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Supporting information

High performance carbon molecular sieving membranes derived from pyrolysis of metal-organic framework ZIF-108 doped polyimide matrix

Wenmei Jiao,[ab] Yujie Ban,*[a] Zixing Shi,*[c] Xuesong Jiang,[c] Yanshuo Li,*[a] and Weishen Yang*[a]

[a] *State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian, 116023, China.*

[b] *University of Chinese Academy of Sciences, Beijing, 100039, China.*

[c] *School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai, 200240, China*

Experimental details:

Chemicals

Chemicals were used as received: $Zn(OAc)_2 \cdot 2H_2O$ (Aldrich, ≥98%), 2-nitroimidazole (nim, 98%, Tongchuang pharma Co., Ltd), N,N-dimethylformamide (BoDi, AR). Polyimide- P84 (BTDA-TDI/MDI, co-polyimide of 3, 3', 4, 4'-benzophenone tetracarboxylic dianhydride and 80% methylphenylene-diamine, 20% methylene diamine) is provided by Shanghai Jiao Tong University.

Preparation of ZIF-108 nanoparticles

ZIF-108 nanocrystals were synthesized at room temperature using the recipe reported previously [S1]. A typical synthesis procedure is as follows: $Zn(OAc)_2 \cdot 2H_2O$ (1.272 g, 5.8 mmol) and 2-nitroimidazole (nim) (1.312 g, 11.6 mmol) were separately dissolved in 224 ml of N,N-dimethylformamide (DMF) at room temperature. Then the linker solution was poured into the zinc solution and light yellow precipitates generated immediately. The product was separated after 2.5 h using centrifugation and washed with plenty of DMF for three times.

Preparation of the free-standing P84 polymer membranes and ZIF-108/P84 mixed matrix membranes

The free-standing P84 polymer membranes and ZIF-108/P84 mixed matrix membranes (MMMs) were prepared using solution mixing-casting method. The obtained ZIF-108 were re-dispersed into DMF using a probe-type sonicator (AiDaPu,

ZJS-500A), with the horn immersed into the sample for 8 min in an ice bath, and then P84 was added into the dispersion to give the weight composition: ZIF-108/P84/DMF = 0.10:1:11.66. The solution was stirred vigorously for at least 24 h. The pure P84 polymer and ZIF-108/P84 solution with other weight ratio (0.05, 0.10, 0.16, 0.23 and 0.59) was prepared in analogous conditions. Then the P84 and ZIF-108/P84 solution were separately casted on a glass using an automatic film applicator (elcometer 4340) and then heated at 80 ^{o}C for 24 h and 150 ^{o}C for 6 h. The free-standing P84 polymer membrane and ZIF-108/P84 MMMs were obtained by peeling off from glass.

Preparation of P84-FSCMSMs and ZIF-108/P84-FSCMSMs and carbon powders

The free-standing CMSMs were prepared from pyrolysis of the free-standing P84 polymer membranes and ZIF-108/P84 MMMs, denoted as P84-FSCMSMs and ZIF-108/P84-FSCMSMs, respectively. P84 polymer membrane and ZIF-108/P84 MMMs were placed on a home-made quartz trough in a quartz tube, and then loaded into a temperature-programmed tube furnace. The pyrolysis setup was similar to the previous method reported by Koros with a little modification [S2]. After purging the tube with Argon for at least 30 min, the membranes were pyrolyzed under a stream of Argon (100 ml min^{-1}). The heating protocol is as below:

(1) 30 ^{o}C-250 ^{o}C at a heating rate of 11.6 ^{o}C min^{-1}.

(2) 250 ^{o}C-585 ^{o}C at a heating rate of 3.75 ^{o}C min^{-1}.

(3) 585 ^{o}C-600 ^{o}C at a heating rate of 0.25 ^{o}C min^{-1}.

(4) Soak at 600 ^{o}C for 2 h.

(5) 600 ^{o}C-300 ^{o}C at a cooling rate of 2 ^{o}C min^{-1}.

