

Ultra-thin Trinity Coating Enabled by Competitive Reactions for Unparalleled Molecular Separations

*Yanqiu Zhang^a, Jun Ma^b, Lu Shao^{*a}*

^aMIIT Key Laboratory of Critical Materials Technology for New Energy Conversion and Storage, State Key Laboratory of Urban Water Resource and Environment, School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin 150001, China.

^bState Key Laboratory of Urban Water Resource and Environment, School of Environment, Harbin Institute of Technology, Harbin, 150090, China.

Correspondence to: shaolu@hit.edu.cn

1. Experimental

1.1 Materials

N-methyl-2-pyrrolidone (NMP), rose bengal (RB), dopamine, tannic acid, gallic acid and O, O' -bis (2-aminopropyl) polypropylene glycol-block-polyethylene glycol-block-polypropylene glycol (Jeffamine® ED-600, MW=600) were received from Sigma-Aldrich. Methyl blue (MB), bromothymol blue (BTB) and crystal violet (CV), Na₂SO₄, MgSO₄, NaCl, and MgCl₂ were obtained from Tianjin (China). Tris(hydroxymethyl)amino methane (Tris), congo red (CR), Co(NO₃)₂, Cu(NO₃)₂, Ni(NO₃)₂, FeCl₃, polyethyleneimine (PEI, average molecular weight=600 g/mol), bovine serum albumin (BSA, Mn=68,000), and humic acid (HA) were obtained from Aladdin Industrial Co., Ltd. Amino functional polyhedral oligomeric silsesquioxanes (POSS-NH₂) was received from Hybrid Plastics Inc. Deionized water as eco-friendly solvent was homemade.

1.2 Preparation of ternary coated nanoporous membrane.

Previously we reported the preparations of PAN-H porous substrates.¹ Briefly, 18 wt% PAN/NMP solutions which contain 2 wt% PEG-800 were cast on a glass plate with stainless steel scraper. Then phase conversion by immersing in water, PAN membranes were fabricated. After, PAN membranes were placed in the 10 wt% NaOH and 0.5M HCl solutions successively, and then placed in water overnight to obtain PAN-H membranes. The SEM and EDX of PAN-H membrane were given in Fig. S1. The membrane show high permeance (183 L m⁻² h⁻¹ bar⁻¹) and low rejection(17.1%) for BTB

with water contact angle 40.2°. The ternary coated nanoporous membrane (pDA/PEI/TMIs) was prepared in a clean assembly room (Fig. 1). 0.2 g dopamine, (0.2-0.8) g PEI and 0.05 mol transition metal ion were added to the 100 mL of Tris buffer solution (pH=8.5, 50 mM). After that, the porous substrate was immersed and gently shaken in the already prepared dip-coating solution for a certain time (2 h, 4 h, 6 h, 8 h). Finally, the membranes were rinsed with deionized water five times. In addition, a similar approach was implemented for a control pDA coated sample and GA/TA ternary system NF membrane. For the UV-vis measurements, the DA ternary coating solution remained for shock reaction 12 h and took the solution for the UV-vis measurements in a certain reaction time. The same method was used to prepare solution without transition metal ion (pDA/PEI) and various others ternary coating system for membrane fabrications.

1.3 Characterizations:

Attenuated total reflection fourier transformed infrared spectroscopy (ATR-FTIR) were carried out using a Spectrum One instrument (Perkin Elmer, USA). X-ray photoelectron spectroscopy (XPS) analysis was determined using Shimadzu AXIS Ultra DLD with an Al-K α X-ray source and the photoelectron take-off angle were 90° in regard to the specimen surface. Scanning electron microscopy (SEM) images were collected from Hitachi S-4500. The specimens were fractured by immersing into liquid nitrogen to observe the cross-sectional SEM images. Atomic force microscopy (AFM) images were measured by Solver P47 AFM (Russia). Water contact angles were

recorded by a SL 200KB measure system. The zeta potentials were recorded by adjusting the solution pH from 3 to 10 by 0.1 mol⁻¹ HCl or NaOH. For the stability test, the membranes were treated with acid and alkali (0.05 M HCl or NaOH) 24 h. Inductively Coupled Plasma Mass Spectrometry (ICP-MS) was performed using a Bruker 820-MS instrument (Bruker).

