Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information

Interfacial Growth of Metal-Organic Frameworks Membrane on Porous Polymer via Phase Transformation

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1. Experimental Section
2. Effect of M3 Assembly Conditions
3. Work Comparison
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1. Experimental Section

1.1 Chemicals

Polyethersulfone (PES, M_w = 58 kDa) was provided by BASF company (German). 2-Methylimidazole (2-MeIM) was obtained from Aladdin Industrial Corporation). Zinc Acetylacetonate ($Zn(acac)_2$) was purchased from Energy Chemical. Poly (sodium 4-styrenesulfonate) (PSS, average M_w of 500000, powder) was provided by Alfa Aesar company. *N, N*-dimethylformamide (DMF) was supplied by Nanjing Chemical Reagent Co., Ltd. Congo Red, Acid Yellow 17, Orange II, Methyl Orange and Bovine Serum Albumin (BSA, M_w = 67 kDa) were purchased from Sinopharm Chemical Reagent Co., Ltd.

1.2 Synthesis of ZIF-8 ($Zn(acac)_2$) powder

$Zn(acac)_2$ (0.12g, 0.46mmol) and 2-MeIM (0.38g, 4.6mmol) were dissolved in 15ml DMF and 15ml DI water, respectively. The solutions were mixed and stirred at room temperature for 12h. The sediment was collected for further characterization after washing three times with DI water followed by centrifugation and drying in a vacuum oven at 80℃.

1.3 Membrane fabrication

The MOF membrane was formed via one-step process. 15wt% of PES, certain amount of $Zn(acac)_2$ and DMF were mixed and stirred at 60℃ for 12h. Then the casting solution was degassed. After that, the solution was cast on clean glass plate using a 300μm pitch spiral bar. The glass plate was immersed in coagulation bath consists of 100g/L 2-MeIM and certain concentration of PSS aqueous solution for a certain time. The as-prepared PSS/ZIF-8/PES membrane, named M3, was then washed and stored in DI water before test.

By contrast, two other samples were prepared via similar process. For the first sample,

named M1, its casting solution contained only water instead of mixture of 2-MeIM and PSS. For the second sample, named M2, its coagulation bath contained water and 2-MeIM, but no PSS.

Table S1. Formulas of casting solution and coagulating bath of M1, M2 and M3.

Membrane	Casting Solution			Coagulating Bath		
Name	PES	DMF	$Zn(acac)_2$	Water	2-MeIM	PSS
M1	√	√	√	√	×	×
M2	√	√	√	√	√	×
M3	√	√	√	√	√	√

1.4 Membrane performance

1.4.1 Filtration experiment

A dead-end filtration system with an effective area of 12.56cm^2 and 2bar operating pressure was employed to test the membrane permeability and selectivity. 100mg/L dye aqueous solution was used as feed solution. Each permeate sample was collected after a 30 minutes filtrating process since the flux could be steady. Each test was measured at the same condition three times. The average and the standard deviation of each test data were employed to get more reasonable results. 100mg/L dye permeance was calculated by Eq.1. Dye rejection was calculated by Eq.2.

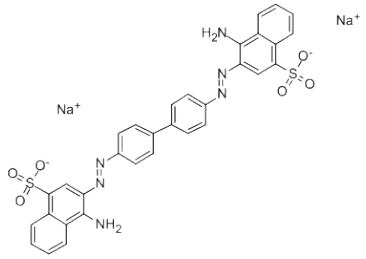
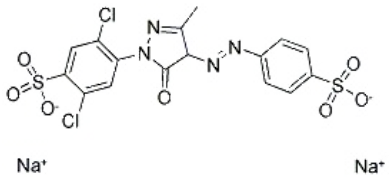
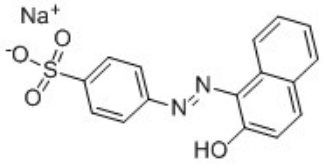
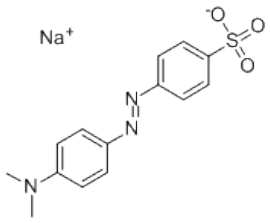
$$J=\Delta V/A\Delta t \quad \text{(Eq.1)}$$

where V is the weight of permeate sample (L) , A is the effective area of the system (m^2) , t is the time (h) .

$$R=(C_f - C_p)/C_f \times 100\% \quad \text{(Eq.2)}$$

Where C_p, C_f represent CR concentration of the permeate and the feed, respectively. The CR concentration was carried out by UV-Vis spectrophotometer (Perkin Elmer, USA).

