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Electronic Supplementary Information

High-performance nanocomposite membranes realized by efficient molecular sieving with CuBDC nanosheets

Yanqin Yang,[a] Kunli Goh,[ab] Rong Wang[ac] and Tae-Hyun Bae*[ab]

[a] Singapore Membrane Technology Centre, Nanyang Technological University, Singapore 637141, Singapore. E-mail: thbae@ntu.edu.sg

[b] School of Chemical and Biomedical Engineering, Nanyang Technological University, Singapore 637459, Singapore

[c] School of Civil and Environmental Engineering, Nanyang Technological University, Singapore 637141, Singapore

1 Experimental

1.1 Materials

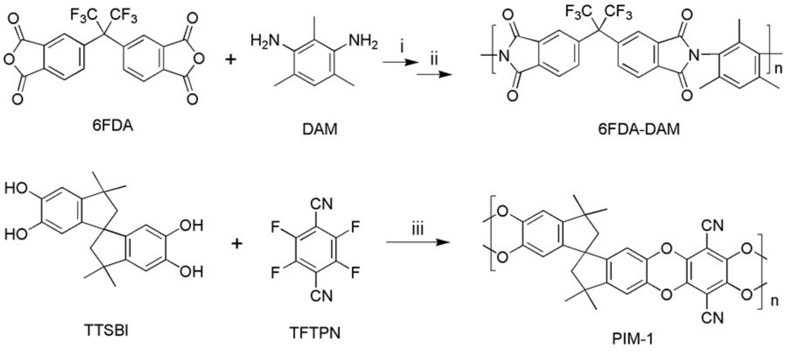
4,4′-(Hexafluoroisopropylidene)diphthalic anhydride (6FDA, 99%, Sigma-Aldrich), diaminomesitylene (DAM, 96%, Sigma-Aldrich) and 2,3,4,5-tetrafluoroterephthalonitrile (TFTPN, 99%, Matrix Scientific) were purified by vacuum sublimation. 5,5′,6,6′-Tetrahydroxy-3,3,3′,3′-tetramethylspirobisindane (TTSBI, 98%, Alfa Aesar) was purified by recrystallization from methanol-dichloromethane solvent. Acetic anhydride (aa), triethylamine (TEA), anhydrous K_2CO_3, $Cu(NO_3)_2\cdot 3H_2O$, 1,4-benzenedicarboxylic acid (H_2BDC), chloroform ($CHCl_3$), acetonitrile (CH_3CN), anhydrous *N*,*N*-dimethylformamide (DMF) and anhydrous *N*-methyl-2-pyrrolidinone (NMP) were purchased from Sigma-Aldrich and used as received. ZIF-8 nanoparticle and submicrometer-sized ZIF-90 were synthesized using the previously reported methods.[1, 2]

1.2 Synthesis of 6FDA-DAM

The 6FDA-DAM polyimide was synthesized with a two-step polycondensation reaction.[3] First, 6FDA (1 mmol, 0.4442 g) was gradually added to a solution of DAM (1 mmol, 0.1502 g) in NMP (1.6 mL) under argon atmosphere. The mixture was stirred at room temperature for 30 min and then was diluted with NMP solvent (9.6 mL). After reacted for 5 h, a viscous polyamic acid/NMP solution was formed. Then it was imidized by adding a mixture of TEA (2 mmol, 0.202 g) and aa (8 mmol, 0.816 g) to the solution and reacted for another 20 h. The polymer was recovered by precipitation in methanol and then washed several time with methanol. The polymer was purified by dissolving in chloroform and reprecipitating in methanol. The write polymer powder was finally collected by filtration, and dried in vacuum oven at 150 °C for 12 h to give 6FDA-DAM.

1.3 Synthesis of PIM-1

The PIM-1 was synthesized following the method described by Guiver and co-workers.[4] All glassware was oven-dried prior to reaction to ensure anhydrous conditions. A one-step polycondensation via TTSBI (30 mmol, 10.213 g) and TFTPN (30 mmol, 6.003 g) was performed in the presence of K_2CO_3 (60mmol, 8.292 g) in anhydrous DMF (200ml). After the mixture has been stirred at 55 °C for about 24 h, the mixture was added to water (300 mL). The polymer was purified by dissolving in chloroform and reprecipitation from methanol.



