Electronic Supplementary Information

Nano-confinement-inspired metal organic framework/polymer composite separation membranes

Xiaoting Li,[a] *Naixin Wang,*[a*] *Xinmin Bao,*[a] *Qian Li,*[a] *Jie Li,*[a] *Ya-Bo Xie,*[a] *Shulan Ji,*[a] *Jiayin Yuan,*[b] *Quan-Fu An*[a*]

Preparation of other MOF particles suspension

ZIF-8 nanocrystals were synthesized at room temperature. 3.28 g 2-methylimidazole (H-mim) was dissolved in 30 mL of ethanol; then 1.48 g $Zn(NO_3)_2$ and 0.01 g Cetyl trimethyl ammonium bromide (CTAB) was dissolved in 20 mL of water. The two solutions were mixed under stirring for 0.5 h at room temperature. Then, the suspension of nanocrystals was separated by centrifugation with 6000 rpm for 0.5 h.

ZIF-11 nanocrystals were synthesized at room temperature. 2.4 g Bim was dissolved in 30 mL of ethanol; then 2.2 g $Zn(NO_3)_2$ was dissolved in the mixed solvent (10 mL of ethanol and 10 mL of toluene). The two solutions were mixed under stirring for 0.5 h at room temperature. Then the suspension of nanocrystals was separated by centrifugation with 6000 rpm for 0.5 h.

ZIF-12 nanocrystals were synthesized at room temperature. 2.4 g Bim was dissolved in 30 mL of ethanol; then 2.9 g $Co(NO_3)_2$ was dissolved in the mixed solvent (10 mL of ethanol and 10 mL of toluene). The two solutions were mixed under stirring for 0.5 h at room temperature. Then, the suspension of nanocrystals was separated by centrifugation 6000 rpm for 0.5 h.

CuBTC nanocrystals were synthesized at room temperature. 0.9 g H_3BTC and 1.66 mL trimethylamine were dissolved in 30 mL of ethanol; then 1 g $Cu(NO_3)_2$ and 0.36 g CTAB was dissolved in the 100 mL water. The two solutions were mixed under stirring for 0.5 h at room temperature. Then, the suspension of nanocrystals was separated by centrifugation with 6000 rpm for 0.5 h.

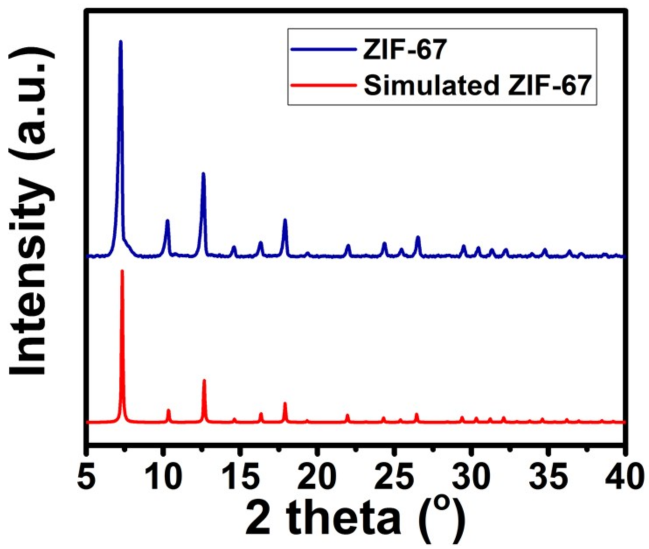

Fig. S1. PXRD patterns of synthetic and simulated ZIF-67 crystals.

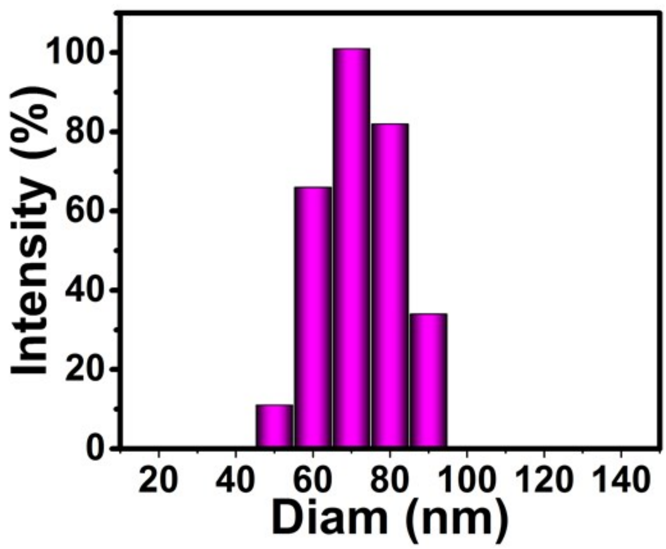

Fig. S2. Particle size distribution of ZIF-67 nanoparticles in solution.

Fig. S3. Digital photograph of a ZIF-67 suspension in ethanol with Tyndall effects.

