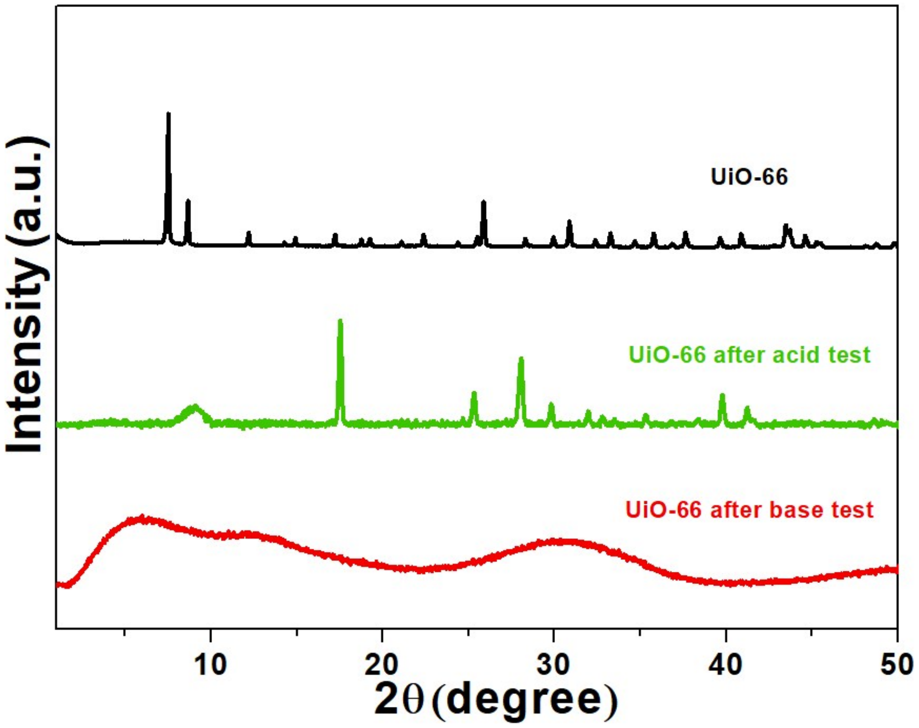
ZIF-8 under NaOH (pH=13) condition for 24 h, is stable. XRD patterns (a) of ZIF-8 and the sample after base test. N_2 adsorption-desorption isotherms (b) of the unmodified ZIF-8, the ZIF-8 sample after stability test. ZIF-8 under H_2SO_4 (pH=1) condition for 24 h, is dissolved completely (c). The surface areas of samples are: as-synthesized ZIF-8 (black, 1788 m^2/g) and ZIF-8 after base test (red, 1710 m^2/g).



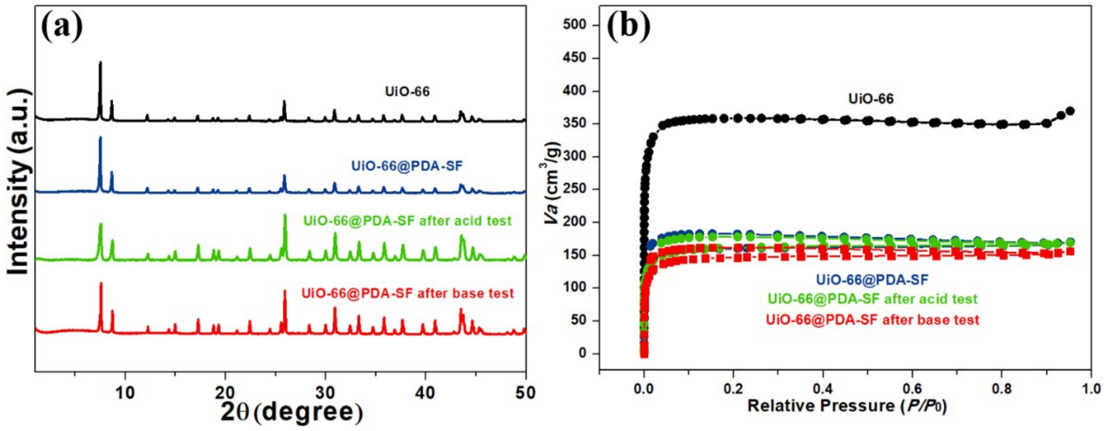
ZIF-8@PDA-SF under H_2SO_4 (pH=1)/NaOH (pH=13) condition for 24 h, is stable. XRD patterns (a) of ZIF-8 and the corresponding modified sample ZIF-8@PDA-SF after acid-base test. N_2 adsorption-desorption isotherms (b) of the unmodified ZIF-8, the modified sample ZIF-8@PDA-SF and ZIF-8@PDA-SF after stability test. The surface areas of samples are: ZIF-8 (black, 1788 m^2/g), ZIF-8@PDA-SF (navy, 1389 m^2/g), ZIF-8@PDA-SF after acid test (green, 1387 m^2/g) and ZIF-8@PDA-SF after base test (red, 1411 m^2/g).



