Supplementary Information (SI) for Nanoscale Horizons.

Piezoelectric PVDF Membrane for Emulsion Separation with Constant Flux and High Efficiency

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Experimental Section

Materials

NMP (AR, > 99.0%), SA (AR) were obtained from Shanghai Aladdin Chemical Co., Ltd., China. CTAB (99%), DA (98%), PVDF (average Mw: ~400000, powder) were purchased from Shanghai Macklin Biochemical Co., Ltd., China. Toluene, Tween 80 (CP), SDS (CP) were purchased from Sinopharm Chemical Reagent Co., Ltd, Shanghai, China. Deionized water was obtained from a water purifier (Ulupure-I-20T, Sichuan Ulupure Technology Co., Ltd.) with a resistivity of 18.25 MΩ cm. None of the reagents were further purified before use.

Preparation of PDS-1 Membrane and Control Sample

PDS-1 membranes were prepared by the NIPS method. The casting solution consisted of NMP, DA, and PVDF powder, with a mass ratio of PVDF to NMP of 15:85, and DA accounting for 0.2 wt% of the PVDF solution. Stirring was used to ensure that DA and PVDF were completely dissolved in NMP. The solution was then left to stand at room temperature for several hours to remove bubbles from the casting solution. After the bubbles were removed, a 250 μm casting knife was used to spread the solution onto a glass plate, it was immediately placed into a 0.25 wt% sodium alginate solution that had been pre-chilled in the refrigerator for a low-temperature solvent exchange for 48 h. After membrane formation, the surface residues were washed off with deionized water, and the membrane was dried at room temperature to obtain the finished membrane PDS-1. Meanwhile, control samples were prepared without the addition of DA and non-solvent is deionized water, without the addition of DA, with DA but with a solvent bath of deionized water, and with an increased content of DA to 0.4 wt%, and were named PVDF, PVDF-SA, PVDF-DA, and PDS-2, respectively.

Table S1 Membrane Codes of the membranes with their corresponding material quality composition.

Membrane Code	PVDF (g)	DA (g)	NMP (g)	SA (g)	H_2O (g)
PVDF	1.5	0	8.5	0	0
PVDF-DA	1.5	0.02	8.5	0	0
PVDF-SA	1.5	0	8.5	5	2000
PDS-1	1.5	0.02	8.5	5	2000
PDS-2	1.5	0.04	8.5	5	2000

Characterization

The morphologies of samples were obtained via Field Emission Scanning Electron Microscope (FESEM, sigma 500). The element distribution on the membrane surface was characterized by Energy Dispersive Spectroscopy (Bruker, XFlash 6/30). XPS (Thermo Scientific ESCALAB 250Xi) was hired to perform surface element composition analysis. The group types of the samples were characterized by FT-IR (is50). The crystal structures of the samples were determined via XRD (Bruker, D8 Advance). Emulsion droplet sizes before and after separation were measured by Particle Size and Z Potential Analyzer (Zetasizer Nano ZS90) and optical microscopy (Olympus). The piezoelectric properties of the materials were tested using a Piezoresponse Force Microscopy (MFP-3D Origin+). A Raman spectrometer (LabRAM HR Evolution, Horiba) was employed to gain a deeper understanding of the structural evolution and the crystalline phases of the samples. The pore distribution and porosity on the material surface were calculated using ImageJ software. Fluorescence signals were detected through fluorescence spectroscopy (RF-6000, Shimadzu) and a fluorescence confocal microscope (Carl Zeiss lsm880).

Oil-in-water Emulsions Separation Experiment

The atmospheric pressure separation experiment was conducted through a dead-end filtration method. The effective separation membrane area was 1.5 × 1.5 cm^2, with a working pressure of 0.1 bar. The variable pressure separation experiment was carried out using a peristaltic pump device, where the effective separation membrane area was 2.1 × 2.1 cm^2, and the separation rotation speed was 0.1-0.3 rpm. Both separation methods lasted for 45 min, with flux tests conducted every 3 min. Toluene was used as the oil for separation, and three emulsifiers with different properties were employed: CTAB, SDS, and Tween 80. The oil-in-water emulsion was prepared as follows: 100 mL of oil/water (1 v/v%) containing the surfactant (75 mg) was stirred at 4200 rpm for 0.5 h using a high-speed mixer (FJ-200-SH). The prepared emulsion was marked with a hydrophobic dye (Sudan IV, 0.1 g L^{-1}). The variable pressure separation samples were tested three times to determine the average flux, and the standard deviation of the error was represented. Flux (*J*) was calculated using the Equation (4):

$$J = \frac{V}{At}$$

Where V is the volume (L) of filtrate, A is the active area (m^2) of the membrane, and t is the recorded permeation time (h) of water.