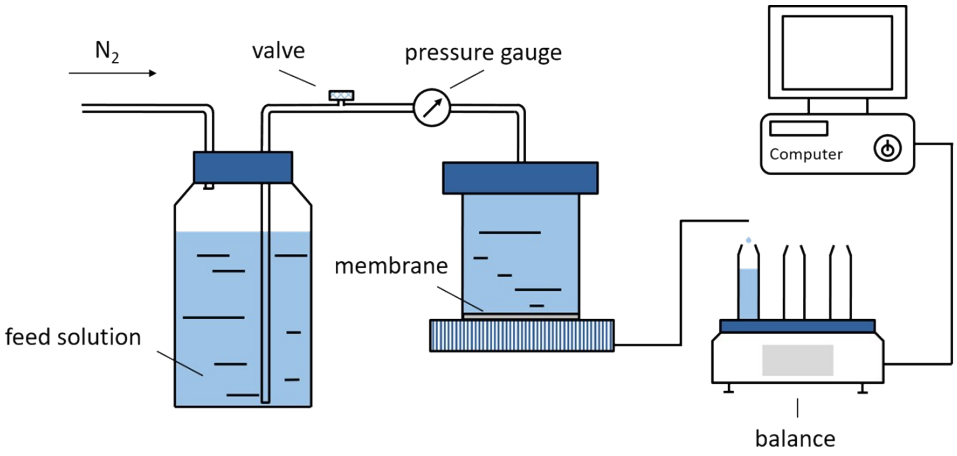
Table S2. Property of dyes used in filtration experiments.

Dye name	Molecular Structure	Mw (Da)	λ_{max}(nm)
Congo Red (CR)		696.7	495
Acid Yellow17 (AY17)		551.3	403
Orange II (OII)		350.3	485
Methyl Orange (MO)		327.3	462

1.4.2 Dye mixture separation experiment

Mixture of CR and another kind of dye aqueous solutions were filtrated to test M3's separation property to them. The feed solution contained 100mg/L CR and 100mg/L AY17.

The permeate solution was collected for detecting dye concentrations.



Scheme S1. Set-up of dead-end filtration system for nanofiltration test.

1.4.3 Long-time stability and anti-fouling performance

A 300-min-long filtration process using 100ppm CR was carried out to investigate the long-time stability of M3 by working out CR flux and rejection. Anti-fouling performance of M2 and M3 was evaluated by filtrating pure water and 1000ppm bovine serum albumin (BSA) aqueous solution in turn for 2 cycles.

1.5 CR adsorption experiment

To investigate the adsorption effect of ZIF-8 on CR. A piece of M3 with an effective area of 12.56cm^2 was immersed into 100ppm Congo Red (CR) aqueous solution (500ml) with stirring at 25 ^{o}C. Samples were collected after certain time for detecting dye concentrations using UV-Vis spectrophotometer (Perkin Elmer, USA).