1.4 Permeance and rejection tests:

The permeance of our membranes were conducted on a homemade dead-end filtration system. The feed dye solutions (50 ppm) were poured into the measurer with valid membrane test area of 21.2 cm⁻² under 5 bar pressure derived from a nitrogen tank. The permeance was calculated using the Equation1.

$$P = \frac{V}{A \times t \times \Delta P} \quad (1)$$

Where P corresponds to the permeance (L m⁻² h⁻¹bar⁻¹), V , A , and t refer to the volume of permeate, effective membrane area, operation time, respectively. ΔP is trans-membrane pressure (bar)

The ternary coated membranes' solute rejections were calculated by Equation 2.

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \quad (2)$$

Where R corresponds to rejection, C_p and C_f refers to the concentrations of dyes in permeate and feed solution, which were determined by a UV-vis Cintra20-GBC measurer. The conductivity of salt aqueous solution was analyzed using a conductivity

meter (INESA Scientific Instrument, DDB-303A, China). During the process of separation test of fabricated nanofiltration membrane, the pure water was allowed to permeate about 1 h until its performance is stable, and then the dye solution was poured into the cell, the rejection of dyes were caught after 2 h. Record the data every 10 minutes and calculate the average value after stabilization. Alkaline solutions, which have high capability to dissolve dyes, are widely used to regenerate membranes after fouled by dyes. Thus, a strong alkaline solution (pH=11) was employed to removed contamination from the membrane after the separation process.

1.5 Dye/salt mixture separations

Dye/salt mixture separation performances of the membrane was observed using BTB and NaCl. The concentration of dye and salt was correspondingly fixed at 50 ppm and 1 g/L during the experiment. At the same time, the influence of salt concentration was observed by varying NaCl concentration in the range of 500-3000 ppm with the 50 ppm BTB aqueous solution at pH=7.

1.6 Antifouling property of the membrane

The antifouling property of the membrane was investigated using organic foulant BSA and HA solution. The membrane was compacted with DI-water at 5 bar for a certain time to achieve a stable state and the pure water permeance of the original membrane (J_0) was measured. Then, the fouling experiment was carried out with 1 g/L BSA aqueous solution as feed solution for another a certain time and the steady value of the permeance was noted as J_1 . The normalized permeance J_1/J_0 refers to the flux

declining ratio during the fouling process. After that, the fouled membrane was thoroughly flushed by DI-water for a certain time. Finally, the pure water permeance (J_2) of the cleaned membrane was measured for a certain time. The above procedure was repeated for 3 times to evaluate the permeance recovery ratio (FRR), which was determined by Equation 3.²

$$FRR = \frac{J_2}{J_0} \times 100\%$$

(3)

During the interception test of charged dyes may be adsorbed on the surface of the membrane and influence the performance analysis. The following formula can be used for quantitative adsorption to determine the influence of adsorption:³

$$Ads = \frac{V_F C_F - (V_R C_R + V_P C_P)}{V_F C_F} \quad (4)$$

Ads is concentration of adsorption percentage. C_F , C_P and C_R , corresponds to the concentration of raw material liquid, the concentration of permeable liquid and the concentration of residual liquid in the upper layer after separation. V_F , V_P and V_R are respectively raw material liquid volume, permeable liquid volume and residual liquid volume.

1.7 Pore size and pore size distribution measurement.

The calculations of mean pore size and pore size distribution were based on the theory established by Michaels's and Singh's work.⁴ It is assumed that the solute rejection relates with solute size using log normal probability function, which can be described in the following Equation 5.

$$R_T = \text{erf}(y) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^y e^{-\frac{u^2}{2}} du, \text{ with}$$
$$y = \frac{\ln r_s - \ln \mu_s}{\ln \sigma_s} \quad (5)$$

Where R_T is the solute rejection, r_s represents the solute radius, μ_s is the geometric mean radius of solute at $R_T = 50\%$, σ_g is the geometric standard deviation of μ_s which is defined as the ratio of the solute radius at $R_T = 84.13\%$ and $R_T = 50\%$. The relationship between R_T and r_s can be expressed using Equation 6.

$$F(R_T) = A + B \ln r_s \quad (6)$$

The values of σ_g and μ_s determine the sharpness and the position of the rejection curves, respectively.