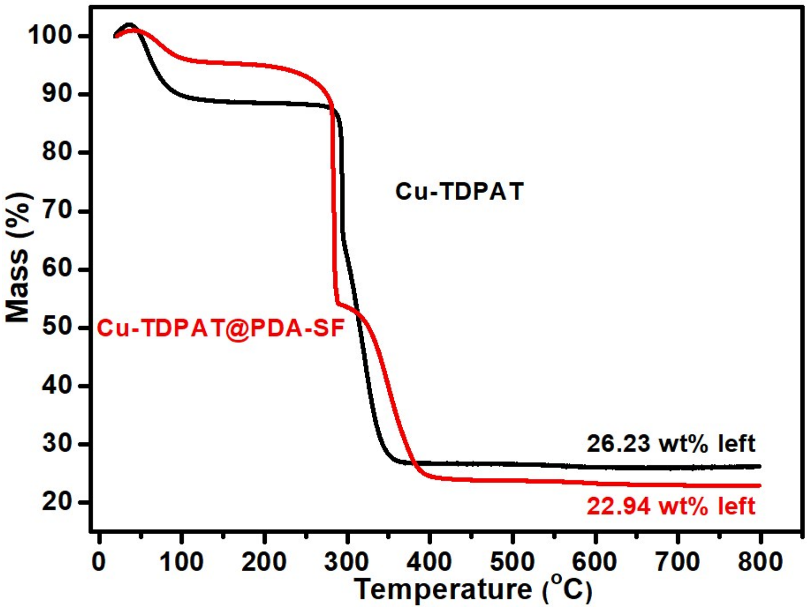
Thermogravimetric analysis of UiO-66 and UiO-66@PDA-SF revealed the UiO-66@PDA-SF composite with polymer loading: (1-36.37/40.56)*100% = 10.3 wt%.



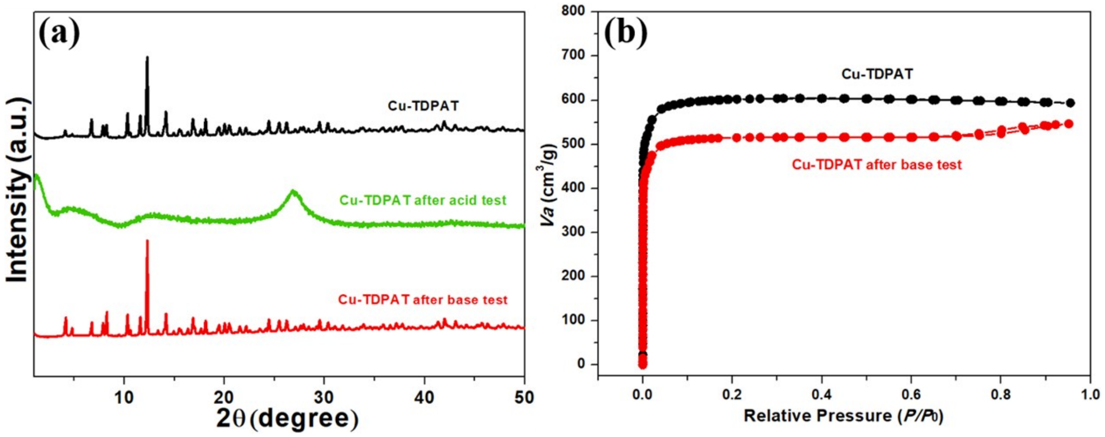
UiO-66 under H_2SO_4 (pH=1)/NaOH (pH=13) condition for 24 h, is unstable.



