

# In-situ Growth of Metal Organic Frameworks on Porous Ultrafiltration Membrane for Separation Applications

(Supporting Information)

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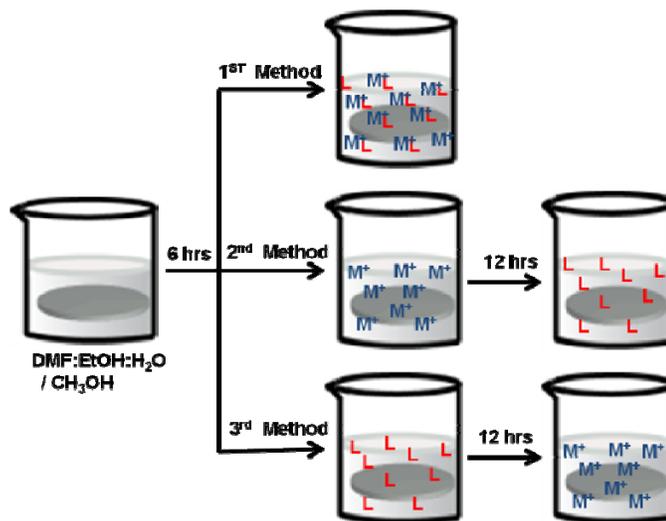
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## **Section S1: Method development for growing MOFs@PSF support**

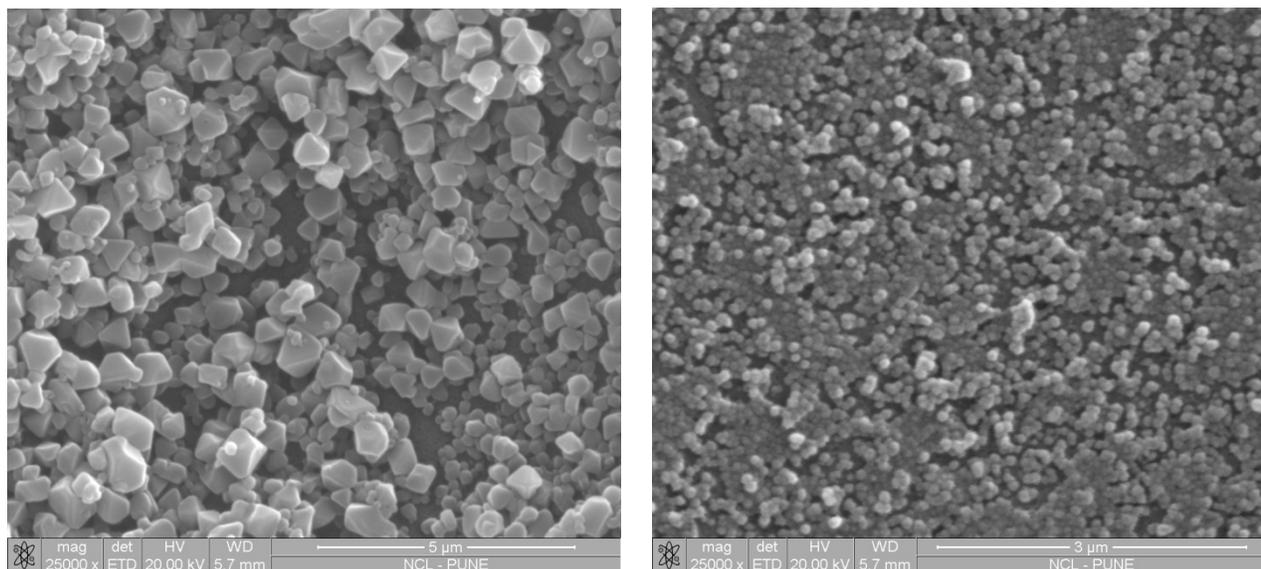
The stability of membrane towards solvents to be used for MOF growth (1:1:1 volume ratio of DMF/EtOH/H<sub>2</sub>O for CuBTC and CH<sub>3</sub>OH for ZIF-8) was evaluated by dipping membrane samples of known water flux for 24 hours and again measuring the water flux. The water flux did not vary to a noticeable extent, concluding stability of PSF membrane towards this solvent mixture.