0.2 g L⁻¹ solutions of PEGs (Mw=200, 400, 600, 800, 1000, 1500 and 2000 g mol⁻¹) were applied to determine the solute rejection. The relationship between molecular weight (Mw or M_w) and stokes radius of these known solutes can be expressed by the below Equation 7.⁵

$$\log r = -1.52517 + 0.47956 \log M_w \quad (7)$$

Without taking into consideration of the effects of the steric and hydrodynamic interaction between solute and pores on the solute rejection, the mean effective pore radius (μ_p) and the geometric standard deviation (σ_p) are assumed as the same as μ_s and σ_g . Hence, the pore size distribution of NF membranes can be depicted as the following probability density function:

$$\frac{dR(d_p)}{d(d_p)} = \frac{1}{d_p \ln \sigma_p \sqrt{2\pi}} \exp \left[-\frac{(\ln d_p - \ln \mu_p)^2}{2(\ln \sigma_p)^2} \right] \quad (8)$$

Where d_p is the pore size in diameter. μ_s is the geometric mean radius of the solute at $R=50\%$, σ_g is the geometric standard deviation about us, which is defined as the ratio of the solute radius at $R=84.13\%$ and $R=50\%$. PEG concentrations were determined by total organic carbon analyser (TOC V CPN, Shimadzu, Japan).

The Stokes radii (m) of PEGs were determined based on molecular weights.⁶

$$r_s = 16.73 \times 10^{-12} \times M_w^{0.557} \quad (9)$$

Where r_s is the corresponding stokes radii of the PEGs and M_w (g mol⁻¹) is the molecular weight of the PEGs. The molecular weights of PEGs used in this study were 200, 400, 600, 800, 1000, 1500 and 2000 g mol⁻¹.

We thank the reviewer for this question. To determine the chemical compositions of the selective layers, a relative composition (ratio) of dopamine, amino substance (AS) and transition metal ions (TMIs) was analyzed based on XPS tests. The results showed

that the selective layer contains the elemental composition of C, N, O, and transition metal ions. The relative composition (ratio) was then calculated according to the chemical formula of the structural units of polymerized dopamine and PEI unit and the XPS results:

$$x_{dopamine}:y_{PEI}:z_{TMI} = \frac{m}{2} : \frac{n - \frac{m}{2}}{11} : p \quad (10)$$

Where m, n and p were the element content of oxygen (O), nitrogen (N) and transition metal ions (TMI), respectively, which were obtained from XPS test. The relative composition (ratio) of dopamine: PEI unit: Co for pDA/PEI/Co²⁺ membrane was 7.6:4.5:1. This method can only give relatively rough ratio, because of the complex reaction system of amino substances with dopamine and metal ions, and the structural formulas of the polymer PEI and polydopamine are difficult to determine exactly. We have added this in revised manuscript as Supporting Information.

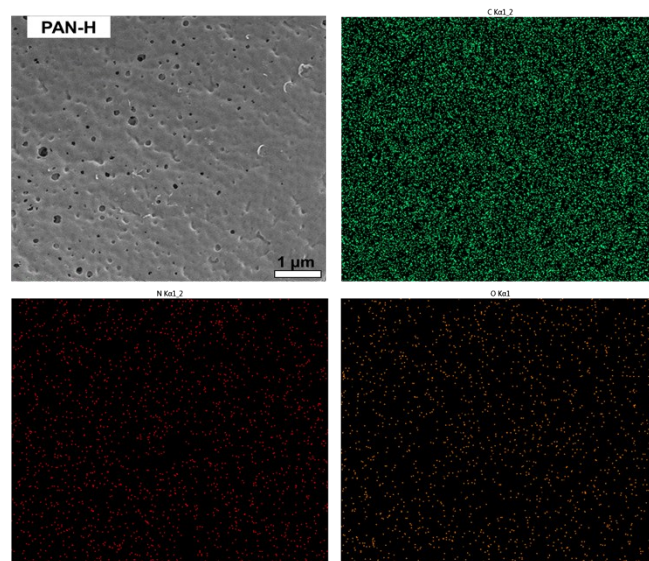


Figure S1. The substrate porous membrane (PAN-H) utilized in this manuscript and the

morphologies, the element distribution on the surface.

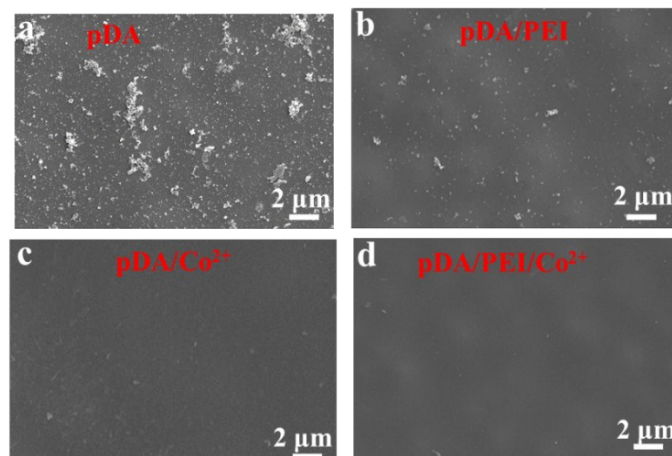


Figure S2. SEM images of pDA, pDA/PEI, pDA/Co²⁺, pDA/PEI/Co²⁺ coated membranes' surfaces.

