Supporting Information

Solvent-Influenced Fragmentations in Free-Standing Three-Dimensional Covalent Organic Framework Membranes for Hydrophobicity Switching

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S-1: General information

General remarks
Tetrakis(4-amino)phenylmethane was purchased from Sigma Aldrich. 2, 5-dibromoterephthaldehyde, and terephthaldehyde were purchased from TCI chemicals. All other chemicals were purchased from commercial sources and used as such without any further purification.

Instruments

**Wide-angle X-ray diffraction (WAXD):** Bruker D2 Phaser XRD (excitation source: Cu K alpha, 1.54 Å) was used to analyze the samples' PXRD pattern. The 3D-COF membranes were directly used on the support for the analysis. We have processed the PXRD data by using XRD software X’pert High Score Plus for the background correction.

**FT-IR:** Fourier transform infrared (FT-IR) spectra were taken on a Bruker Optics ALPHA-E spectrometer with a universal Zn-Se ATR (attenuated total reflection) accessory in the 600-4000 cm⁻¹ region or using a Diamond ATR (Golden Gate) with 24 scan rate and 4 cm⁻¹ resolution.

**Thermogravimetric analyses (TGA):** TGA was carried out on a PerkinElmer Simultaneous Thermal analyzer STA 6000 under N₂ atmosphere at a heating rate of 15 °C min⁻¹ within a temperature range of 30-900°C.

**Gas adsorption:** Porosity measurements were conducted on a Micromeritics 3-Flex gas sorption analyzer. A weighed amount of the sample (50-80 mg) was first degassed at 130 °C for 12 h. Adsorption isotherms were then measured in the volumetric method with Micromeritics 3-Flex device at 273 K (maintained by ice-water bath) and 298K for CO₂ adsorption. The micropore size distributions were calculated from Horvath-Kawazoe method by using cylinder pore geometry. The BET surface area was calculated by the CO₂ adsorption at 273 K.

**Scanning Electron Microscopy (SEM):** The JEOL JSM-7610F FEG-SEM was used for the SEM analysis of 3D-COF membranes. It combines an electron column with semi-in-lens detectors and an in-the-lens Schottky field emission gun – to deliver ultrahigh-resolution with a wide range of probe currents (1pA to more than 200 nA). The images were recorded with 2.0 k eV voltage. SEM images of thin-sheet sections were taken after the vertical alignment of COF samples on the holder by pasting with a conducting carbon tape. Prior to imaging, the samples were sputtered with Pt (nano-sized film) using JEOL JEC-300FC Auto Fine Coater.
Transmission Electron Microscopy (TEM): The TEM images were recorded by FEI Tecnai TEM 20 kV. The TEM samples were prepared by the crushed and ground COF thin-films and dispersed in acetonitrile solvent by 20-minute sonication and drop cast on copper grids TEM Window (TED PELLA, INC. 200 mesh).

Nuclear Magnetic Resonance Spectroscopy: Magic Angle Spinning (MAS) solid-state NMR experiments were carried out on a Bruker Avance-HD 600 MHz spectrometer operating at a static field of 14.1 T using a 4.0 mm MAS probe. Samples were packed into 4.0 mm zirconia rotors and were spun at a MAS frequency of 14 kHz. $^1$H-$^{13}$C Cross-Polarization Magic Angle Spinning (CP/MAS) experiments were performed using a standard linearly ramped cross-polarization pulse sequence. $^{113}$C chemical shifts were externally referenced to the adamantane CH$_2$ signal at 38.48 ppm on the TMS scale. NMR data were processed using TopSpin software.

Atomic Force Microscopy (AFM): The topography of 3D-COF membranes was analyzed by Asylum Research MFP-3D Origin™. Bruker NCHV0.01 – 0.025 ohm-cm Antimony (n) doped Silicon AFM probe with the resonance frequency of 320 kHz was used.

Contact Angle: Contact angle measurements were taken in Kruss Drop Shape Analyzer –DSA instrument.

Optical Microscopy: Optical microscopic images were analyzed by OPTICA B-383MET instrument.

Tensile strength analysis: The tensile mechanical strength was measured by DEBEN MICROTEST instrument. The elongation capacities of Tam Dbta-1 and Tam Dbta-2 films were measured by pasting the film between two paper pieces. The rectangle COF films with size 0.5 cm X 0.5 cm was prepared and strongly taped in between two rectangle papers by using adhesive tapes. Two paper pieces were connected with a COF film which was subjected to the tensile measurement. Both ends of paper pieces were attached to the instrument and stretched with a motor speed 0.0083 mm sec$^{-1}$.