(6) Cooling to room temperature naturally.

Carbon powders were prepared by carefully grinding P84-FSCMSMs and ZIF-108/P84-FSCMSMs, denoted by P84-CPs and ZIF-108/P84-CPs, respectively.

Preparation of P84-ASCMSMs and ZIF-108/P84-ASCMSMs

Asymmetric γ-Al_2O_3 discs (Inocermic) were used as supports in this study to synthesis of supported CMSMs for gas separation. Prior to use, the supports were washed with water at 60 ^{o}C for 2 h, washed with acetone at 30 ^{o}C for another 2 h, and finally dried overnight. The supports were dipped into the membrane solution for 10 s and withdrawn at a speed of 2 mm s^{-1} using an automatic dip coater (WPTL0.01). Then the membranes were dried in a temperature-programmed tube furnace with a heat-treatment at 80 ^{o}C for 24 h and 150 ^{o}C for 6 h under an inert atmosphere (Argon 30 ml min^{-1}). The obtained membranes were placed on a home-made quartz trough in a quartz tube, and then loaded into a temperature-programmed tube furnace. The pyrolysis setup was analogous with FSCMSMs described above. The membranes carbonized from the γ-Al_2O_3 supported P84 polymer membranes and ZIF-108/P84 MMMs was denoted as P84-ASCMSM and ZIF-108/P84-ASCMSM, respectively.

Characterization methods

Powder X-ray Diffraction (PXRD) patterns were obtained on Rigaku D/MAX 2500/PC instrument (Cu Kα radiation with a wavelength of 0.154 nm at 40 kV and

200 mA) with a scan speed of 5° min^{-1} and 2θ range of 2-50°. The *d* spacing was estimated by Brag's equation according to the following formula:

$$n\lambda = 2d \sin \theta$$

Where n is an integral number (1, 2, 3,…), λ represents the X-ray wavelength, *d* denotes the inter-segmental spacing between polymer chains and θ indicates the diffraction angle. Nitrogen adsorption-desorption isotherms were measured at 77 K, on a Quantachrome Autosorb Automated Gas Sorption instrument. Brunauer-Emmett-Teller (BET) surface area was obtained with N_2 at 77 K. The pore size distribution (PSD) was analyzed with Horváth-Kawazoe (HK) method. Thermogravimetric analysis (TGA) was performed on a Netzsch STA449F3 TGA instrument at a heating rate of 10 °C min^{-1} from room temperature to 900 °C under nitrogen atmosphere with a flow rate of 50 ml min^{-1}. Morphological features were observed by Scanning Electron Microscopy (Quanta 200 FEG, FEI Co., 30kV). High resolution transmission electron microscopy images (HRTEM, FEI Tecnai F30) were obtained at an accelerating voltage of 300 kV. Infrared spectra were recorded on a Nicolet 6700 FTIR-ATR (Fourier Transform Infrared Spectroscopy-Attenuated Total Reflectance) spectrophotometer with 32 scans at a resolution of 4 cm^{-1}. Raman spectra were recorded on a "Bruker Optics Senterra" Raman spectrometry using a green laser with a wavelength of 532 nm, setting to a power of 10 mW and 50 scans per minute.

Gas permeation experiments

The obtained membranes were sealed in a home-made stainless steel permeation cell to measure their separation performance for pure and mixed gas mixture, respectively. All the measurements were performed using the Wicke-Kallenbach method with an online gas chromatography (Agilent 7890). Single and binary gas permeations were measured at room temperature with feed pressure of 3 bar. The flow rate of single and binary gas feed was constant with a volumetric flow rate of 50 ml min^{-1} and 100 ml min^{-1}, (each gas of 50 ml min^{-1}), respectively. Helium was used as a sweep gas in all measurements.