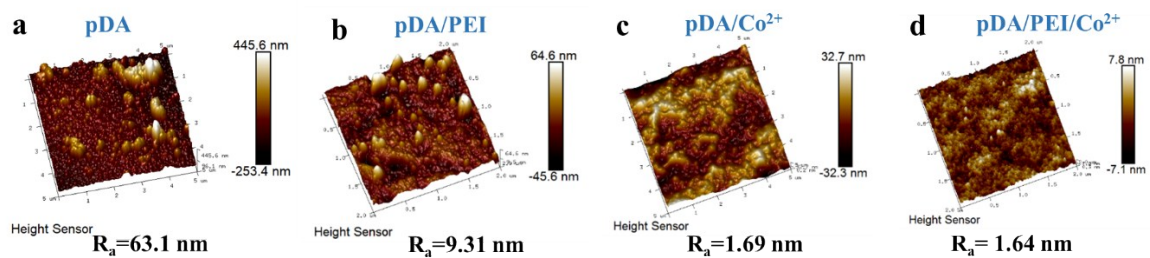


Figure S3. AFM of the pDA, pDA/PEI, pDA/Co²⁺, pDA/PEI/Co²⁺ coated membranes.

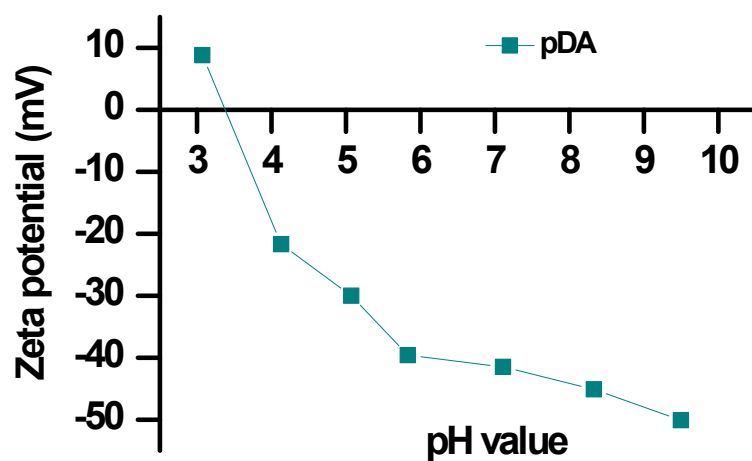


Figure S4. Zeta potentials of the unary (pDA) coated membranes.

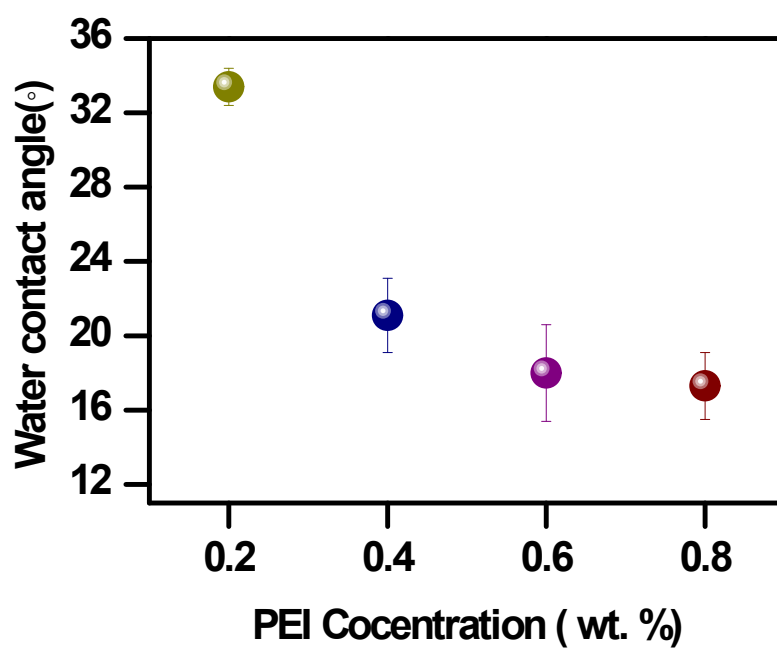


Figure S5. Water contact angle (WCA) of the ternary coated membranes with different concentrations of PEI.