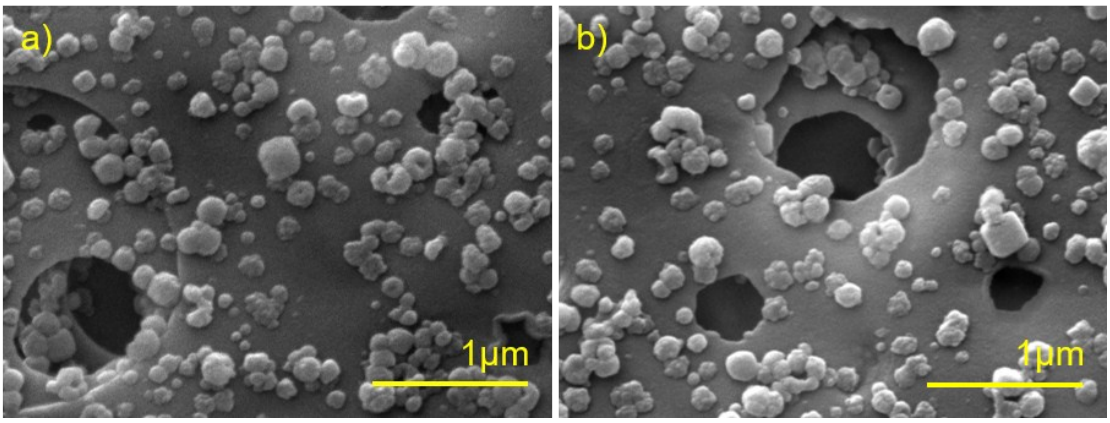


Figure S1. SEM images of the reverse side of M2 (a) and M3 (b).

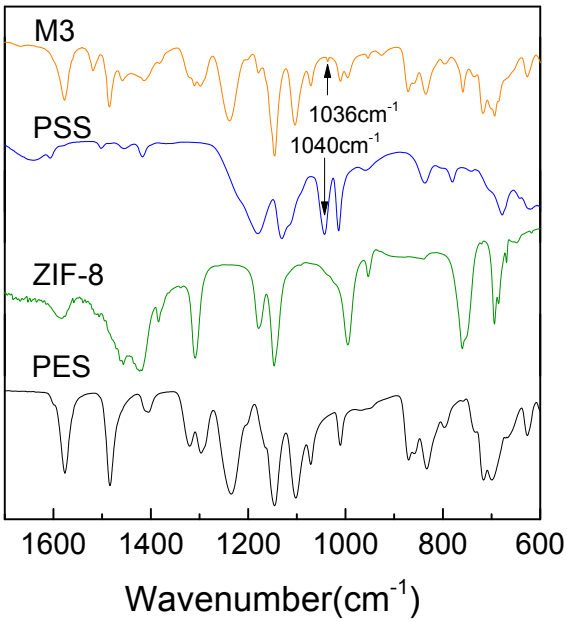


Figure S2. FT-IR spectra of pure PES membrane, ZIF-8, PSS and M3.

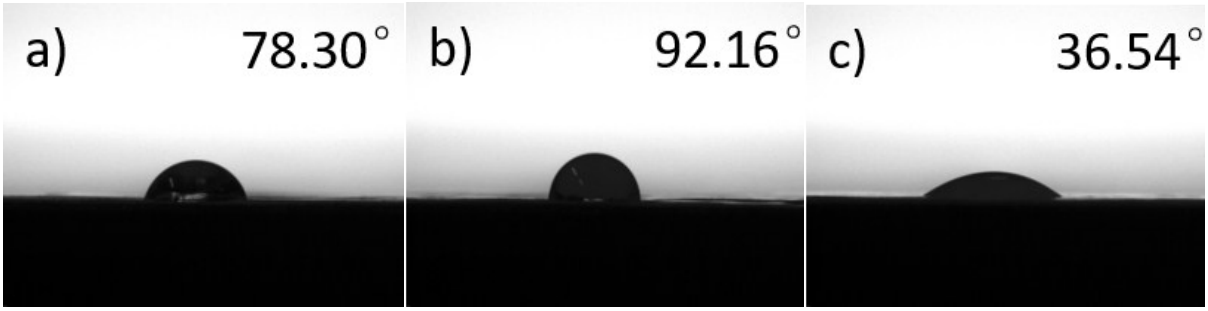


Figure S3. Images of contact angle of M1 (a), M2 (b) and M3 (c).

