

## Supplementary Information

# Diffusion-Induced *In situ* Growth of Covalent Organic Frameworks for Composite Membranes

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## Experimental details

### Materials

Polyacrylonitrile (PAN) with molecular weight >100.000 g/mol was kindly supplied by GMT Membrantechnik GmbH Germany, polypropylene nonwoven was purchased from Sojitz Europe, Germany. 2,5-Dimethoxybenzene-1,4-dicarboxaldehyde (97 %), N,N-dimethylformamide, hydrazine monohydrate (60-65%), dioxane, mesitylene, dimethylformamide (DMF) (99.8%), acetone (99%), tetrahydrofuran (THF) (99%), scandium(III) triflate (Sc(OTf)<sub>3</sub>) were purchased from Sigma-Aldrich and used without further purification, 1,3,5-tris(4-aminophenyl)benzene was purchased from Tokyo Chemical Industry used without further purification.

### Fabrication of XPAN supports

PAN asymmetric porous supports were prepared, following a previous report<sup>1</sup>, using a 12 % PAN solution in DMF cast on a polypropylene support and immersed in water. The resulting PAN porous support was then cross-linked using hydrazine hydrate.

### Fabrication of COF-XPAN composite

The TMP-DMTP COF was *in-situ* grown on a XPAN support, using a PermeGear diffusion cell. In a typical procedure, 4.9 cm<sup>2</sup> of the XPAN support described above was placed between the two halves of the diffusion cell and clamped together. The selective crystalline COF growth on the XPAN surface was conducted with a dioxane:mesitylene (4:1 v/v) mixture on both sides. The cell half with the polypropylene side of the support contained a solution having a stoichiometric concentration of the monomers 1,3,5-tri-(4-aminophenyl)benzene (TPB) (0.080 mmol, 28.1 mg) and 2,5-dimethoxybenzene-1,4-dicarboxaldehyde (DMTP) (0.120 mmol, 23.3 mg), dissolved in 5 ml of dioxane:mesitylene (4:1, v/v) and stoppered. The other half of the cell contained scandium

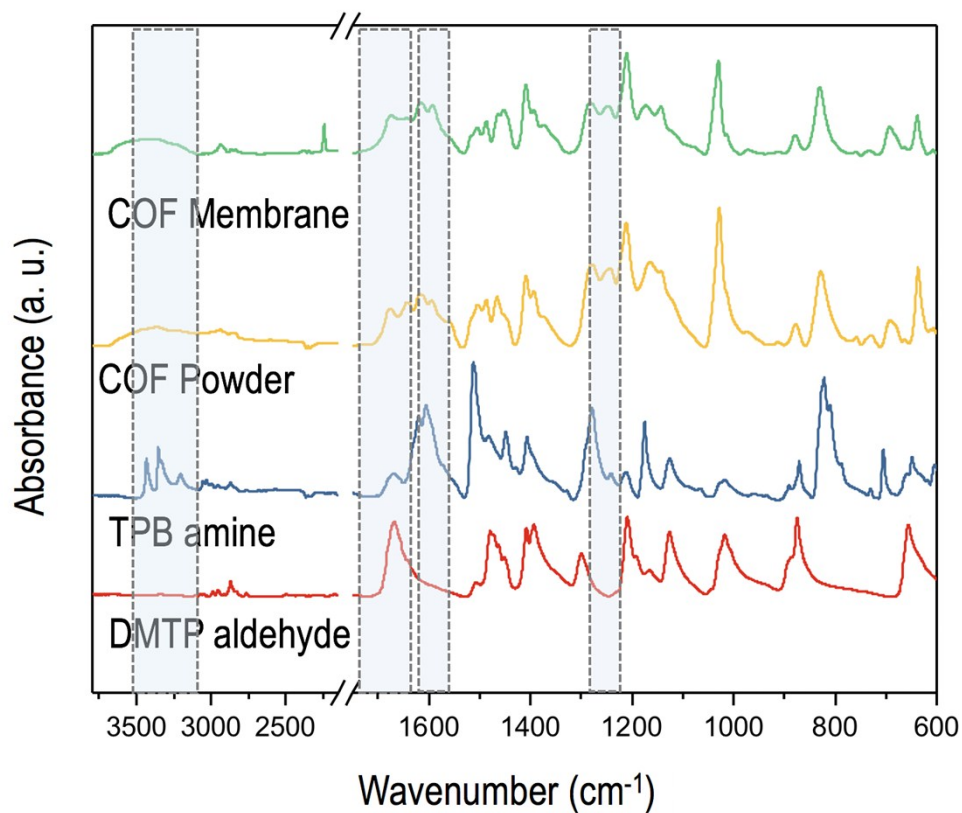
triflate (0.007 mmol, 3.5 mg), dissolved in 5 ml of dioxane:mesitylene (4:1, v/v) (Fig. 1). The diffusion assembly was left undisturbed in different time intervals. The formed COF-XPAN composite was gently removed from the diffusion cell assembly and immersed in a dioxane:mesitylene (4:1) mixture, washed (3 x 20 ml) with the same mixture to remove the unreacted monomers, followed by washing with THF and water.



