Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Highly Propylene-Selective Supported Zeolitic-imidazolate Framework ZIF-8 Membranes by Rapid Microwave-assisted Seeding and Secondary Growth

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Experimental details:

Chemicals: Chemicals were used as purchased without further purification. Zinc nitrate hexahydrate ($Zn(NO_3)_26H_2O$, 98%, Sigma-Aldrich,)) were used as metal sources. 2-methylimidazole ($C_4H_5N_2$, 97%, Sigma-Aldrich, hereafter m-Im), benzimidazole ($C_7H_6N_2$, 98%, Sigma-Aldrich, hereafter b-Im), and 4-methyl-5-imidazolecarboxaldehyde ($C_5H_6N_2O$, 95%, Santa Cruz Biotechnology, hereafter m-Imca) were used as ligand sources. Sodium formate (HCOONa, 99%, Sigma-Aldrich, denoted as S.F.) was used as a deprotonating agent. Graphite powder (-300 mesh, 99%, Alfa Aesar) was used for coating a conductive layer on a support for MITD seeding. Methanol (99.8%, Alfa Aesar), ethanol (99.5%, Sigma-aldrich), and dimethylformamide (99.88%, Alfa Aesar, hereafter DMF) were used as solvents for membrane synthesis.

Preparation of α-Al_2O_3 supports*:* First, 1.9 g of alumina powder (CR6, Baikowski) was mixed with 8 mg of D.I. water (binder) and grinded in mortar to eliminate aggregated powder. Then the powder was injected into a die and compressed uniaxially with 10 ton for 1 min. The molded disks were dried at room temperature for 4 days and subsequently sintered at 1100^{o}C for 2 hr. The disks were polished with a sand paper (grid #1200) and washed with methanol under sonication for 1min. Finally, the disks were dried at 120^{o}C in an oven before usage. The prepared disks have a dimension of 22 mm in diameter and 2 mm in thickness with 46% of porosity.

Formation of ZIF-8 seed layer and secondary growth: A metal precursor solution was prepared by dissolving 2.43 g of zinc nitrate hexahydrate in 40 ml of methanol while a ligand precursor solution was prepared by dissolving 2.59 g of m-Im and 0.125 g of S.F. in 30 ml of

methanol. After a support was soaked in the metal precursor solution for 1 hr, it was placed vertically using a Teflon holder in the ligand solution contained in microwave-inert glass tube and immediately followed by the microwave radiation with the power of 100 W for 1.5 min. The seeded support was then thoroughly washed in fresh methanol under stirring for 4 hr followed by drying at 60^{o}C for 4 hr. The secondary growth of the ZIF-8 seed layer was done using the recipe reported by Pan et al.[1] Briefly, an aqueous precursor solution was prepared by dissolving 0.11 g of zinc nitrate hexahydrate and 2.27 g of m-Im in 40 ml of DI water. The seeded support was immersed vertically in the aqueous precursor solution and kept in an oven at 8^{o}C and 30^{o}C for 6 hr, respectively. The membrane was washed in fresh methanol under stirring for 5 days. Finally the sample was dried at 60^{o}C for 6 hr before further characterization.

Formation of ZIF-7 seed layer and secondary growth: Similarly, the seed layer was prepared by irradiating the microwave with the power of 100 W for 3 min onto the disk saturated with a metal precursor solution (3.06 g of zinc nitrate hexahydrate in 40 ml of DMF) positioned vertically inside of a ligand solution (1.62 g of b-Im and 0.01 g of S.F. in 40 ml of DMF). The seeded disk was thoroughly washed in ethanol under stirring for 4 hr and consecutively dried at 60^{o}C for 4 hr. Then the seeded disk was placed in an autoclave containing precursor solution (0.57 g of zinc nitrate hexahydrate and 0.31 g of b-Im in 40 ml of DMF) and kept at 100^{o}C for 6 hr in a convective oven. The membrane was rinsed in ethanol under stirring for 5 days. Lastly the sample was dried at 60^{o}C for 6 hr before further characterization.