The separation efficiency of the membranes was calculated by Equation (5) based on the difference in the oil concentration in the emulsion and filtrate:

$$R = \left(\frac{C_i - C_f}{C_i}\right) \times 100\%$$

where C_i is the concentration of oil in the emulsion before separation (g cm^{-1}) and C_f is the concentration of oil in the filtrate after separation (g cm^{-1}).

Dye Degradation Experiment

Before conducting the experiment, the methylene blue solution (10 mg L^{-1}) was directly sonicated for 0.5 h, and the absorbance before and after sonication was measured using a UV-Vis spectrophotometer (UV-8000S, Shanghai Yuanxi Instruments Co., Ltd.). Then, the PDS-1 membrane, cut into pieces of 1.5 × 1.5 cm, was immersed in the methylene blue solution and left in a dark environment for 2 h, with a UV test conducted every hour to reach adsorption-desorption equilibrium. Afterward, the equilibrium system was sonicated with a power output of 150 W and a working frequency of 40 kHz (KQ3200E, Kunshan Ultrasonic Instruments Co., Ltd.) for 1 h, with a test conducted every 15 min to obtain the degradation curve.

ROS Detection Experiment

Cut the PDS-1 membrane into pieces of 1 × 1 cm in size and place them into 1 mL of water, then add 10 μL of fluorescence detection reagent. After shaking to ensure even dispersion, conduct a test on the sample labeled as "0" using a fluorescence spectrometer. Provide mechanical energy through vertexing to generate ROS, and perform a fluorescence spectrum test after each 1 min vortex.

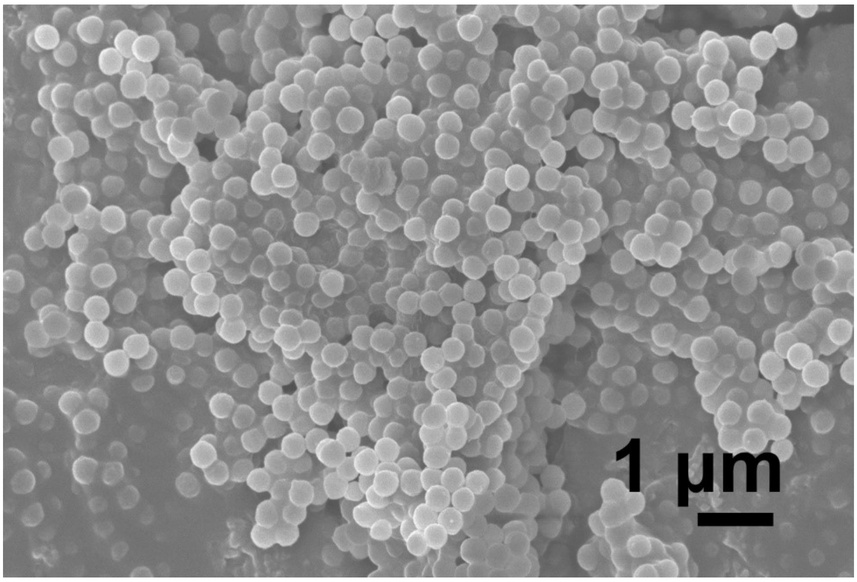

Figure S1. The FESEM image of PVDF powder.

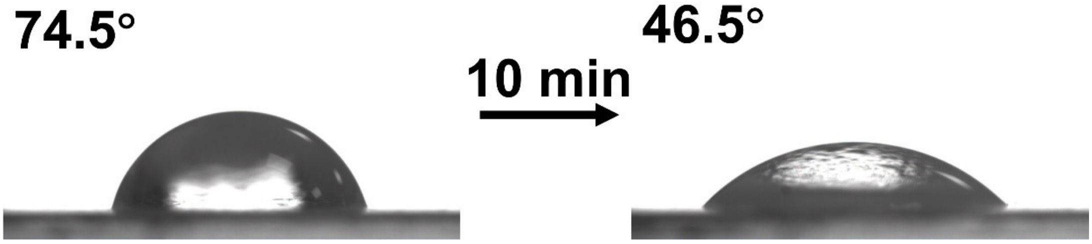

Figure S2. The water contact angle value of PDS-1 and the water contact angle value after 10 minutes of permeation.