**Figure S1.** Experimental setup for the diffusion-assisted fabrication of COF-XPAN composite along with the digital images of the front and back side of the resultant composite.

#### **Fourier Transform Infrared (FTIR) spectroscopy analysis**

The formation of the imine was confirmed by using attenuated total reflectance (ATR) FTIR on a FTIR-iS10 in the wavenumber range of 500–4000  $\text{cm}^{-1}$  at an average of 32 scans with 4  $\text{cm}^{-1}$  resolution.

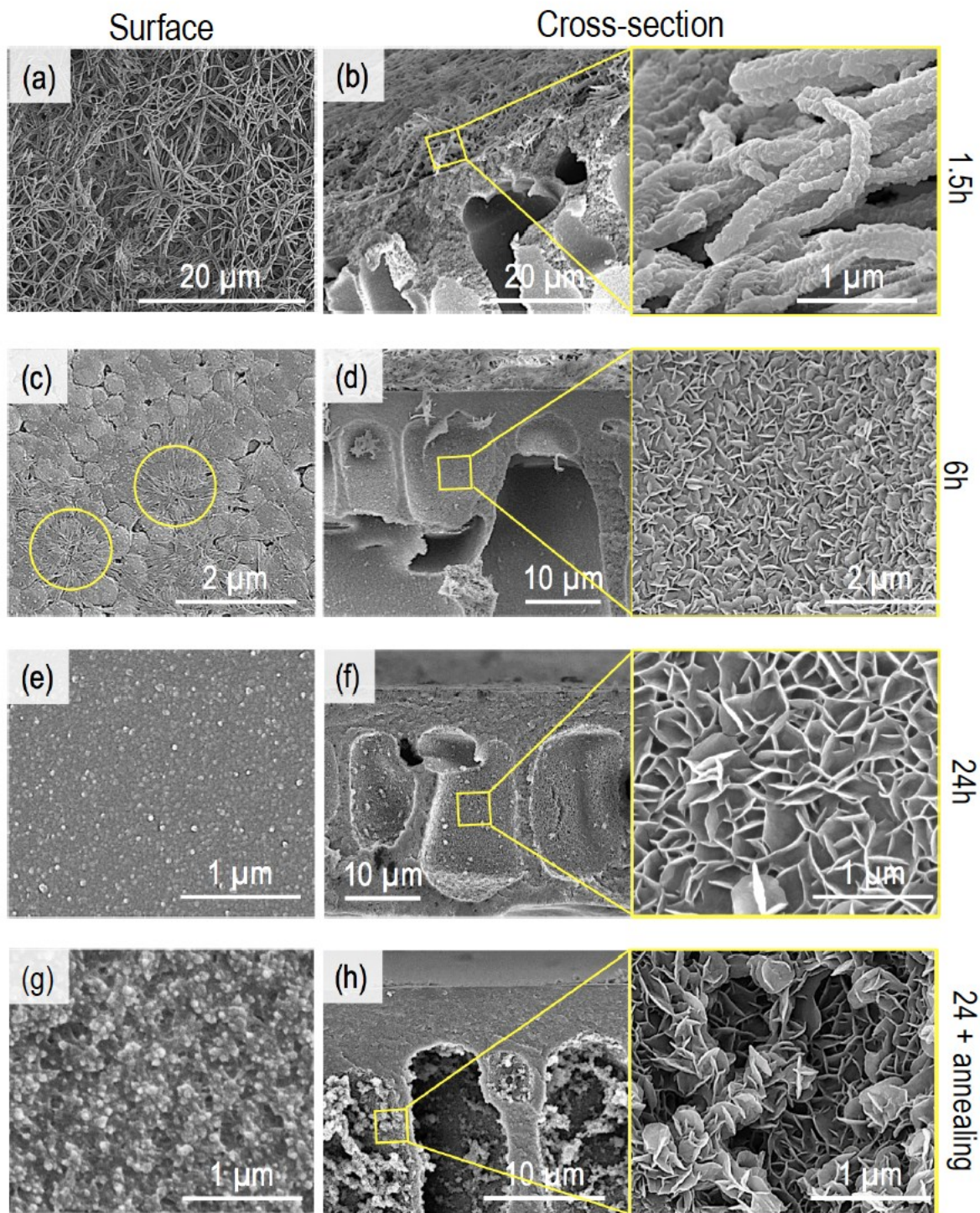


**Figure S2.** ATR-FTIR spectra of the monomer (DMTP and TPB), TPB-DMTP COF as powder and TPB-DMTP COF-XPAN composite.