Formation of SIM-1 seed layer and secondary growth: The disk soaked in metal solution (2.5 g of zinc nitrate hexahydrate in 30 ml of ethanol) for 1 hr was injected into ligand solution (0.35g of m-Imca in 30 ml ethanol). Then the microwave with a power of 100 W was irradiated on the

system for 3 min. Then the seeded disk was thoroughly washed in ethanol under stirring for 4 hr and consecutively dried at 60^{o}C for 4 hr. Afterward the seeded layer was solvothermally treated at 85^{o}C for 4 hr in an autoclave containing a precursor solution (0.1 g of zinc nitrate hexahydrate and 0.1 g of m-Imca in 40 ml of ethanol). Then, the membrane was rinsed in ethanol under stirring for 5 days. Lastly the sample was dried at 60^{o}C for 6 hr before further characterization.

Binding strength of ZIF-8 seed layers: The binding strength of seed layers were tested by sonication method.[2] Briefly, the seed layers were sonicated with a power of 90 W (RF frequency, 35 kHz) in methanol as a function of time (20 min, 1 hr, 1.5hr, and 2 hr). XRD diffraction patterns were collected at each time intervals and (110) diffraction peaks were normalized by the (110) peak intensity obtained from the initial seed layers. Then the tendencies of variation in the normalized intensities as a function of sonication time were compared to judge the binding strength to supports between the seed layers prepared in different ways such as dip-coating,[1] MITD,[3] and microwave-assisted seeding. The dip-coated seed layers were prepared by following the recipe reported by Pan et al.[1] In case of MITD seeding, first, the conductive graphite layer was coated on a support by manually rubbing graphite powder. Then the graphite coated supports were placed in the solution, a mixture of 0.04 ml of metal solution (2.43 g of zinc nitrate hexahydrate in 40 ml methanol) and 30 ml of ligand solution (2.59 g of m-Im and 0.125 g of S.F. in 30 ml of methanol). Subsequently, the system was exposed to the microwave with the power of 100 W for 1.5 min. The seeded support was then thoroughly washed in fresh methanol under stirring for 4 hr followed by drying at 60^{o}C for 4 hr.

Characterization: Crystal phases of the seed layers and membranes were identified by a Rigaku Miniflex II powder X-ray diffractometer using Cu-Kα radiation (λ = 1.5406 Å) which were scanned with a step size of 0.02°. Scanning electron micrographs were collected using a JEOL JSM-7500F operating at 5 keV acceleration voltage and 15 mm working distance. The gas separation performance of ZIF-8 membranes was tested using the Wicke-Kallenbach technique under atmospheric pressure. The 50:50 mixture of propylene and propane was supplied to a feed side while a permeate side was swept by argon with the total flow rates of both sides maintained at 100 ml/min. The gas composition of the permeate side was analyzed using a gas chromatography (Agilent GC 7890A equipped with HP-PLOT/Q column).

Figure S1

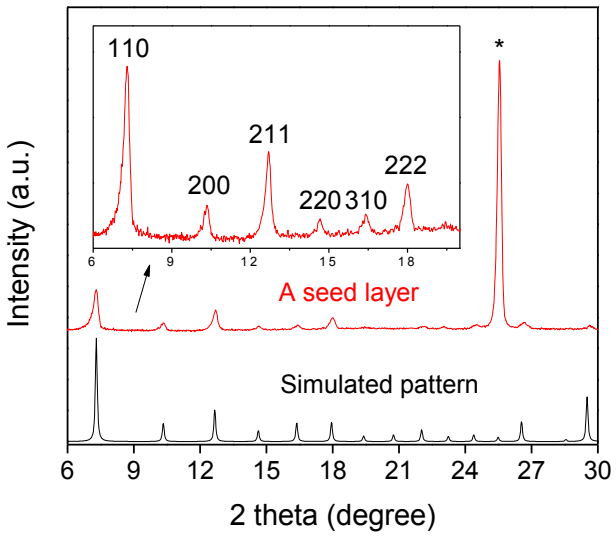

Fig. S1. X-ray diffraction pattern of a ZIF-8 seed layer on an α-Al_2O_3 support prepared under microwaves in comparison with a simulated pattern. The characteristic peak of α-Al_2O_3 support is marked with an asterisk.

