

Electronic Supplementary Information

***In situ* fabrication of bendable epitaxial metal-organic framework films via spraying**

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EXPERIMENTAL SECTION

Materials

Copper acetate ($\text{Cu}(\text{CH}_3\text{COO})_2$), 1,4-benzenedicarboxylic acid (H_2BDC) and Sudan III were supplied from Energy Chemical (Shanghai, China). *N,N*-dimethyl formamide (DMF), acetonitrile (CH_3CN) and *n*-hexane were purchased from Tianjin fuyu fine Chemical Reagent Co., Ltd (Tianjin, China). Sodium dodecyl benzene sulfonate (SDBS) and sodium dodecyl sulfate (SDS) were obtained from Tianjin zhiyuan Reagent Co., Ltd (Tianjin, China). Polyvinylidene fluoride (PVDF), Al_2O_3 and nylon filter film with average pore size of $0.22\ \mu\text{m}$ were purchased from Shanghai Xingya Purification Material Co., Ltd (shanghai, China). All chemicals were of analytical grade and used as received without further purification.

Preparation of the MOF film.

In this study, CuBDC was selected to fabricate the MOF layer. Commercially available porous PVDF, Al_2O_3 , and nylon filter film with an average pore size of $0.22\ \mu\text{m}$ were selected as substrates. Taking PVDF substrate as an example, H_2BDC (79.8 mg, 0.41 mmol) was dissolved in 12 mL of a mixture of DMF and CH_3CN solvents in a 2:1 volumetric ratio of (*v:v*), and the resultant mixture was then ultrasonicated for 8 min to ensure even stirring. $\text{Cu}(\text{CH}_3\text{COO})_2$ (28 mg, 0.15 mmol) was dissolved in 7.5 mL of a 1:2 *v:v* mixture of DMF : CH_3CN , and ultrasonicated for 5 min to ensure even mixing of the solution. Then, the porous substrate was immersed in the solution containing H_2BDC for a residence time of around 15 min to allow the solution containing the organic ligand to penetrate into the pores of the substrate. After that, a squeegee roller was employed to remove the excess solution from the top surface of the substrate. Finally, an ultrasonic sprayer was used to evenly spray the solution containing the metal on the surface of the PVDF film at a spray liquid flow rate of $1\ \mu\text{L}\ \text{s}^{-1}$ under static conditions. As this process, a blue homogeneous MOF layer appeared on the surface of the PVDF film.

Oil-in-water emulsion separation experiments

To prepare an oil-in-water emulsion, oil and water were mixed in a volume ratio of 1:9 *v:v* ratio, and the resultant mixture was then ultrasonicated for 6 h at $25\ ^\circ\text{C}$ until it become uniform milky white in color. The prepared solution could be stable for about 4 h at room temperature. To prepare a surfactant-stabilized oil-in-water emulsion, SDBS $100\ \text{mg}\ \text{L}^{-1}$ was selected as the surfactant, and oil and water were mixed with it in a 1:9 *v:v* ratio. After ultrasonicated for 6 h at $25\ ^\circ\text{C}$, the prepared solution was stabilized for around 12 h at ambient temperature. After that, the emulsion was filtered through a PVDF-supported CuBDC film using an adsorption filtration device. The water flux through the film was calculated using the following equation:

$$F = \Delta V / (S \cdot \Delta t)$$

where F ($\text{L}\ \text{m}^2\ \text{h}^{-1}$) is the volumetric water flux, ΔV (L) is the volume of the permeate solution collected over a period of time Δt (h), and S (m^2) is the effective film area. Dye emulsion separation experiments

To prepare a surfactant-stabilized dye emulsion, SDS $100\ \text{mg}\ \text{L}^{-1}$ was selected as a surfactant, and oil and water were mixed in a 1:50 *v:v* ratio. To this, Sudan III dye was added ($0.005\ \text{g}\ \text{L}^{-1}$) and the resultant mixture was ultrasonicated at $25\ ^\circ\text{C}$ for 6 h to ensure its uniform dispersion. The prepared solution could be stored for around 24 h at ambient temperature.

