Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information for

Facile modification of ZIF-8 mixed matrix membrane for CO_2/CH_4 separation: synthesis and preparation

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Thermal analysis of virgin and modified ZIF-8

The thermal stability of the prepared ZIF-8 samples was characterized with TGA analysis under N_2 atmosphere as shown in **Fig. S1**. No apparent weight loss was observed below 150°C for virgin and modified ZIF-8s indicating the absence of guest molecules (i.e. ammonium hydroxide, moisture) within their pores. Hence, this result further suggested that the ammonium hydroxide chemically altered the ZIF-8 particles without being impregnated within the pores. Second weight losses observed around 250°C associate with carbonization of guest molecule (2-MeIM) in ZIF-8 pores. The third weight losses that occurred at approximately 600°C for all prepared ZIF-8s can be ascribed to the decomposition of the organic linkers and ZIF-8 crystal. From the TGA analysis, it can be concluded that the modification introduced does not alter thermal stability of ZIF-8 and it remains thermally stable up to 600°C in inert environment.

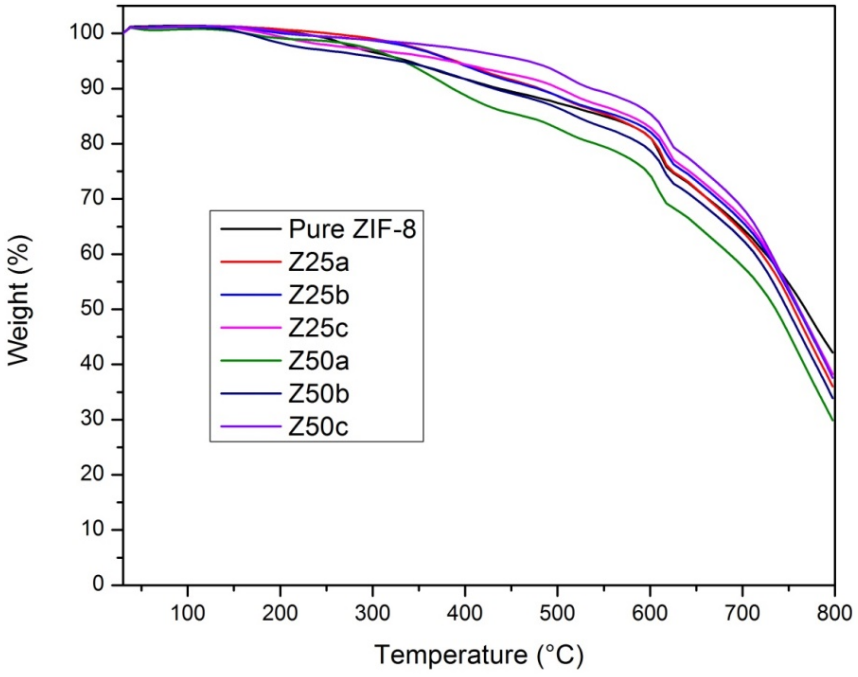

Fig. S1. TGA curves of virgin and modified ZIF-8s

Pores distribution of virgin and modified ZIF-8

The pores dsitribution of virgin and modified ZIF-8s were calculated using commercial software. The virgin ZIF-8 pores well-distributed in macro- (>50 nm), meso- (2-50 nm) and micropores (<2 nm) ranges (**Fig. S2**). After modification, significant changes in the pores distribution were observed. For Z25-series modification, the macropores and mesopores began to diminish, while micorpores shows increased when modification temperature increased (**Fig. S3**). Similar observation were also experienced by Z50-series with different magnitude of changes (**Fig. S4**). It can be postulate that different modification parameters (i.e. the amount of ammonia solution and temperature) induce the evolution of the pore distribution due to pore reopening[1] and/or formation of new pores due to cage reordering[2] .

