Electronic supplementary information

Highly permeable zeolite imidazolate framework composite membranes fabricated via chelation-assisted interfacial reaction

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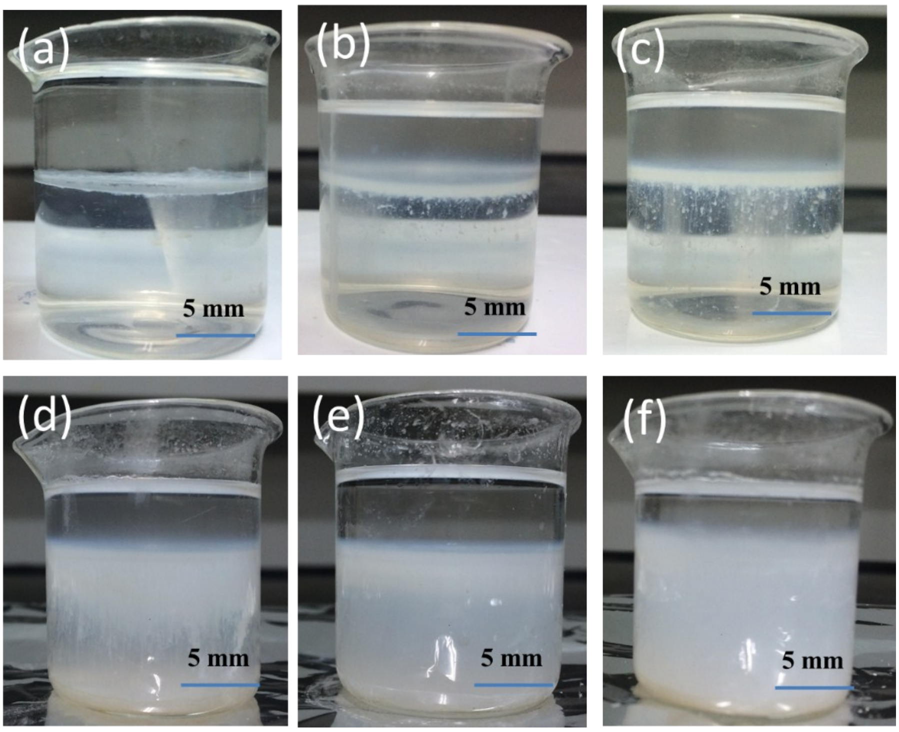

Fig. S1. Photos of ZIF-8 crystals synthesizing on the interface between water and hexane solutions with reaction times of (a) 10s, (b) 20s (c) 30s, (d) 2 min (e) 5 min and (f) 10 min.

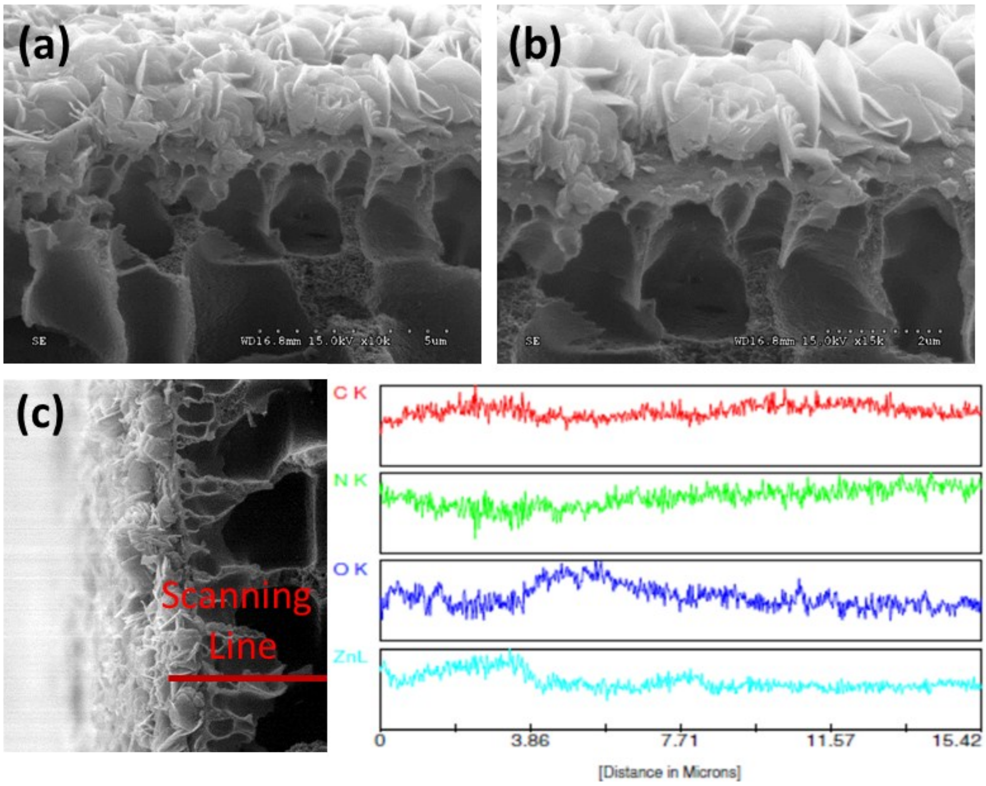

Fig. S2. (a), (b) SEM images and (c) EDX analysis of cross section of the ZIF-8/PEI-HPAN composite membrane.