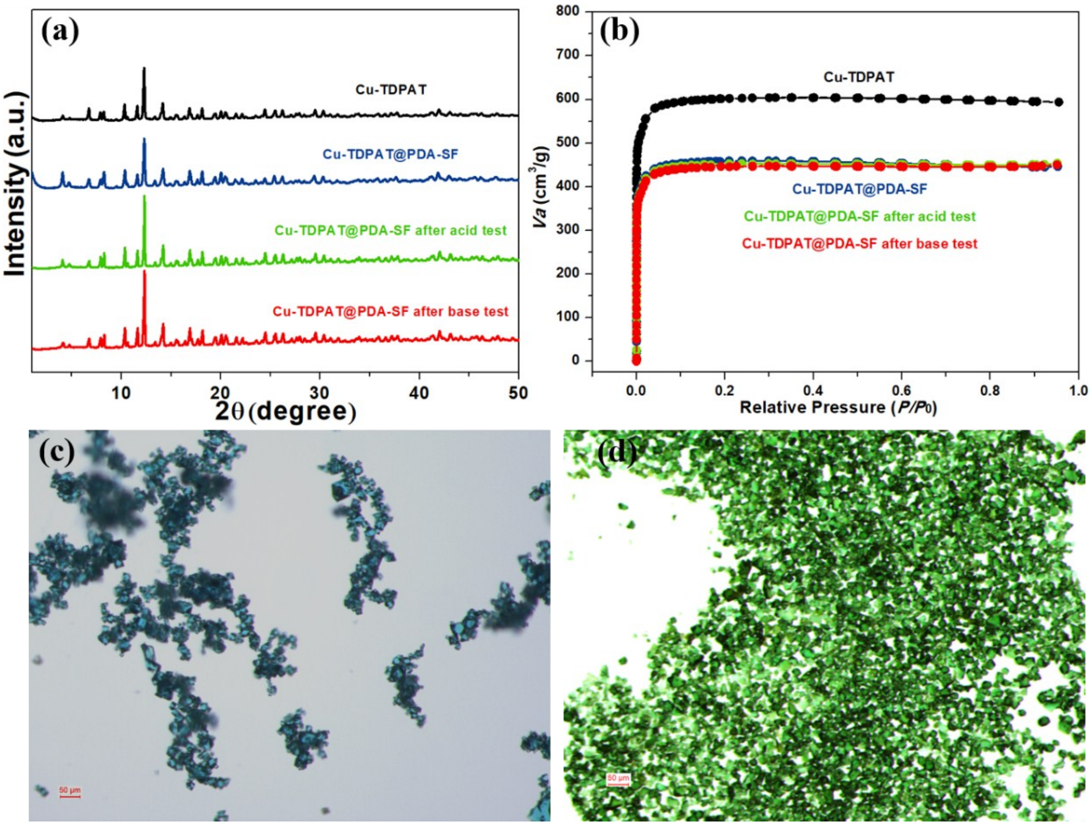
UiO-66@PDA-SF under H_2SO_4 (pH=1)/NaOH (pH=13) condition for 24 h, is stable. XRD patterns (a) of UiO-66, UiO-66@PDA-SF and the corresponding modified sample UiO-66@PDA-SF after acid-base test. N_2 adsorption-desorption isotherms (b) of the unmodified UiO-66, the modified sample UiO-66@PDA-SF and UiO-66@PDA-SF after stability test. The surface areas of samples are: as-synthesized UiO-66 (black, 1430 m^2/g), UiO-66@PDA-SF (navy, 638 m^2/g), UiO-66@PDA-SF after acid test (green, 626 m^2/g) and UiO-66@PDA-SF after base test (red, 581 m^2/g).