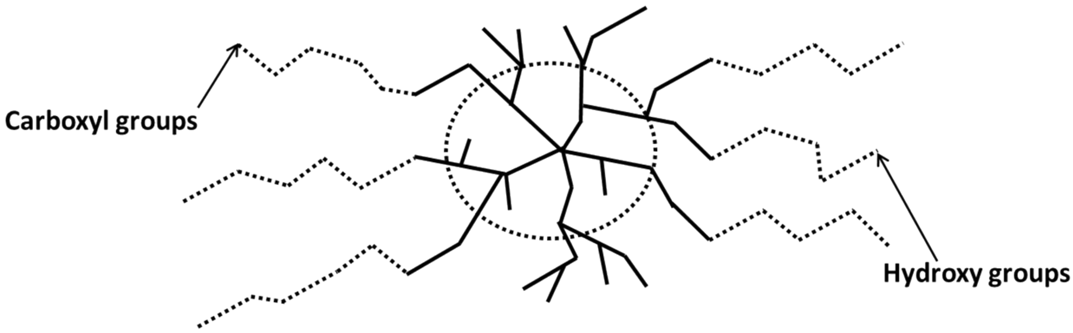

Fig. S4. Schematic representation of HBP Boltorn W3000 molecular structure.

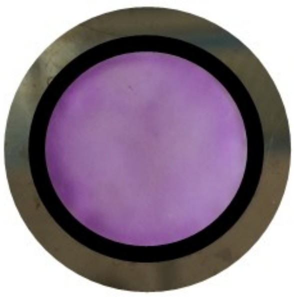

Fig. S5. Digital photograph of the ZIF-67/W3000-nc membrane on PS support.

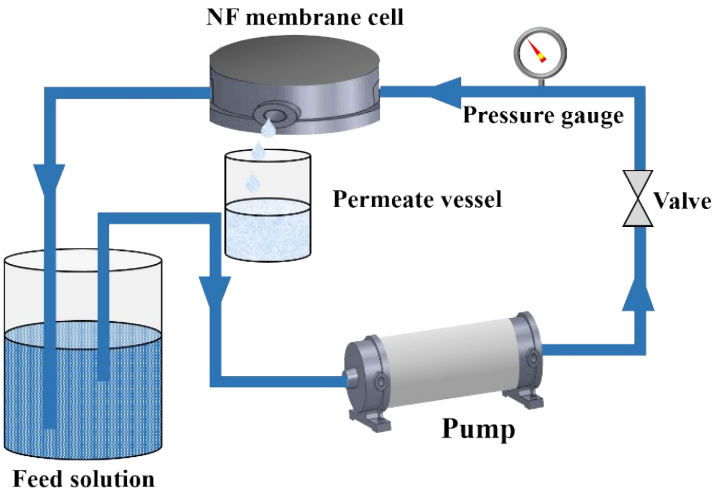

Fig. S6. Schematic diagram of a flat-sheet cross-flow separation device.

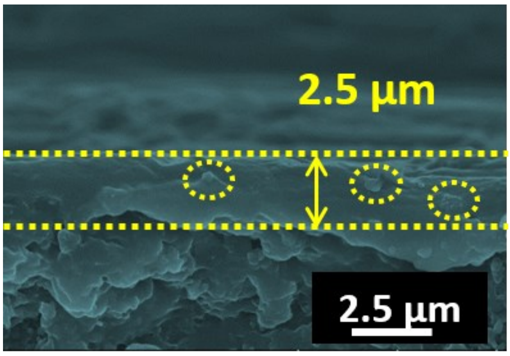

Fig. S7. The cross-sectional SEM image ZIF-67/W3000-tr membrane on PS support.

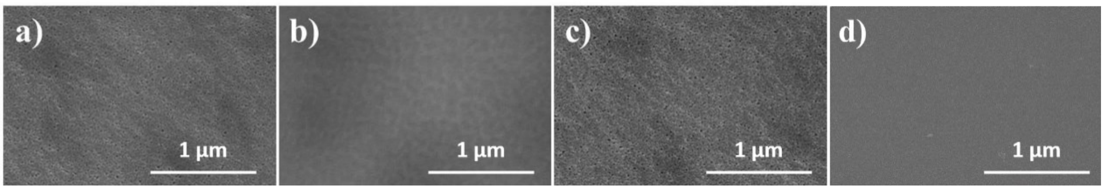

Fig. S8. Top-view SEM images of a) PS support; b) W3000 membrane; c) ZIF-67 membrane; ZIF-67/W3000-nc membrane.