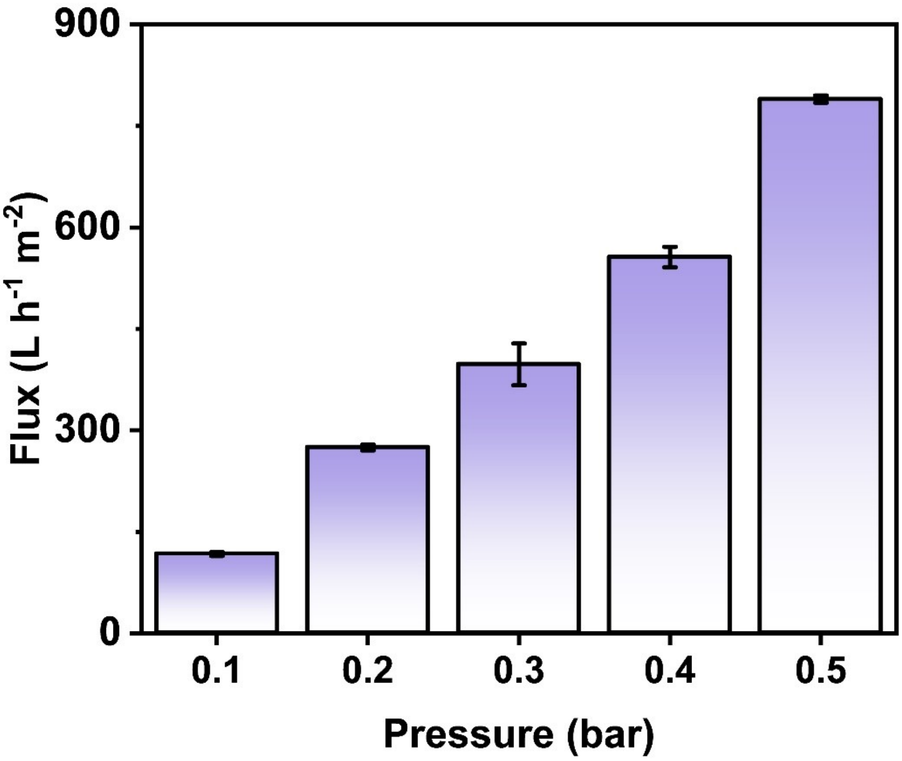

Figure S3. The water flux of PDS-1 under atmospheric pressure for 5 min at different pressures after pre-wetting.