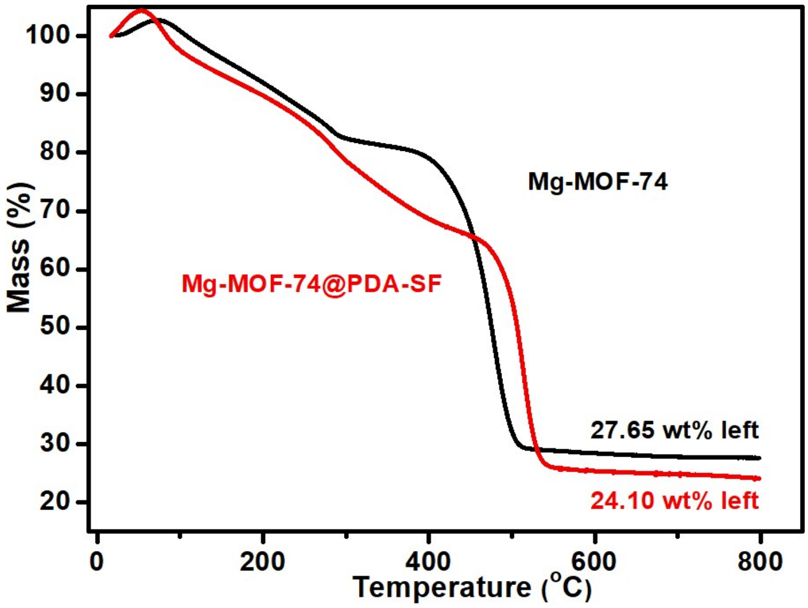
Thermogravimetric analysis of Cu-TDPAT and Cu-TDPAT@PDA-SF revealed the Cu-TDPAT@PDA-SF composite with polymer loading: (1-22.94/26.23)*100% = 12.5 wt%.



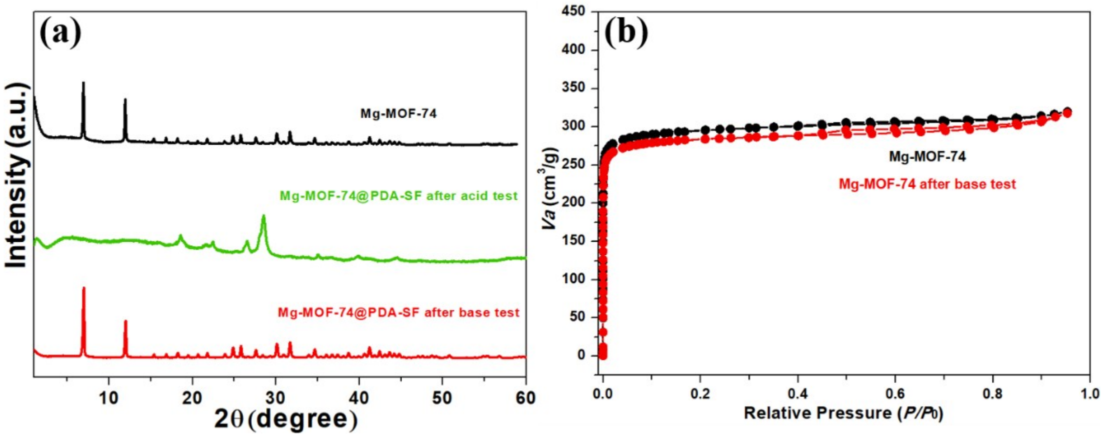
Cu-TDPAT under H_2SO_4 (pH=2) condition for 24 h, is unstable; even though the XRD pattern of Cu-TDPAT under NaOH (pH=12) condition for 24 h is maintained, the surface area decreased. The surface areas of samples are: as-synthesized Cu-TDPAT (black, 2254 m^2/g) and Cu-TDPAT after base test (red, 2042 m^2/g).