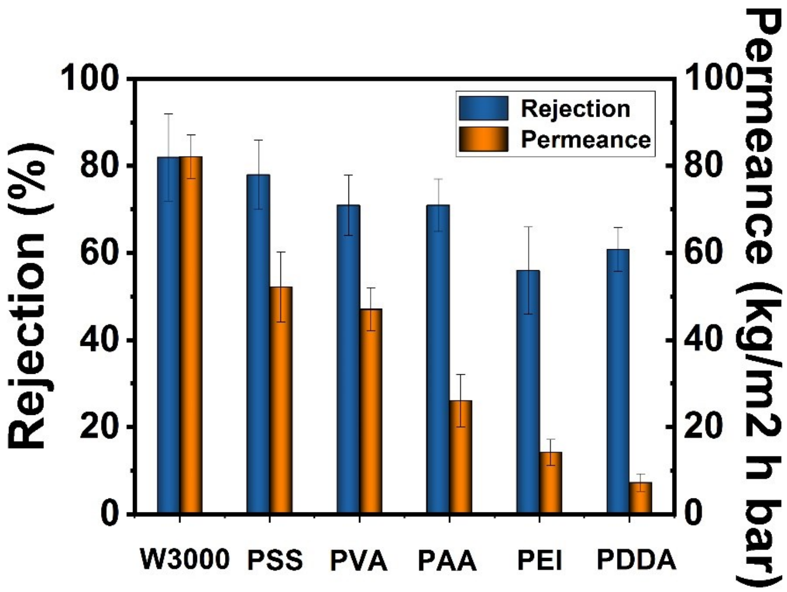

Fig. S9. Desalination performance of ZIF-67/polymer-nc membranes with different polymers. (Separation condition: 100 mg/L Na_2SO_4 aqueous solution)

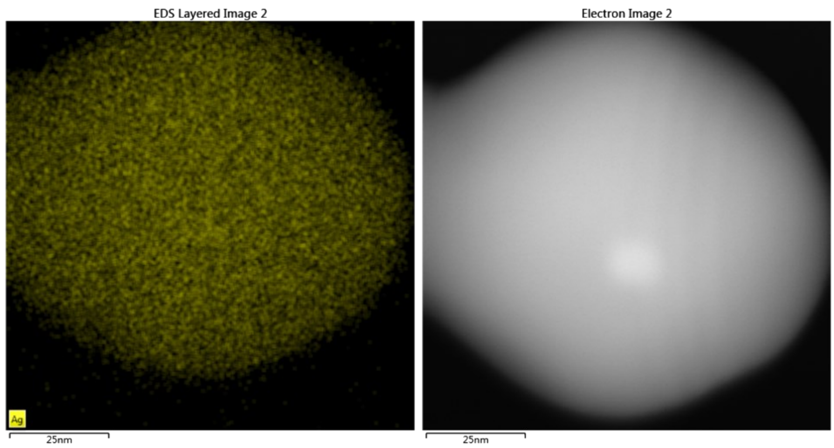

Fig. S10. EDX mapping and TEM images of Ag particles.

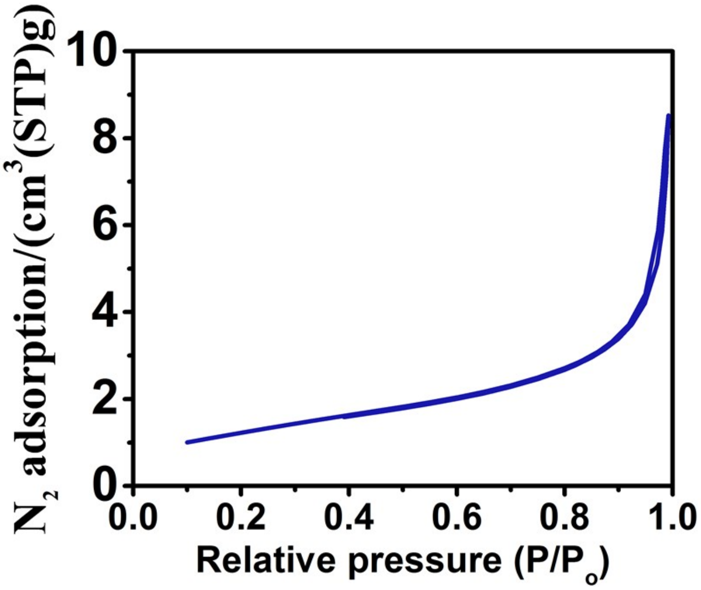

Fig. S11. N_2 sorption isotherms of Ag particles.

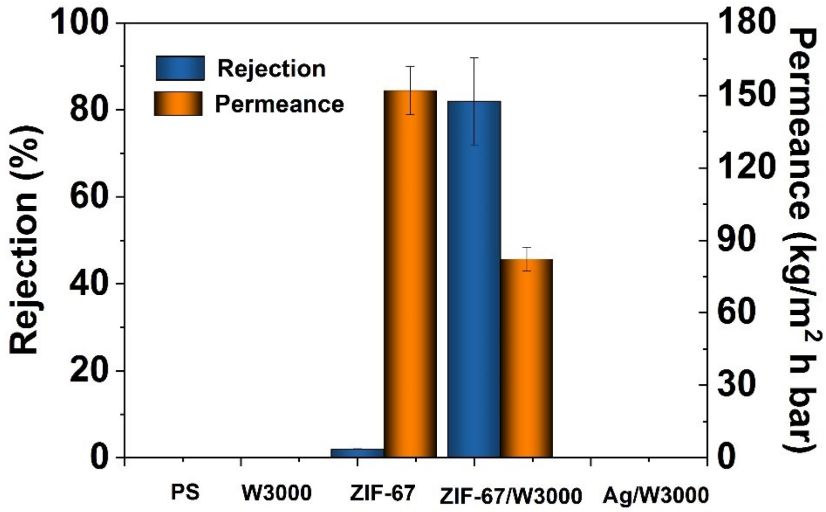

Fig. S12. Desalination performance of different kinds of membranes.