In the first method, the PSF membranes that were immersed in 1:1:1 volume ratio of DMF/EtOH/H<sub>2</sub>O [for CuBTC] and CH<sub>3</sub>OH [for ZIF-8] were subsequently kept in a 250 ml beaker containing a 120 ml solution of Cu(NO<sub>3</sub>)<sub>2</sub> (8.6 g), BTC (5.0 g) and TEA (5 ml) [for CuBTC] and 100 ml solution of Zn(NO<sub>3</sub>)<sub>2</sub> (1.46 g) and 2-MIM (3.2 g) [for ZIF-8] for 12 hrs. Thus obtained membranes were washed with water and dried at RT or 60 °C for 2 hrs. In the second method, the PSF membranes that were dipped in 1:1:1 volume ratio of DMF/EtOH/H<sub>2</sub>O [for CuBTC] and CH<sub>3</sub>OH [for ZIF-8] were taken out and first immersed in the metal salt solution [Cu(NO<sub>3</sub>)<sub>2</sub> for CuBTC and Zn(NO<sub>3</sub>)<sub>2</sub> for ZIF-8] for 12 hrs and then the membranes were immersed into ligand solutions [BTC for CuBTC and 2-MIM for ZIF-8] for 12 hrs and dried at RT or 60 °C for 2 hrs. In the third method the PSF membranes immersed in 1:1:1 volume ratio of DMF/EtOH/H<sub>2</sub>O [for CuBTC] and CH<sub>3</sub>OH [for ZIF-8] were subsequently immersed in ligand solution [BTC for CuBTC and 2-MIM for ZIF-8] for 12 hrs and then was immersed into 250 ml beaker containing 100 ml of metal salt solution [Cu(NO<sub>3</sub>)<sub>2</sub> for CuBTC and Zn(NO<sub>3</sub>)<sub>2</sub> for ZIF-8] and dried at RT or 60 °C for hrs.



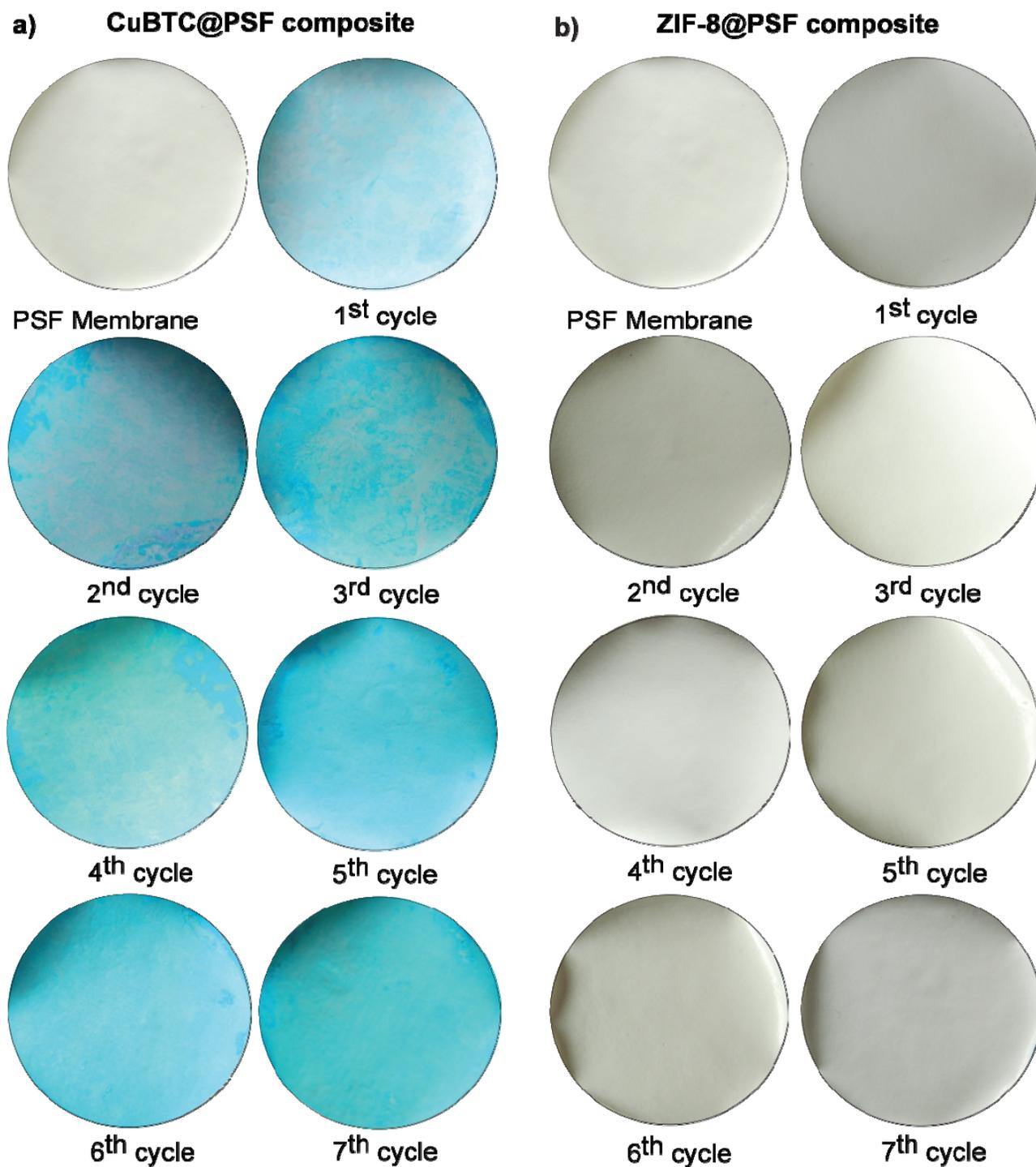
**Fig. S1** Growth scheme for MOFs@PSF support helped us in obtaining a denser crystal growth of MOFs without causing any physical defects to the PSF. Consistent reduction in water flux after every cycle of growth gave the clear indication of pores getting filled by MOF. Method-2 showed good crystal growth for CuBTC@PSF, while method-3 for ZIF-8@PSF composites.