Characterization of the films

The morphologies of the MOF films were estimated by field-emission scanning electron microscopy (FE-SEM, Hitachi SU8010). Energy-dispersive X-ray spectroscopy (EDX, Oxford Instruments)

was used to characterize the chemical composition of the MOF films. Power X-ray diffractometry (PXRD, Shimadzu XRD-6000) was conducted on a diffractometer equipped with a Cu K α radiation source ($\lambda=1.5406 \text{ \AA}$) to analysis the crystallographic information of the films. The organic groups of the film were analyzed by Fourier-transform infrared (FT-IR) spectroscopy (Bruker VERTEX70). The water content of the film was measure using a Karl Fischer moisture analyzer (870 KF Titrino plus, Switzerland). Optical microscopy images were made use of biological microscope (Dilun Optics TL2800A, Shanghai, China). The ultrasonic spray nozzle and system used to spray the film were manufactured by Siansonic Technology Co., Ltd (DP30 ultrasonic generator and ZPQ-S-95 nozzle).

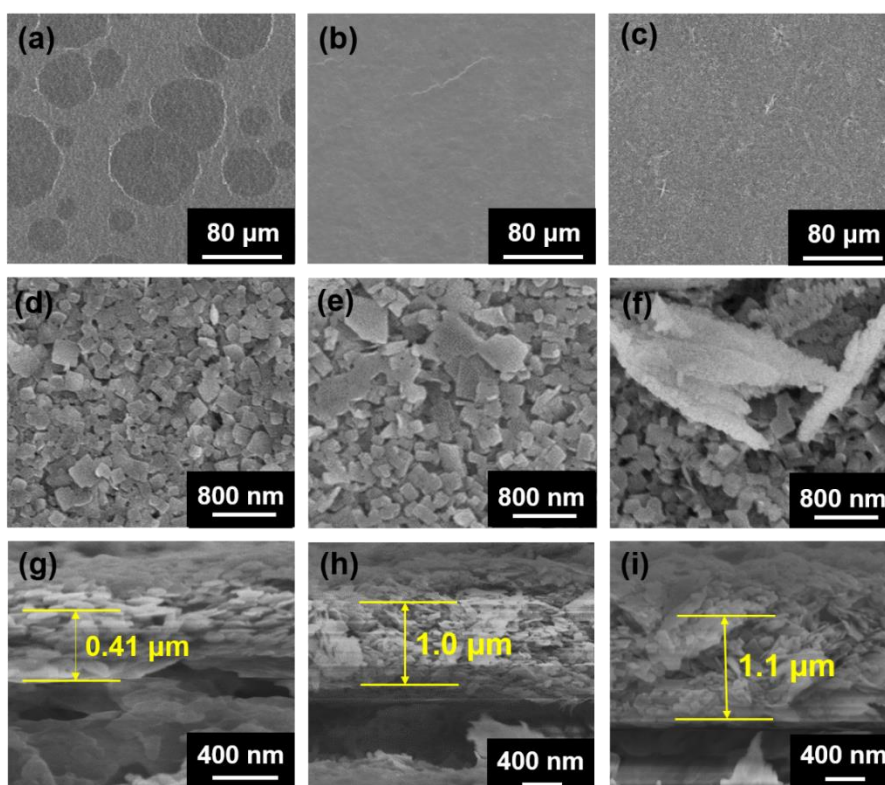


Figure S1. The change of MOF layer morphology and thickness with different spray numbers. (a, d, g) Spraying twice. (b, e, h) Spraying sixth. (c, f, i) Spraying eighth.

After spraying twice, the porous substrate is covered completely. The MOF layer is composed by nanosheet and the thickness is $0.41\ \mu\text{m}$. As spraying time increased, flat square nanosheets begin to gather and the thickness increased to $1.0\ \mu\text{m}$ after spraying sixth. After that, the nanosheets agglomerated into a rod-like structure and the thickness of the film reach $1.1\ \mu\text{m}$ under spraying eighth.