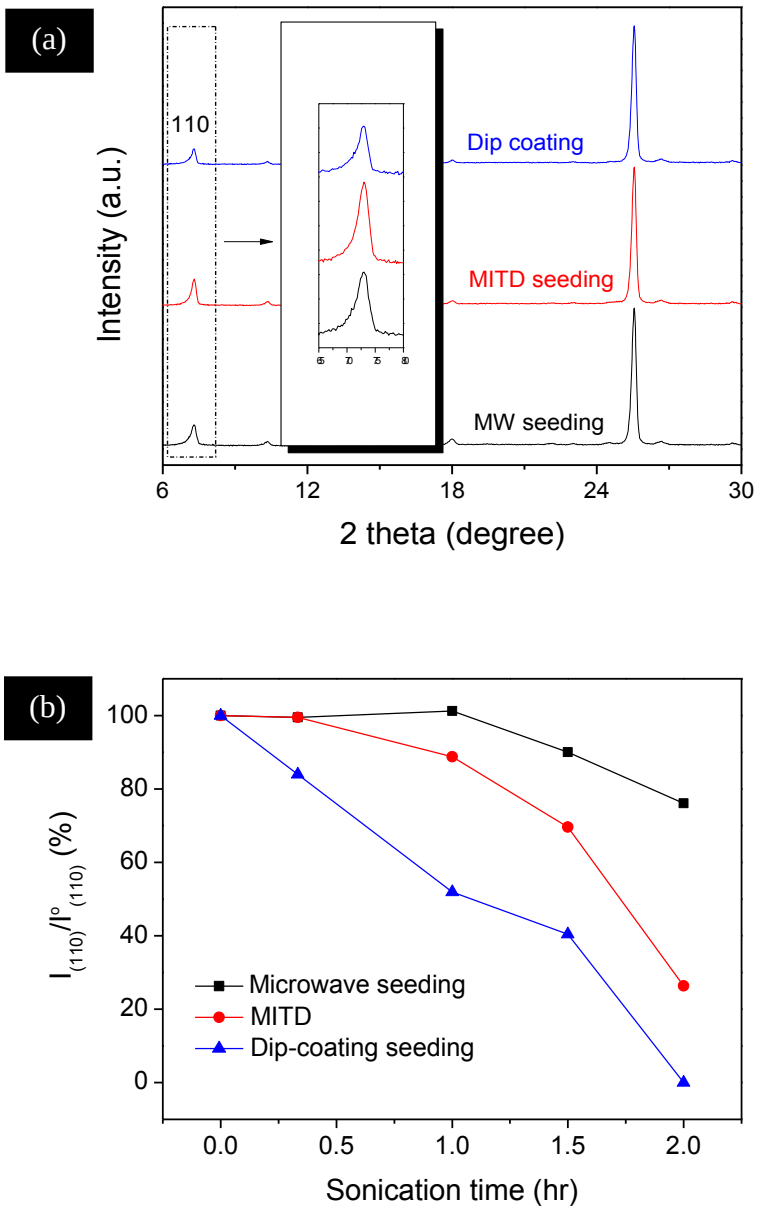

Fig. S2. (a) XRD patterns of initial seed layers prepared by various method and (b) binding strength of the ZIF-8 seed crystals on α-Al_2O_3 supports.