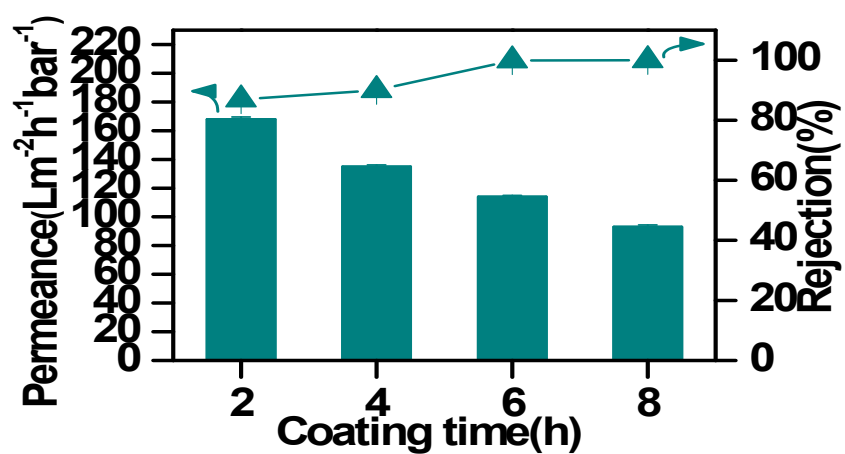


Figure S6. The effects of the reaction time on the performances of the pDA/PEI/Co²⁺ ternary coated membrane.

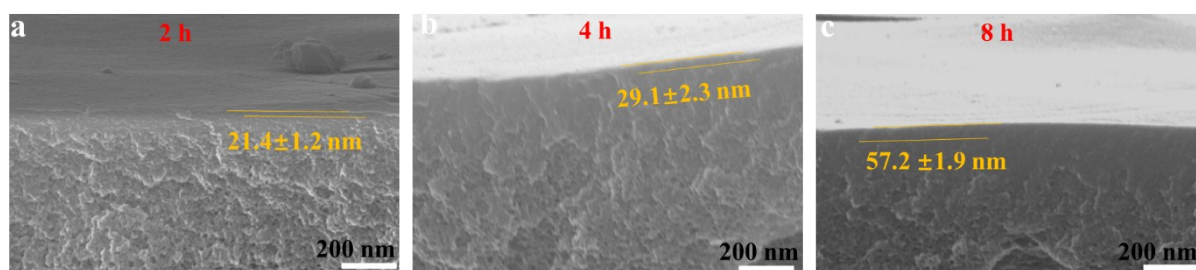


Figure S7. The cross-sectional SEM image of pDA/PEI/Co²⁺ ternary coated membranes with the different reaction time.

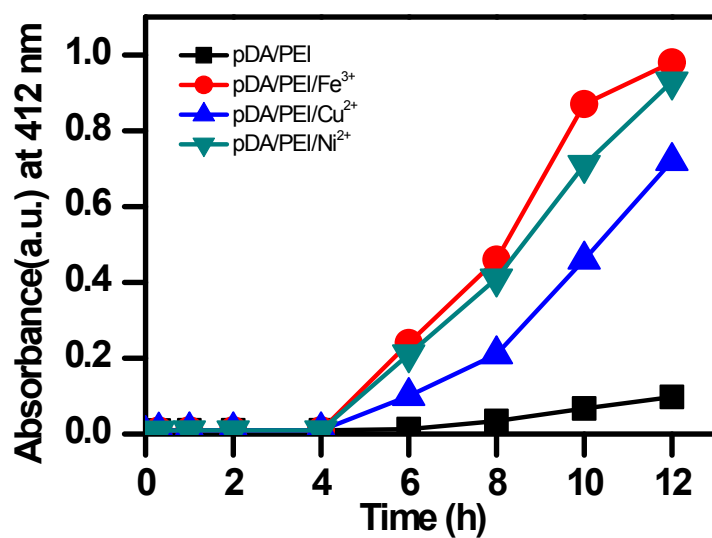


Figure S8. Time-dependence of UV-Vis absorbance at 412 nm for various diluted pDA/PEI and pDA/PEI/TMIs solutions.