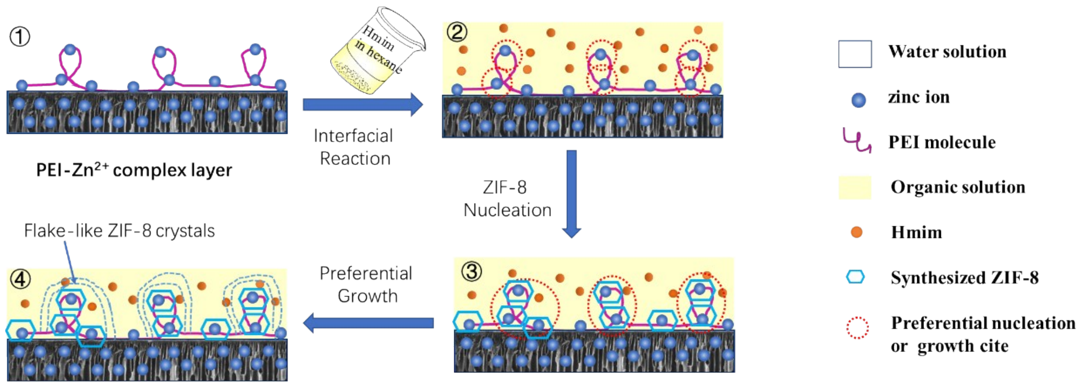

Fig. S3. The proposed formation mechanism of ZIF-8 via chelation assisted interfacial reaction.

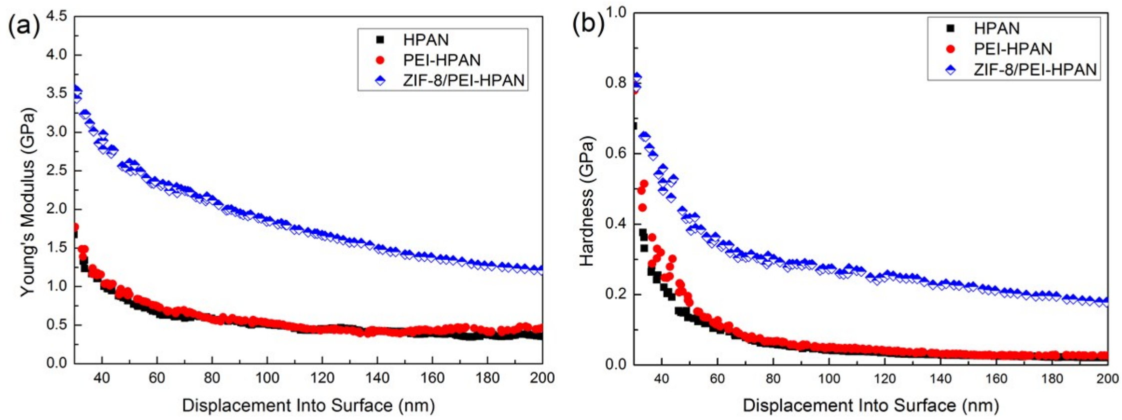

Fig. S4. (a) The modules and (b) hardness of different membranes.