Figure S3

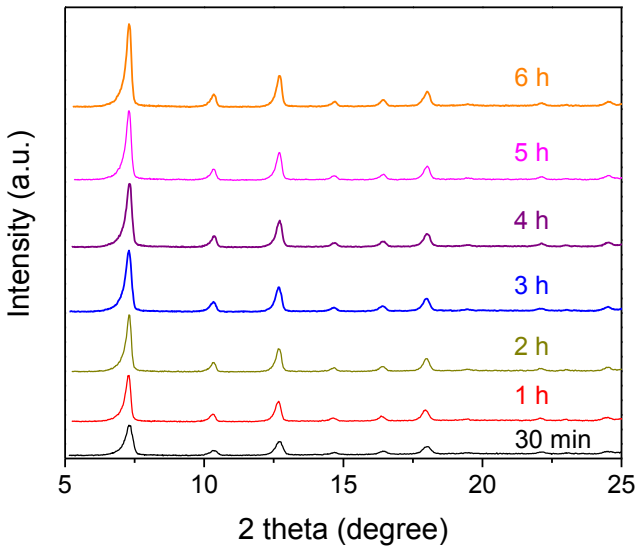

Fig. S3. XRD patterns of ZIF-8 membranes as a function of growth time

Figure S4

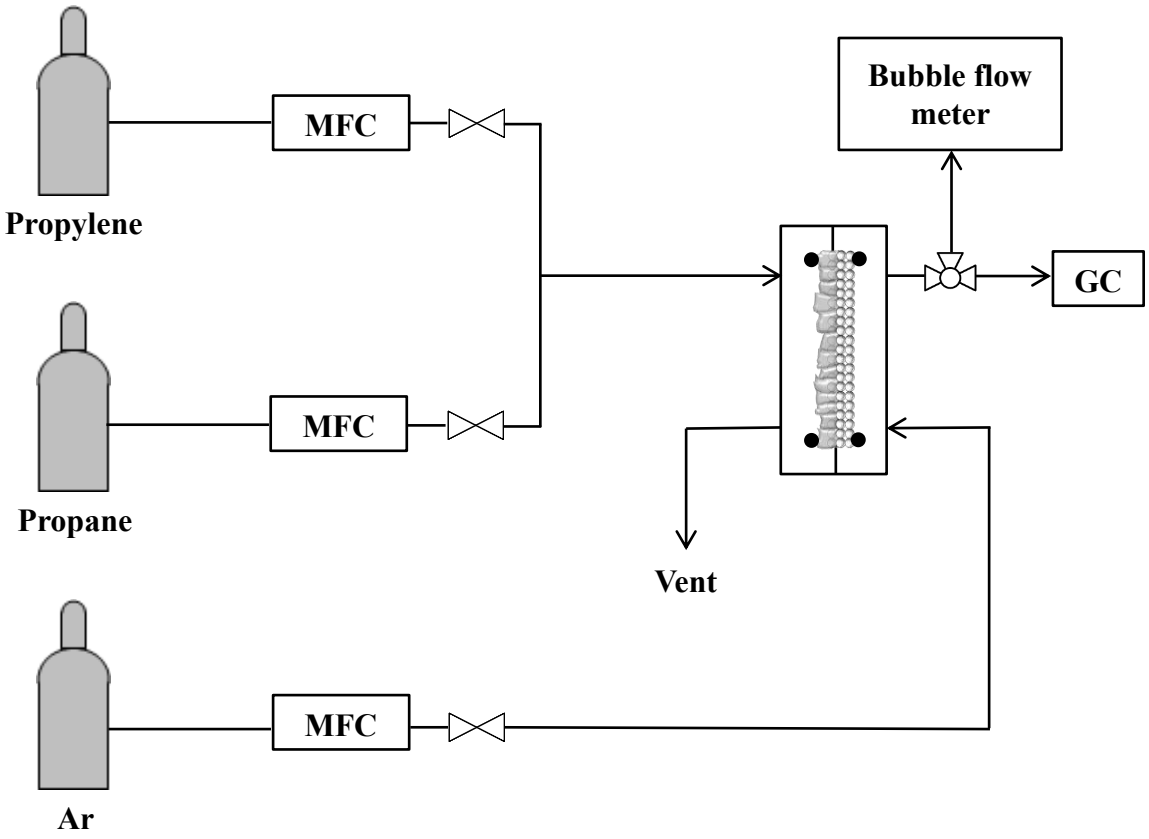