The permeability Pi of membranes was calculated using the equation 1.

$$P_i = \frac{N_i\, l}{A\, \Delta P_i} \qquad [1]$$

Where P_i is the gas permeability of component i (mol m^{-2} s^{-1} Pa^{-1}), N_i is permeate rate of component i (mol s^{-1}), A refers to the effective membrane area (m^2), ΔP_i is the transmembrane pressure difference of component i (Pa), and membrane thickness l (m).

The most common unit for permeability is the Barrer which is defined as:

$$1 \text{ Barrer} = 10^{-10} \frac{cm^3\,(STP)\,cm}{cm^2\,s\,cmHg}$$

The ideal selectivity is defined as the ratio of the single gas permeability, as shown in equation 2.

$$\alpha_{ij}^{ideal} = \frac{P_i}{P_j} \qquad [2]$$

The separation factor of binary mixture was calculated by dividing the molar ratio of the permeate x_i/x_j by the molar ratio of retentate y_i/y_j. We assumed that the flow rate through the membrane is negligible compared to the feed flow rate and the sweep flow rate and therefore the concentration of a component in the retentate is nearly the same as in the feed. The mixed gas separation factor α_{ij} was defined as follows:

$$\alpha_{ij} = \frac{x_i/x_j}{y_i/y_j} \qquad [3]$$

Where y_i (y_j) is the molar fraction of component i (j) in the permeate, x_i (x_j) is the molar fraction of component i (j) in the feed.

Fig. S1

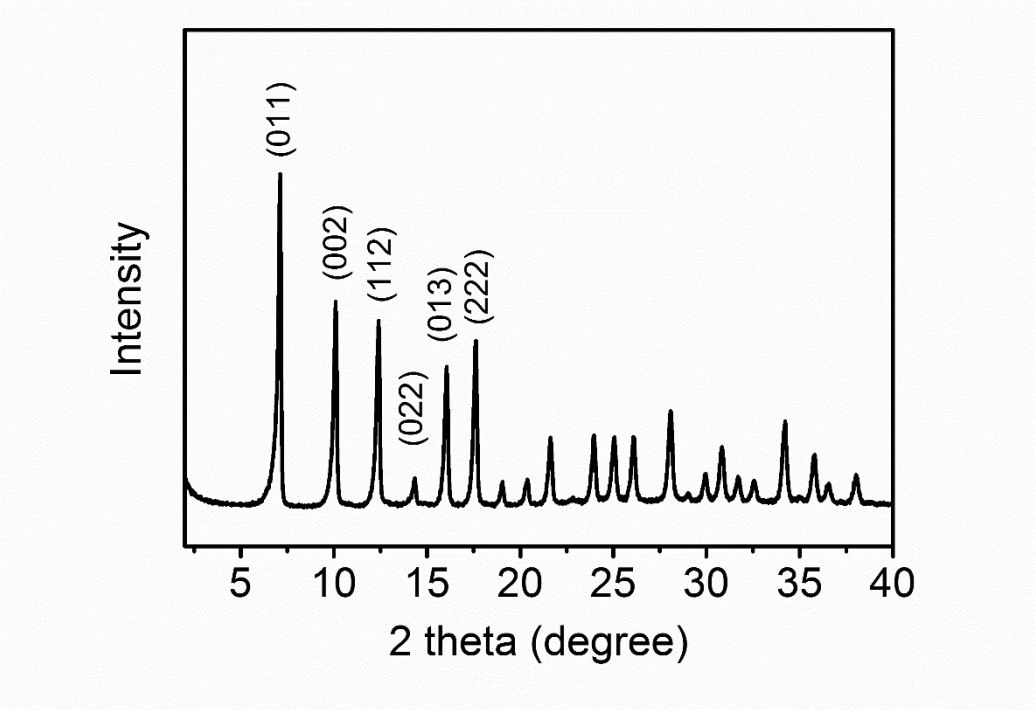

Fig. S1 PXRD pattern of the as-synthesized ZIF-108.