(Separation condition: 100 mg/L Na_2SO_4 aqueous solution)

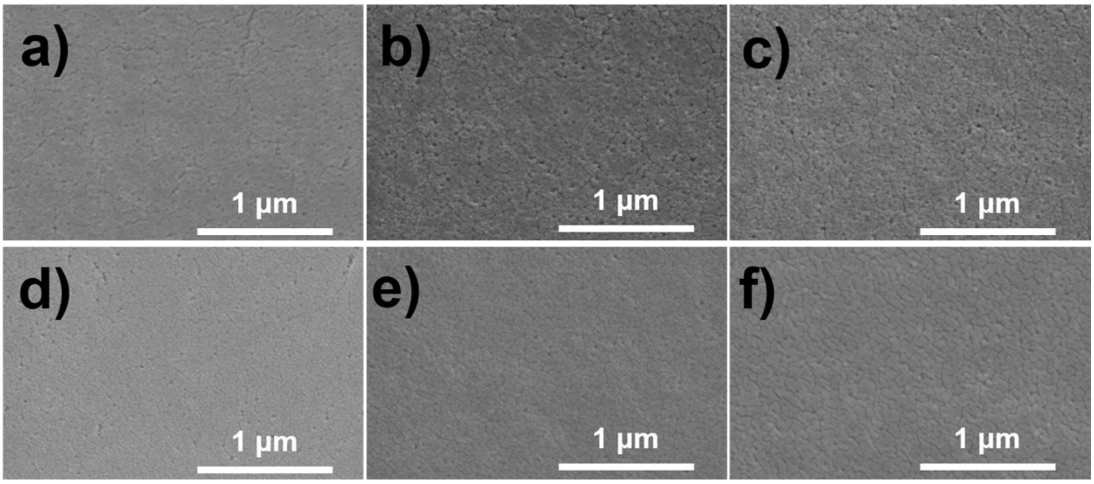

Fig. S13. Surface SEM images of a) PS support and PS support with different annealing temperature: b) 90 °C; c) 100 °C; d) 110 °C; e) 120 °C; f) 130 °C.

Table S1. Pore size and porosity for PS support before and after heated.

	PS support	Heated PS support
Most probable aperture/μm	0.21	0.065
Minimum pore size/μm	0.079	0.063
Average pore size/μm	0.17	0.095
Porosity/%	61	49

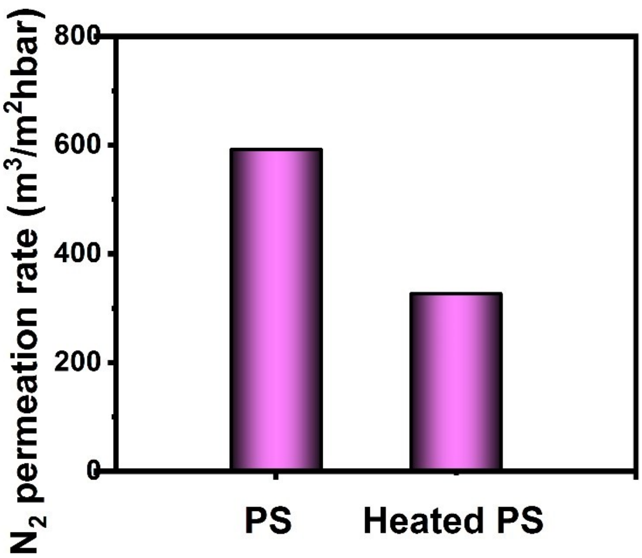

Fig. S14. N_2 permeation rate for a PS support before and after being heated.

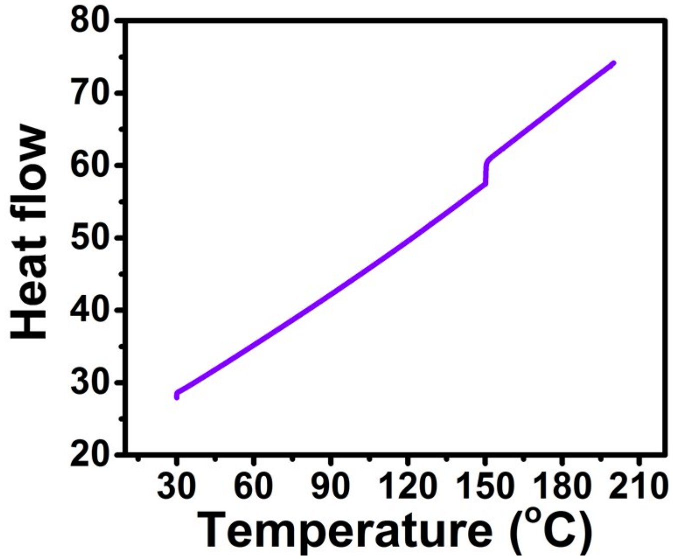

Fig. S15. DSC trace of the PS support.