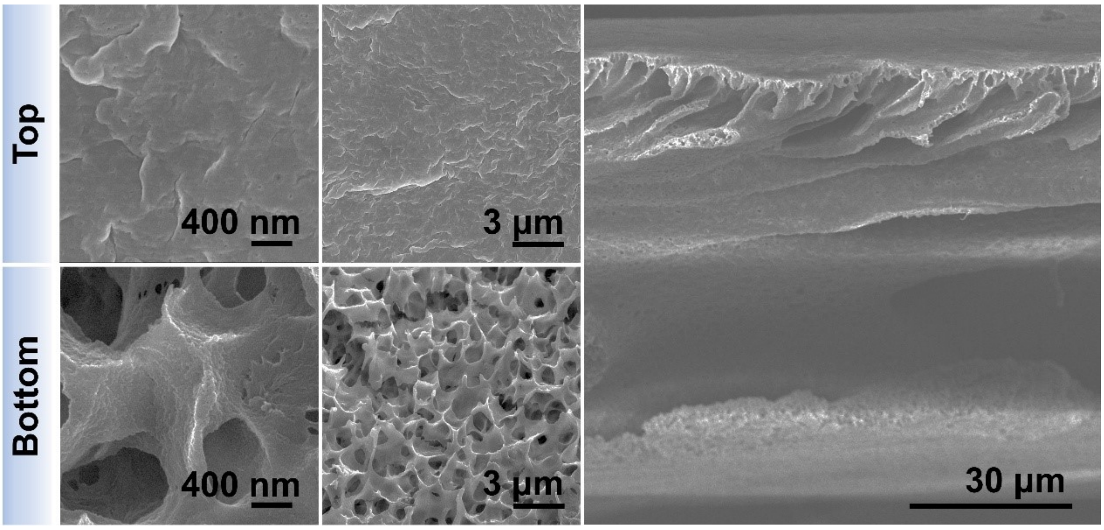

Figure S4. The FESEM images of the top, bottom, and cross-section of PVDF

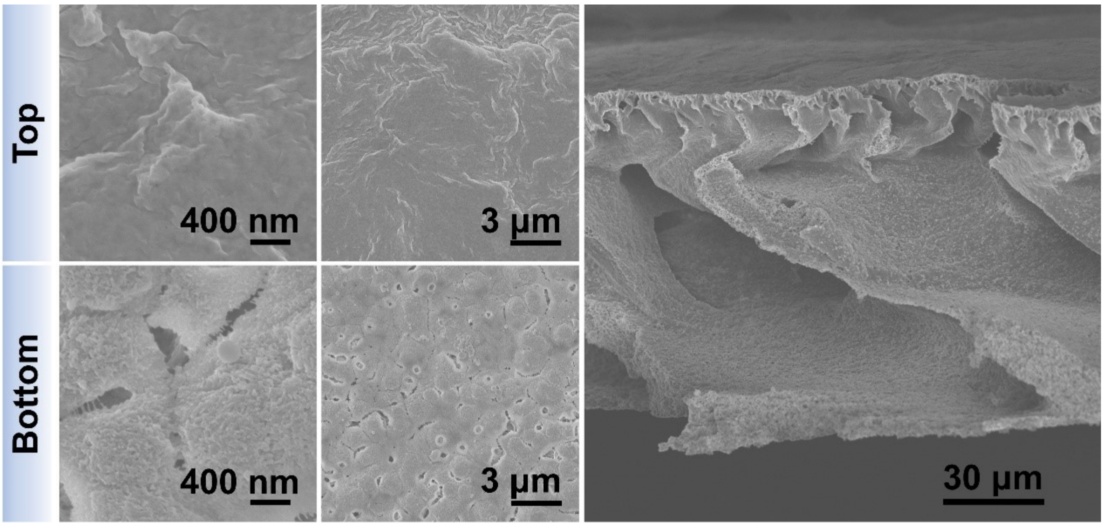

Figure S5. The FESEM images of the top, bottom, and cross-section of PVDF-DA.

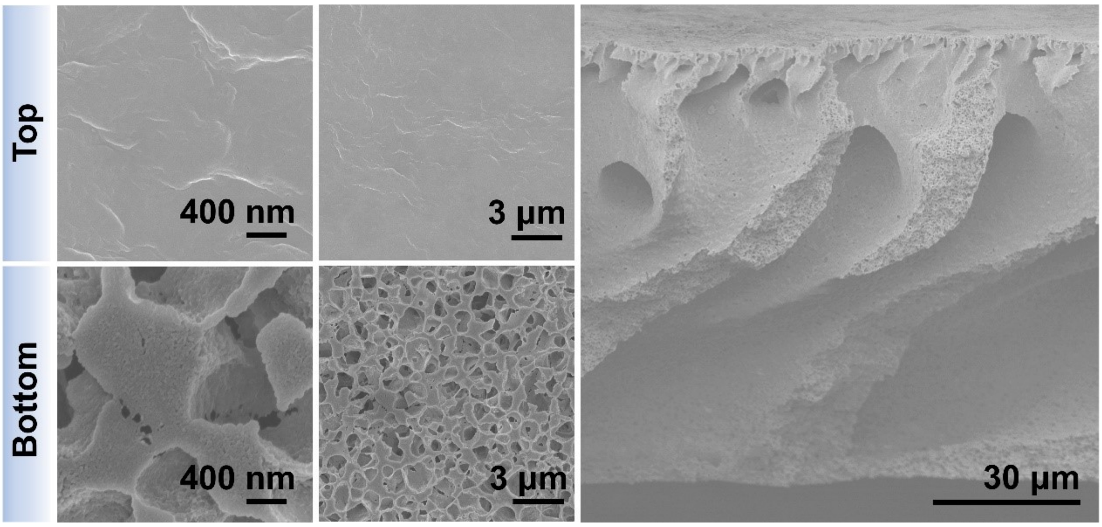

Figure S6. The FESEM images of the top, bottom, and cross-section of PVDF-SA.

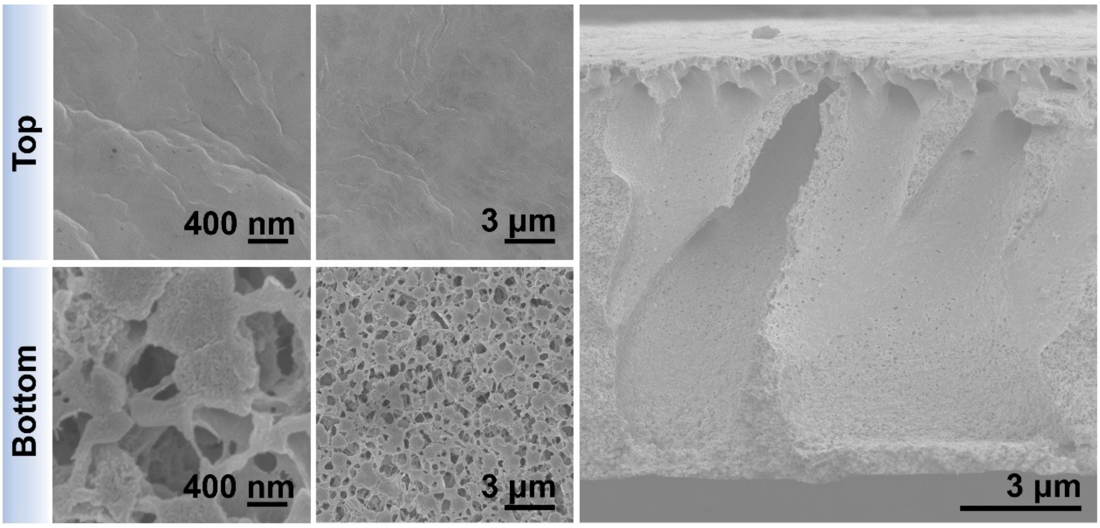

Figure S7. The FESEM images of the top, bottom, and cross-section of PDS-2.