Fig. S2

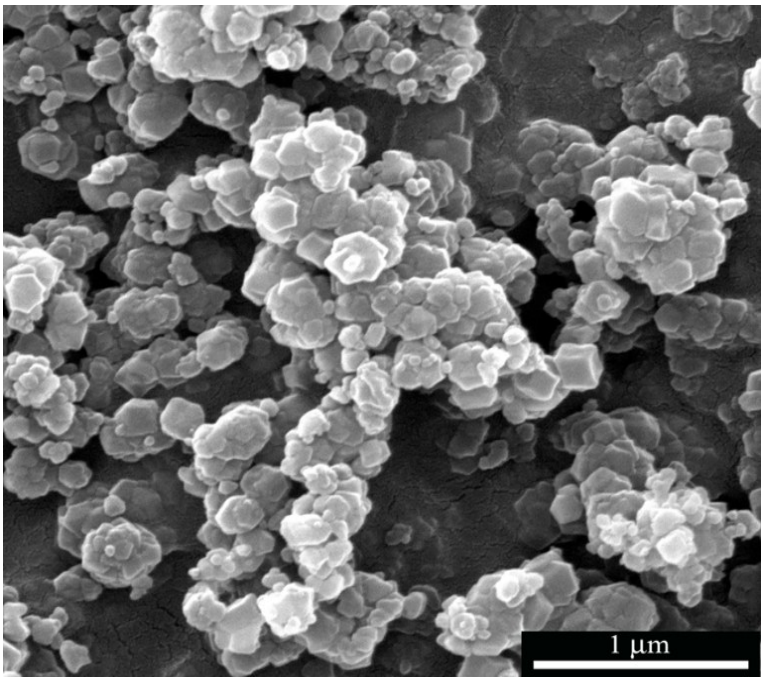

Fig. S2 SEM image of the as-synthesized ZIF-108.

Fig. S3

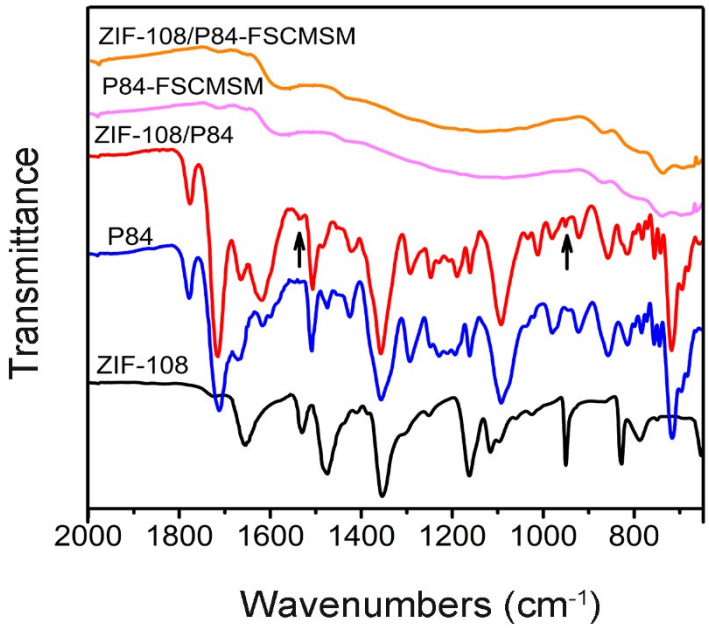

Fig. S3 ATR-FTIR spectrums of ZIF-108, P84 polymer membranes, ZIF-108/P84 MMMs, P84-FSCMSM and ZIF-108/P84-FSCMSM.