Calculation of the % of elongation = \( \frac{\text{Final length} - \text{Initial length}}{\text{Initial length}} \times 100 \)

Oil-water separation: A Swinny filter apparatus (purchased from Sigma) has been used for the gravity-driven flux analysis of solvents and demulsification. The 3D-COF membrane (~10 µm thickness) was cut into a circular shape with a 1.3 cm diameter. The membrane was directly kept on the steel disk of the Swinny filter apparatus without any further support. The oil-water emulsion has been prepared by the ultra-sonication of the water in oil (0.25%, 0.5%, and 1%) mixture for 30 minutes. The white emulsion has been used for the separation analysis. 5 ml of solvents and emulsions were taken for the flux analysis.
The solvent permeation flux were calculated by using the following formula:

\[ \text{Flux} = \frac{\text{Volume}}{(\text{Area} \times \text{Time})} \]

Volume – liter (L); Area – m²; Time – hours

The recyclability test was carried out by using fresh volume of emulsion (5 ml) each time of the separation. The recyclability test was performed by two ways: 1) The membrane after separation directly used for another batch of separation without removing any water droplets/drying it. 2) The membrane was dried properly and then used for separation analysis.

**S-2: Synthetic procedures**

**Synthesis of Tam Dbta-1:** A mixture of tetrakis(4-amino)phenylmethylene (Tam) (0.0394 mmol) and p-toluenesulphonic acid (PTSA) (0.157 mmol) was dissolved in 10 ml of distilled water. A solution of 2,5-dibromoterephthaldehyde (Dbta)(0.0786 mmol) in ethylacetate (10 ml) was slowly added to the surface of the aqueous solution. The reaction was allowed for 48 hours at room temperature. A yellow film was formed at the interface of the solvents which was collected and washed with hot water, hot N, N-dimethylacetamide, and acetone. The dried thin film was used for further characterizations and measurements.

**Synthesis of Tam Dbta-2:** A mixture of tetrakis(4-amino)phenylmethylene (Tam) (0.0394 mmol) and p-toluenesulphonic acid (PTSA) (0.157 mmol) was dissolved in 10 ml of distilled water. The prepared aqueous solution was slowly added on the surface of a solution of 2,5-dibromoterephthaldehyde (Dbta) (0.0786 mmol) in chloroform (10 ml). The reaction was allowed for 48 hours at room temperature. A yellow film was formed at the interface of the solvents which was collected and washed with hot water, hot N, N-dimethylacetamide and acetone. The dried thin film was used for further characterizations and measurements.

**Synthesis of Tam Dbta (powder):** The synthesis of Tam Dbta powder was performed by the Schiff base condensation reaction between Tam (Tam; 62.4 mg, 0.3 mmol) and 2, 5-dibromoterephthaldehyde (Tp; 42 mg, 0.2 mmol) in mesitylene (0.75 ml) – dioxane (0.75 ml) solvent mixture with catalytic amount of 6M acetic acid (0.1 ml) by solvothermal reaction. After sealing, the tube was kept at 120°C for 48 hours. A yellowish precipitate was collected by centrifugation and subsequent washing by N, N-dimethylacetamide, water and acetone.

**Synthesis of Tam Ta-1:** A mixture of Tam (0.0394 mmol) and PTSA (0.0786 mmol) was dissolved in 10 ml of distilled water. A solution of Ta (0.0786 mmol) in ethylacetate (10 ml) was slowly added on the surface of aqueous solution. The reaction was allowed for 48 hours at room temperature. A transparent yellowish narrow film was formed at the interface of the solvents which was collected and washed with water; N, N-dimethylacetamide; and acetone.

**Synthesis of Tam Ta-2:** A mixture of Tam (0.0394 mmol) and PTSA (0.0786 mmol) was dissolved in 10 ml of distilled water. The prepared aqueous solution was slowly added on the surface of a solution of Ta (0.0786 mmol) in chloroform (10 ml). The reaction was allowed for 48 hours at room temperature. An yellow transparent film was formed at the interface of the
solvents which was collected and washed with hot water; \textit{N, N}-dimethylacetamide; and acetone.

**Figure S1**: The digital photographs of interfacial synthesis of Tam Dbta-1 and Tam Dbta-2.

**Figure S2**: The digital photographs of membranes. a) Tam Dbta-1; b) Tam Dbta-2; and large-scale Tam Dbta-1 (8 cm diameter).
**Figure S3:** The digital photographs of free-standing a) Tam Dbta-1 and 2) Tam Dbta-2.

**Figure S4:** The schematic diagram of Tam Dbta powder through solvothermal synthesis (inset: the digital photograph of Tam Dbta (powder)).
Figure S5: a) Graphical representation of the interfacial synthesis of (i) Tam Ta-1 and (ii) Tam Ta-2. b) The schematic representation of the synthesis of Tam Ta.