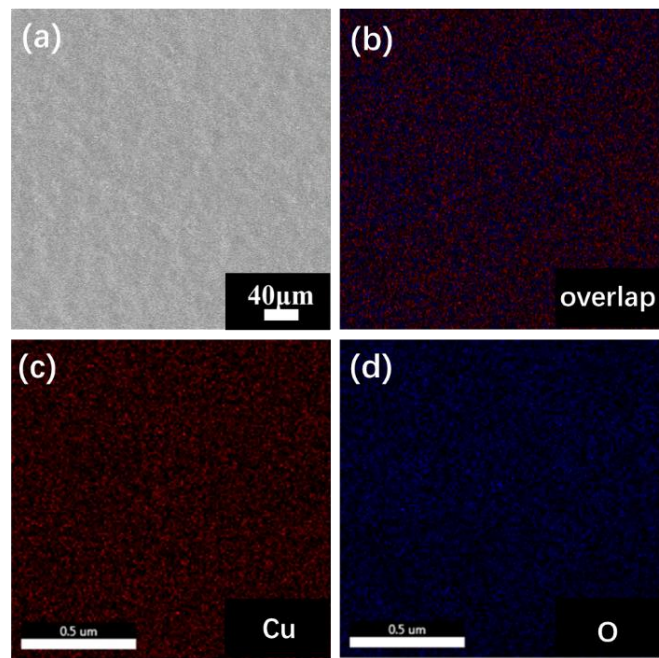


Figure S2. (a) SEM image. (b-d) EDX elemental mapping images of CuBDC films.

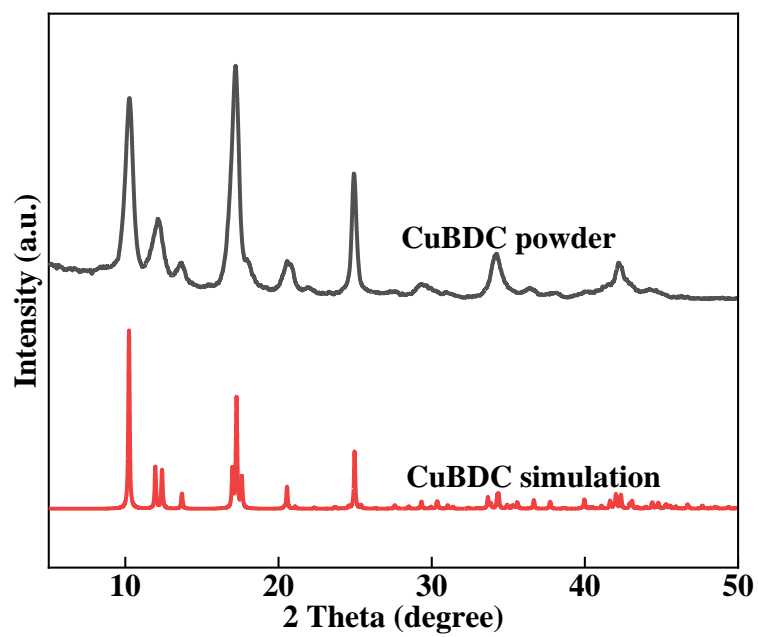


Figure S3. PXRD patterns of the CuBDC powder scratched from the film, and the simulated powder pattern of CuBDC.