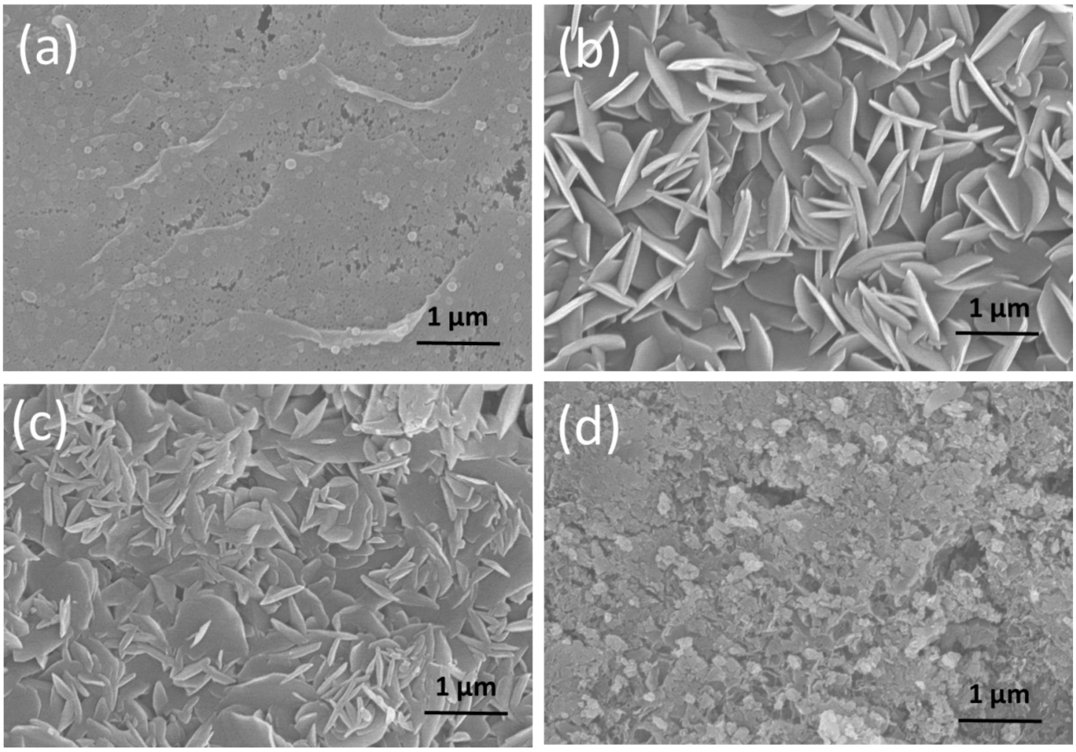

Fig. S5. Effects of different pH value of PEI-Zn(II) complex solutions on membrane surface morphology: (a) pH 5, (b) pH 6, (c) pH 7, (d) pH 8.

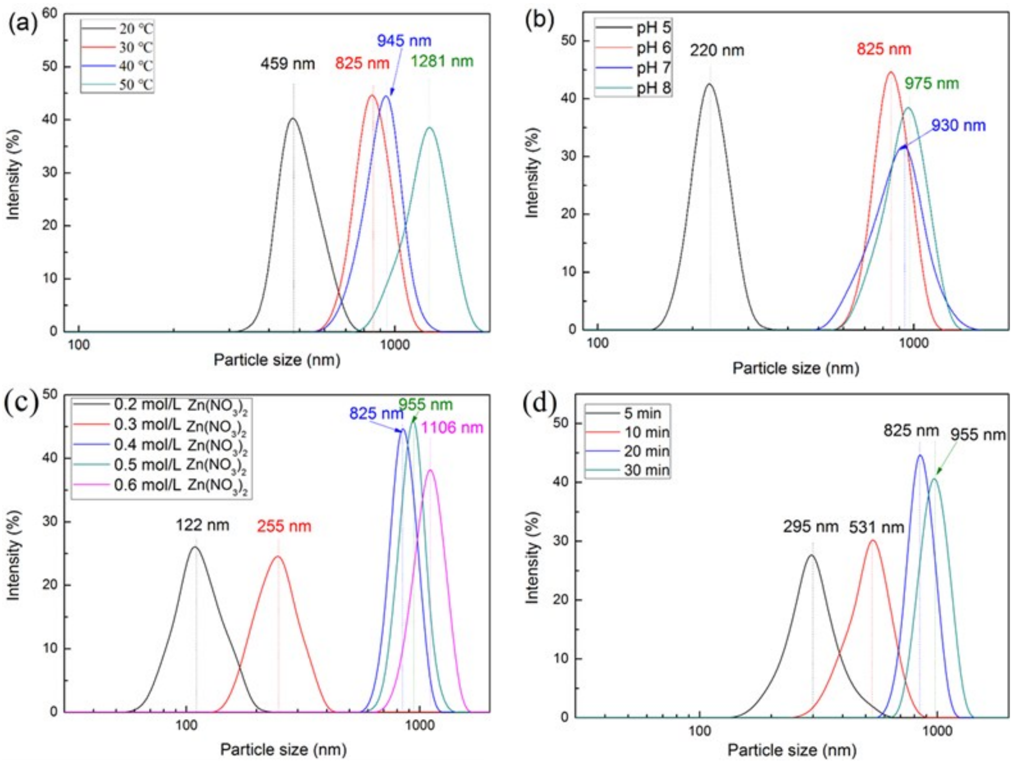

Fig. S6. Particle size distribution of ZIF-8 crystals prepared by (a) different chelation temperature, (b) pH value of aqueous solutions, (c) prepared by different $Zn(NO_3)_2$ concentrations and (d) prepared with different interfacial reaction time.