## Section S2: SEM images of CuBTC@PSF and ZIF-8@PSF composites after 5<sup>th</sup> cycle



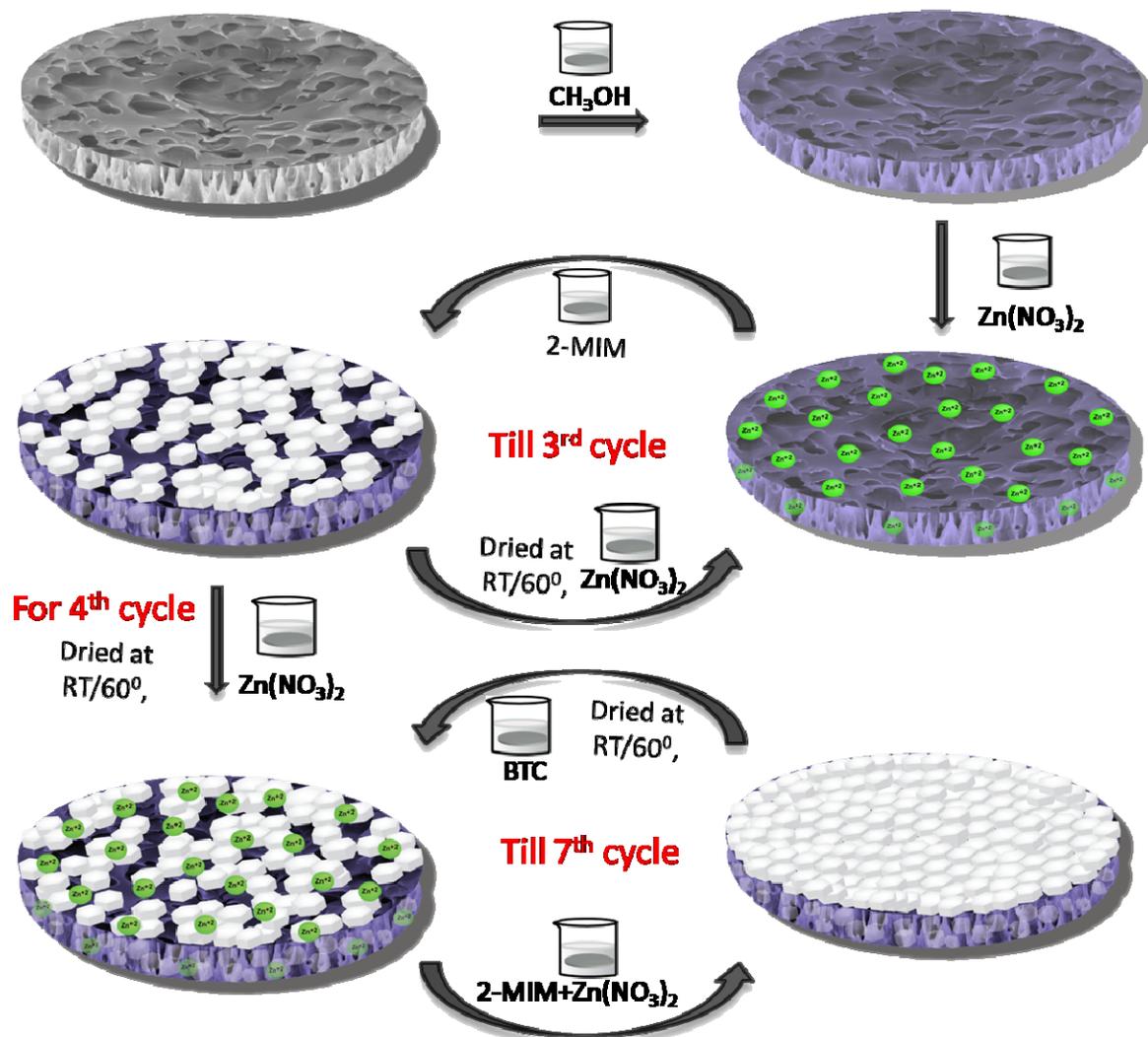
**Fig. S2** Surface SEM images reveal that when growth was followed through swapping of membranes in just the metal salt solution followed by the ligand solution, led to increase in crystal amount but there existed gaps which were not covered by crystals and henceforth demanded a change in crystal growing technique.