Fig. S4. Schematic diagram of a Wicke-Kallenbach gas permeation test setup

Figure S5

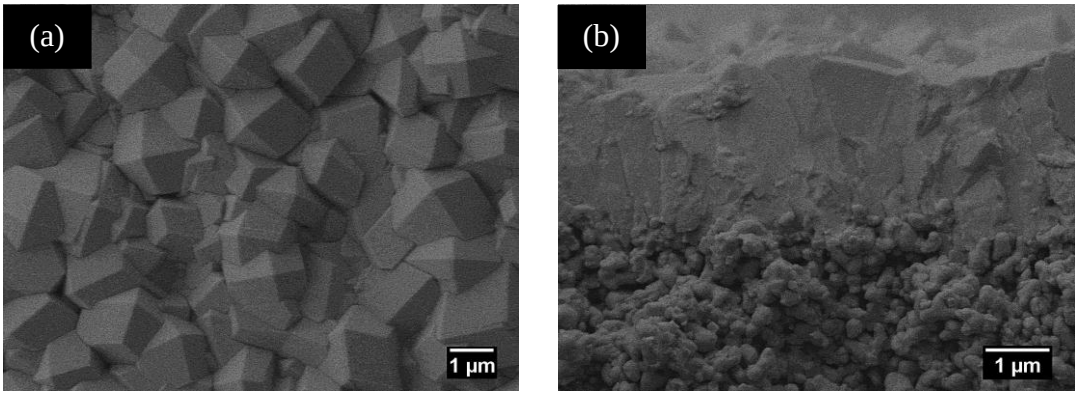

Fig. S5. SEM images of ZIF-8 memrbanes grown: at 30 ^{o}C (a) top view and (b) cross-section