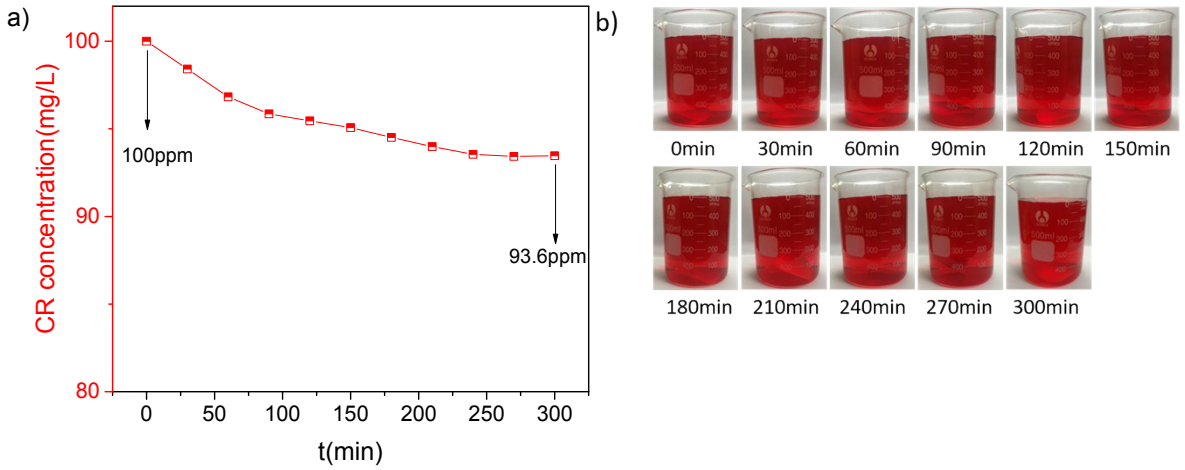


Figure S4. (a) Effect of time on adsorption of Congo Red over M3 at 25 °C. (b) Photographs of CR aqueous solution during adsorption experiment.

2. Effect of M3 assembly conditions

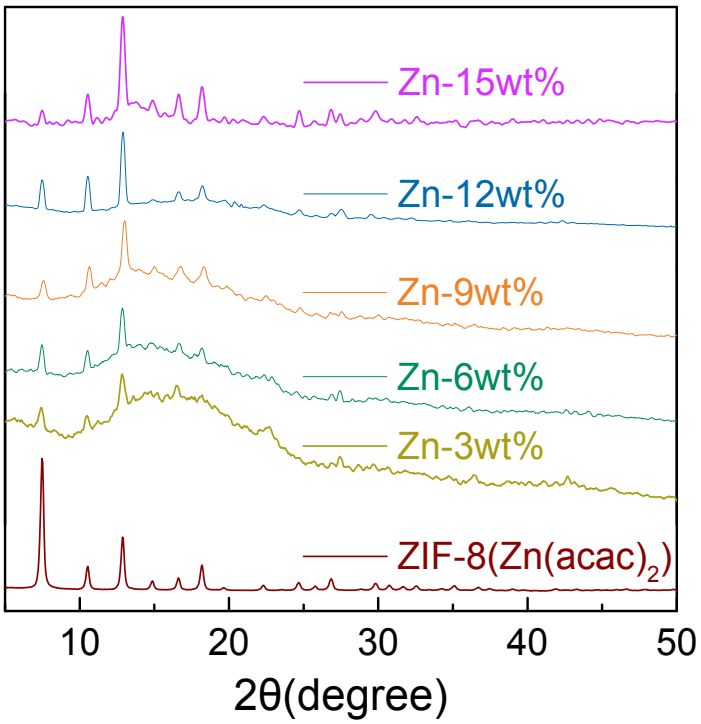


Figure S5. XRD patterns of M3 with different $Zn(acac)_2$ wt% in dope solution.