### Section S3: Digital photographs of CuBTC@PSF and ZIF-8@PSF composites



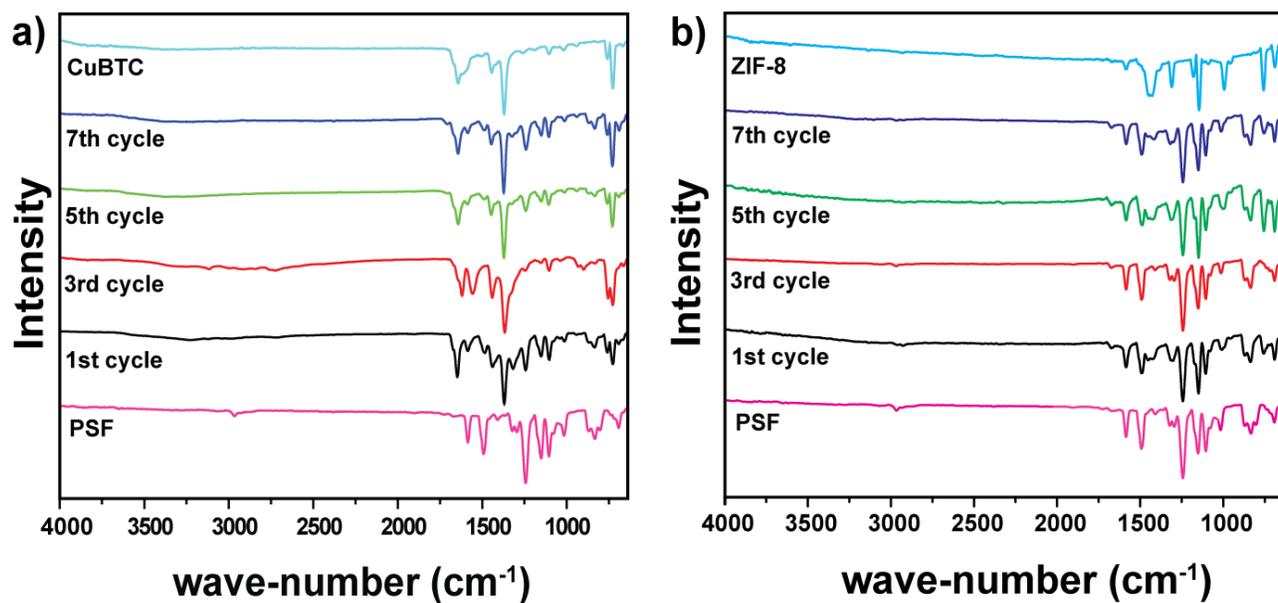
**Fig. S3** Digital photographs of the PSF@CuBTC and PSF@ZIF-8 composites membranes taken after every cycle of growth. In PSF@CuBTC we can see increased crystal growth after every cycle because of the blue color imparting from the crystals but in case of ZIF-8, as they are colorless, they does not make much difference to the naked eye.