Fig. S4

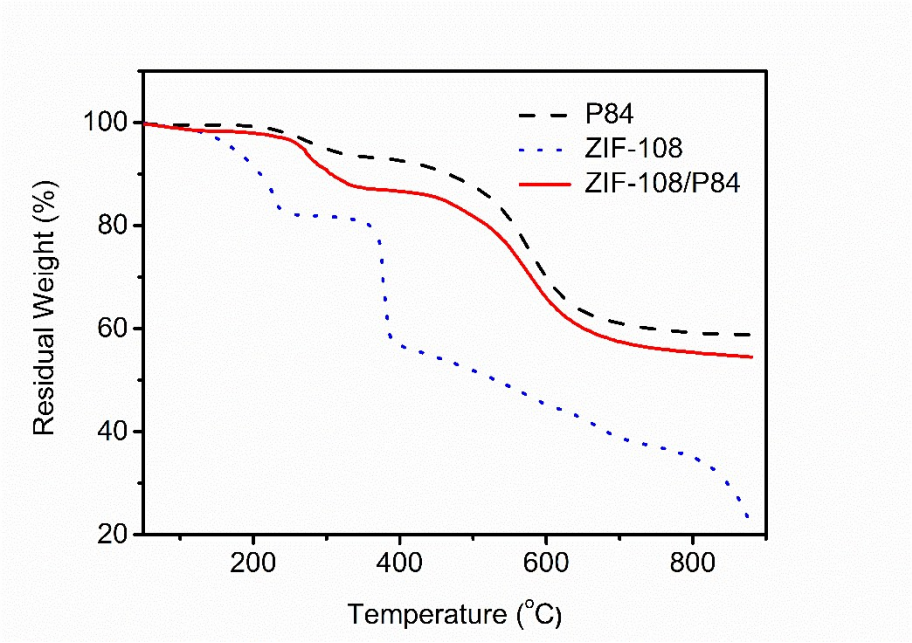

Fig. S4 TG curves of ZIF-108, P84 polymer membranes and ZIF-108/P84 MMMs.

Table S1 Raman shifts of three different carbon materials. [S3]

Virbration bands (cm^{-1})	Amorphous carbon	Turbostratic carbon	Crystalline carbon
1^{th} order D1	1387.3	1338.9	1350
1^{th} order G	1532.7	1597.5	1580
2^{nd} order 2*D1	2738.4	2835	2720

Fig. S5

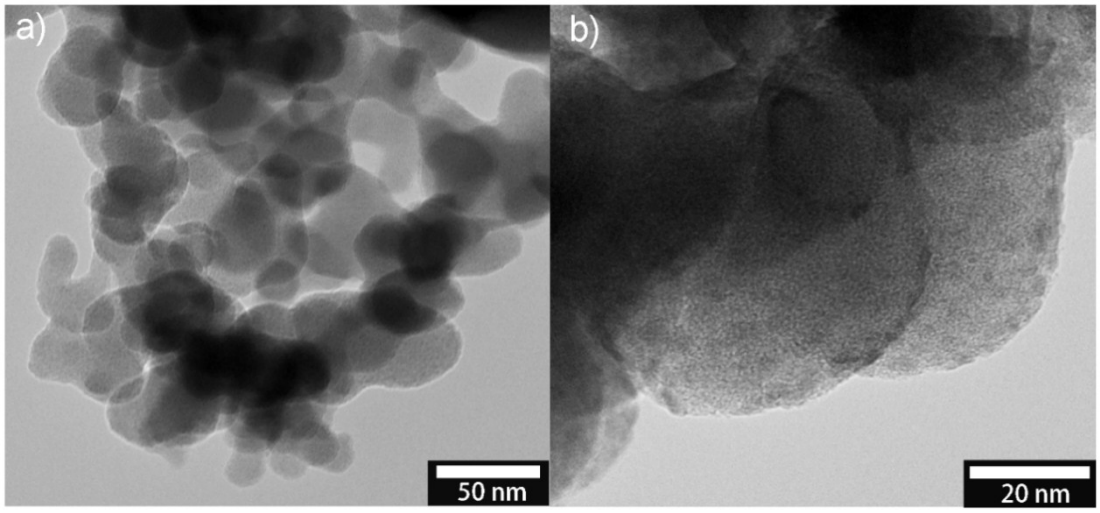

Fig.S5 HRTEM images of nanocarbons derived from pyrolysis of ZIF-108 powders at low (a) and high (b) magnification.