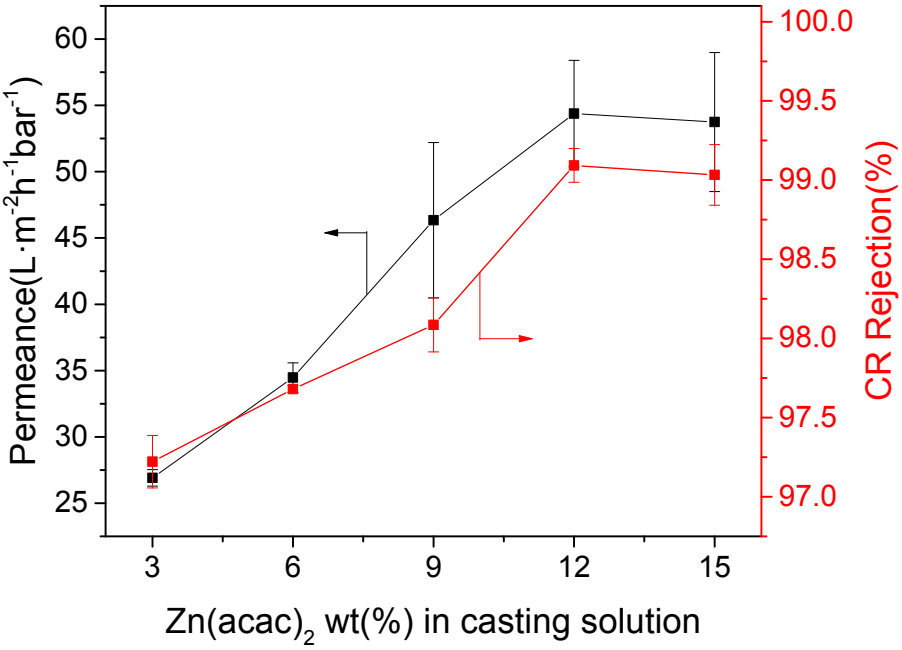


Figure S6. Effect of Zn(acac)2 wt% in casting solution on CR permeance and rejection of M3. (Membrane preparation and test conditions: PSS in coagulating bath: 0.4wt%; ZIF-8 assembly time: 1h; operating pressure: 2bar)

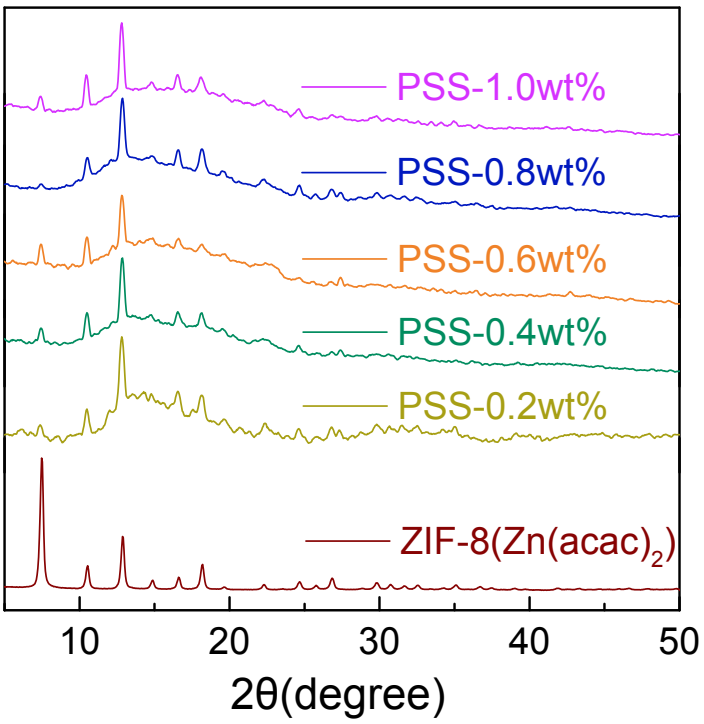


Figure S7. XRD patterns of M3 with different PSS wt% in coagulating bath.