Scheme S1 Synthesis of 6FDA-DAM and PIM-1. Reagents and conditions: (i) NMP, RT, 5h; (ii) Acetic anhydride, Triethylamine, RT, 20 h; (iii) DMF, K_2CO_3, 50 °C, 24 h.

1.4 Synthesis of CuBDC nanosheet

The CuBDC nanosheets (ns-CuBDC) were synthesized based on the three-liquid-layer method described elsewhere.[5] A glass tube with 13 mm of inner diameter was used to synthesize ns-CuBDC. The bottom solution (composed of H_2BDC (30 mg) dissolved in a mixture of 2 mL of DMF and 1 mL of CH_3CN), intermediate solvent layer (a mixture of 1 mL of DMF and 1 mL of CH_3CN) and topmost solution (composed of $Cu(NO_3)_2{\cdot}3H_2O$ (30 mg) dissolved in a mixture of 1 mL of DMF and 2 mL of CH_3CN) were successively and carefully added to the tube to prevent premature mixing of the solutions. After leaving the tube at 40 °C for 24 h in static conditions, the product was collected by centrifugation and consecutively washed 3 times with DMF (1 mL each step) followed by another 3 times with $CHCl_3$ (1 mL each step). The resulting material was left suspended in CH_2Cl_2 until the synthesis of the composite membranes.

1.5 Fabrication of mixed matrix membranes

Mixed matrix membranes were fabricated by the solution casting technique. After dispersing ns-CuBDC in anhydrous chloroform by applying sonication, the polymer, previously degassed at 150 ºC overnight under vacuum to remove the adsorbed water, was stepwise added. The resulting suspensions were gently shacked in a laboratory shaker at room temperature for 24 hours. Before the casting of the membranes, two cycles were carried out each consisting of dispersing the suspension of ns-CuBDC/polymer in an ultrasounds bath for 15 minutes, followed by shaking for 15 minutes. Afterwards, the dope solution was cast on a glass plate with the casting knife in a glove bag filled with N_2 and chloroform vapor that can prevent a rapid solvent evaporation from the nascent membrane. After solvent evaporation at room temperature for 24 hours, the resulting membranes were removed from the glass plate and further treated in a vacuum oven at 180 ºC for 24 h. The final thickness of the membranes was evaluated using a micrometer, and was in the range of 40-50 µm and 60-70 µm for 6FDA-DAM and PIM-1 containing membranes, respectively. For reference purposes, pure polymer membranes were prepared following an identical procedure without filler incorporation.

15wt%-ZIF-90@6FDA-DAM and 20wt%-ZIF-8@PIM-1 were fabricated by using the similar methods reported previously.[1, 2]

2. Characterization methods

2.1 Scanning Electron Microscopy (SEM)

SEM experiments for ns-CuBDC were conducted in a field-emission scanning electron microscope (FE-SEM JSM6700) at an accelerating voltage of 5 kV. Before SEM observation, the ns-CuBDC specimens were prepared by applying a few drops of suspensions of the material in DCM on a silicon wafer and letting it dry. The membrane cross-sectional morphology was imaged using a field-emission scanning electron microscope (FE-SEM JSM-7600F) at an accelerating voltage of 2 kV. The membranes were cryogenically fractured in liquid nitrogen. Both CuBDC nanosheet and mixed-matrix membranes were coated with gold prior to imaging using FESEM.

2.2 Atomic Force Microscopy (AFM)

The lateral dimensions and height profile of the ns-CuBDC were elucidated via atomic force microscopy (AFM, MFP-3D) in the AC mode. The ns-CuBDC specimens were prepared by applying a few drops of suspensions of the material in DCM on a silicon wafer and letting it dry.

2.3 powder X-ray diffraction

The XRD data were collected with a Bruker D2 phaser diffractometer with a Cu Kα radiation. the ns-CuBDC specimen was prepared by slow evaporation of a couple of drops from a suspension of the material in dichloromethane over a zero-background single-crystal silicon sample holder.

2.4 Tensile measurement

Tensile measurement was performed with a tensile force tester (Instron. Model 5543) at a speed of 10 mm min^{-1} at ambient humidity (70% relative humidity).

2.5 Gas sorption isotherms

Nitrogen sorption isotherms at 77 K were performed on an Autosorb-6B instrument (Quantachrome) measured in liquid-nitrogen baths. Pure component CO_2 and CH_4 isotherms at 25 °C were obtained by a gas sorption analyzer (Quantachrome, iSorp HP1). Both powders and membranes were degassed at 180 °C for 8 h under high vacuum before the measurements.