Fig. S6

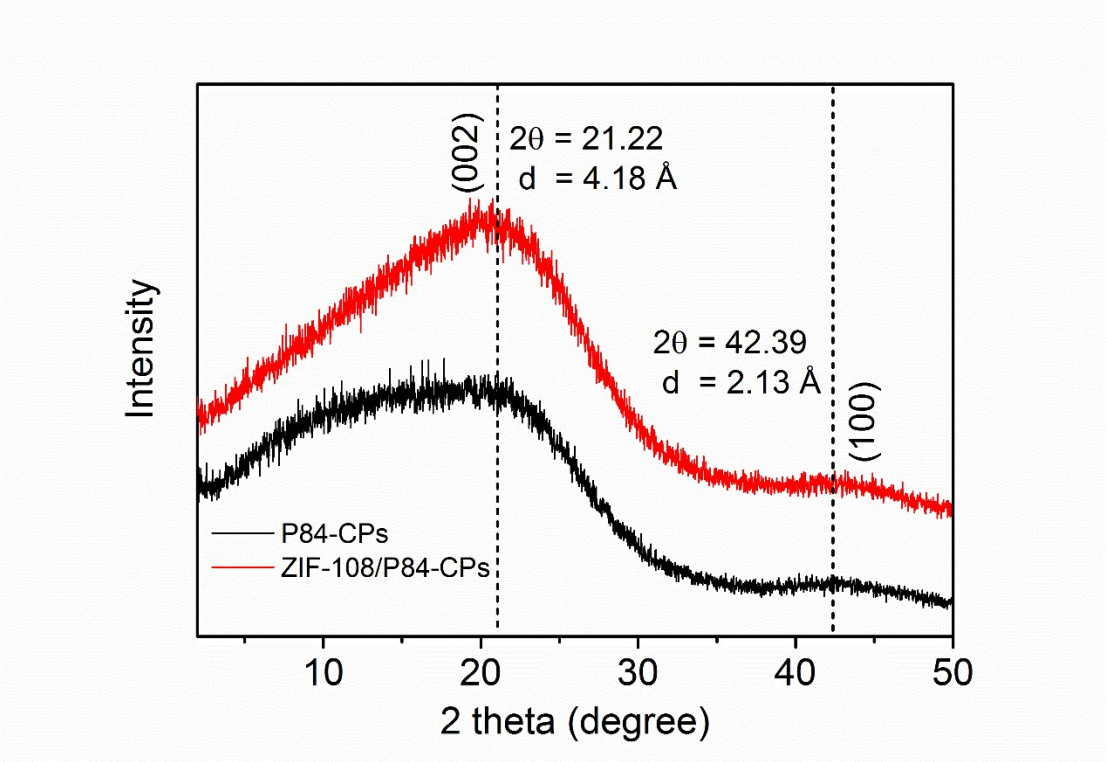

Fig. S6 PXRD patterns of P84-CPs (black) and ZIF-108/P84-CPs (red).