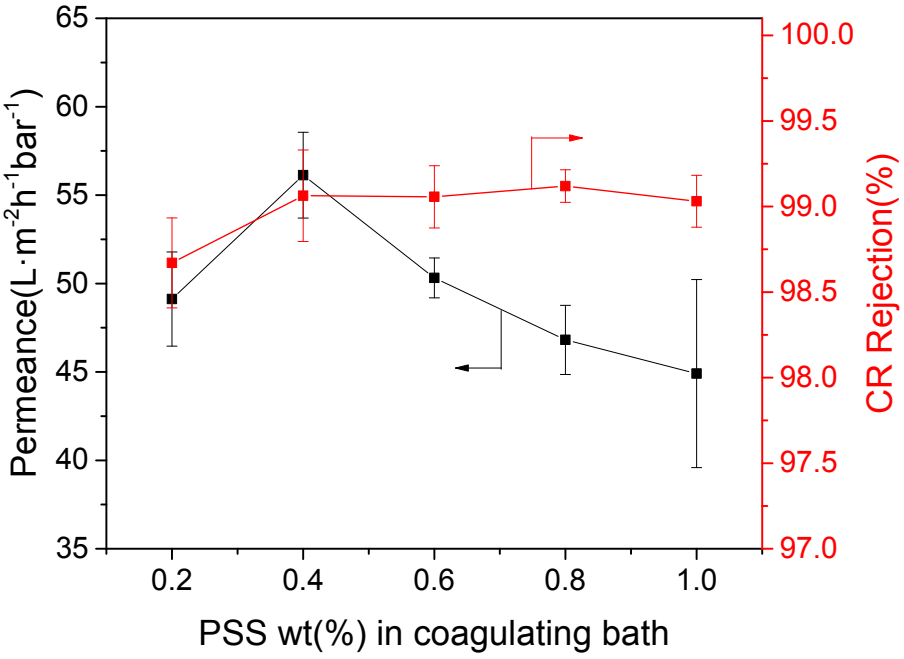


Figure S8. Effect of PSS wt% in coagulating bath on CR permeance and rejection of M3. (Membrane preparation and test conditions: $Zn(acac)_2$ in dope solution: 12wt%; ZIF-8 assembly time: 1h; operating pressure: 2bar)

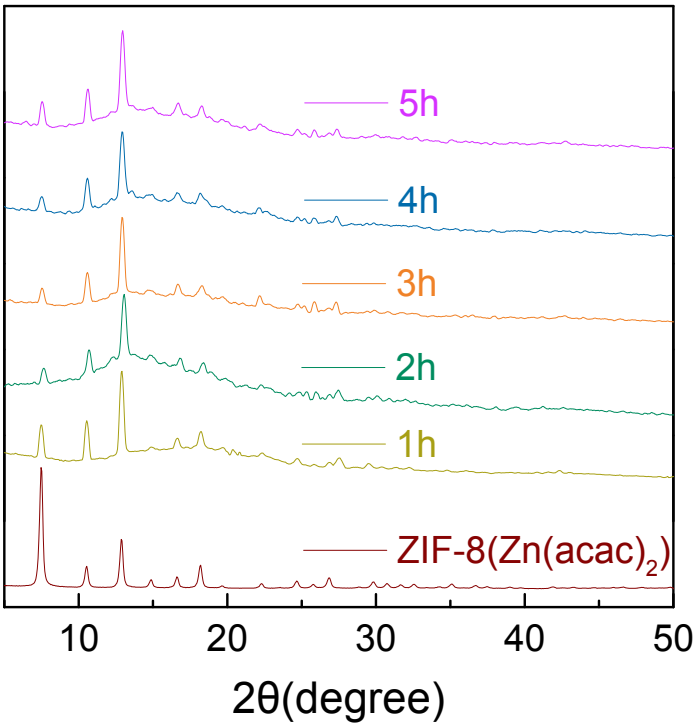


Figure S9. XRD patterns of M3 with different ZIF-8 assembly time.