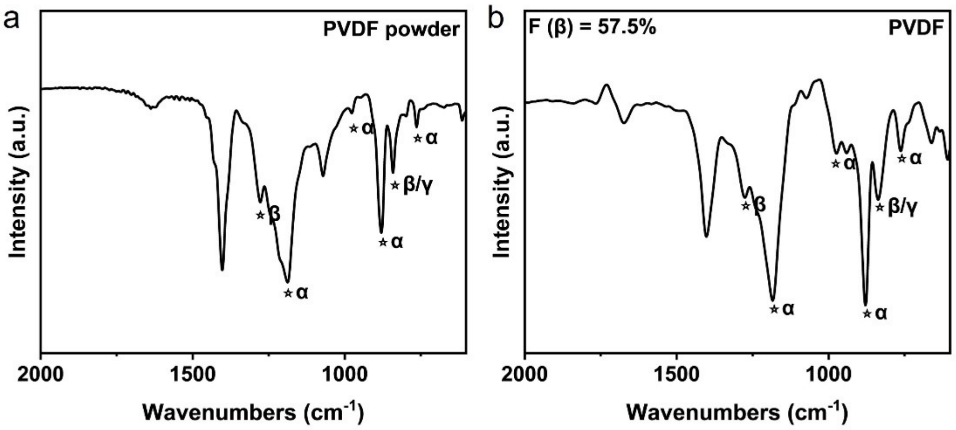

Figure S8. The FT-IR spectra of PVDF powder (a) and PVDF (b).

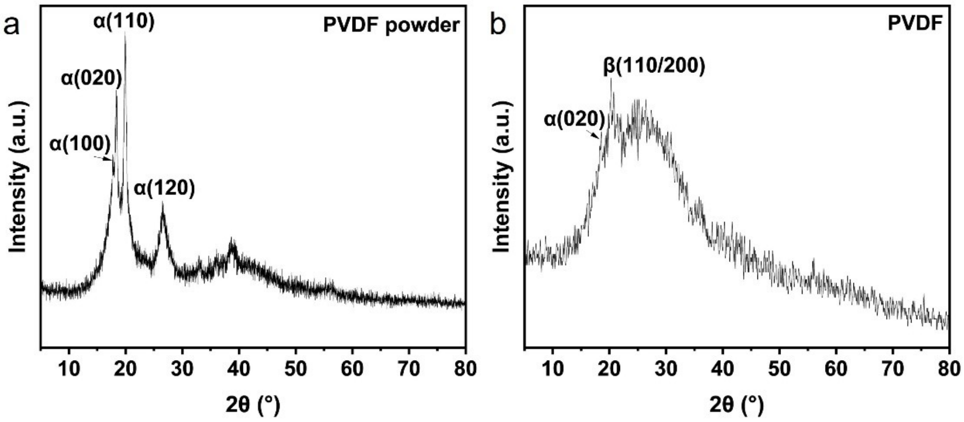

Figure S9. The XRD spectra of PVDF powder (a) and PVDF (b).

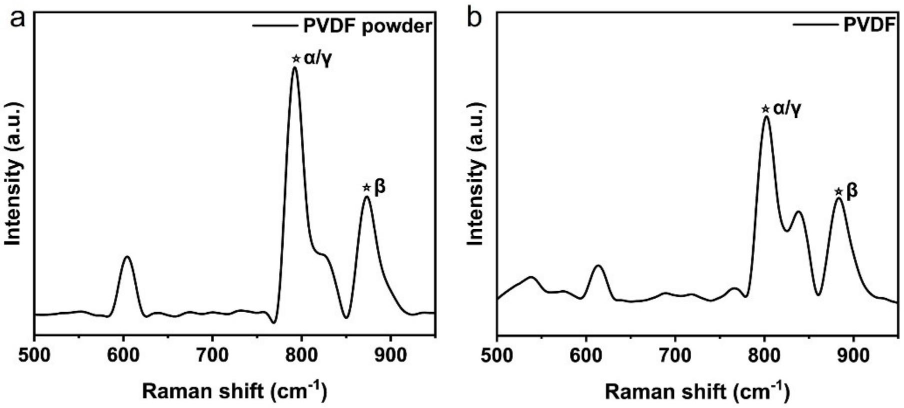

Figure S10. The Raman spectrum of PVDF powder (a) and PVDF (b).