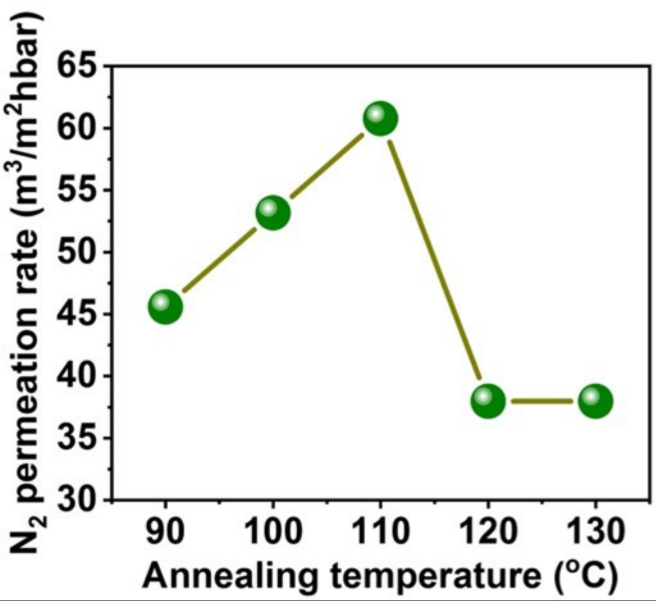

Fig. S16. N_2 permeation rate of ZIF-67/W3000-nc membrane at different annealing temperatures.

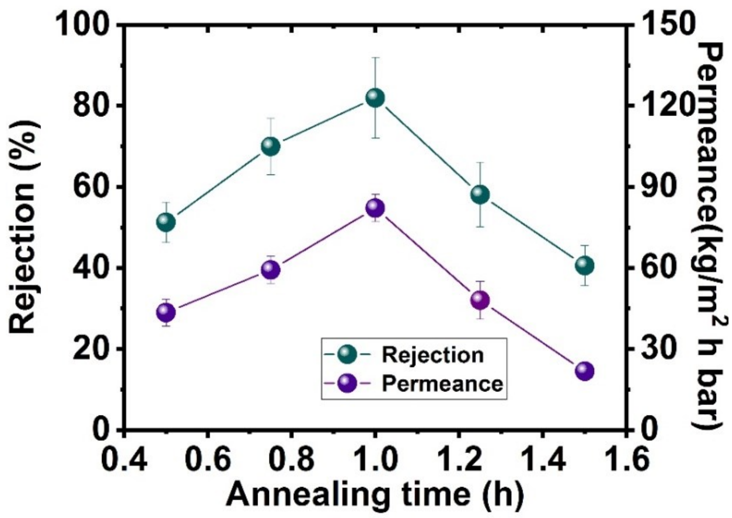

Fig. S17. Effects of annealing time on the separation performance of the ZIF-67/W3000-nc membranes. (Separation condition: 100 mg/L Na_2SO_4 aqueous solution)

(Preparation conditions: $C_{Co(NO3)2}$ = 1.6 mol/mL; $C_{H\text{-}mim}$ = 0.5 mol/mL; concentration of W3000, 0.05 wt.%; liquid level interval, 6 cm; annealing temperature, 110 ^{o}C)

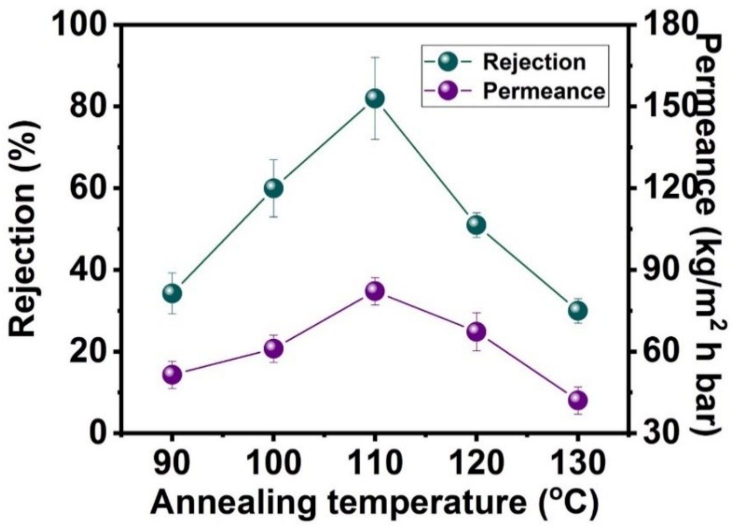

Fig. S18. Effects of annealing temperature s on the separation performance of the ZIF-67/W3000-nc membranes.