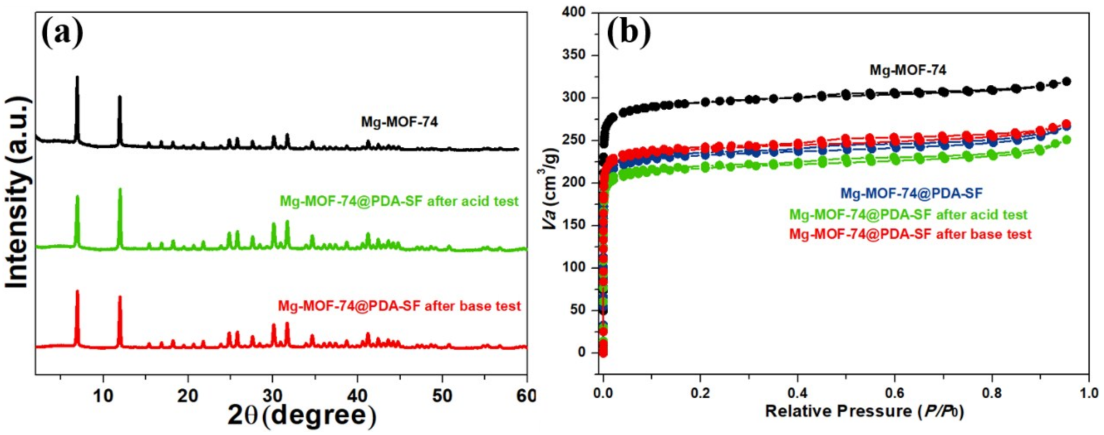
Cu-TDPAT@PDA-SF under H_2SO_4 (pH=2)/NaOH (pH=12) condition for 24 h, is stable. XRD patterns (a) of Cu-TDPAT, Cu-TDPAT@PDA-SF and the corresponding modified sample Cu-TDPAT@PDA-SF after acid-base tests. N_2 adsorption-desorption isotherms (b) of the unmodified Cu-TDPAT, the modified sample Cu-TDPAT@PDA-SF and Cu-TDPAT@PDA-SF after stability test. The surface areas of samples are: Cu-TDPAT (black, 2254 m^2/g), Cu-TDPAT@PDA-SF (red, 1835 m^2/g), Cu-TDPAT@PDA-SF after acid test (green, 1784 m^2/g) and Cu-TDPAT@PDA-SF after base test (red, 1778 m^2/g). Light microscope images of Cu-TDPAT (c) and Cu-TDPAT@PDA-SF (d).



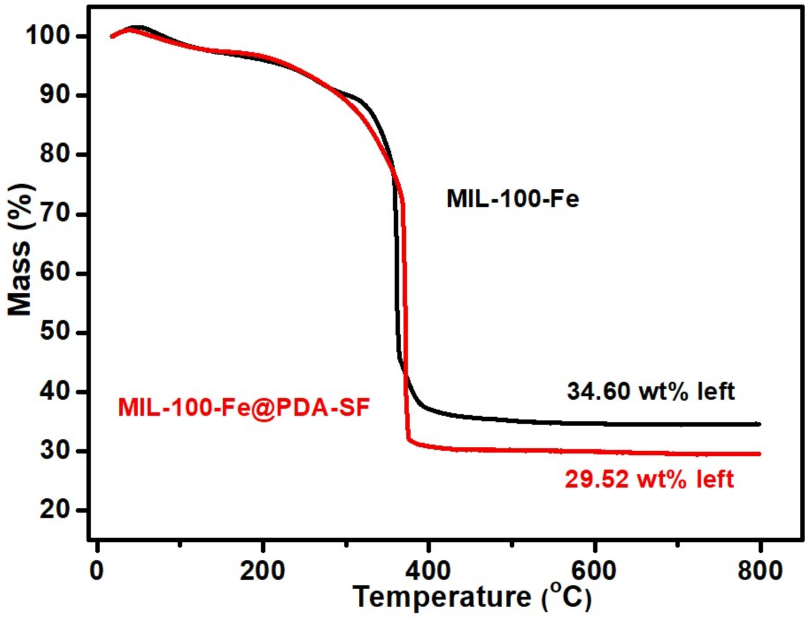
Thermogravimetric analysis of Mg-MOF-74 and Mg-MOF-74@PDA-SF revealed the Mg-MOF-74@PDA-SF composite with polymer loading: (1-24.10/27.65)*100% = 12.8 wt%.