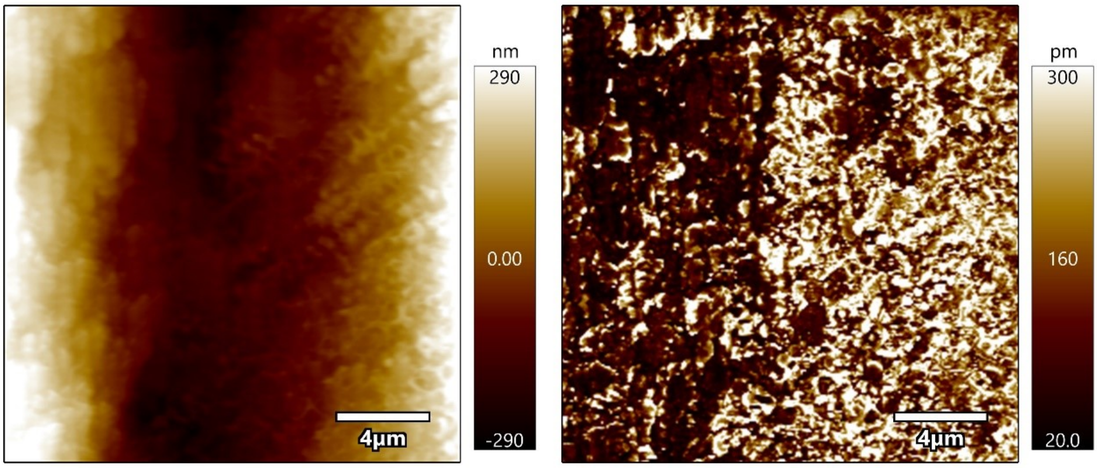

Figure S11. The topography and amplitude images of PDS-1.

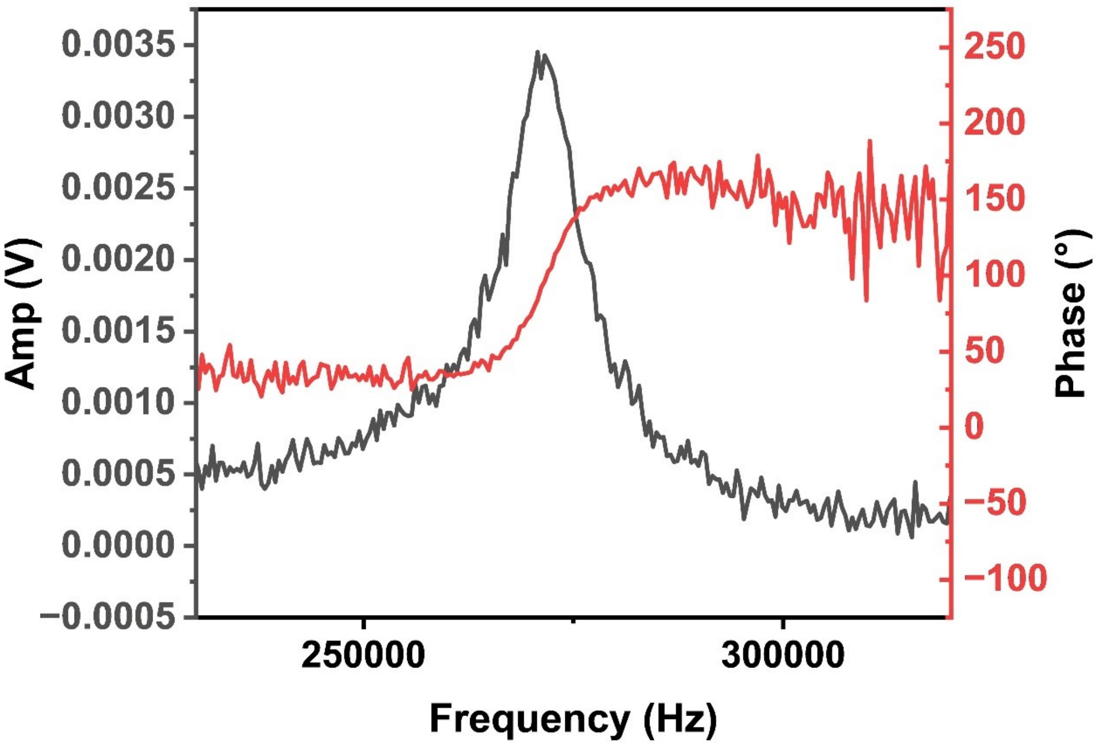

Figure S12. The Piezoresponse Force Microscopy resonance frequency peak of PDS-1.