### Scanning electron microscopy

The morphology of the COF-polymer composites was investigated by SEM on a Nova Nano microscope, using an accelerating voltage of 2 to 5 kV and a working distance of 1.5 to 5 mm. The samples were sputter-coated before the analysis with iridium or platinum on a Quorum Q150TES equipment. The samples for cross-section image were fractured in liquid nitrogen.

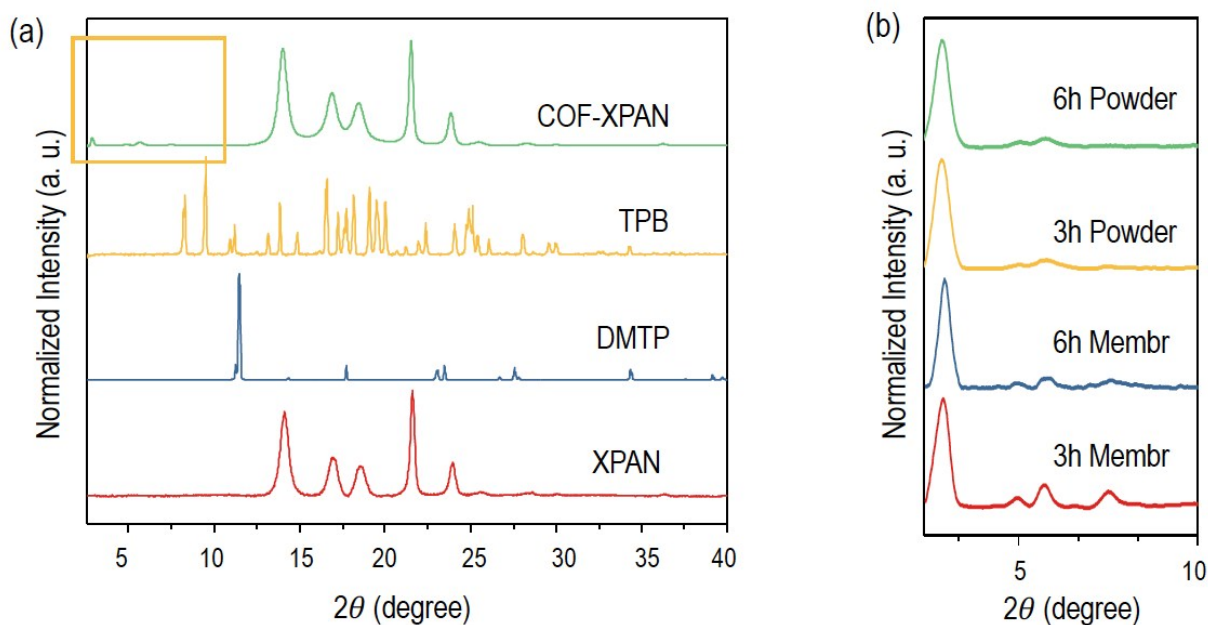




**Figure S3.** SEM (a, c, e, g) surface and (b, d, f, h) cross-section images of COF membranes obtained by using 3.5 mg of  $\text{Sc}(\text{OTf})_3$  and reaction times of (a, b) 1.5, (c, d) 6, and (e, f) 24h without and (g, h) with 24h annealing.