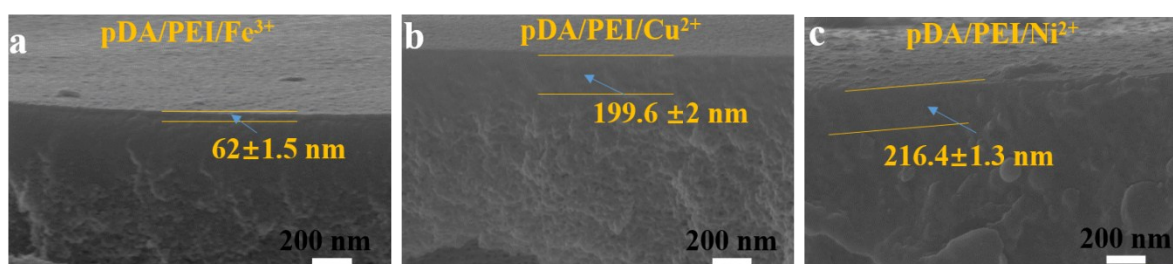


Figure S9. Cross-sectional SEM image of the pDA/PEI/Fe³⁺, pDA/PEI/Cu²⁺, pDA/PEI/Ni²⁺ coated membranes.

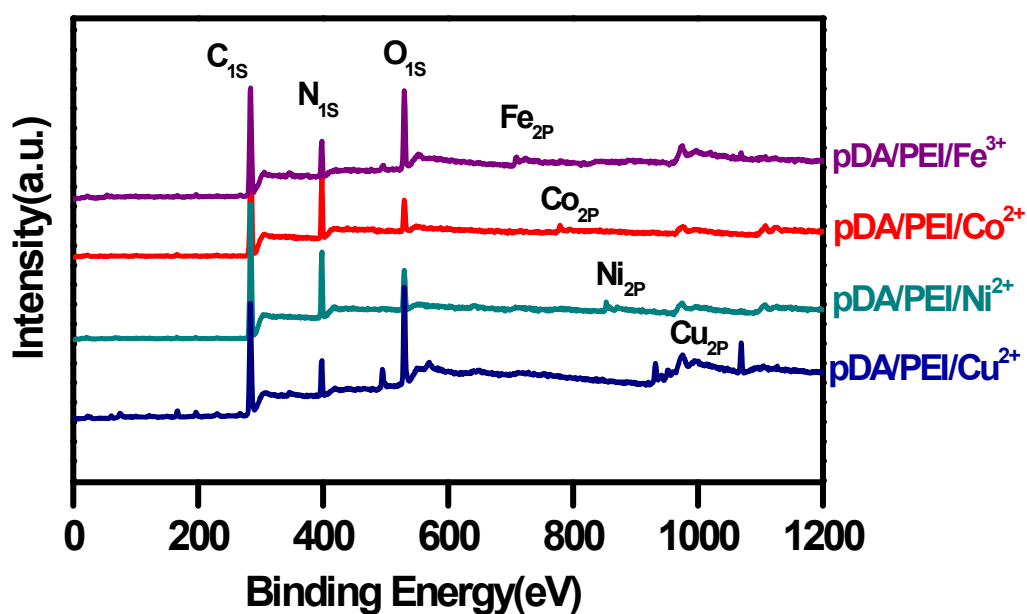


Figure S10. XPS of pDA/PEI/TMIs

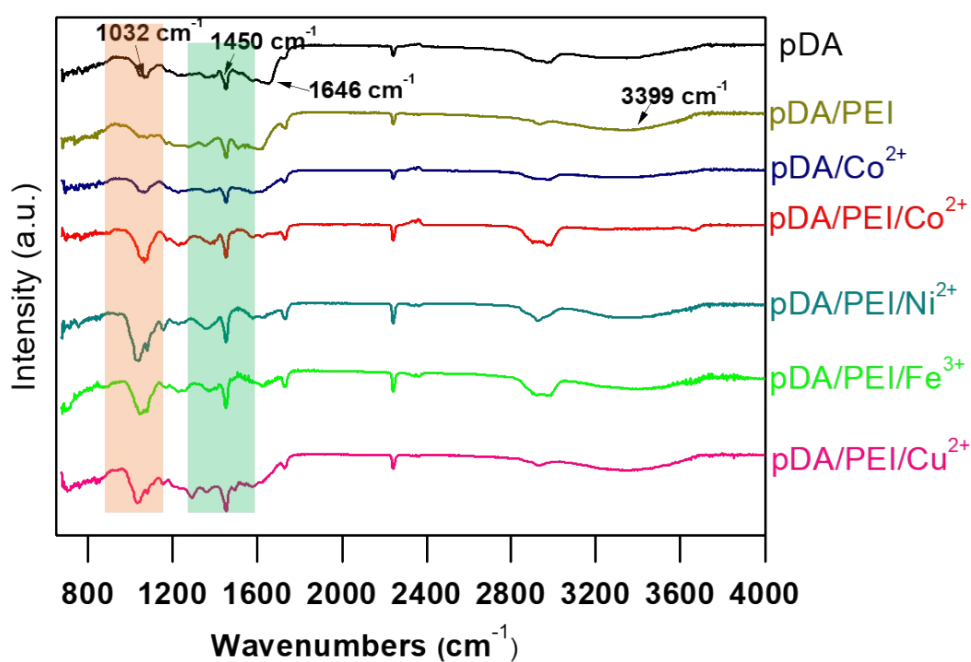


Figure S11. The FT-IR image of pDA, pDA/PEI, pDA/Co²⁺, pDA/PEI/Co²⁺, pDA/PEI/Ni²⁺, pDA/PEI/Fe³⁺, pDA/PEI/Cu²⁺ coated membranes.

The FT-IR spectrum of pDA coated membrane showed a strong peaks at ~1646 and ~1450 cm⁻¹ resulted from the aromatic rings in the pDA. After PEI grafting, the peak intensity at ~3399