### Section S4: Schematic representation of synthesis for ZIF-8@PSF composite membranes



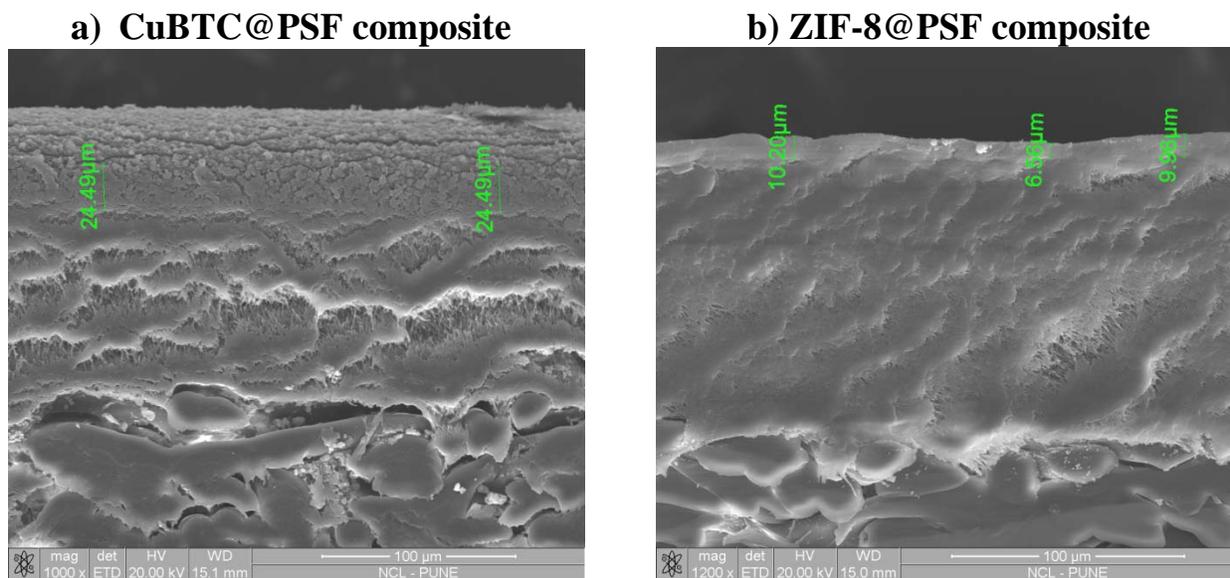
**Fig. S4** Scheme of synthesis of ZIF-8@PSF composite membranes by the in-situ crystallization and layer by layer deposition of crystals. Till 3<sup>rd</sup> cycle the crystallization is followed by in-situ method which leads to heterogeneous nucleation and from 4<sup>th</sup> cycle layer by layer deposition of crystals helps in forming the denser crystal layers which cover the gaps developed initially due to the heterogeneous nucleation.

### Section S5: FTIR analysis



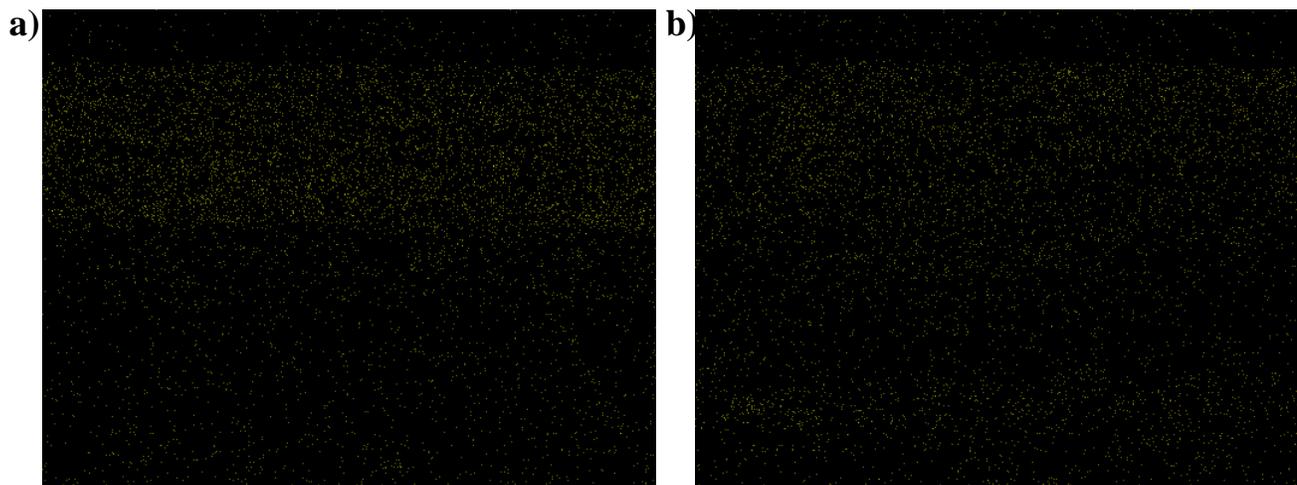
**Figures S5.** FTIR data collected after every alternative cycle of growth a) CuBTC@PSF and b) ZIF-8@PSF composite membranes.