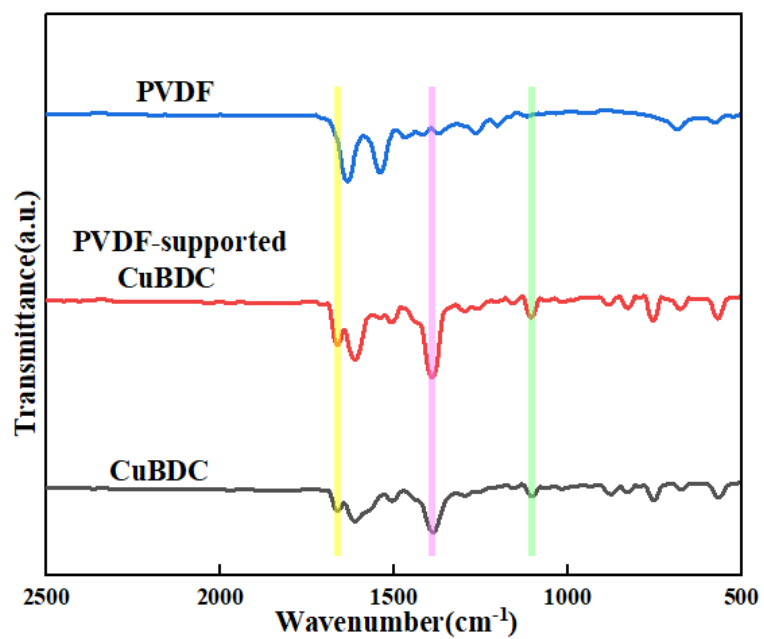


Figure S4. FT-IR spectra of the PVDF film, PVDF-supported CuBDC film and CuBDC power.

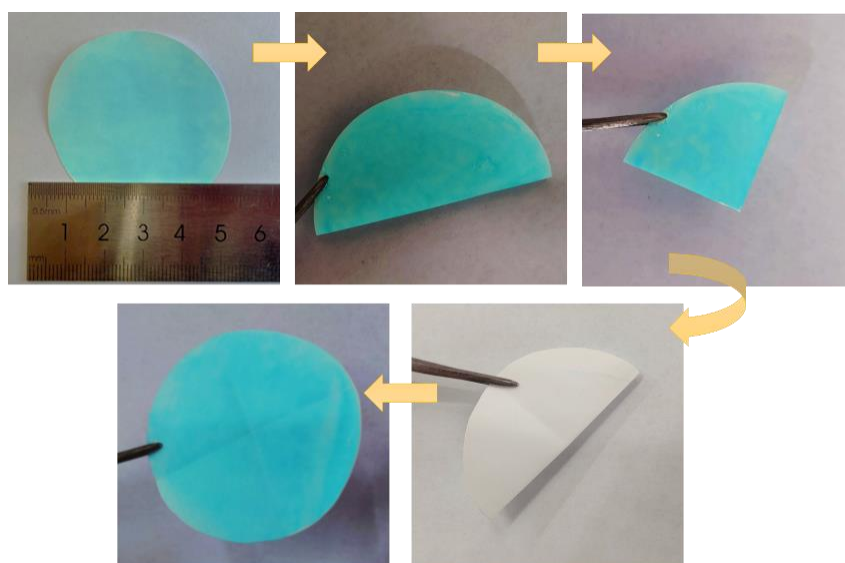


Figure S5. Photographs of the PVDF-supported CuBDC film after folded in half.

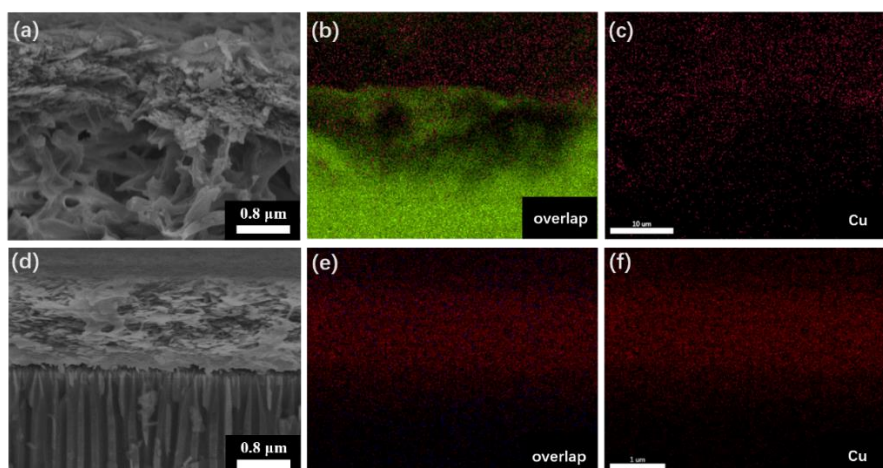


Figure S6. (a) SEM cross-section image and (b-c) EDX images of CuBDC films supported by PVDF matrix. (d) SEM cross-section image and (e-f) EDX images of CuBDC films supported by the Al₂O₃ matrix.