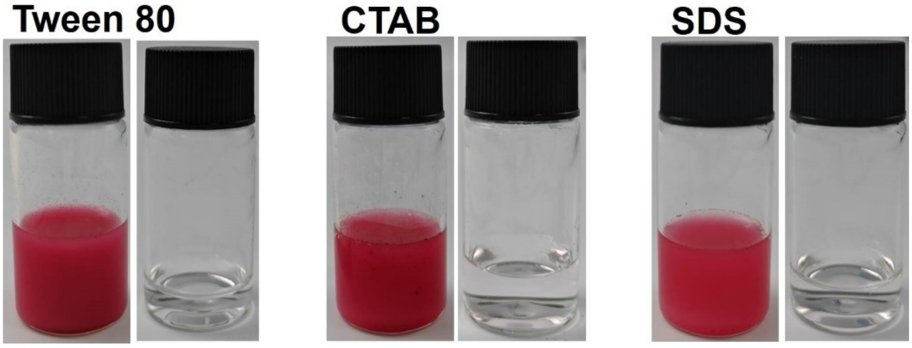

Figure S13. Optical photographs of the separation before and after of the three emulsions under atmospheric pressure.

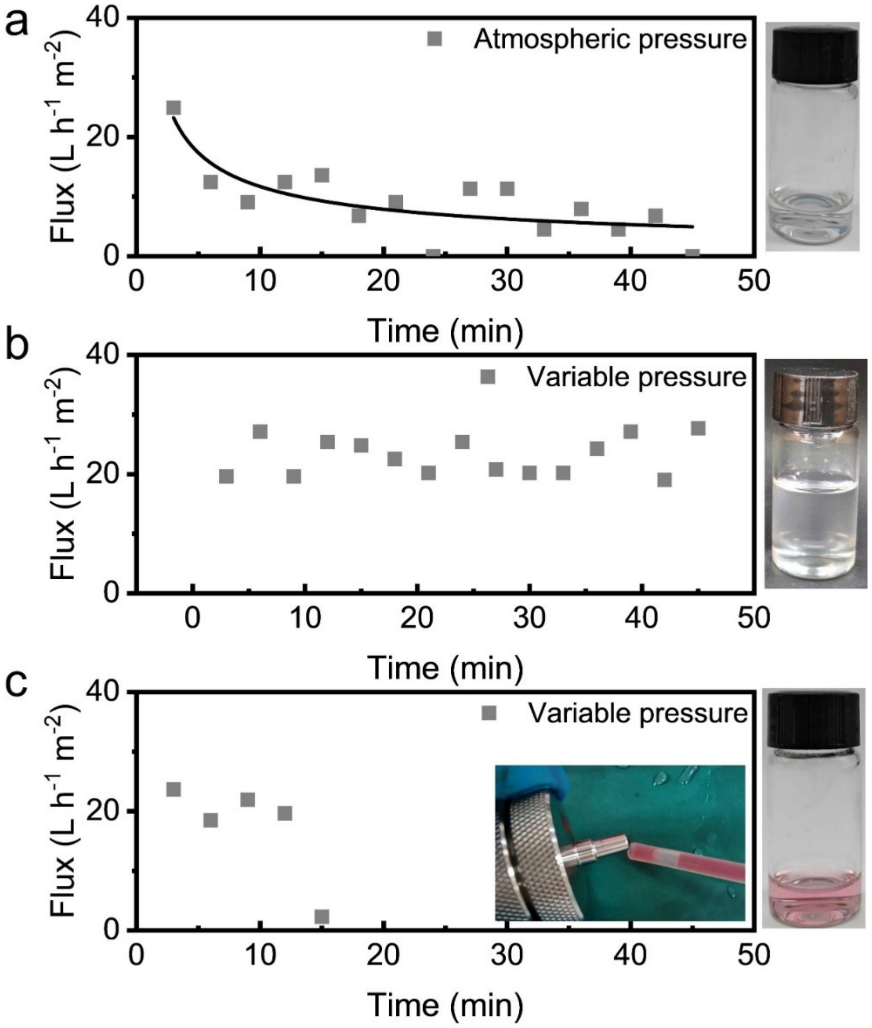

Figure S14. Separation of toluene emulsions by PVDF at atmospheric (a) and variable pressures (b, Without Sudan IV staining and c, Sudan IV stain) and optical photographs of the corresponding separated filtrates.

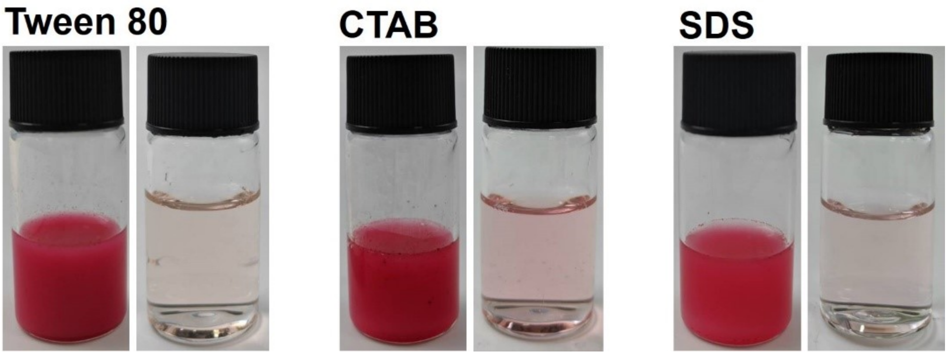

Figure S15. Optical photographs of the separation before and after of the three emulsions under variable pressure.