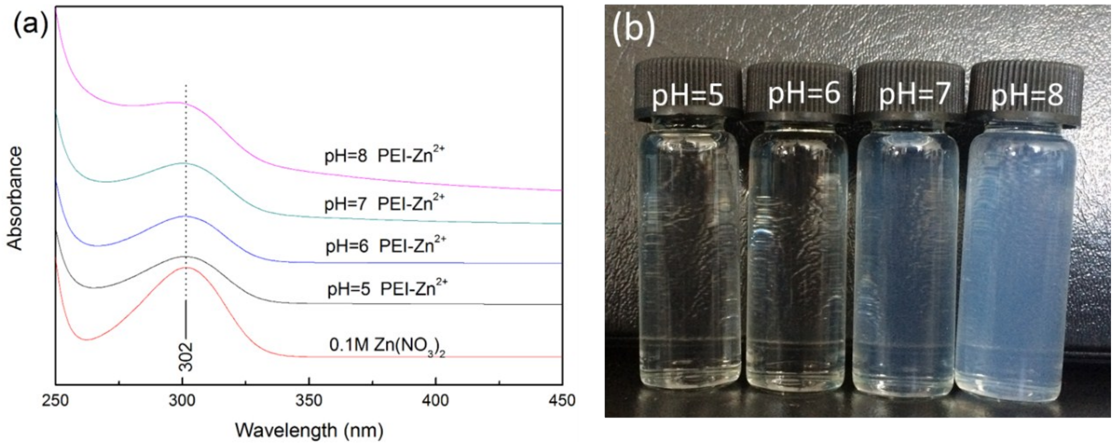

Fig. S7. (a) UV–vis absorption spectra and (b) digital photos of PEI-Zn(II) complex at different pH values.

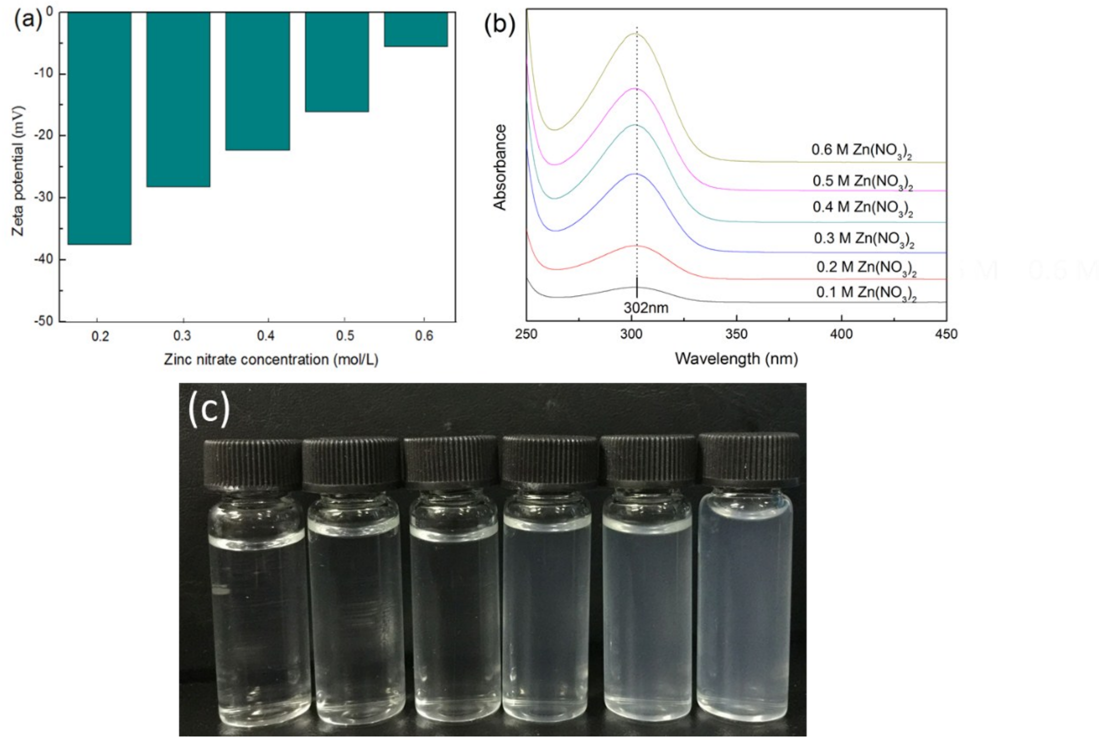

Fig. S8. (a) zeta potential of HPAN-Zn(II) membrane prepared with different $Zn(NO_3)_2$ concentration (b) UV–vis absorption spectra and (c) digital photos of PEI-Zn(II) complex at different $Zn(NO_3)_2$ concentrations.