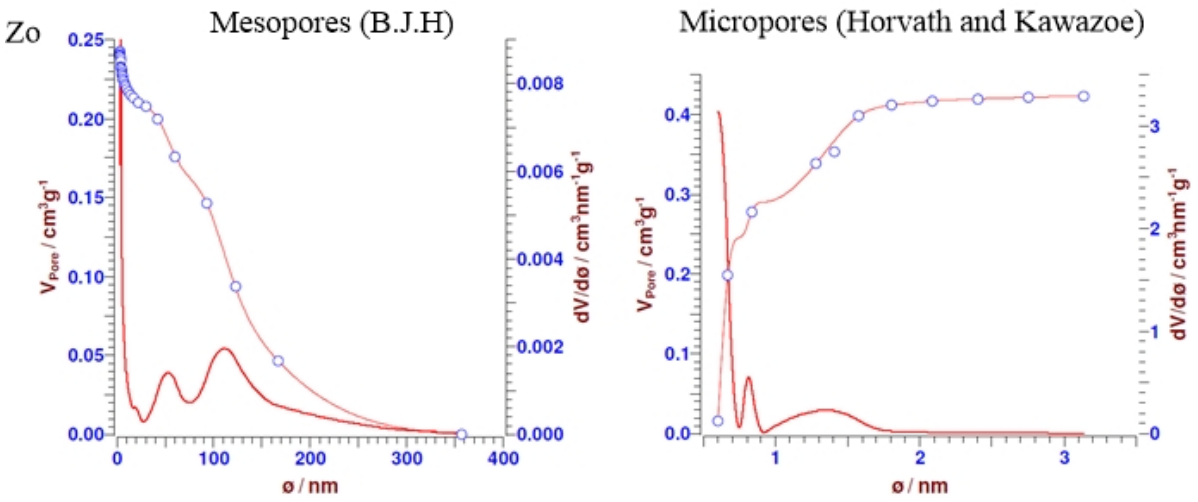

Fig. S2 Pores distribution of virgin ZIF-8

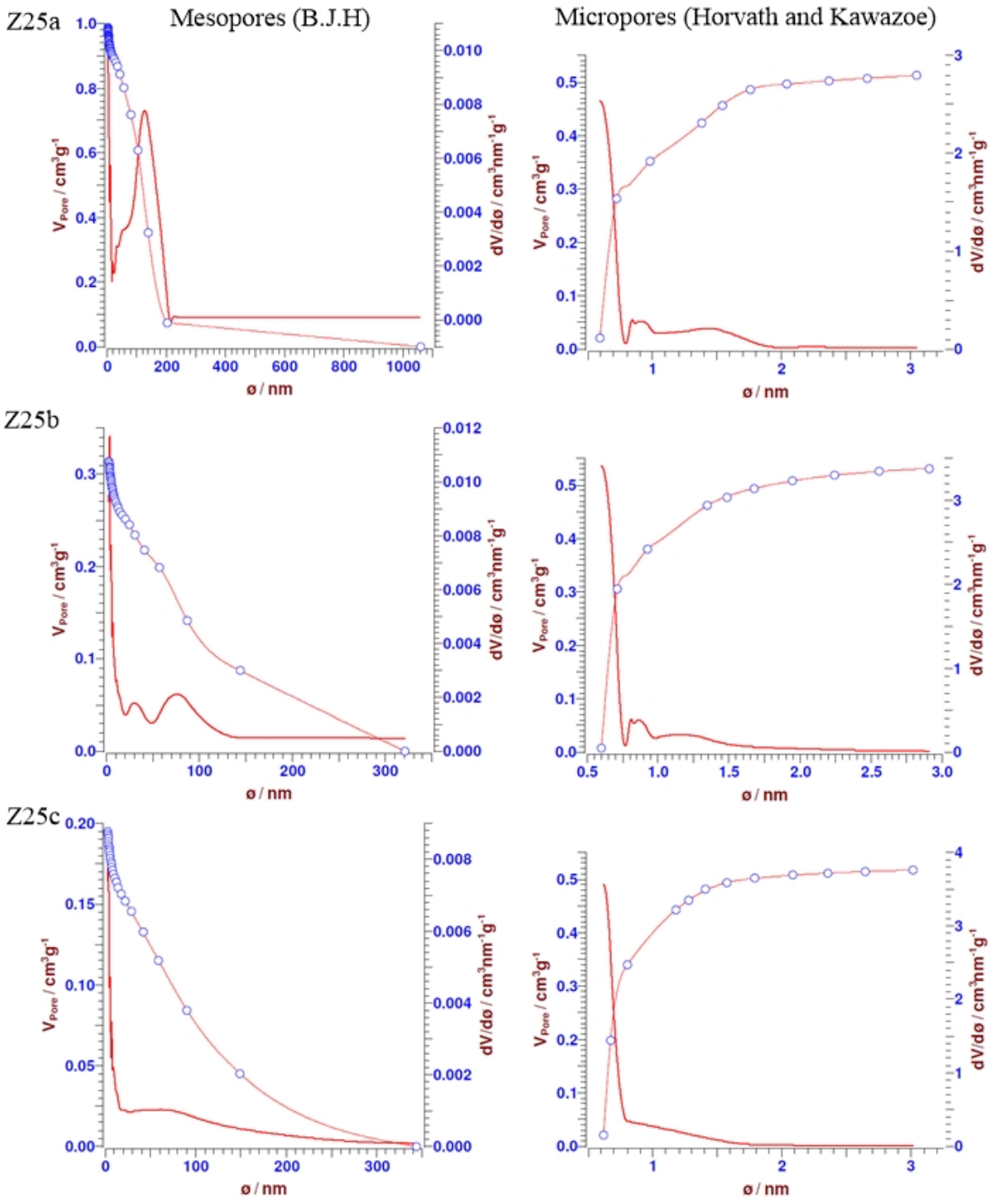

Fig. S3 Pores distribution of Z25-series

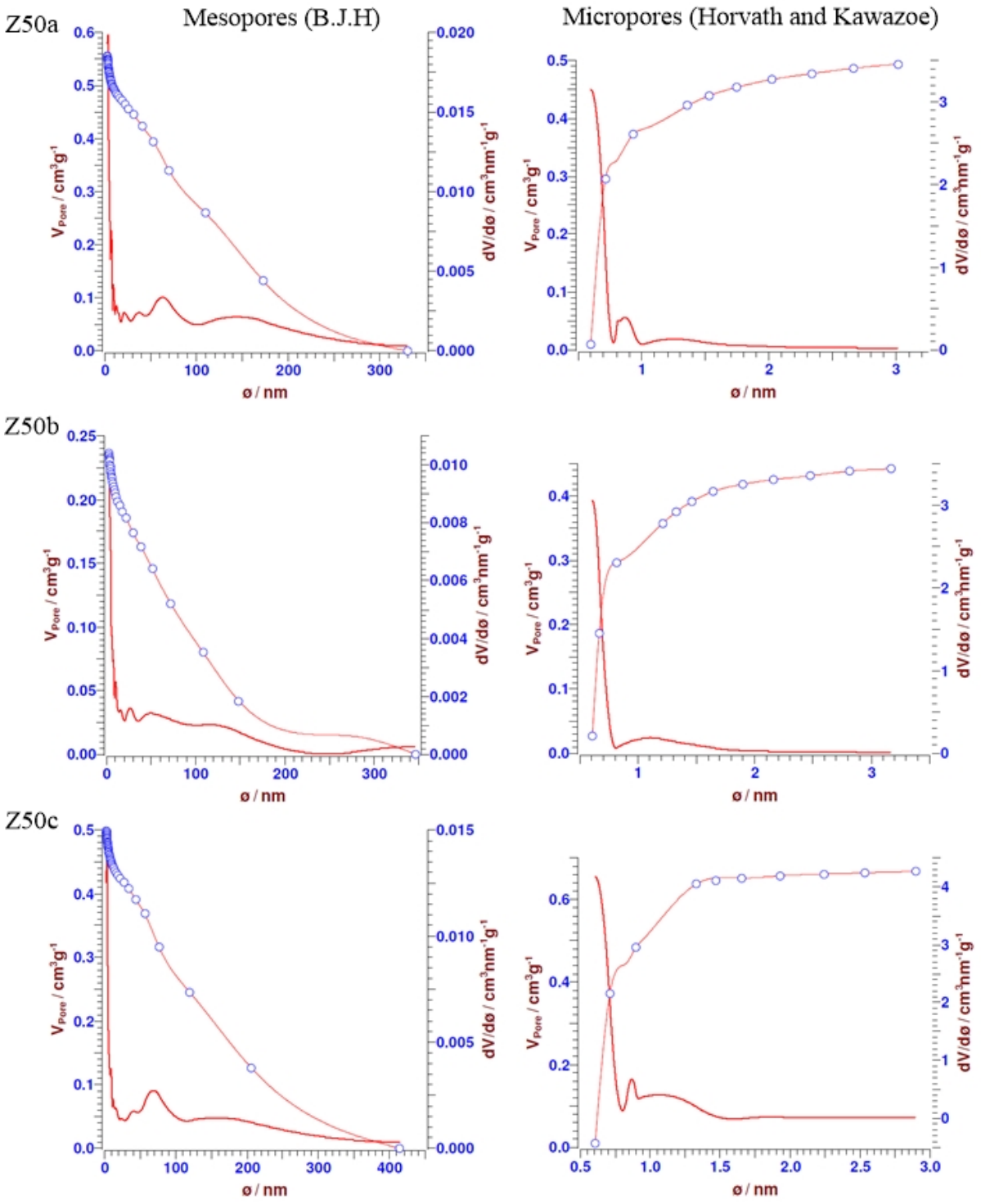

Fig. S4 Pores distribution of Z50-series

Cross-sectional morphology of PSf/modified ZIF-8 MMMs

The cross-sectional morphology of M25-series and M50-series membranes are presented in **Fig. S5** and **Fig. S6**, respectively. The resulting membranes show an asymmetric structure, with an apparent active layer accompanied by a sponge-like substructure, which cause by different phase inversion rate during dry and wet inversion. There was no apparent different compared to neat PSf membrane and virgin ZIF-8 membrane (see **Fig. 4** in the main manuscript) due to only small amount of fillers were incorporated and similar preparation protocol was used for fabrication.