## Powder X-Ray Diffraction (PXRD) analysis

The crystallinity of COF polymer composite membrane prepared under different conditions was investigated using a Bruker D8 Advance diffractometer with Cu-K $\alpha$  radiation source ( $\lambda = 0.154$  nm), operating at 40 kV and 40 mA. The diffraction profiles were obtained in the range of 2°–30° using a low angle kit accessory.

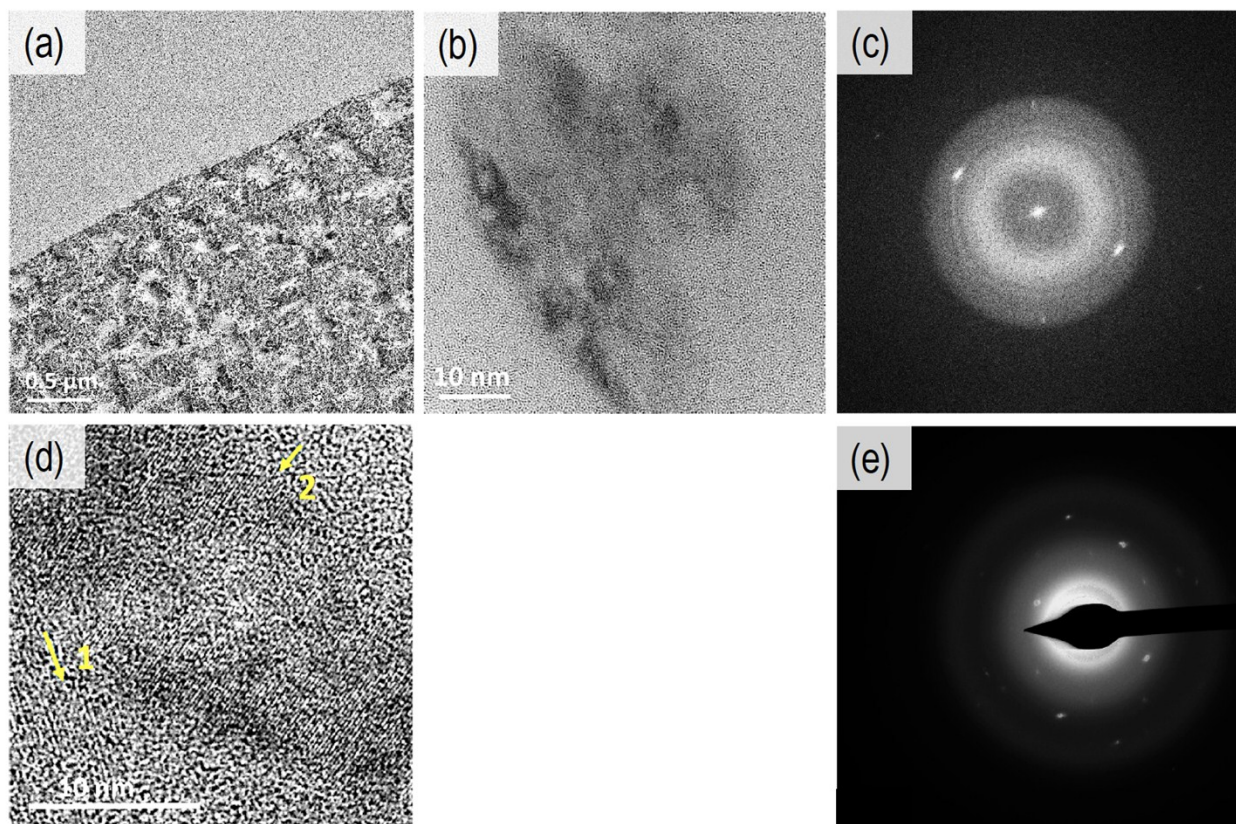


**Figure S4.** (a) PXRD profiles with  $2\theta$  varying from 2 to 40°, for the crosslinked (XPAN) support, for the pure monomers, and for the COF-XPAN membranes; (b) expanded PXRD profiles with  $2\theta$  varying from 2 to 10° for the COF powder and for the COF-XPAN composite membranes obtained by reacting for 3 and 6h, using 7 mg of Sc(OTf)<sub>3</sub>.