Figure S6

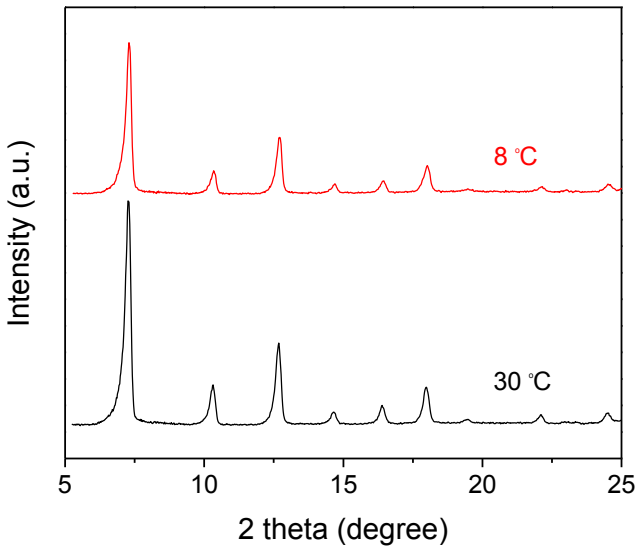

Fig. S6. XRD patterns of ZIF-8 membranes prepared at 8°C and 30°C

Figure S7

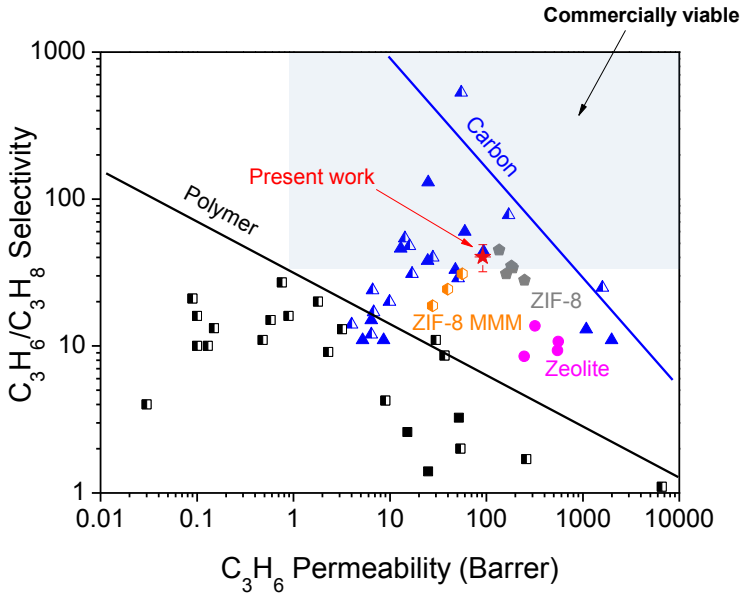

Fig. S7. Comparison of ZIF-8 membrane performances for propylene/propane separation with other literature data. Half-filled and full-filled symbols indicate separation data from singles gas permeation and binary gas permeation test, respectively. The shaded area in the graph implies the performance requirement of a membrane (a minimum permeability of 1barrer and selectivity of 35) for commercial application.[4] ((triangle : Carbon membrane,[5-8] circle : zeolite membrane,[9] rectangle : polymer membrane,[10] pentagon : ZIF-8 membrane,[1] hexagon : ZIF-8 mixed matrix membrane,[11] star : ZIF-8 membrane in this work)