2.6 Gas permeability measurements

Gas permeability measurements were performed using the permeation system produced by Labthink (G2-110) at a feed pressure of 1 bar and feed temperature of 25 °C following the same procedure as reported before.[6] The testing gas was equalmolar CO_2/CH_4 mixture. To check the reproducibility of experiments and obtain the error bars of results, three samples of each mixed-matrix membrane were tested.

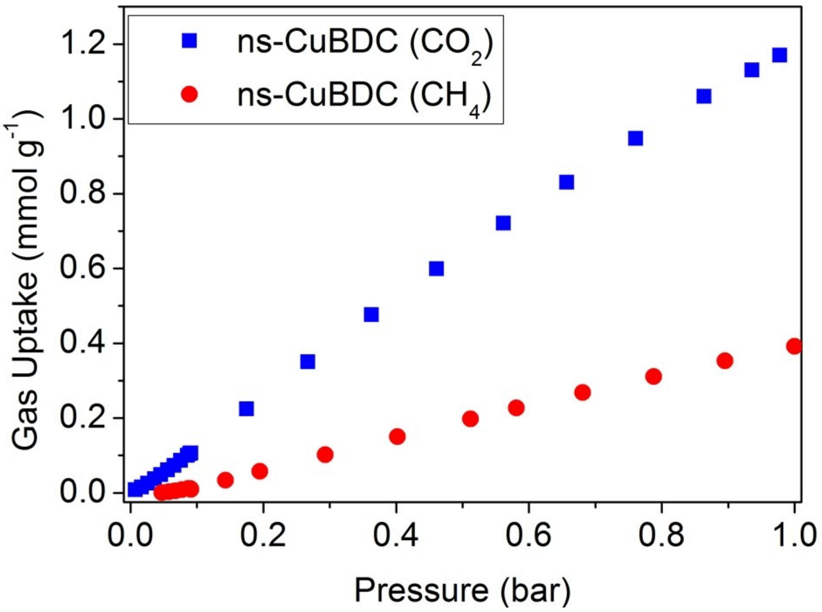


Fig. S1 CO_2 and CH_4 adsorption isotherms of ns-CuBDC at 25 °C.

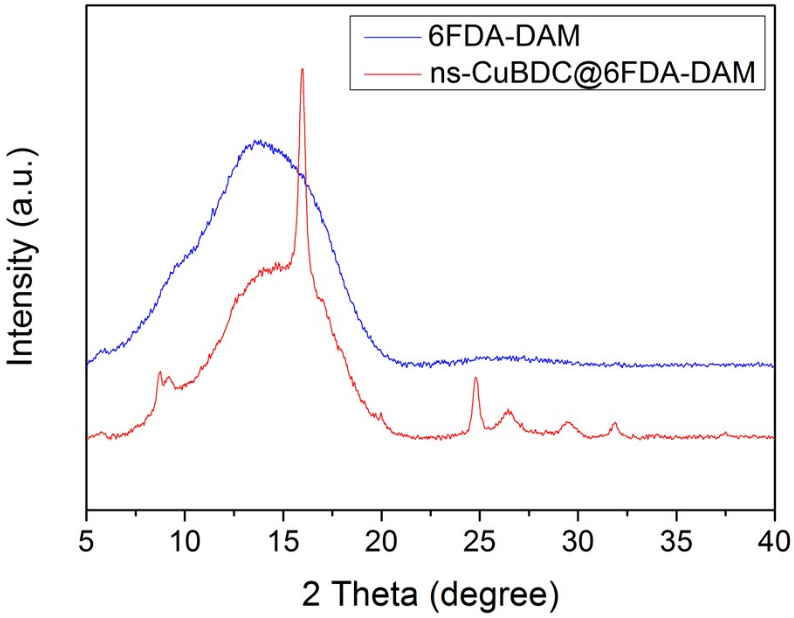


Fig. S2 XRD patterns of pure 6FDA-DAM and 4 wt%-ns-CuBDC@6FDA-DAM membranes.