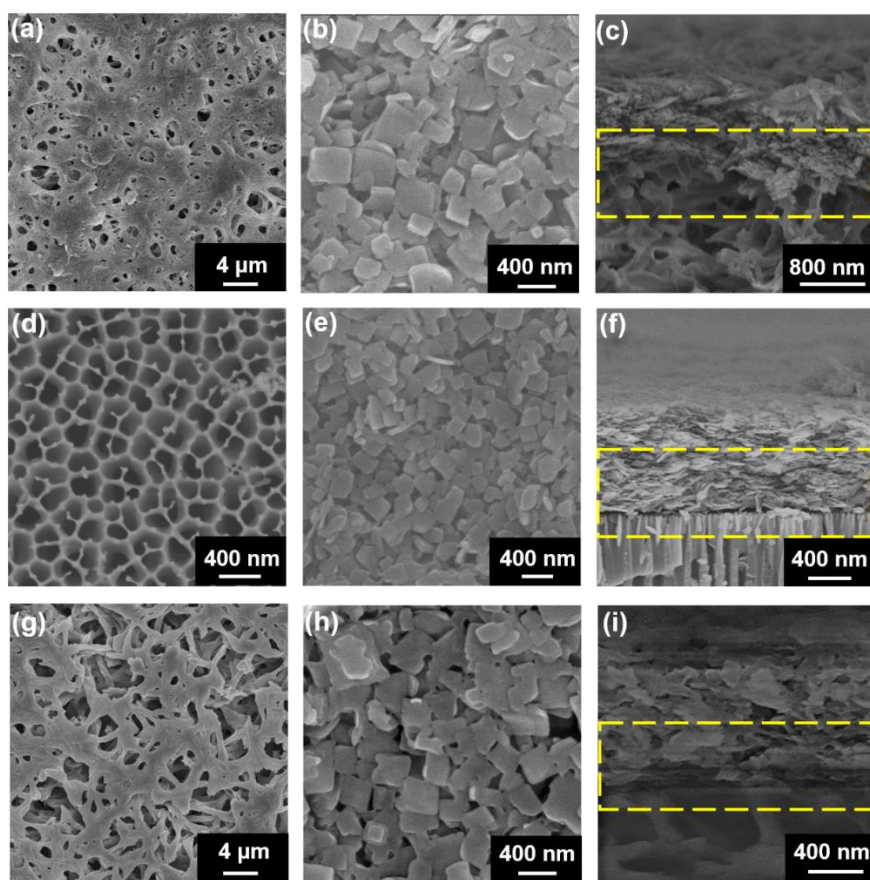


Figure S7. SEM images of different commercially available substrates and MOF layer prepared on it. (a-c) PVDF matrix; (d-f) Al₂O₃ matrix; (g-i) nylon filter matrix.

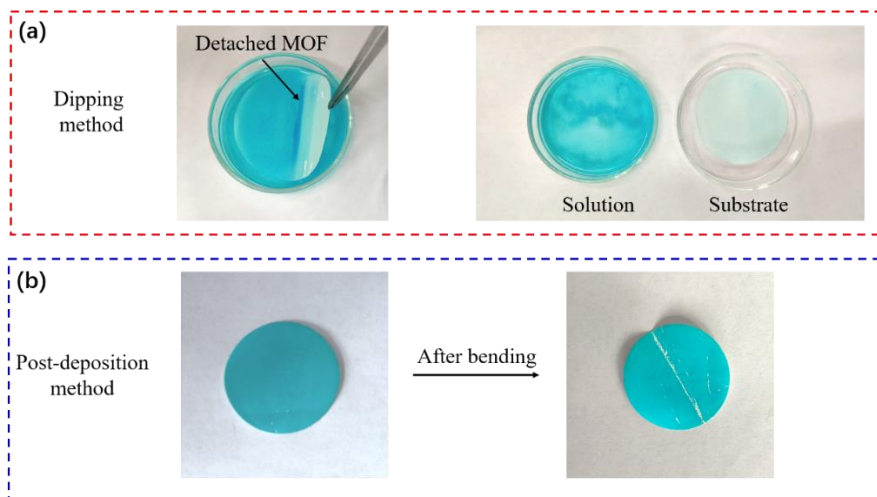


Figure S8. The membrane prepared by dipping (a) and post-deposition (b).

