Electronic Supplementary Information

Nano-confinement-inspired metal organic framework/polymer composite separation membranes
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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$_3$BTC 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$_2$SO$_4$ 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$_2$SO$_4$ 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.

<table>
<thead>
<tr>
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<th>PS support</th>
<th>Heated PS support</th>
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<tbody>
<tr>
<td>Most probable aperture/μm</td>
<td>0.21</td>
<td>0.065</td>
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<tr>
<td>Minimum pore size/μm</td>
<td>0.079</td>
<td>0.063</td>
</tr>
<tr>
<td>Average pore size/μm</td>
<td>0.17</td>
<td>0.095</td>
</tr>
<tr>
<td>Porosity/%</td>
<td>61</td>
<td>49</td>
</tr>
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</table>

Fig. S14. N₂ permeation rate for a PS support before and after being heated.
**Fig. S15.** DSC trace of the PS support.

**Fig. S16.** $\text{N}_2$ 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$_2$SO$_4$ aqueous solution) (Preparation conditions: C$_{\text{Co(NO}_3)_2}$ = 1.6 mol/mL; C$_{\text{H-mim}}$ = 0.5 mol/mL; concentration of W3000, 0.05 wt.%; liquid level interval, 6 cm; annealing temperature, 110 °C)

**Fig. S18.** Effects of annealing temperature on the separation performance of the ZIF-67/W3000-nc membranes. (Separation condition: 100 mg/L Na$_2$SO$_4$ aqueous solution) (Preparation conditions: C$_{\text{Co(NO}_3)_2}$ = 1.6 mol/mL; C$_{\text{H-mim}}$ = 0.5 mol/mL; concentration of W3000, 0.05 wt.%; 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$_2$SO$_4$ aqueous solution)  
(Preparation conditions: $C_{\text{Co(NO}_3)_2}$ = 1.6 mol/mL; $C_{\text{H-mim}}$ = 0.5 mol/mL; liquid level interval, 6 cm; contra-diffusion time, 5 min; annealing time, 1 h; annealing temperature, 110 °C)

Fig. S20. Effects of contra-diffusion time on the separation performance of the ZIF-67/W3000-nc membranes.  
(Separation condition: 100 mg/L Na$_2$SO$_4$ aqueous solution)  
(Preparation conditions: $C_{\text{Co(NO}_3)_2}$ = 1.6 mol/mL; $C_{\text{H-mim}}$ = 0.5 mol/mL; concentration of W3000, 0.05wt.%; liquid level interval, 6 cm; annealing time, 1 h; annealing temperature, 110 °C)
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$_2$SO$_4$, AlCl$_3$, MgCl$_2$, NaCl aqueous solution)
(Preparation conditions: $C_{Co(NO3)2} = 1.6$ mol/mL; $C_{H-mim} = 0.5$ mol/mL; concentration of W3000, 0.05wt.%; liquid level interval, 6 cm; annealing time, 1 h; annealing temperature, 110 °C)
Table S2. Pore size of different polymer supports.

<table>
<thead>
<tr>
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<th>PS support</th>
<th>PVDF support</th>
<th>PAN support</th>
<th>PES support</th>
</tr>
</thead>
<tbody>
<tr>
<td>Most probable aperture/μm</td>
<td>0.21</td>
<td>0.28</td>
<td>0.039</td>
<td>0.017</td>
</tr>
<tr>
<td>Minimum pore size/μm</td>
<td>0.079</td>
<td>0.23</td>
<td>0.016</td>
<td>0.011</td>
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<tr>
<td>Average pore size/μm</td>
<td>0.17</td>
<td>0.29</td>
<td>0.027</td>
<td>0.023</td>
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</table>

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$_2$SO$_4$ aqueous solution)
(Preparation conditions: $C_{Co(NO3)2} = 1.6$ mol/mL; $C_{H-mim} = 0.5$ mol/mL; concentration of W3000, 0.05 wt.%; liquid level interval, 6 cm; annealing time, 1 h; annealing temperature, 110 °C)

Supplementary References