Fig. S7

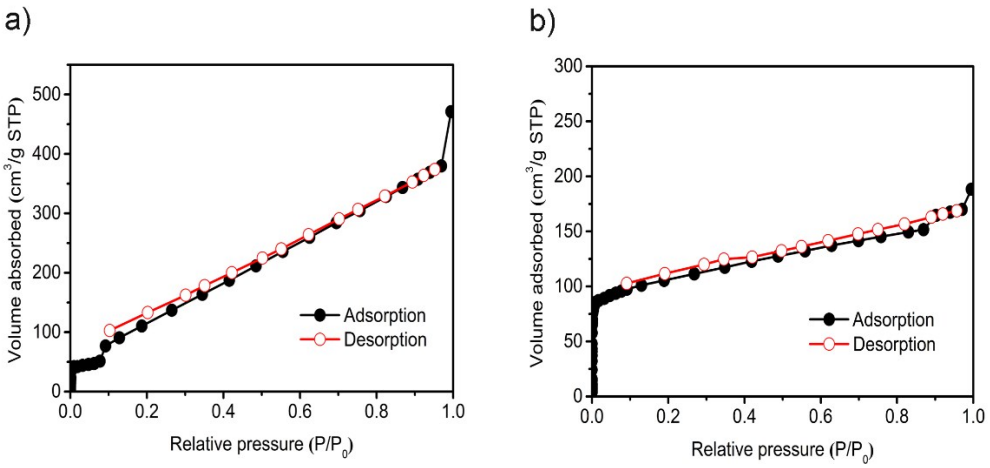

Fig. S7 N_2 adsorption and desorption isotherms for (a) P84-CPs and (b) ZIF-108/P84-CPs.

Fig. S8

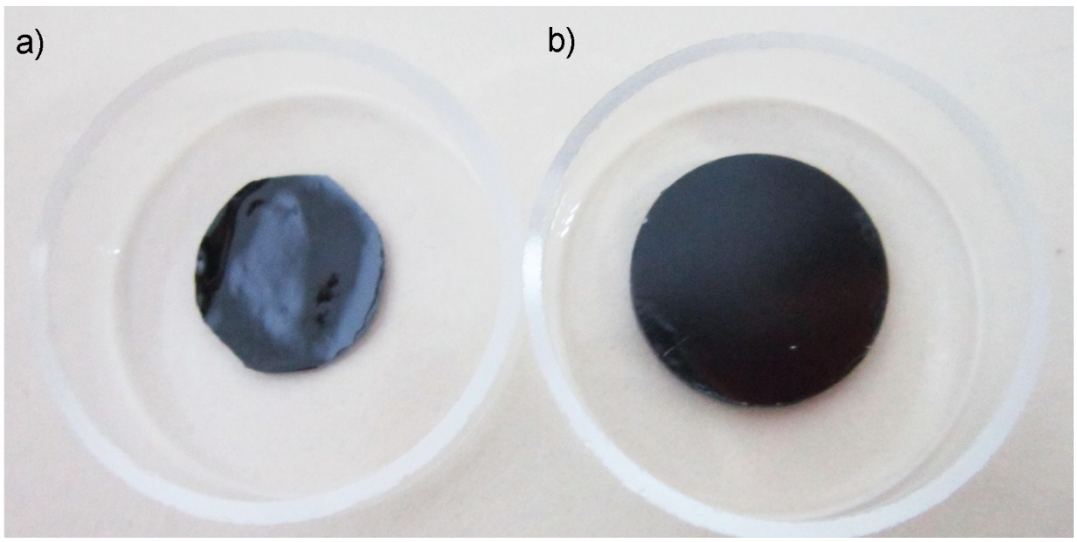

Fig. S8 Photographs of free-standing P84 CMSMs (a) and γ-alumina supported P84 CMSMs.

Table S2 Mixed gas permeability and separation factor for P84-FSCMSMs and ZIF-108/P84-FSCMSMs with different weight composition of precursor at 1 bar and 298K.

Weight ratio (ZIF-108/P84)	CO_2 permeability (Barrers)	CO_2/CH_4 Separation factor
0.00	7.10	72.4
0.05	29.3	71.3
0.10	40.9	174
0.16	102	63.6
0.23	99.9	2.27
0.59	165	0.65

Table S3 Single gas permeability and ideal selectivity for P84-FSCMSMs and ZIF-108/P84-FSCMSMs

Membrane	Permeability (Barrers)				
	H_2	CO_2	O_2	N_2	CH_4
P84-FSCMSM	26.17±0.6	5.52±0.05	1.57±0.07	0.21±0.00	0.07±0.00
ZIF-108/P84-FSCMSM	126.8±9.0	24.75±2.13	6.09±0.41	0.58±0.04	0.19±0.01
Membrane	Ideal selectivity (α_{ij}^{ideal})				
	H_2/N_2	CO_2/CH_4	CO_2/N_2	O_2/N_2	N_2/CH_4
P84-FSCMSM	125±7.0	78.9±7.1	26.2±1.0	7.50±0.54	3.00±0.21
ZIF-108/P84-FSCMSM	219±33	130±27	43.0±7.4	10.5±1.7	3.05±0.25