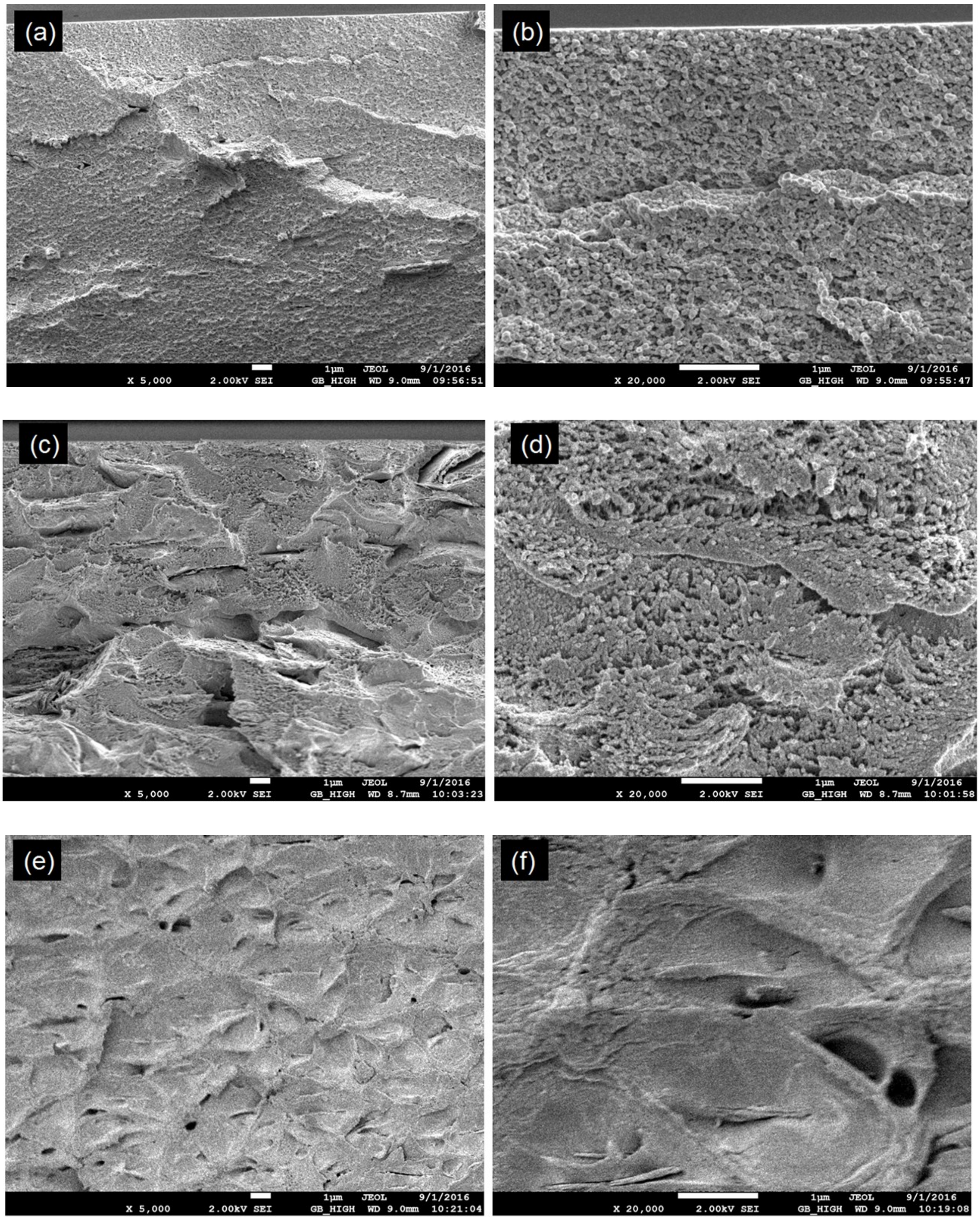


Fig. S3 Cross-sectional SEM images of 2 wt%-ns-CuBDC@PIM-1 (a and b), 4 wt%-ns-CuBDC@PIM-1 (c and d) and 2 wt%-ns-CuBDC@6FDA-DAM (e and f).