cm^{-1} dramatically increased, which can be a merged peak from amine $-\text{NH}$ of PEI. After the transition metal modification, pDA/PEI/TMIs coated membranes exhibited an enhance peak at $\sim 1032 \text{ cm}^{-1}$ comparing to coordination bond formed by metal ions with $-\text{OH}$ and $-\text{NH}$.

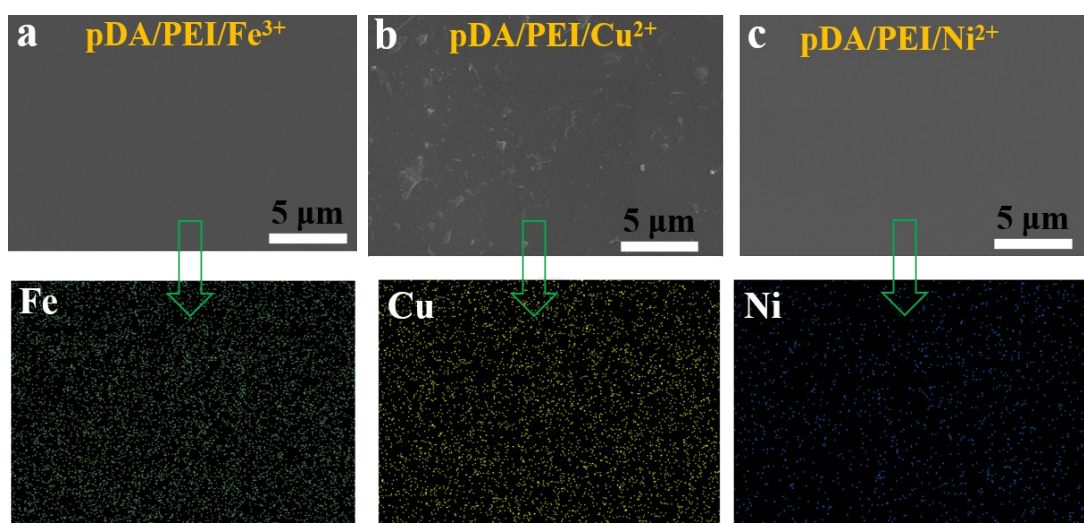
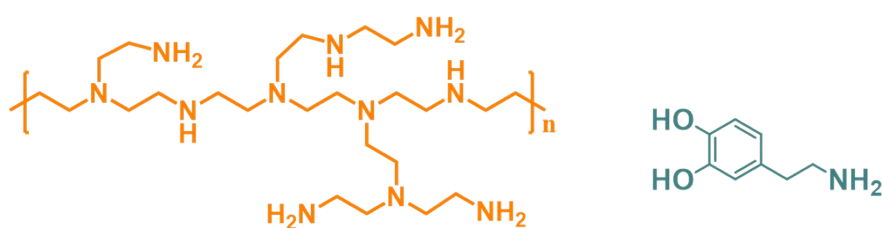


Figure S12. The SEM image and EDX mapping of pDA/PEI/ Fe^{3+} , pDA/PEI/ Cu^{2+} , pDA/PEI/ Ni^{2+} coated membranes.



Chemical Formula: $y \text{ C}_{26}\text{H}_{65}\text{N}_{11}$

Chemical Formula: $x \text{ C}_8\text{H}_{11}\text{NO}_2$

Figure S13. The structural formulas of the polymer PEI and polydopamine unit.