Fig. S9

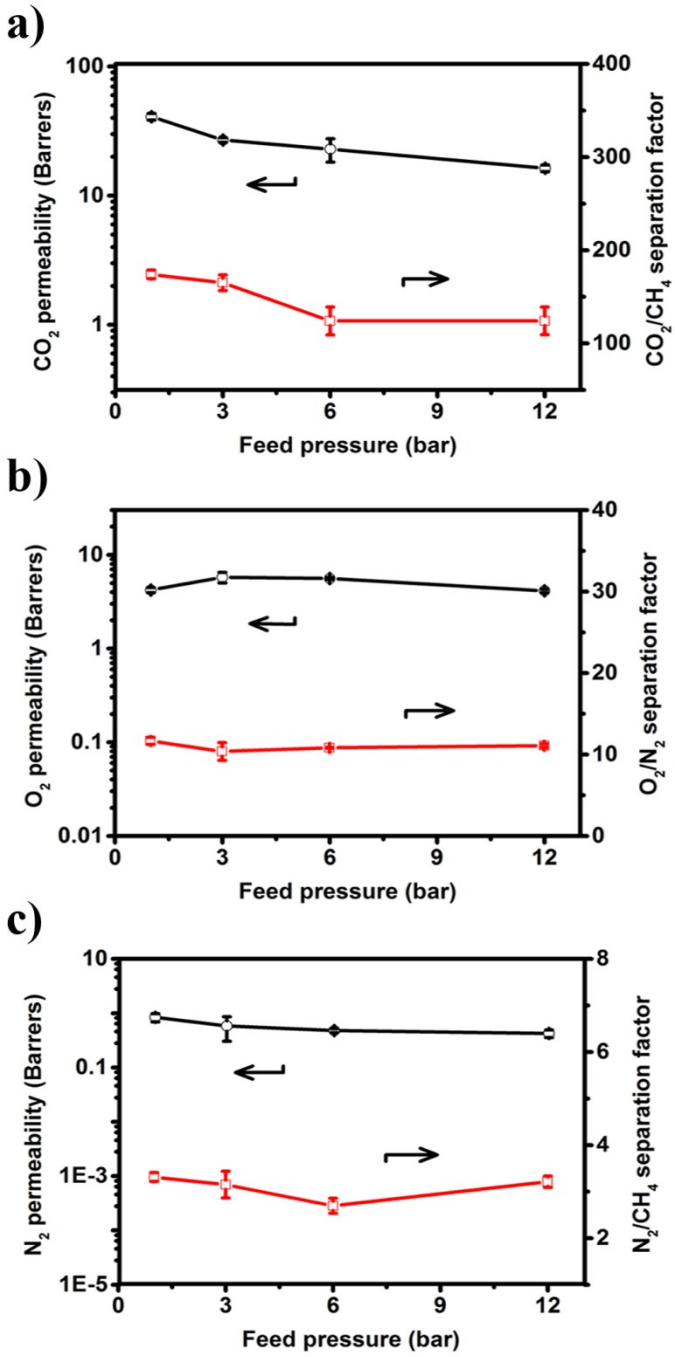

Fig. S9 Gas permeability and separation factor of binary mixtures with feed pressure for ZIF-108/P84-ASCMSM. (a) CO_2/CH_4, (b) O_2/N_2, and (c) N_2/CH_4.

References

S1 Y.J. Ban, Y.S. Li, Y. Peng, H. Jin, W.M. Jiao, X.L. Liu, W.S. Yang, *Chem. Eur. J.* 2014, **20**, 11402-11409.

S2 M. Rungta, L. Xu, W.J. Koros, *Carbon*, 2012, **50**, 1488-1502.

S3 A. Sadezky, H. Muckenhuber, H. Grothe, R. Niessner, U. Pöschl, *Carbon*, 2005, **43**, 1731-1742.