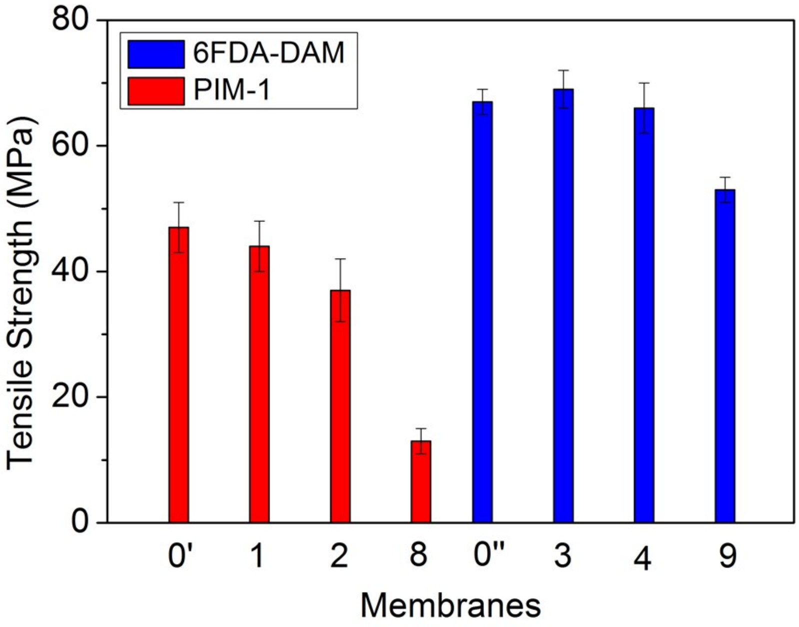


Fig. S4 Tensile strength of pure and composite membranes. [0’, neat PIM-1; 1, 2wt%-ns-CuBDC@PIM-1; 2, 4wt%-ns-CuBDC@PIM-1; 8, 24.2wt%-ZIF-8@PIM-1; 0’’, neat 6FDA-DAM; 3, 2wt%-ns-CuBDC@6FDA-DAM; 4, 4wt%-ns-CuBDC@DAM; 9, 15wt%-ZIF-90@6FDA-DAM.]