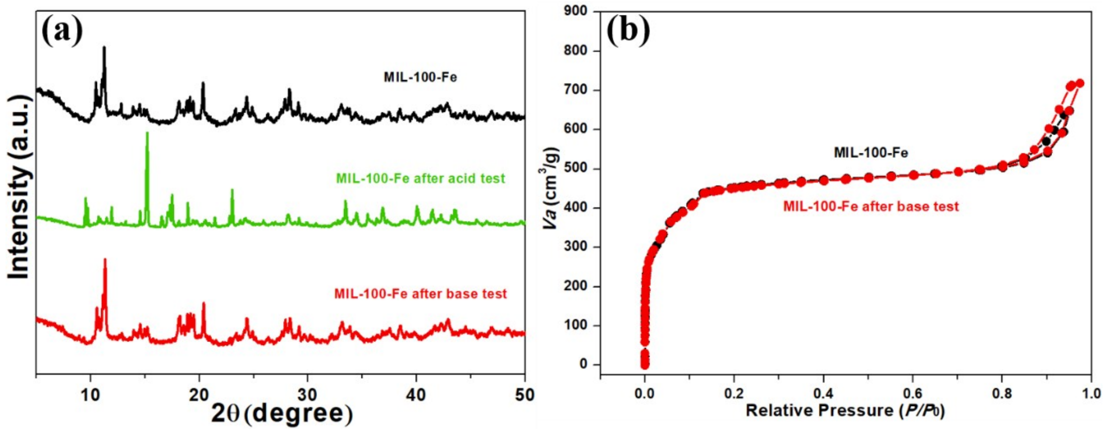
Mg-MOF-74 under H_2SO_4 (pH=1) condition for 24 h, is unstable; Mg-MOF-74 under NaOH (pH=12) condition for 24 h, is stable. The surface areas of samples are: as-synthesized Mg-MOF-74 (black, 1182 m^2/g) and Mg-MOF-74 after base test (red, 1138 m^2/g).



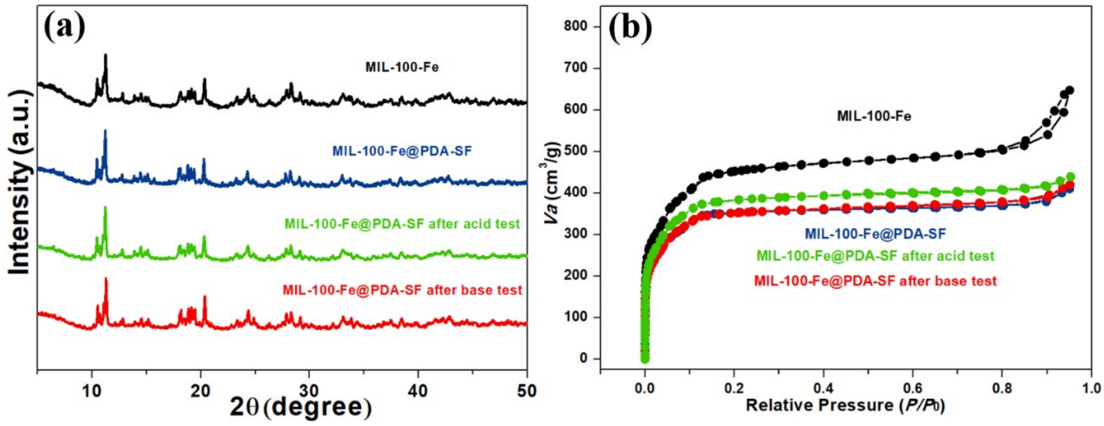
Mg-MOF-74@PDA-SF under H_2SO_4 (pH=1)/NaOH (pH=12) condition for 24 h, is stable. The surface areas of samples are: as-synthesized Mg-MOF-74 (black, 1182 m^2/g), Mg-MOF-74@PDA-SF (navy, 918 m^2/g), Mg-MOF-74@PDA-SF after acid test (green, 867 m^2/g) and Mg-MOF-74@PDA-SF after base test (red, 952 m^2/g).



Thermogravimetric analysis of MIL-100-Fe and MIL-100-Fe@PDA-SF revealed the MIL-100-Fe@PDA-SF composite with polymer loading: (1-29.52/34.60)*100% = 14.7 wt%.



MIL-100-Fe under H_2SO_4 (pH=0) condition for 24 h, is unstable; MIL-100-Fe under NaOH (pH=12) condition for 24 h, is stable. XRD patterns (a) of MIL-100-Fe and the MIL-100-Fe after acid-base test. N_2 adsorption-desorption isotherms (b) of the MIL-100-Fe, the MIL-100-Fe after stability test. The surface areas of samples are: as-synthesized MIL-100-Fe (black, 1587 m^2/g) and MIL-100-Fe after base test (red, 1579 m^2/g).