(Separation condition: 100 mg/L Na_2SO_4 aqueous solution)

(Preparation conditions: $C_{Co(NO3)2}$ = 1.6 mol/mL; $C_{H\text{-}mim}$ = 0.5 mol/mL; concentration of W3000, 0.05wt.%; liquid level interval, 6 cm; contra-diffusion time, 5 min; annealing time, 1 h)

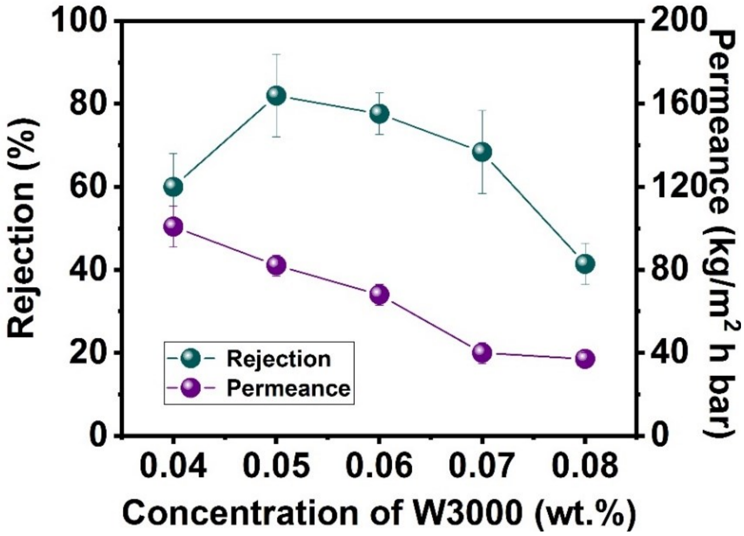

Fig. S19. Effects of W3000 concentration on the separation performance of the ZIF-67/W3000-nc membranes.

(Separation condition: 100 mg/L Na_2SO_4 aqueous solution)

(Preparation conditions: $C_{Co(NO3)2}$ = 1.6 mol/mL; $C_{H\text{-}mim}$ = 0.5 mol/mL; liquid level interval, 6 cm; contra-diffusion time, 5 min; annealing time, 1 h; annealing temperature, 110 ^oC)

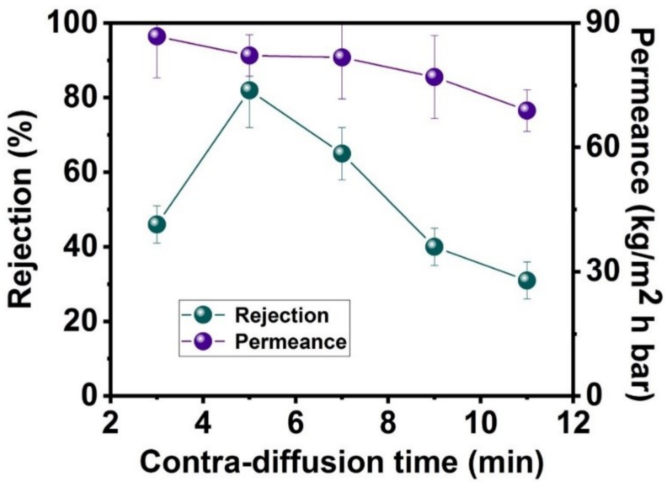

Fig. S20. Effects of contra-diffusion time on the separation performance of the ZIF-67/W3000-nc membranes.

(Separation condition: 100 mg/L Na_2SO_4 aqueous solution)

(Preparation conditions: $C_{Co(NO3)2}$ = 1.6 mol/mL; $C_{H\text{-}mim}$ = 0.5 mol/mL; concentration of W3000, 0.05wt.%; liquid level interval, 6 cm; annealing time, 1 h; annealing temperature, 110 ^oC)

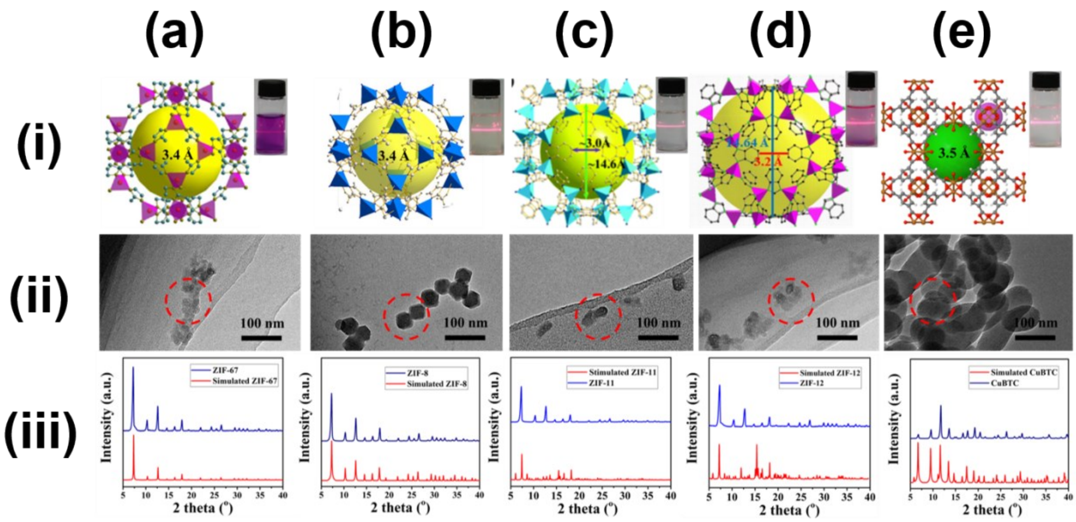

Fig. S21. a) ZIF-67; b) ZIF-8; c) ZIF-11; d) ZIF-12; e) HKSUT-1 crystals with i)-iii) TEM images and PXRD patterns.