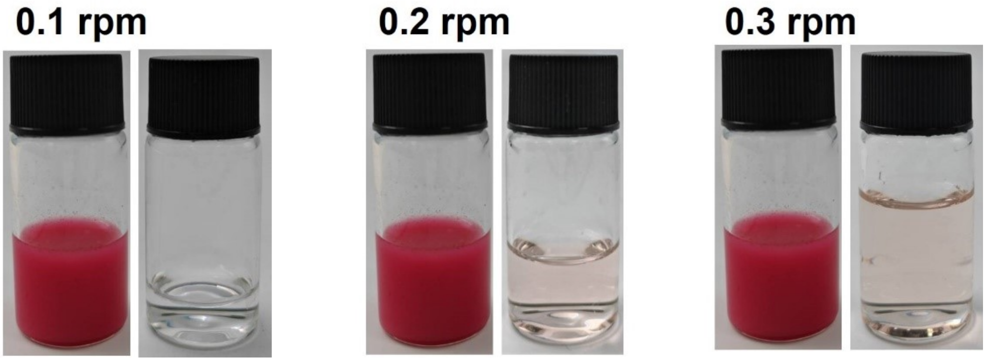

Figure S16. Optical photographs of the separation before and after of emulsions containing Tween 80 under variable pressure at different rotation speeds.

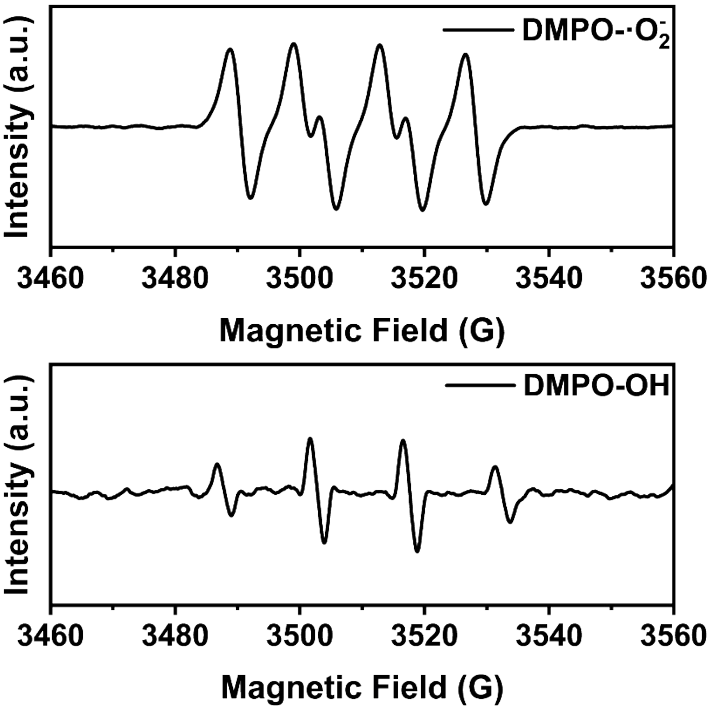

Figure S17. ROS produced by PDS-1 under vibration.

Text S1. Calculation of β phase content of PVDF

To quantitatively analyze the relative β-phase content in PVDF, unique FT-IR absorption bands of 765 cm^{-1} and 840 cm^{-1} were selected to evaluate the α and β phase content in all samples. Assuming that infrared absorption complies with Lambert-Beer's law, the β phase content was calculated by the following formula.

$$F_\beta = \frac{A_\beta}{(K_\beta/K_\alpha)A_\alpha + A_\beta} \times 100\% \qquad \text{(S1)}$$

where A_α and A_β correspond to the absorbance of the α (765 cm^{-1}) and β phase (840 cm^{-1}) in PVDF, respectively. K_α and K_β are the absorption coefficients for their respective wave numbers ($K_\alpha = 6.1 \times 10^4$, $K_\beta = 7.7 \times 10^4$ cm^2 mol^{-1}). F_β represents the relative β fraction.

Text S2. Degradation efficiency and first-order kinetic calculation of PDS-1

$$\eta = \left(1 - C_t/C_0\right) \times 100\%. \qquad \text{(S2)}$$

C_0 and C_t (mg/L) are the original concentration of organic pollutants and the concentration after degradation, respectively.

The kinetics of the degradation process was fitted using the simplified Langmuir Hinshelwood first-order kinetic model, and the first-order rate constant was calculated by Eq. S3.

$$\ln (C_t/C_0) =- kt \qquad \text{(S3)}$$

where k (min^{-1}) is the rate constant and t is the reaction time.