MIL-100-Fe@PDA-SF under H_2SO_4 (pH=0)/NaOH (pH=12) condition for 24 h, is stable. XRD patterns (a) of MIL-100-Fe, MIL-100-Fe@PDA-SF and the corresponding modified sample MIL-100-Fe@PDA-SF after acid-base test. N_2 adsorption-desorption isotherms (b) of the unmodified MIL-100-Fe, the modified sample MIL-100-Fe@PDA-SF and MIL-100-Fe@PDA-SF after stability test. The surface areas of samples are: as-synthesized MIL-100-Fe (black, 1587 m^2/g), MIL-100-Fe@PDA-SF (navy, 1266 m^2/g), MIL-100-Fe@PDA-SF after acid test (green, 1369 m^2/g) and MIL-100-Fe@PDA-SF after base test (red, 1262 m^2/g).

Fig. S21 Stability test results. Compared with that of the parent materials, the modified ZIF-8@PDA-SF, UiO-66@PDA-SF and Cu-TDPAT@PDA-SF showed improved stability under harsh condition (acidic or basic environment).

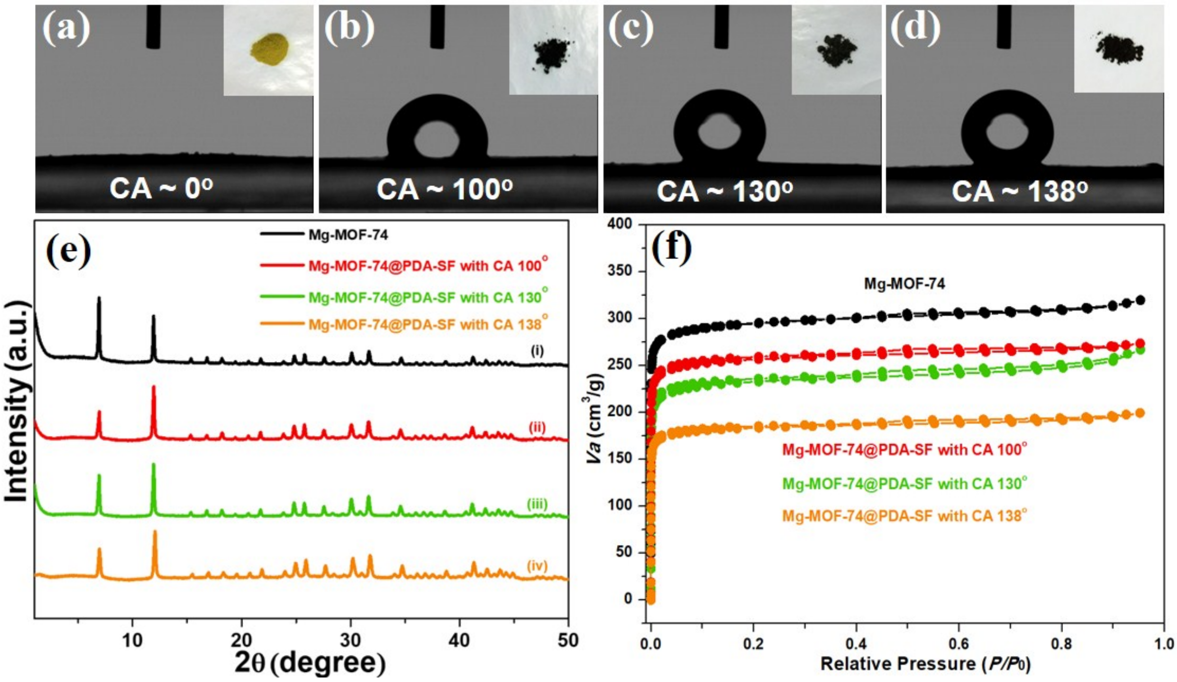


Fig. S22 The water contact angle of Mg-MOF-74 (a), Mg-MOF-74@PDA-SF with CA 100° (b), Mg-MOF-74@PDA-SF with CA 130° (c) and Mg-MOF-74@PDA-SF with CA 138° (d). The insets of Figure a-d are the corresponding sample photographs. XRD patterns (e) and N_2 adsorption-desorption isotherms (f) of Mg-MOF-74 and the modified samples. The surface areas of samples are: as-synthesized Mg-MOF-74 (black, 1182 m^2/g), Mg-MOF-74@PDA-SF with CA 100° (red, 1010 m^2/g), Mg-MOF-74@PDA-SF with CA 130° (green, 918 m^2/g) and Mg-MOF-74@PDA-SF with CA 138° (orange, 704 m^2/g).

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