**Section S6: SEM images showing the thickness of Cubtc@PSF and ZIF-8@PSF composites.**



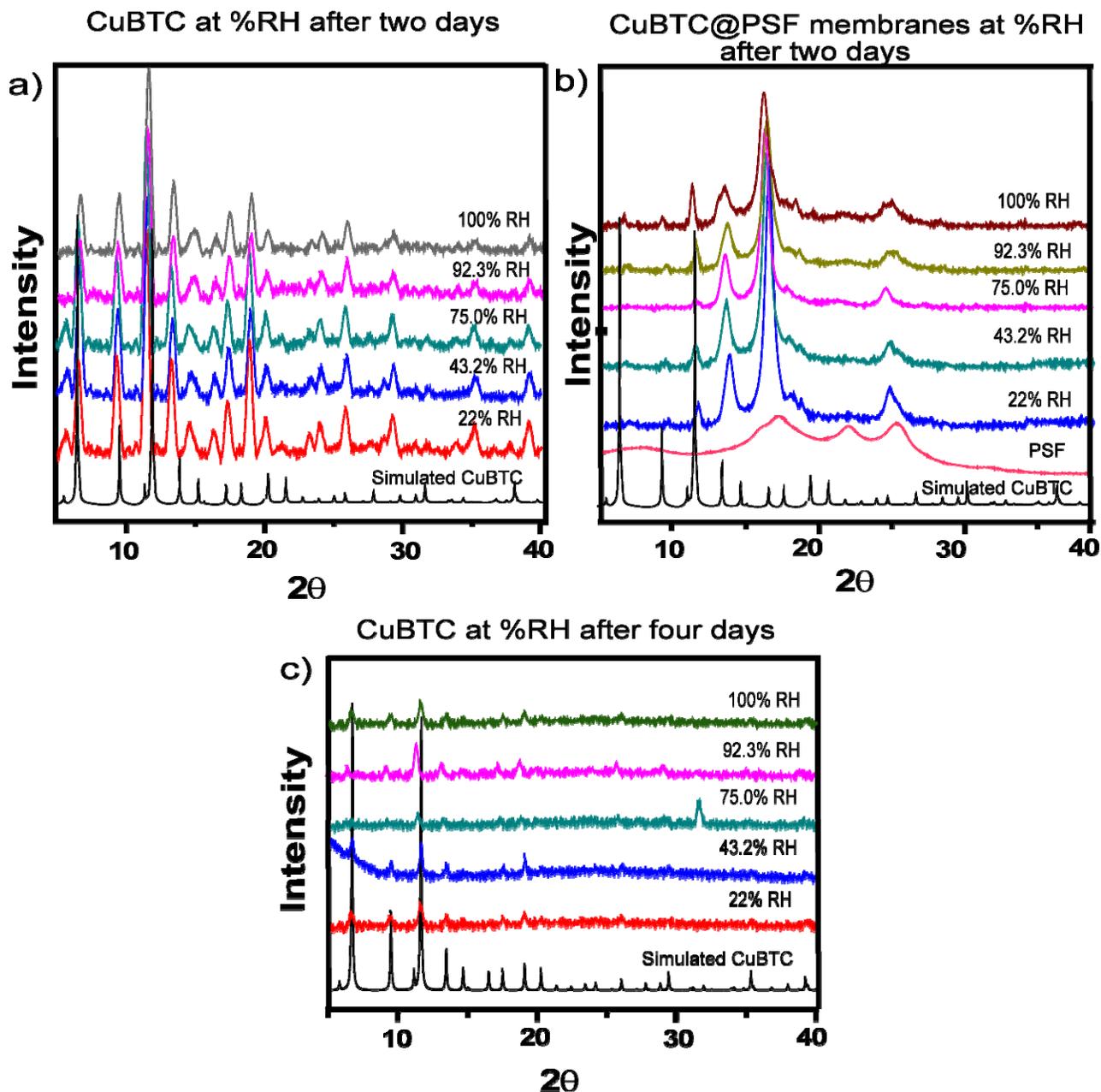
**Fig. S6** Cross section of Cubtc@PSF and ZIF-8@PSF composites which are about 25 μm and 6-10 μm, respectively.