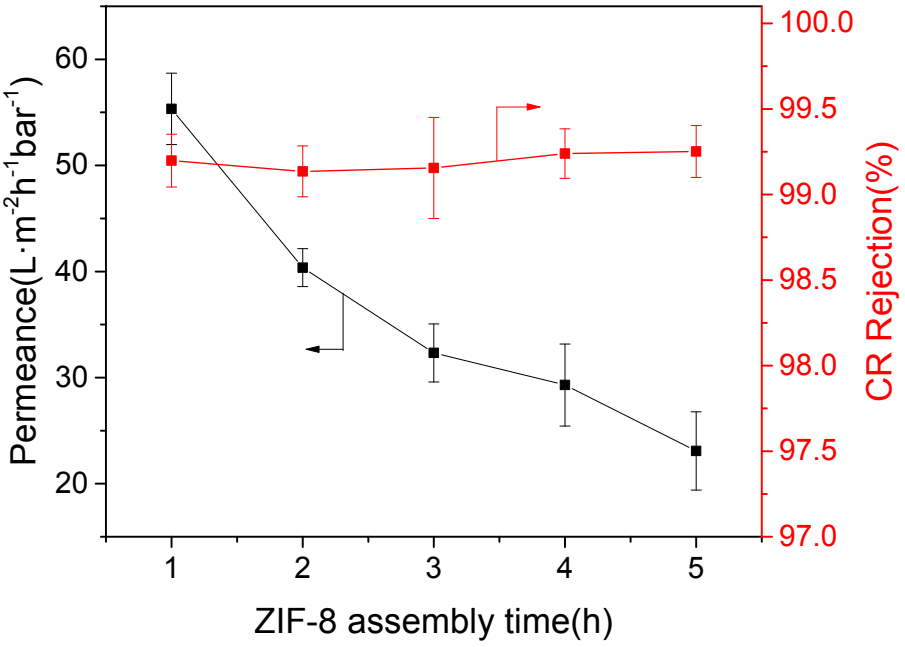


Figure S10. Effect of ZIF-8 assembly time on CR permeance and rejection of M3. (Membrane preparation and test conditions: $Zn(acac)_2$ in dope solution: 12wt%; PSS in coagulating bath: 0.4wt%; operating pressure: 2bar)