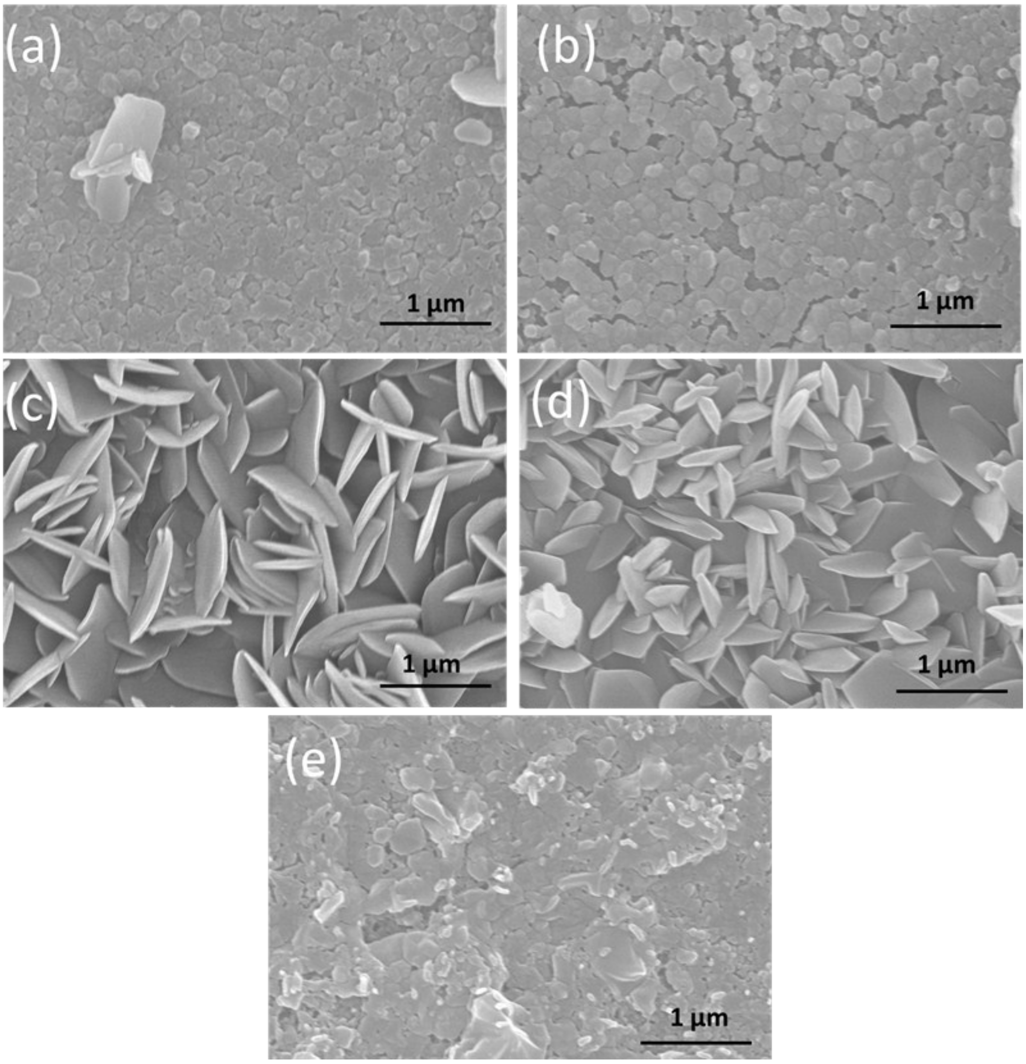

Fig. S9. Effects of different zinc nitrate concentration on membrane surface morphology: (a) 0.2 mol/L, (b) 0.3 mol/L, (c) 0.4mol/L, (d) 0.5 mol/L and (e) 0.6 mol/L.