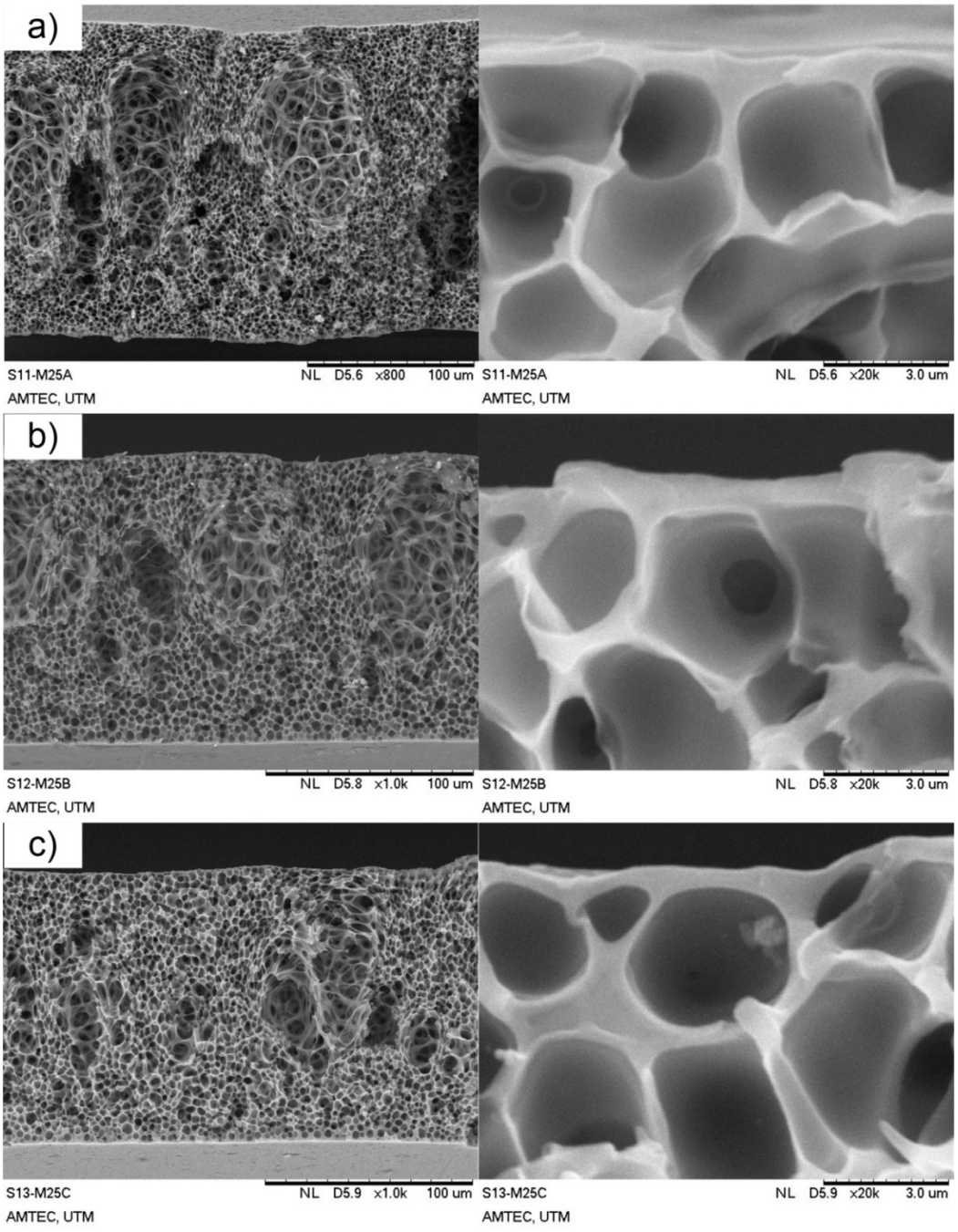

Fig. S5. Cross-sectional membrane morphology of a)M25a, b) M25b, and c) M25c

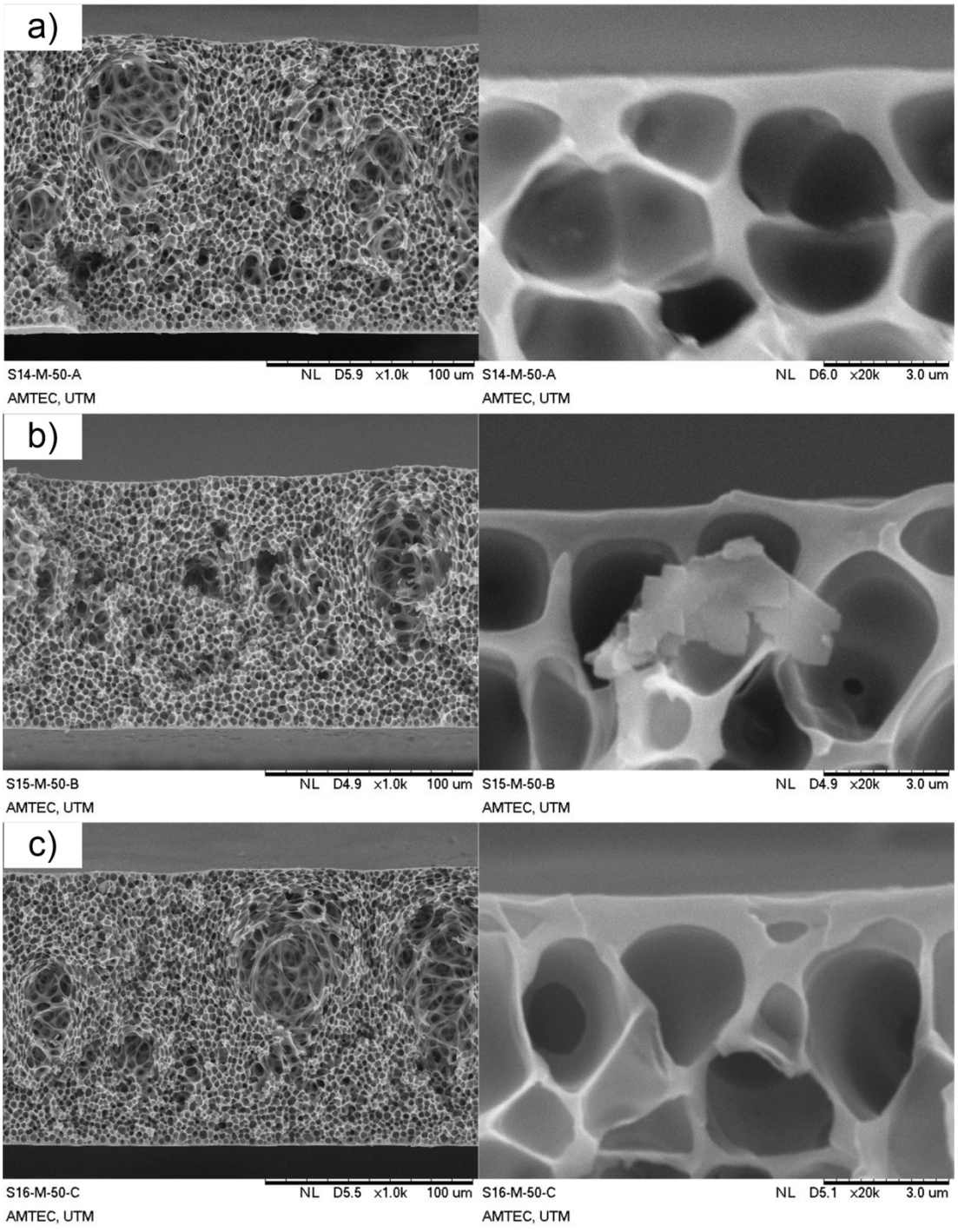

Fig. S6. Cross-sectional membrane morphology of a)M50a, b) M50b, and c) M50c

ATR-IR of membranes

The prepared membranes prepared undergo ATR-IR analysis to identify the changes in functional group after filler incorporation is presented in **Fig. S7**. For this analysis, M25c was use to represent modified ZIF-8 MMM and compared with virgin ZIF-8 MMM (M0) and neat PSf membrane. The ATR-IR of neat PSf membrane shows good agreement with literature[3]. The characteristic IR peaks of PSf presence at 1577 cm^{-1} (aromatic in-plane ring bend) and 1325 cm^{-1} (sulfone functional group). Two weak bands represent 1385 cm^{-1} and 1365cm^{-1} represents the methyl groups in the PSf matrix. The incorporation of fillers (virgin and modified ZIF-8) into PSf matrix showed no distinctive IR spectrum conforming that there is no new functional group introduced and the PSf matrix remain intact even after the fillers were embodied.