Figure S8

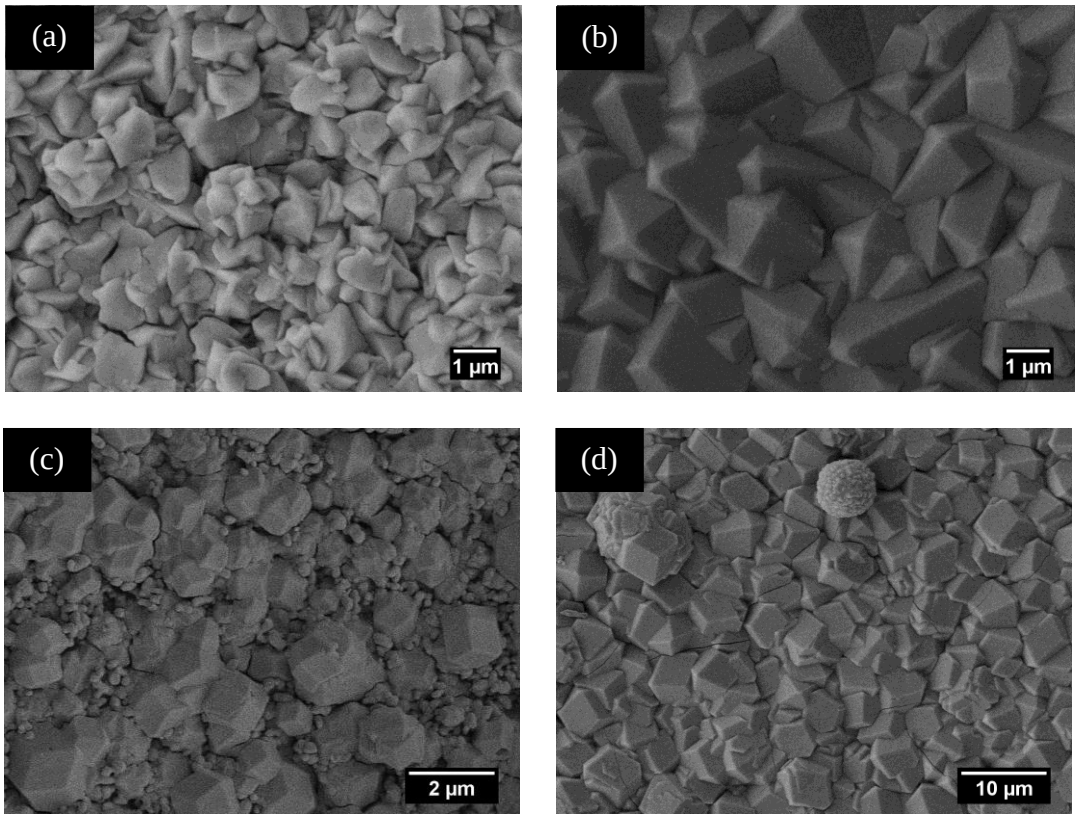

Fig. S8. SEM images of (a) a ZIF-7 seed layer, (b) a ZIF-7 membrane, (c) a SIM-1 seed layer, and (d) a SIM-1 membrane prepared by rapid microwave-assisted seeding and secondary growth.

Figure S9

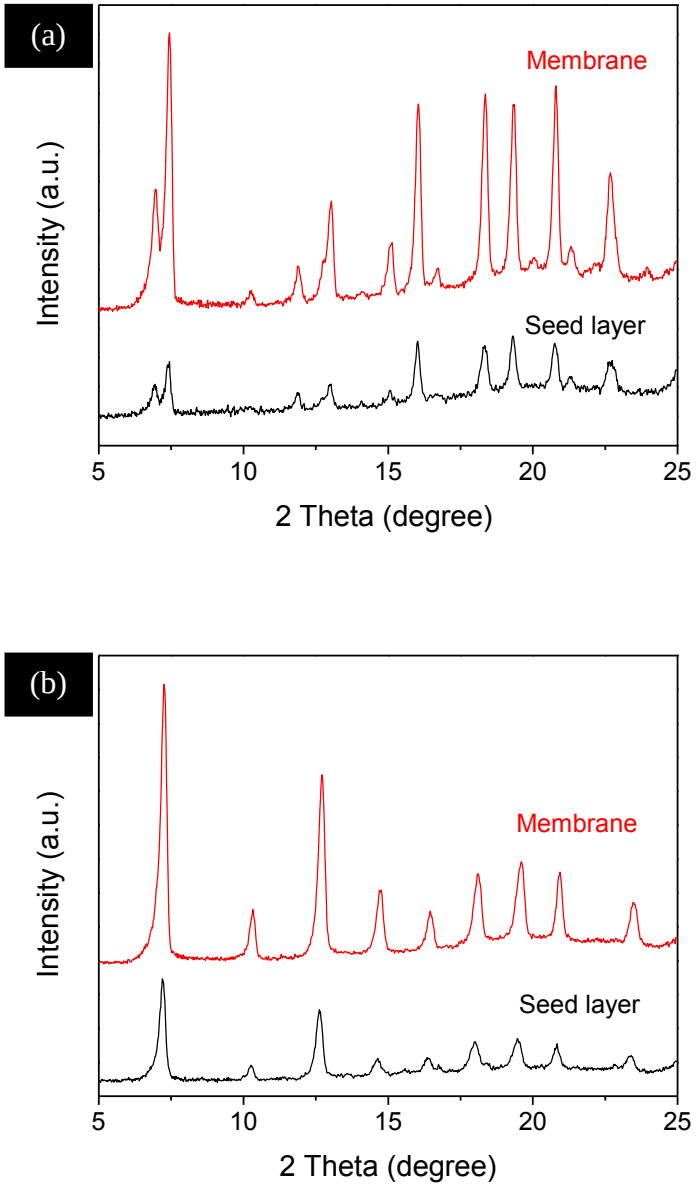

Fig. S9. XRD patterns of (a) a ZIF-7 seed layer and a ZIF-7 membrane and (b) a SIM seed layer and a SIM-1 membrane

Reference

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