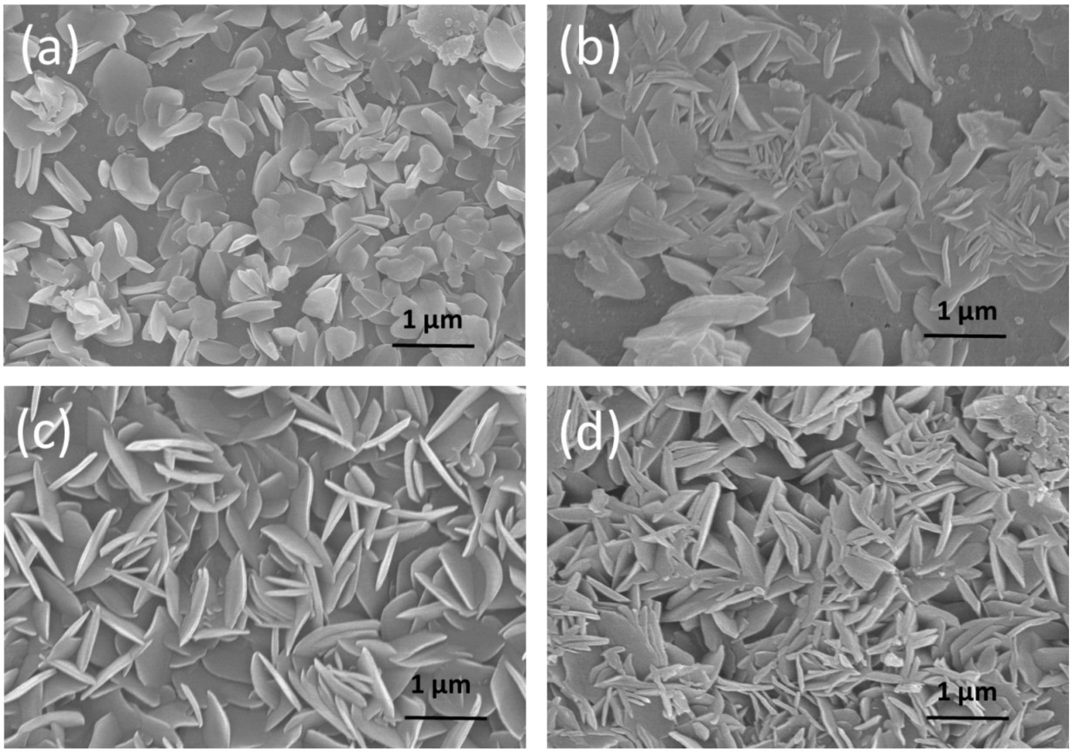

Fig. S10. Effects of different reaction times on membrane surface morphology: (a) 5 min, (b) 10 min, (c) 20 min and (d) 30 min.

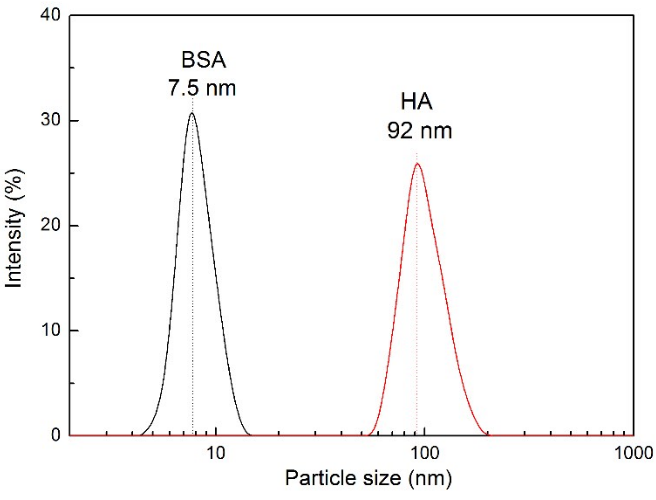

Fig. S11. Particle size distribution of foulant BSA and HA.

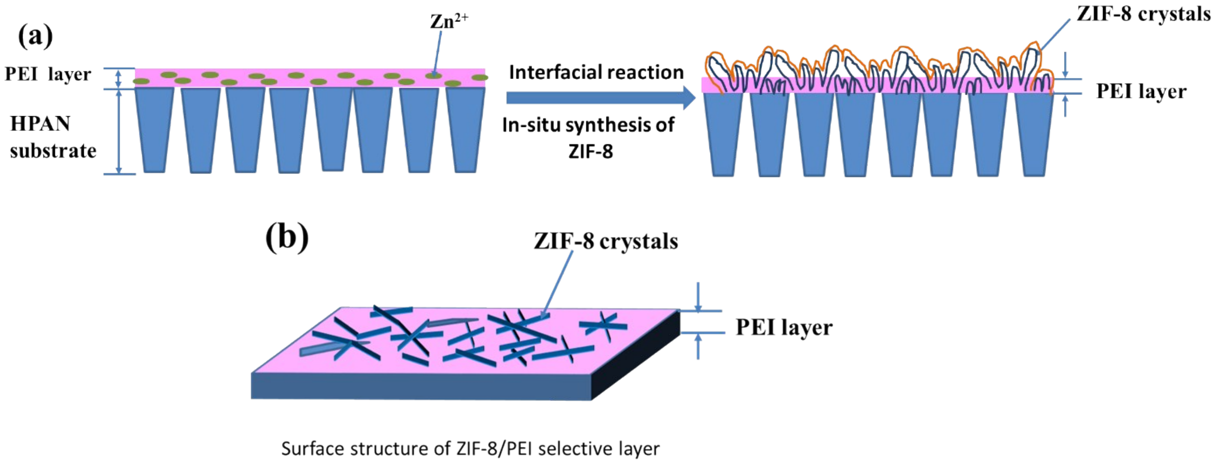

Fig. S12. (a) The proposed membrane formation process and (b) the surface structure of ZIF-8/PEI selective layer.