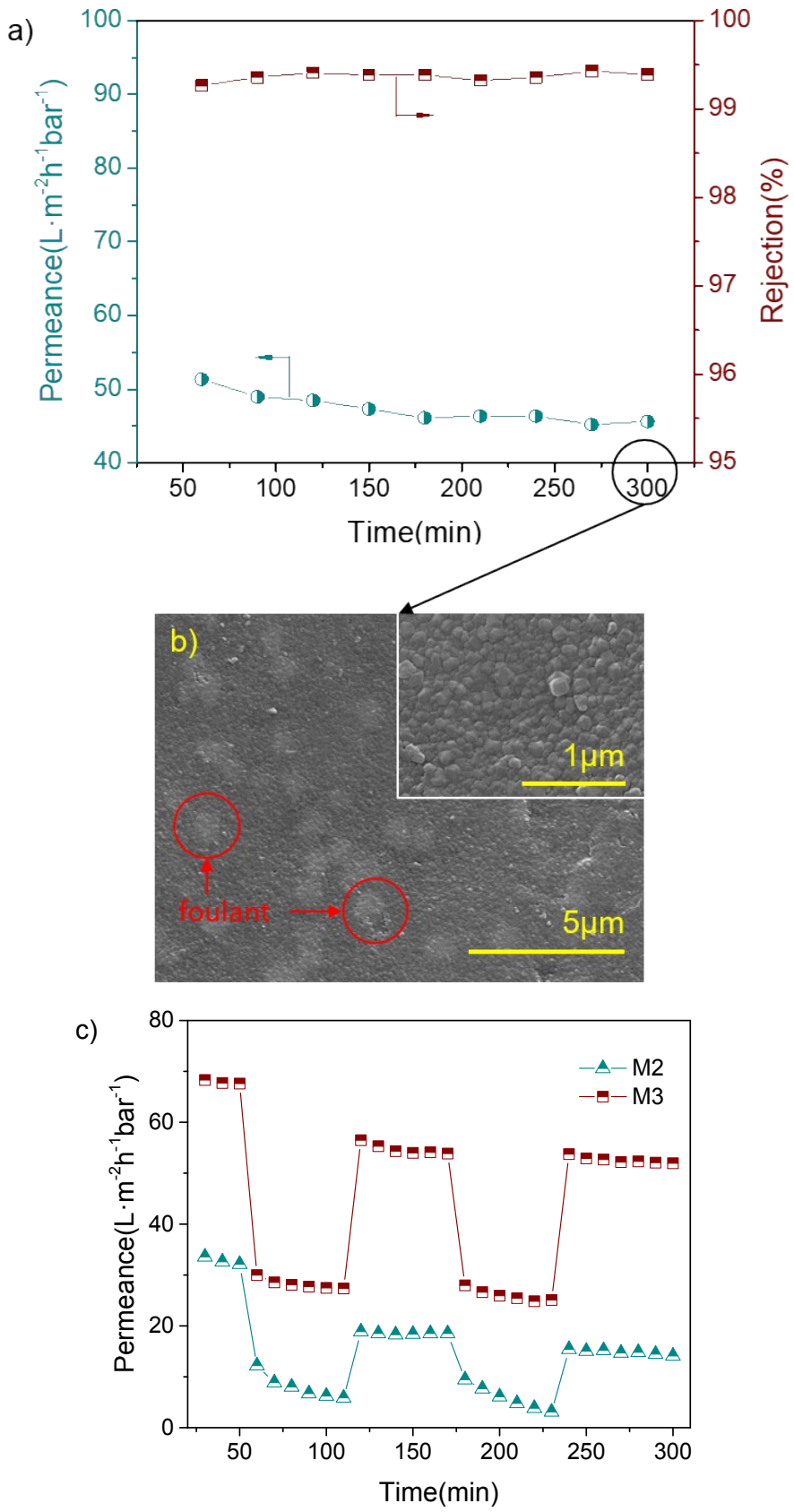


Figure S11. (a) Longtime stability of M3, (b) SEM image of M3 surface after 300-min-long filtration, (c) anti-fouling performance of M2 and M3.

Table S3. Comparison of dye removal property of different membranes.

Membrane	Dye molecule	Permeance (LMH/bar)	Rejection (%)	Pressure (bar)	Reference
PSS/ZIF-8/PAN	methyl blue	26.5	98.6	5	1
PA/ZIF-8/PSf	congo red	2.7	99.2	10	2
ZIF-8/PES	rose bengal	1.3	98.9	ungiven	3
ZIF-8/PES	rose bengal	37.5	98.5	2	4
PA/PSS/ZIF-8/PAN	reactive black 2	14.9	99.2	4	5
brGO/PVDF	methyl blue	19.6	99.2	5	6
AGO/PC	brilliant blue	8.7	99	5	7
ZIF-11/PAN	methyl blue	46.4	98.4	2-8	8
PA/UIO-66/PAN	rose bengal	15.4	~100	5	9
PEI/ZIF-8/PAN	congo red	37.4	99.2	2	10
TMC-PEI/cellulose	direct yellow 50	5.4	99	4	11
PEI/CMCNa/PP	victoria blue B	12.8	99.6	3	12
Chitosan/nanoclay/PVDF	methyl blue	50	75	1	13
UIO-66@GO/PES	direct red 80	16	98.6	3	14
SiO_2/CS/PDA/PS	methyl blue	5.2	99.5	4	15
Catechol-PEI/PAN	bromothymol blue	5.9	99.6	5	16
D-A-HNTs@PVDF	direct blue 14	34.2	93.7	1	17
DEA/PA/PSf	methyl blue	13.1	99.8	5	18

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