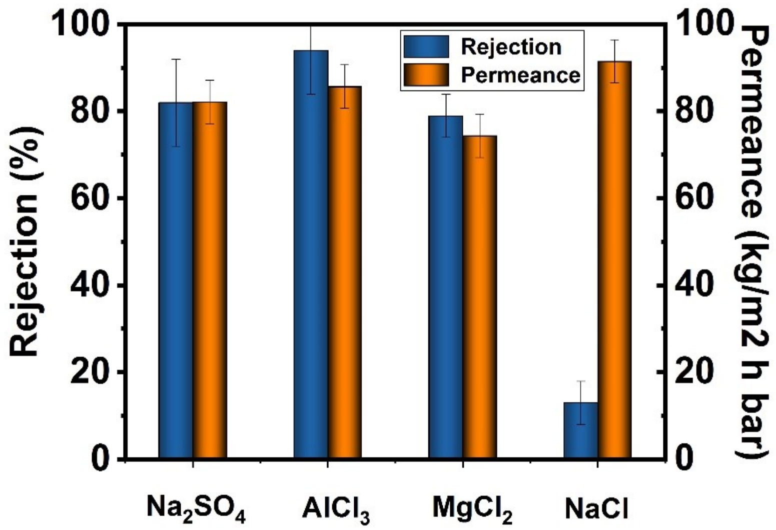

Fig. S22. Separation performance of the ZIF-67/w3000-nc membranes.

(Separation condition: 100 mg/L Na_2SO_4, $AlCl_3$, $MgCl_2$, NaCl aqueous solution)

(Preparation conditions: $C_{Co(NO3)2}$ = 1.6 mol/mL; $C_{H\text{-}mim}$ = 0.5 mol/mL; concentration of W3000, 0.05wt.%; liquid level interval, 6 cm; annealing time, 1 h; annealing temperature, 110 ^{o}C)

Table S2. Pore size of different polymer supports.

	PS support	PVDF support	PAN support	PES support
Most probable aperture/μm	0.21	0.28	0.039	0.017
Minimum pore size/μm	0.079	0.23	0.016	0.011
Average pore size/μm	0.17	0.29	0.027	0.023

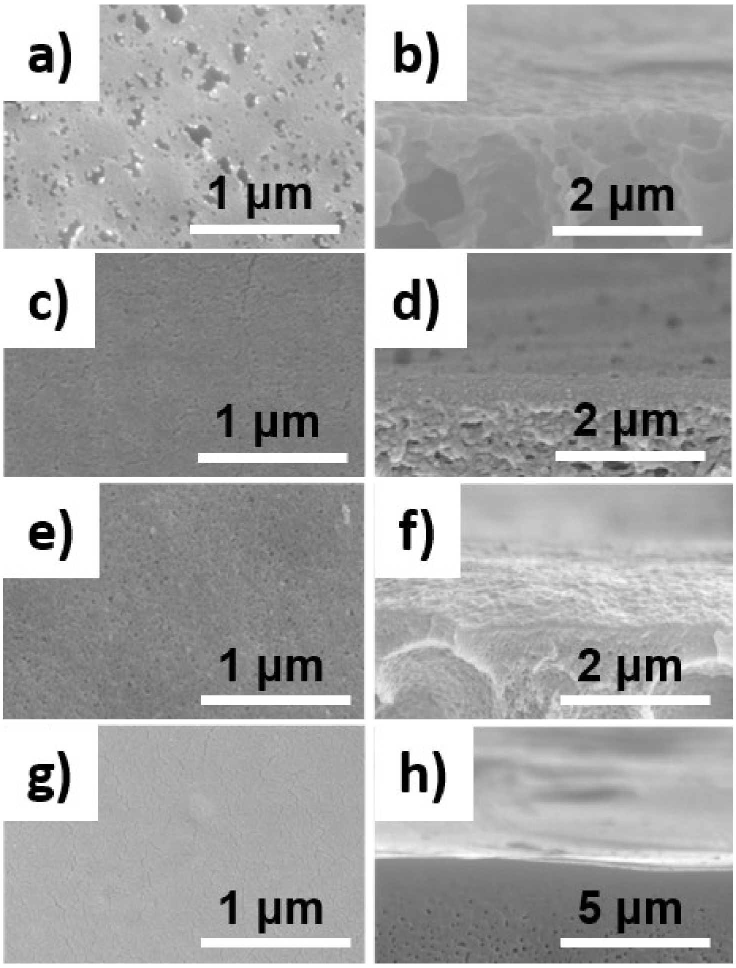

Fig. S23. Top-view and cross-section images of different polymer supports: a-b) PVDF support; c-d) PS support; e-f) PAN support; g-h) PES support.

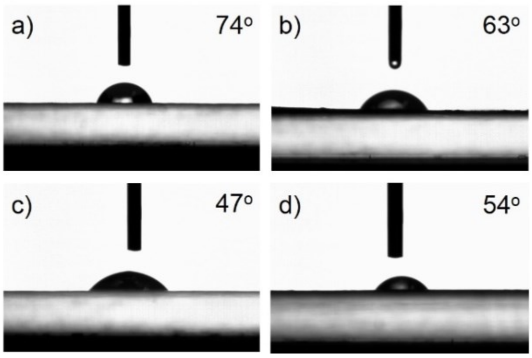

Fig. S24. Static water contact-angle of various substrates. a) PVDF; b) PS; c) PAN; d) PES.