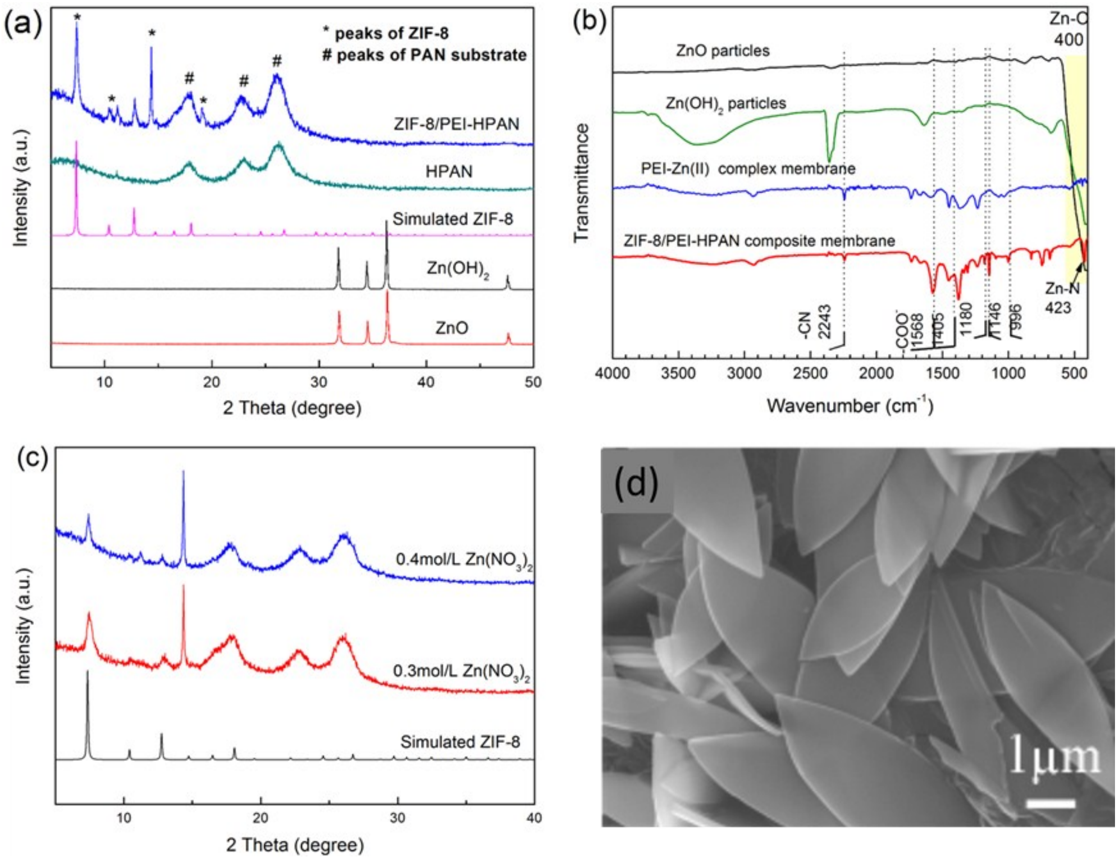

Fig. S13. (a) XRD pattern of the HPAN substrate, the ZIF-8/PEI-HPAN composite membrane, the simulated ZIF-8 particles, ZnO and $Zn(OH)_2$ particles, (b) FTIR sepetra of the ZIF-8/PEI-HPAN composite membrane, PEI-Zn(II) complex membrane, (c) XRD pattern of the ZIF-8/PEI-HPAN composite membrane prepared by different $Zn(NO_3)_2$ concentrations and (d) leaf-like ZIF crystals from the literature [S1].

(ZnO and $Zn(OH)_2$ particles. (ZnO and $Zn(OH)_2$ particles were purchased from Macklin Inc. and Tianjin Guangfu Fine Chemical Insititute in China, respectively.)

Table S1. Surface roughness of different membrane characterized by AFM.

Membrane	Surface roughness		
	R_a (nm)	R_{ms} (nm)	R_z (nm)
HPAN	21.1	27.8	43.0
PEI-Zn(II)	16.1	20.0	19.0
ZIF-8/PEI-HPAN	83.7	105	94.4

Table S2. Zeta potential of HPAN-Zn(II) membrane prepared with different zinc nitrate concentrations.

Samples	Concentration(mg/L)	Zeta potential (mV)
ZIF-8/PEI hybrid membrane	--	32.2 ± 1.5
Methyl blue	100	-32.0 ± 3.0
Congo red	100	-29.2 ± 2.8
Acid fuchsin	100	-25.6 ± 0.9
Crystal violet	100	12.3 ± 1.0
Humic Acid	1000	-41.6 ± 0.8
Bovine Serum Albumin	1000	-9.8 ± 1.3

Table S3. Performance comparison of nanofiltration membrane obtained in this work and those from literatures.