The membrane prepared by dipping as following: the PVDF substrate was immersed in the organic ligand solution, then took out and put it in the solution containing metal ions. As shown in Figure S8a, the MOF layer could not grow on the substrate and detached when the membrane was taken out.

The membrane prepared by post-deposition as following: the solution containing metal ions was spray on the surface of the organic ligand solution, then the solution was removed carefully, and the MOF layer deposited onto the substrate. As shown in Figure S8b, the MOF film showed obvious cracks when it was folded in half.

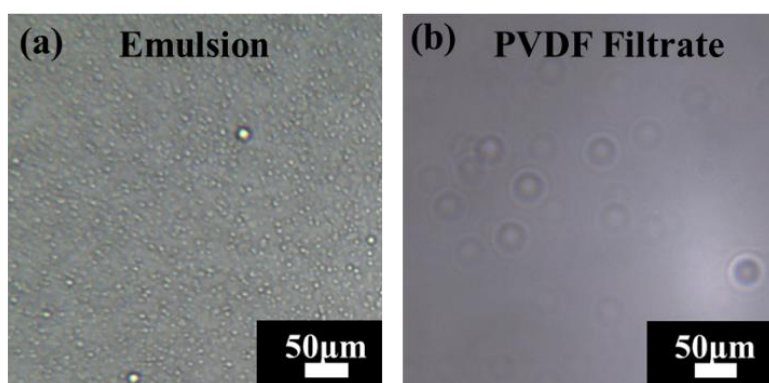


Figure S9. (a) Optical microscopy of oil-in-water emulsion. (b) Emulsion separation with bare PVDF substrate.

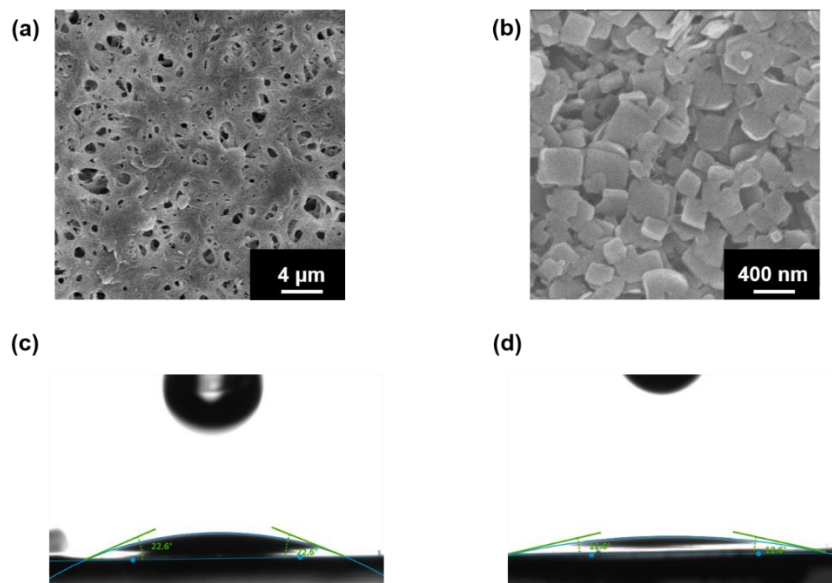


Figure S10. SEM images the PVDF substrate (a), and the MOF film (b). Water contact angle images of PVDF substrate (c), and the MOF film (d).