### Section S7: EDAX Mapping



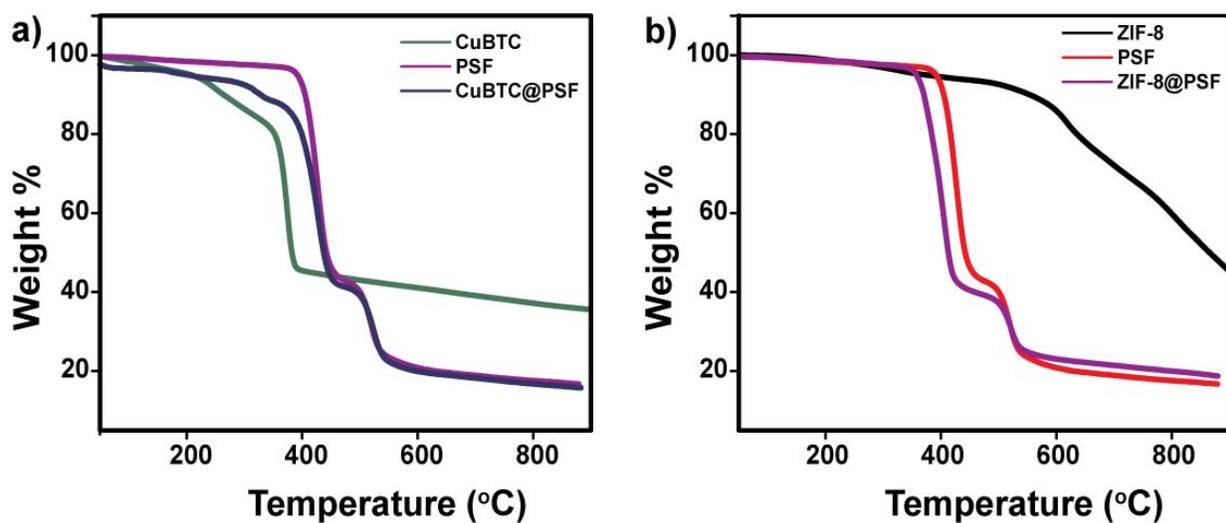
**Fig. S7** EDAX mapping confirming the presence a)  $\text{Cu}^{+2}$  ions in CuBTC@PSF composites and b)  $\text{Zn}^{+2}$  ions in ZIF-8@PSF composites. This also shows that there are denser crystal at the surface and the presence of crystals within the pores of the polymer as well.

### Section S8: Water stability analysis.



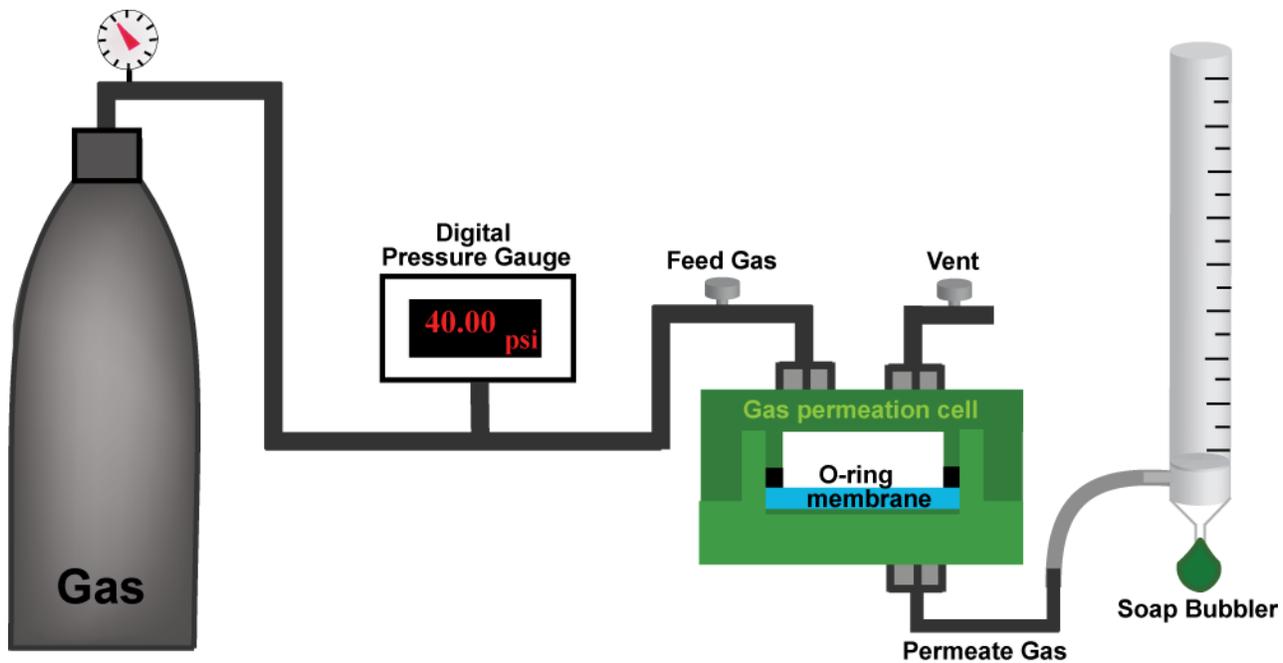
**Fig. S8** The XRD patterns of a) CuBTC exposed at different %RH (exposure time: 48 hr) and b) CuBTC@PSF membranes at different % RH (exposure time: 48 hr) and (c) CuBTC exposed at different %RH (exposure time: 96 hr). The XRD patterns in (a) matches well with the simulated pattern, indicating the stability of CuBTC. The XRD of CuBTC@PSF membranes at 100 % RH seems to differ indicating instability of CuBTC at this RH.