Membrane	Permeance / $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$	Dye Rejection/ %	NaCl rejection/%	References
ZIF-8/PEI-HPAN	75.1	98.9%, methyl blue	4.3%	This study
ZIF-8/PEI-HPAN	78.4	99.2%, congo red	4.3%	This study
ZIF-8/PEI-HPAN	97.0	87.2%, acid fusion	4.3%	This study
mHT/PES	6.3	95−98%, reactive black 5	8%	S2
HNTs-PIL/PES	11.8	94−96%, reactive black 5	6%	S3
ZIF-8-PSS/PAN	26.5	98.6%, methyl blue	-	S4
ZIF-8/PES	5.0	92.5%, rose bengal	-	S5
ZIF-8-PSS/Ceramic	21.0	98.6%, methyl blue	-	S6
ZIF-8-PA/PSf	2.3	99.9%, congo red	-	S7
CS–MMT/PES	17.8	87.1%, reactive black 5	5%	S8
Sepro NF 6	14.0	99.9%, direct red 80	2.6−17.9%	S9
Sepro NF 2A	10.1	99.9%, direct red 80	8.3-23.5%	S9
SiO_2-PIL/PES	37.5	90%, reactive black 5	5%	S10
Tanic acid-TMC/PES	16.8	99.8%, orange GII	15%	S11
DK1812 (Commercial)	5.1	99.9%, reactive black 5	70%	S12
DL1812 (Commercial)	6.7	99.9%, reactive black 5	61%	S12
Ceramic (Commercial)	57	96.8%, reactive black 5	7%	S12
PEI-GA/PAN	25.5	97.1%, congo red	5%	S13
TiO_2-Ceramic	30.0	99.0%, congo red	-	S14
ZrO_2-Ceramic	26.0	99.2%, direct red	16.5%	S15
TiO_2-Ceramic	65.0	97.5%, direct red	3.1%	S15

Notes and references

[S1] R. Chen, J. Yao, Q. Gu, S. Smeets, C. Baerlocher, H. Gu, D. Zhu, W. Morris, O.M. Yaghif and H. Wang, *Chem. Commun.*, 2013, **49**, 9500-9502.

[S2] L. Yu, J. Deng, H. Wang, J. Liu and Y. Zhang, *ACS Sustain. Chem. Eng.*, 2016, **4**, 3292−3304.

[S3] L. Yu, Y. Zhang, H. Zhang and J. Liu, *Desalination*, 2015, **359**, 176−185.

[S4] R. Zhang, S. Ji, N. Wang, L. Wang, G. Zhang and J. R. Li, *Angew. Chem. Int. Ed.*, 2014, **53**, 9775−9779.

[S5] Y. Li, L. H. Wee, A. Volodin, J. A. Martens and I. F. J. Vankelecom, *Chem. Commun.*, 2015, **51**, 918−920.

[S6] N. Wang, R. Zhang, T. Liu, H. Shen, S. Ji and J. R. Li, *AIChE J.*, 2016, **62**, 538-546.

[S7] L. Wang, M. Fang, J. Liu, J. He, L. Deng, J. Li and J. Lei, *RSC Adv.*, 2015, **5**, 50942–50954.

[S8] J. Zhu, M. Tian, Y. Zhang, H. Zhang and J. Liu, *Chem. Eng. J.*, 2015, **265**, 184–193.

[S9] J. Lin, W. Ye, H. Zeng, H. Yang, J. Shen, S. Darvishmanesh, P. Luis, A. Sotto and B. Van der Bruggen, *J. Membr. Sci.*, 2015, **477**, 183−193.

[S10] L. Yu, Y. Zhang, Y. Wang, H. Zhang and J. Liu, *J. Hazard. Mater.*, 2015, **287**, 373−383.

[S11] Y. Zhang, Y. Su, J. Peng, X. Zhao, J. Liu, J. Zhao and Z. Jiang, *J. Membr. Sci.*, 2013, **429**, 235–242.

[S12] P. Chen, X. Ma, Z. Zhong, F. Zhang, W. Xing and Y. Fan, *Desalination*, 2017, 404, 102–111.

[S13] S. Zhao and Z. Wang, *J. Membr. Sci.*, 2017, **524**, 214-224.

[S14] H. Chen, X. Jia, M. Wei and Y. Wang, *J. Membr. Sci.*, 2017, **528**, 95-102.

[S15] S. Benfer, U. Popp, H. Richter, C. Siewert and G. Tomandl, *Sep. Purif. Technol.*, 2001, **22-23**, 231–237.