## Transmission Electron Microscopy

TEM images were obtained on a FEI Titan CT microscope operating at 300 kV. The membrane was previously immersed in an epoxy resin and cured overnight at 65 °C, then thin sections (100 nm) were cut with an ultramicrotome, collected on a 300 mesh copper grid and imaged.

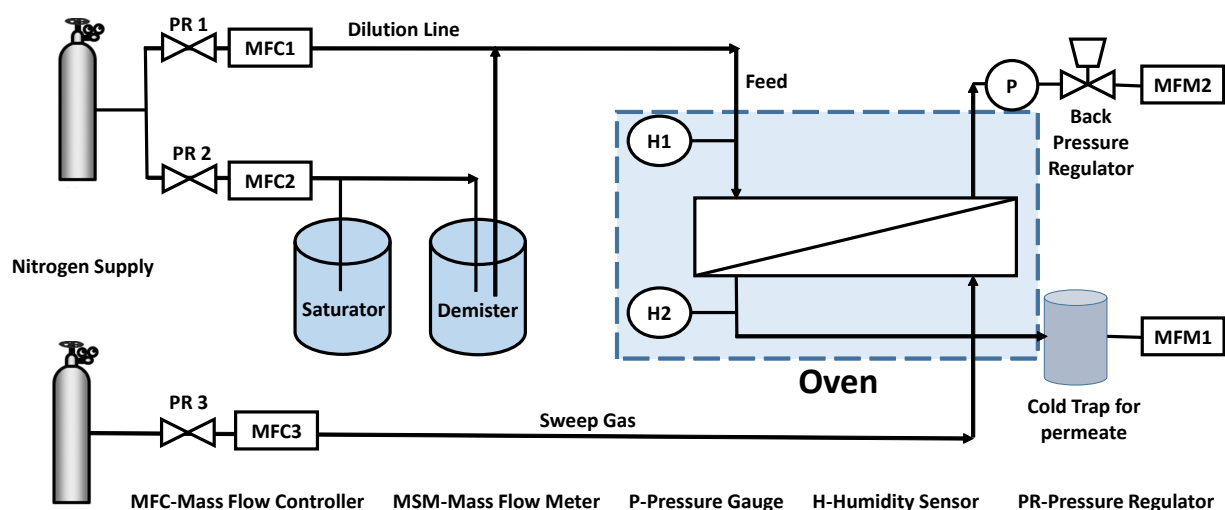




**Figure S5.** TEM images of the membrane cross-section for membrane prepared on XPAN support with 24h reaction, 24h annealing and 3.5 mg catalyst. (a) area close to the surface; (b) detail of a COF ordered area in the membrane cross-section; (c) Fourier Transform; (d) higher magnification images of selected parts of Fig. S5b, with area and (e) electron diffraction pattern of the b area.

## Water Vapor Transport

The modified upright permeability cup method (ASTM E96 standards)<sup>2</sup> is used to analyze the permeance of the composite membrane. The modified method is required over a traditional inverted cup method due to the use of a composite membrane to avoid the destruction of the membrane top active layer during the contact with water. Here the sweep gas is maintained at the permeate side acting as a driving force for extracting the water vapor from feed side. The humidity and temperature sensors were used to measure the accurate humidity and temperature on the feed as well as permeate side. The configuration of the setup is as shown below:



**Figure S6.** Schematic representation of the membrane dehumidification system.

## Contact Angle

The hydrophilicity of the COF membranes was investigated by measuring the water contact angle ( $\theta$ ) using Attension Theta Optical Tensiometer (KSV Instruments) at room temperature. A stipulated volume of 1  $\mu\text{L}$  of deionized water was dropped onto the surface of the membrane with a micro syringe using sessile drop method. The measurement was performed after the water drop stabilized. Each sample was measured at five different locations and the average is reported.

## References

1. Liliana Pérez-Manríquez, Jamaliah Aburabi'e, Pradeep Neelakanda, Klaus-Viktor Peinemann, Cross-linked PAN-based thin-film composite membranes for non-aqueous nanofiltration, *Reactive and Functional Polymers*, 2015, **86**, 243-247.
2. Standard test methods for water vapor transmission of materials, Annual book of ASTM standards. Designation E96–E80, 1989, 730–739.