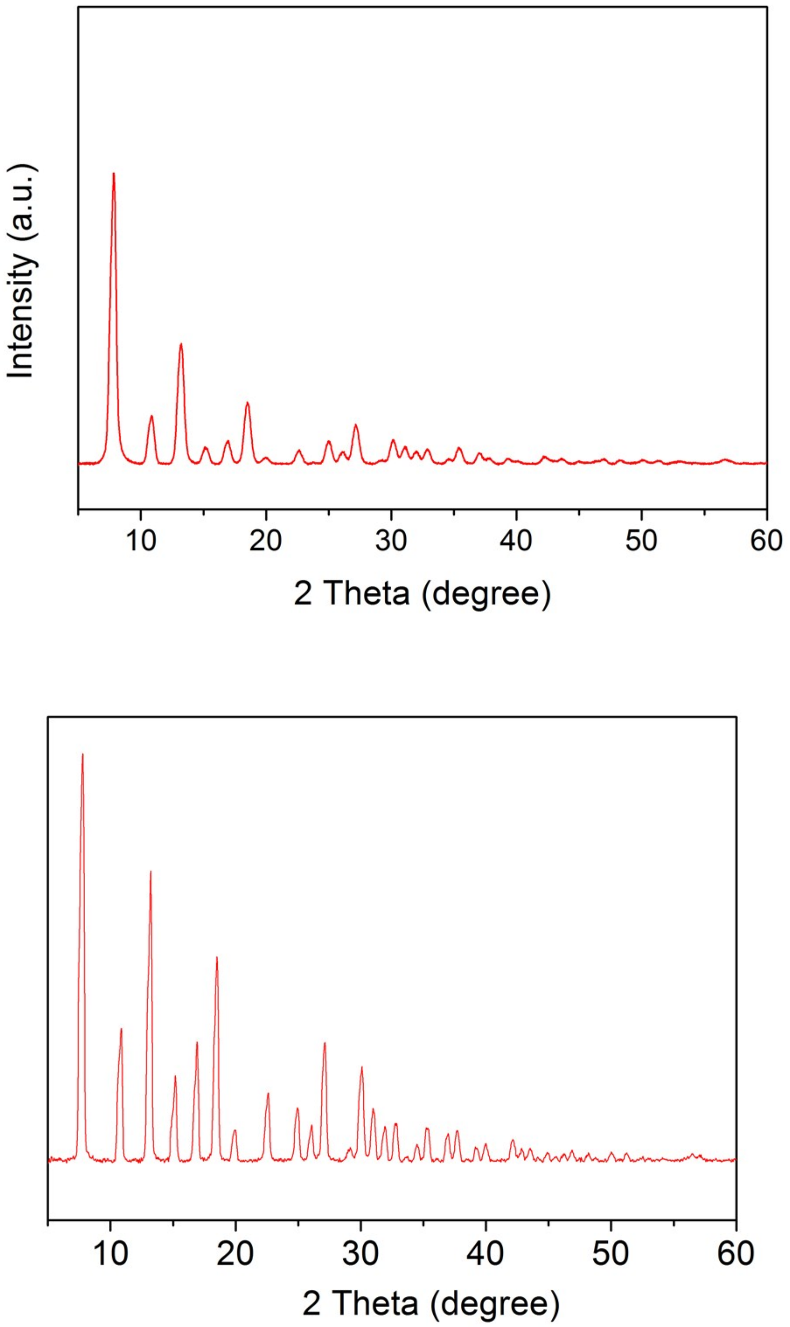


Fig. S5 XRD of ZIF-8 nanoparticle (top) and submicrometer-sized ZIF-90 (bottom).

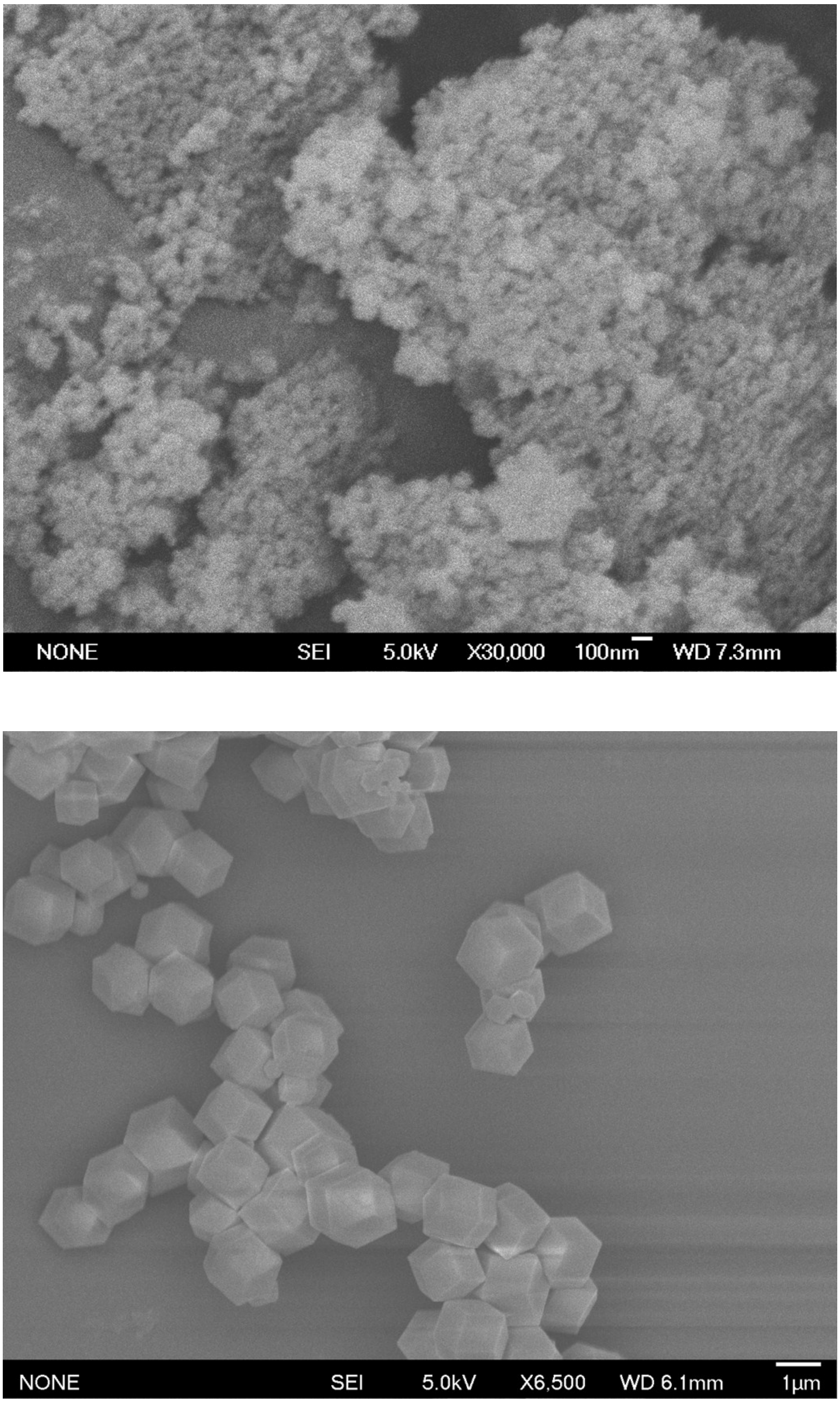


Fig. S6 SEM images of ZIF-8 nanoparticle (top) and submicrometer-sized ZIF-90 (bottom).