Figure S6: The digital photograph of a) Tam Ta-1 and b) Tam Ta-2 (at 2 eq. PTSA)
Figure S7: The powder X-ray diffraction profiles of Tam Dbta-1 & 2 membranes and its corresponding monomers and simulated PXRD of dia-C5 model.
Figure S8: Experimental (Red) compared with refined (Blue) PXRD profiles of Tam Dbta-1 with diamond topology model; difference plot is given in (black).

Figure S9: Experimental (Red) compared with refined (Blue) PXRD profiles of Tam Dbta-2 with diamond topology model; difference plot is given in (black).

Figure S10: The PXRD of Tam Dbta (powder).
**Figure S11:** Diamond topology (dia-c5) model of Tam Dbta membranes. Atomic positions and cell sizes of the Tam Dbta layers were optimized using the SelfConsistent-Charge Density-Functional Tight-Binding (SCC-DFTB) method, including LennardJones dispersion. C, N, O, H atoms were described using the mio-0-1 parameter set. ²
Figure S12: FT-IR spectra of TamDbta-1 & 2 and monomers. The characteristic N-H peak of Tam is absent in Tam Dbta-1 and Tam Dbta-2. Tam Dbta-1 exhibits a sharp C=N peak, whereas Tam Dbta-2 shows a sharp C=O peak.
Figure S13: FT-IR spectra of TamDbta-1 and TamDbta-2. Tam Dbta-1 exhibits a sharp C=N peak, whereas Tam Dbta-2 shows a sharp C=O peak.
Figure S14: The FT-IR spectra of Tam Dbta (powder) with monomers.

Figure S15: The FT-IR profiles of Tam Dbta-1, Tam Dbta-2, and Tam Dbta (powder)
Figure S16: The FT-IR spectra of Tam Ta-1 and Tam Ta-2 with corresponding monomers.
Figure S17: FT-IR spectra of solvent ratio analysis. The ethylacetate ratio in the organic layer directly connect with the formation of C=O in Tam Dbta. When the ethylacetate ratio increases, the intensity of C=O also increases.
Figure S18: FT-IR spectra of excess amine reaction. The excess amine in the aqueous layer does not have any impact on the fragmentation in ethylacetate-water interfacial reaction. The formation of C=O remains the same even after the double amount of Tam in water.
Figure S19: FT-IR spectra of mechanism study of TamDbta-1. The intensity of C=O peak increases as time progress, whereas the intensity of C=N peak is decreasing.
Figure S20: FT-IR spectra of mechanism study of TamDbta-2. The steady formation of C=N with a weak C=O peak during the reaction process has been observed.
Figure S21: $^{13}$C CP MAS solid-state NMR of Tam Dbta and monomers. The intensity of C=O in Tam Dbta-1 is higher than in Tam Dbta-2.
**Figure S22:** $^{13}$C CP MAS solid-state NMR peak ratio of Tam Dbta-1. The peak integration of carbonyl carbon (C=O) by taking the $sp^3$ carbon as a reference.

**Figure S23:** $^{13}$C CP MAS solid-state NMR peak ratio of Tam Dbta-2.

Even though CP MAS experiments are usually not quantitative, here we are only comparing the relative area of the $sp^3$ carbon and carbonyl carbon (C=O) from Tam Dbta-1 and Tam Dbta-2 samples to highlight the intensity difference of carbonyl groups. Both the spectra were obtained under identical experimental conditions.
S-6: TGA and gas adsorption

**Figure S24**: TGA of Tam Dbta-1 and Tam Dbta-2.

**Figure S25**: The TGA of Tam Dbta (powder).
Figure S26: TGA of Tam Ta-1 and Tam Ta-2.

Figure S27: CO$_2$ adsorption analysis of Tam Dbta-1 and Tam Dbta-2 at 298 K. Solid circles and open circles represent adsorption points and desorption points respectively. The reversible adsorption-desorption indicates the physisorption nature of Tam Dbta-1 & 2.
**Figure S28**: The CO$_2$ gas adsorption isotherm of Tam Dbta (powder) at 273 K.

**Figure S29**: The BET surface area calculation from CO$_2$ gas adsorption at 273 K.
Figure S30: Horvath-Kawazoe micropore size distribution of Tam Dbta-1 and Tam Dbta-2.

Figure S31: Horvath-Kawazoe micropore size distribution of Tam Dbta (powder).
Figure S32: TEM images of a) Tam Dbta-1 and b) Tam Dbta-2.
Figure S33: The TEM images of Tam Dbta (powder).
Figure S34: SEM images of Tam Dbta-1.
Figure S35: SEM images of Tam Dbta-2.
**Figure S36:** SEM images of time dependent growth of Tam Dbta-1.
Figure S37: SEM images of time dependent growth of Tam Dbta-2.
Figure S38: The SEM images of Tam Dbta (powder).
**Figure S39:** The SEM images of Tam Ta-1.