### Section S9: Thermo Gravimetric Analysis.



*Fig. S9* TGA data confirms the presence of CuBTC and ZIF-8 in Cubtc@PSF and ZIF-8@PSF respectively.

**Section S10: Gas permeation unit.**



*Fig S8.* Setup of gas permeation equipment

## Section S11: Permeance and selectivity data

**Table S1.** Single gas permeances (GPU) and separation factors for the composite membranes at 25 °C and 40 psi.

Variable Conditions	Permeances			Separation factors	
	P*( H <sub>2</sub> )	P(C <sub>3</sub> H <sub>6</sub> )	P(CO <sub>2</sub> )	P(H <sub>2</sub> )/ P(C <sub>3</sub> H <sub>6</sub> )	P(H <sub>2</sub> )/ P(CO <sub>2</sub> )
PSF-60	6089	2759	2057	2.2	3.0
PSF RTD	6004	2626	2027	2.3	3.0
ZIF8@PSF-60	1592	479	417	3.3	3.8
ZIF8@PSF -RTD	1190	314	317	3.8	3.8
CuBTC@PSF -60	503	95	131	5.3	3.8
CuBTC@PSF – RTD	236	41	33	5.7	7.2
CuBTC@PSF – humidified gases	259.4	75.7	74.5	3.4	3.5

\* Permeance expressed in GPU, (1 GPU = 1x10<sup>-6</sup> cm<sup>-3</sup>/cm.s.cmHg<sup>-1</sup>).

**Table S2.** Comparison of the ideal selectivity and permeation properties in the hybrid membranes with CuBTC@PSF composite membranes.

Membranes	T (°C)	Support	Permeance		Ideal Separation factor H <sub>2</sub> /CO <sub>2</sub>	Ref.
			H <sub>2</sub>	CO <sub>2</sub>		
CuBTC	25	Twin copper source	3792.7 <sup>a</sup> (127) <sup>b</sup>	839.2 (28.1)	4.52	1
	25	α-Alumina	5972.8 (200)	1493.2 (50)	4	2
	25	Alumina	2233.8 (74.8)	442 (14.8)	5.05	3
	25	PMAA coated Si wafers	4151.1 (139)	477.8 (16)	8.68	4
	40	α-Alumina	216.5 (7.25)	16.4 (0.55)	13.18	5
	25	α-Alumina	8511.2 (285)	1991.9 (66.7)	4.27	6
	25	Porous Polysulfone	236 (7.9)	33 (1.1)	7.2	This work
ZIF-8	25	α-Alumina	516.6 (17.3)	132.9 (4.45)	3.89	7
	25	α-Alumina	1075.1 (36)	418.1 (14)	2.57	8
	25	Alumina	1633.6 (54.7)	50.8 (1.7)	32.2	9
	25	APTES functionalized α-Alumina	17110.7 (5730)	10034.3 (336)	17.05	10
	25	Porous Polysulfone	1190 (39.8)	317 (10.6)	3.8	This work

<sup>a</sup>: Permeance values are expressed in GPU, where 1 GPU = 1x10<sup>-6</sup> cm<sup>-3</sup>/cm.s.cmHg<sup>-1</sup> ; while,

<sup>b</sup>: Permeance values in the parenthesis are expressed in mol.m<sup>-2</sup>.s<sup>-1</sup>.Pa<sup>-1</sup> x 10<sup>-8</sup>.

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