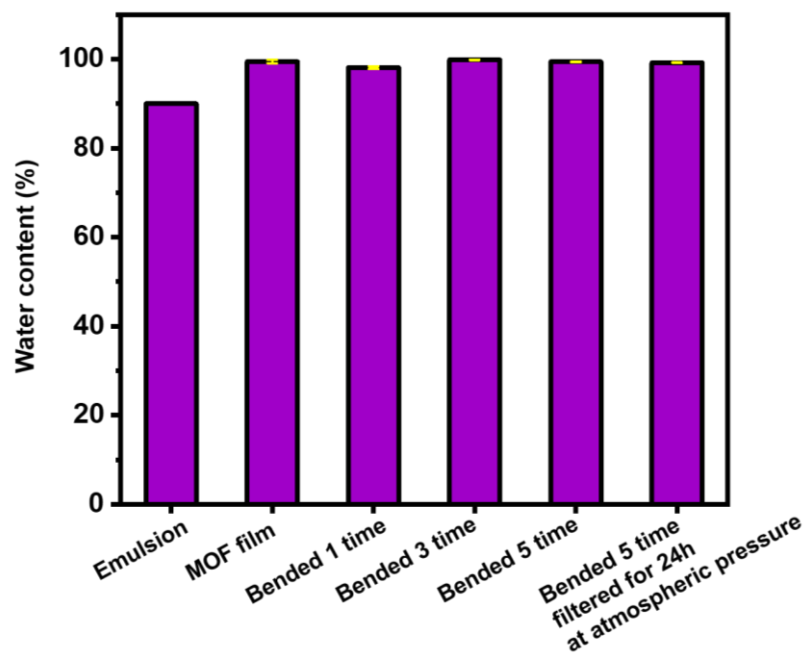


Figure S11. The separation efficiency of the MOF film before and after bending for different times at curvature $K= 400 \text{ m}^{-1}$.

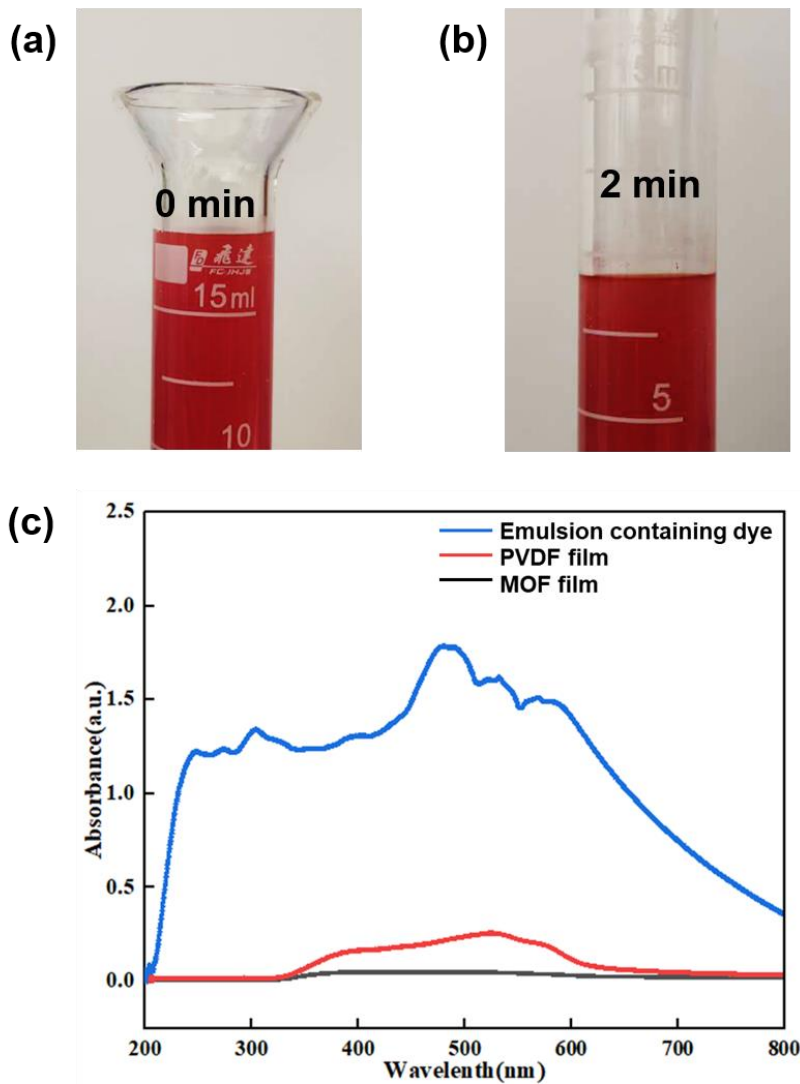


Figure S12. The separation process of oil-in-water surfactant stabilized emulsion. (a) Before separation. (b) Separation after 2 min. (c) The UV absorption of the solvents after filtrated with different films.