Table S1 CO_2 and CH_4 permeabilities, diffusivities, and solubilities in 6FDA-DAM, 2wt%-ns-CuBDC@6FDA-DAM, PIM-1 and Matrimid membranes at 1 bar upstream pressure and 25 °C. The solubility (mol/m^3·bar) is calculated by:[7]

$$\text{Solubility} = \frac{\text{Uptake} \times \text{Density}}{\text{Pressure}}$$

where uptake (mol/kg) was gas adsorption capacity of membranes at partial pressure of 0.5 bar, which was estimated by the fitting of CO_2 and CH_4 adsorption isotherms in Fig. 4a with dual-site Langmuir and Single-site Langmuir models respectively. Subsequently, gas diffusivities (m^2/s) were calculated using the following relationship:

$$\text{Diffusivity} = \frac{\text{Permeability}}{\text{Solubility}}$$

here permeability is in mol·m/m^2·s·bar.

membranes	CO_2 permeability (mol·m/m^2·s·bar)	CO_2 solubility (mol/m^3·bar)	CO_2 diffusivity (m^2/s)	CH_4 permeability (mol·m/m^2·s·bar)	CH_4 solubility (mol/m^3·bar)	CH_4 diffusivity (m^2/s)	CO_2/CH_4 solubility selectivity	CO_2/CH_4 diffusivity selectivity
6FDA-DAM	2.00×10^{-8}	1800[a]	1.11×10^{-11}	6.68×10^{-10}	260[a]	2.57×10^{-12}	6.92	4.32
2wt%-ns-CuBDC @6FDA-DAM	1.93×10^{-8}	1770[b]	1.09×10^{-11}	5.23×10^{-10}	250[b]	2.09×10^{-12}	7.08	5.22
PIM-1	1.05×10^{-7}	1760[c]	5.97×10^{-11}	6.10×10^{-9}	430[c]	1.42×10^{-11}	4.09	4.20
Matrimid[d]	3.46×10^{-10}	438[e]	7.90×10^{-13}	1.02×10^{-11}	56[e]	1.82×10^{-13}	7.82	4.34

[a] The density of 6FDA-DAM was found in literature[8].

[b] As the filler loading of our composite membrane was quite low, we assumed the density of composite membrane was same as its counterpart pure membrane.

[c] The gas uptake properties of PIM-1 was from literature[9].

[d] The gas permeation properties of Matrimid was from literature[10].

[e] The gas uptake properties of Matrimid was from literature[11].

Table S2 Mechanical properties of neat and mixed matrix membranes.

Membranes	Tensile Strength (MPa)	Young's Modulus (MPa)
Neat 6FDA-DAM	67 ± 2	1800 ± 20
2wt%-ns-CuBDC@6FDA-DAM	69 ± 3	2000 ± 110
4wt%-ns-CuBDC@6FDA-DAM	66 ± 4	2080 ± 180
Neat PIM-1	47 ± 4	1580 ± 30
2wt%-ns-CuBDC@PIM-1	44 ± 4	1440 ± 160
4wt%-ns-CuBDC@PIM-1	37 ± 5	1440 ± 120
15wt%-ZIF-90@6FDA-DAM	53 ± 2	1970 ± 55
20wt%-ZIF-8@PIM-1	13 ± 2	1000 ± 200

Table S3 CO_2/CH_4 mixture gas permeation properties of membranes.

Membranes	CO_2 Permeability (Barrer)	CO_2/CH_2 selectivity
Neat 6FDA-DAM	590 ± 15	30 ± 1
2wt%-ns-CuBDC@6FDA-DAM	570 ± 20	37 ± 2
4wt%-ns-CuBDC@6FDA-DAM	430 ± 10	43 ± 3
Neat PIM-1	3100 ± 200	17 ± 1
2wt%-ns-CuBDC@PIM-1	2030 ± 120	24 ± 1
4wt%-ns-CuBDC@PIM-1	2300 ± 320	22 ± 2

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