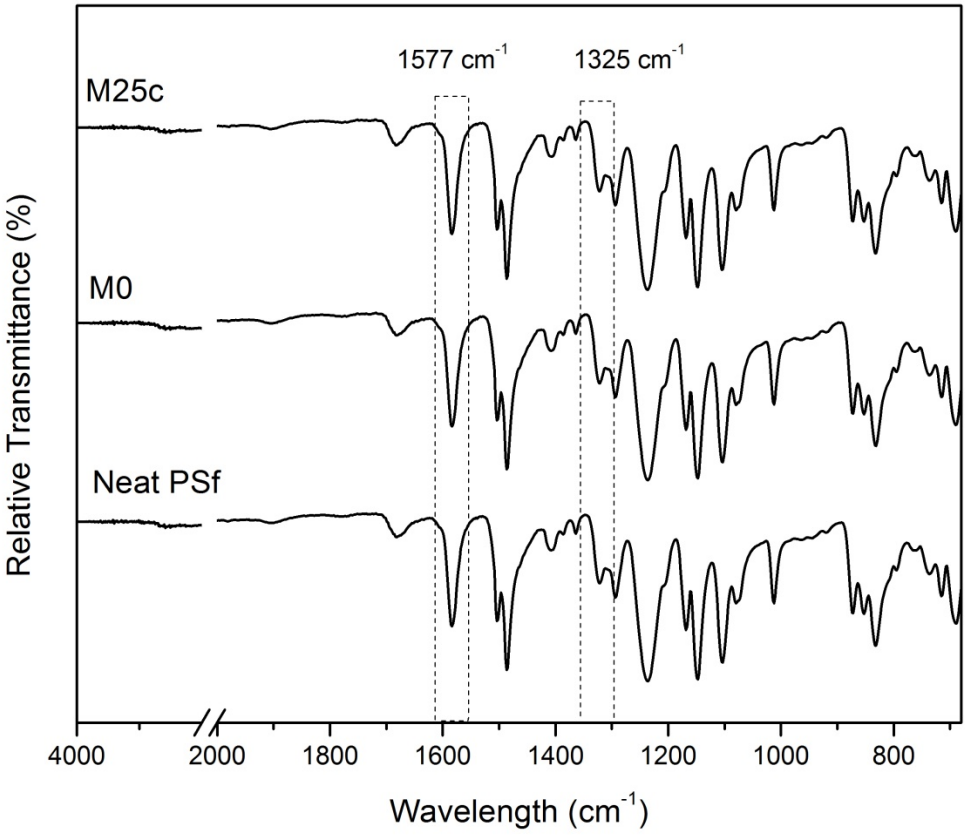

Fig. S7 ATR-IR spectrum of neat PSf, M0 and M25c

Thermal stability of prepared membranes

Thermal stability of prepared membranes is presented in **Fig. S8**. Neat membrane exhibits the first weight loss (%) at temperature around 100°C, which is attributed to the presence of water trapped in the membrane during the wet phase inversion. Whereas, MMMs show insignificant weight loss at this temperature due to hydrophobic nature of ZIF-8 that has minimized water trap within the membrane[4]. Second weight loss at approximately 500°C is attributed to degradation of polymer matrix[5]. No significant difference between thermal stability of pristine PSf and MMMs was observed, which suggested that low ZIF-8 loading did not affect overall thermal stability of prepared membranes.

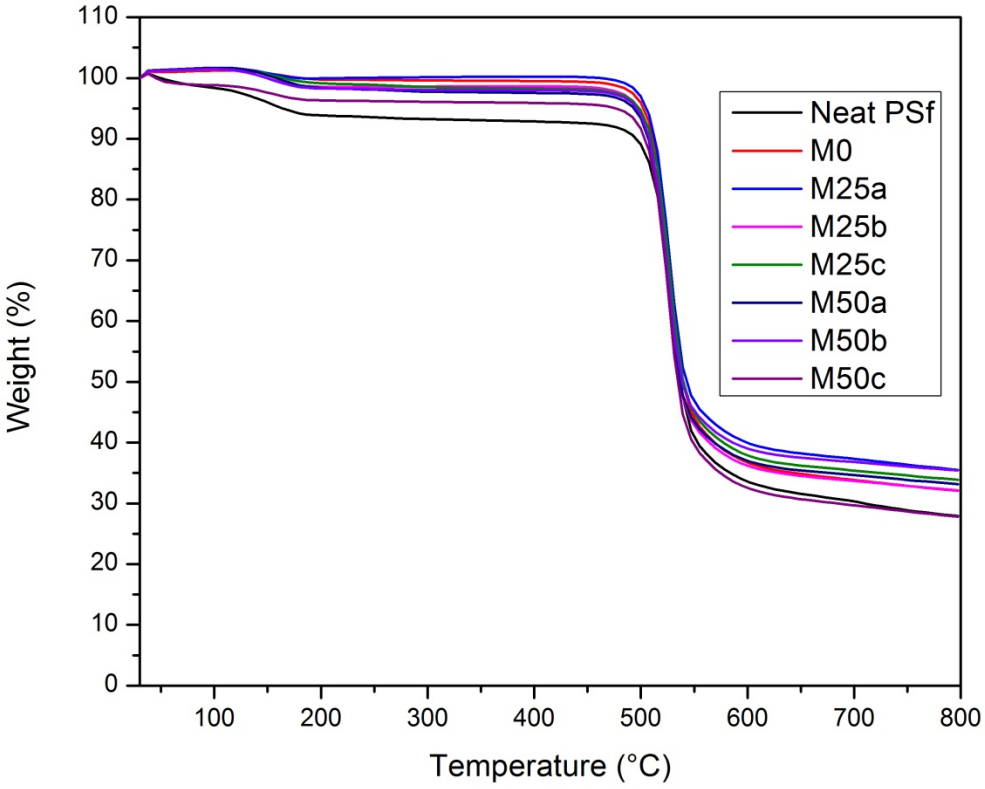

Fig. S8 TGA curve of prepared membranes

References

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