**Figure S40:** The SEM images of Tam Ta-2.
Figure S41: AFM height profiles of Tam Dbta-1.

Figure S42: AFM height profiles of Tam Dbta-2.
S-10: Miscellaneous data

Figure S43: The tensile strength analysis of Tam Dbta-1 and Tam Dbta-2.

Figure S44: The FT-IR spectra of Tam Dbta-1 and Tam Dbta-2 after the acidic treatment at pH = 1.
Figure S45: The PXRD of Tam Dbta-1 and Tam Dbta-2 after the acidic treatment at pH.

Figure S46: A representative DFT model for free aldehyde sites (oxygen in red colour) in Tam Dbta. A 3x3x3 super cell with a total of 216 linkers has been taken as a model and introduced 11 defects.
Figure S47: The water molecule interaction with various sites of Tam Dbta. Water is strongly binding in between the COF layers.

Figure S48: The water molecule interaction with various sites molecular fragment of Tam Dbta-1. The water molecule weakly binds with bromine atom.

To determine the structure and energetics of the interaction of water with Tam Dbta, a single water molecule was added stochastically to the dia-c5 structure of Tam Dbta and the position of the water molecule was optimised using GFN-xTB as implemented in AMS2021. Following optimisation, the binding energy \( \text{E}_{\text{binding}} = \text{E}_{\text{COF}+\text{H}_2\text{O}} - (\text{E}_{\text{COF}} + \text{E}_{\text{H}_2\text{O}}) \) was calculated on the GFN-xTB optimised geometries, using PBE-D3/DZ.
Figure S49: Halogen bond possibilities in a representative molecular fragment.
Figure S50: Electrostatic potential mapping (ESP) of discrete molecules. The phenomena has been indicated in the electrostatic potential mapping (ESP) of a discrete molecule to the periodic framework. The ESP ranges from -0.3 au (red) to +0.3 au (blue) demonstrating the nucleophilic and electrophilic regions respectively. The nucleophilicity of the carbonyl oxygen atom (-0.219 au) is higher than the imine nitrogen atom (-0.137 au) in discrete molecules. The nucleophilicity of imine nitrogen is further decreased in the corresponding periodic structure.
**Figure S51**: Hydrophobicity of Tam Dbta-1. The water drop on the membrane.

**Figure S52**: a) Contact angle measurement of Tam Dbta (powder). b) The digital photographs of (i) dry Tam Dbta (powder) pellet and (ii) after dropping water.
Figure S53: The digital photograph of Tam Dbta-1 and Tam Dbta (powder) pellet after placing one drop of water on the surface.

Figure S54: The contact angle measurement of Tam Ta-1 & 2 films.
Figure S55: The digital photographs of water drop on Tam Ta-1 and Tam Dbta-1 films.
**Figure S56**: Optical microscopic images of oil-water emulsion before and after separation.
**Figure S57:** a) Free-standing Tam Dbta-1 membrane in Swinny filter apparatus. b) Tam Dbta-1 wet with hexane. c) Water drop on Tam Dbta-1.

**Figure S58:** Water droplet recovery by a) dropper and b) tissue paper.
Figure S59: The demulsification flux at various pH (1 to 5) of water.

Figure S60: The FT-IR spectra of Tam Dbta-1 after the separation of oil-water emulsion with pH = 1.
**Figure S61:** Continuous recyclability of demulsification by Tam Dbta-1.

**Figure S62:** The PXRD profile of recycled Tam Dbta-1 membrane.
Figure S63: The FT-IR profile of recycled Tam Dbta-1 membrane.

Figure S64: The SEM images of recycled Tam Dbta-1 membrane.
| Separation material | Physical nature | Oil-water physical state | Separation Flux / Efficiency | Reference |
|---------------------|-----------------|--------------------------|-----------------------------|-----------|
| Tam Dbta-1 (3D-COF) | Free-standing membrane | Oil-water emulsion | ~1536 L m⁻² h⁻¹ (gravity driven) | This Work |
| JUC-530/531 (3D-COF) | Pressed powder pellet | Oil-water in two phase | 99% | 6 |
| COF-DhaTab/PAN (2D-COF) | Composite membrane of COF and PAN | Oil-water emulsion | 2039.5 L m⁻² h⁻¹ | 7 |
| TAPB-TFA-COF (2D-COF) | Powder | Oil-water emulsion | 99.5% (manual syringe pressure) | 8 |
| COF@SSN (2D-COF) | COF-coated Stainless steel network | Oil-water in two phase | (2.22±0.07) 10⁻⁵ L m⁻² h⁻¹ | 9 |
| COF/rGO (2D-COF) | Aerogel | Oil-water in two phase | ----- | 10 |

**Table S1**: The comparison table (based on physical nature and efficiency) of COF-based oil-water separation.

**S-11: Reference**

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