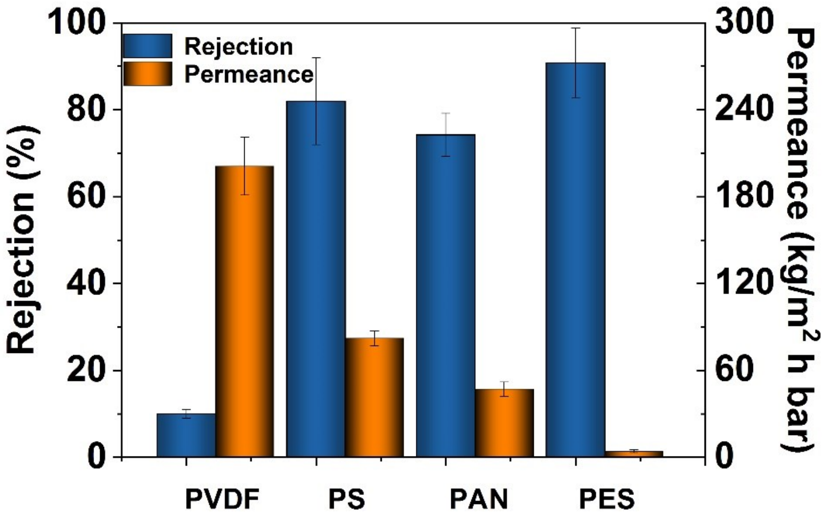

Fig. S25. Effects of polymer supports on the desalination performance of membranes.

(Separation condition: 100 mg/L Na_2SO_4 aqueous solution)

(Preparation conditions: $C_{Co(NO3)2}$ = 1.6 mol/mL; $C_{H\text{-}mim}$ = 0.5 mol/mL; concentration of W3000, 0.05 wt.%; liquid level interval, 6 cm; annealing time, 1 h; annealing temperature, 110 ^{o}C)

Supplementary References

[1] J. Kujawa, S. Cerneaux, X. Kujawski, *J. Membr. Sci.*, 2015, **474**, 11.

[2] X. Chen, M. Qiu, H. Ding, K. Fu, Y. Fan, *Nano,* 2016, **8**, 5696.

[3] Y. Li, L. H. Wee, J. A. Martens, I. F. J. Vankelecom, *J. Membr. Sci.,* 2017, **523**, 561.

[4] H. Huang, Z. Song, N. Wei, L. Shi, Y. Mao, Y. Ying, *Nat. Commun.,* 2013, **4**, 2979.

[5] A. Ali, A. Ahmed, A. Gad, *Water Sci. Technol.,* 2017, **75**, 439.

[6] S. You, J. Lu, C. Y. Tang, X. Wang, *Chem. Eng. J.*, 2017, **320**, 532.

[7] Z. Wang, Z. Wang, S. Lin, H. Jin, S. Gao, Y. Zhu, J. Jin, *Nat. Commun*., 2018, **9**, 2004.

[8] A. K. Basumatary, R.V. Kumar, A. K. Ghoshal, G. Pugazhenthi, *J. Membr. Sci*., 2015, **475**, 521.

[9] X. Liu, N. K. Demir, Z. Wu, K. Li, *J. Am. Chem. Soc.,* 2015, **137**, 6999.

[10] C. Yacou, S. Smart, J. C. Dinz da Costa, *Sep. Purif. Technol.,* 2015, **147**, 166.

[11] Z. Wang, Y. Wei, Z. Xu, Y. Gao, Z. Dong, X. Shi, *J. Membr. Sci.,* 2016, **503**, 69.

[12] Y. Chu, C. Lin, F. Kleitz, X. Zhao, S. Smart, *Chem. Commun.,* 2013, **49**, 4534.

[13] M. Elma, D. K. Wang, C. Yacou, J. C. Diniz da Costa, *J. Membr. Sci.,* 2015, **553**, 376.

[14] M. Elma, D. K. Wang, C. Yacou, J. C. Diniz da Costa, *Desalination,* 2015, **365**, 308.

[15] S. Bano, A. Mahmood, S.-J. Kim, K.-H. Lee, *J. Mater. Chem. A,* 2015, **3**, 2065.

[16] Y. Han, Z. Xu, C. Gao, *Adv. Funct. Mater.,* 2013, **23**, 3693.

[17] Y. Han, Y. Jiang, C. Gao, *ACS Appl. Mater. Interfaces,* 2015, **7**, 8147.

[18] J.-J. Wang, H.-C. Yang, M.-B. Wu, X. Zhang, Z.-K. Xu, *J. Mater. Chem. A,* 2017, **5**, 16289.

[19] M. Hu, B. Mi, *Environ. Sci. Technol.,* 2013, **47**, 3715.

[20] Y. Wei, Y. Zhang, X. Gao, Y. Yuan, B. Su, C. Gao, *Carbon,* 2016, **108**, 568.