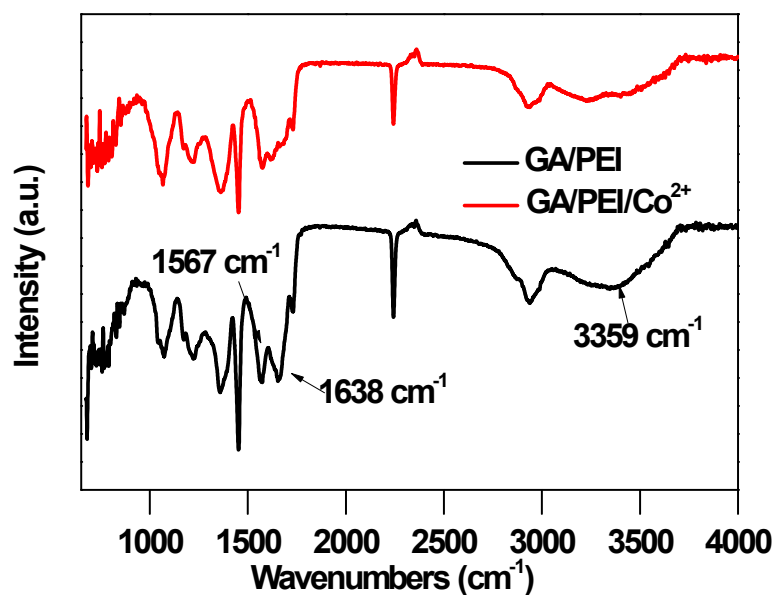


Figure S14. The FT-IR image of GA/PEI, GA/PEI/Co²⁺ coated membranes.

For GA/PEI coated membrane, peaks at 1638 cm⁻¹ and 1567 cm⁻¹ were belong to the C=O stretching peak and C-N stretching peak, respectively, indicating the formation of -CO-NH-. Furthermore. The peaks appeared around 3359 cm⁻¹ stretching peaks of -NH₂, indicating the formation of the GA/PEI coatings. Furthermore, the peak around 3359 cm⁻¹, 1638 cm⁻¹ and 1567 cm⁻¹ became weaker after adding Co²⁺. Coordination reaction of Co²⁺ with GA and PEI occurred. The GA/PEI/Co²⁺ ternary coated membranes was fabricated.

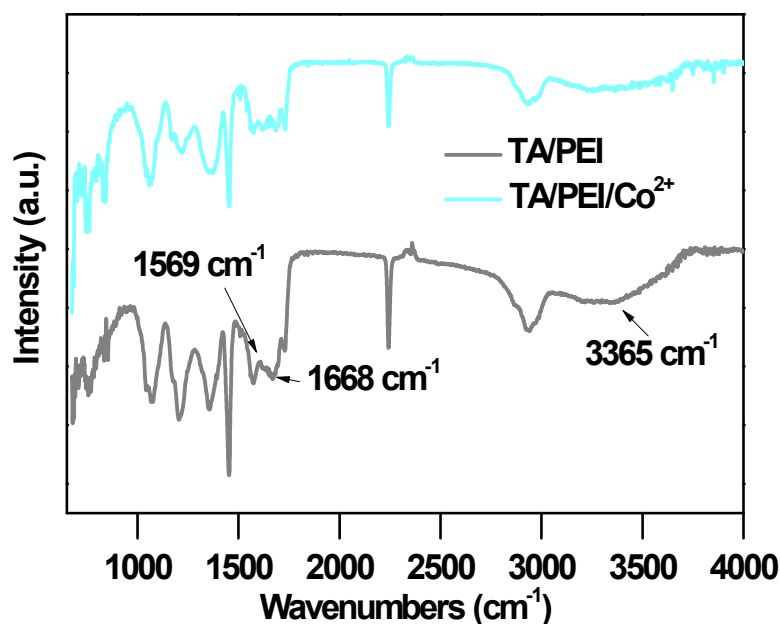


Figure S15. The FT-IR image of TA/PEI, TA/PEI/Co²⁺ coated membranes.

For GA/PEI membrane, peaks at 1668 cm⁻¹ and 1569 cm⁻¹ were belong to the C=O stretching peak and C-N stretching peak, respectively, indicating the formation of -CO-NH-. Furthermore. The peaks appeared around 3365 cm⁻¹ stretching peaks of -NH₂, indicating the formation of the TA/PEI coatings. Furthermore, the peak around 3365 cm⁻¹, 1668 cm⁻¹ and 1569 cm⁻¹ became weaker after adding Co²⁺. Coordination reaction of Co²⁺ with TA and PEI occurred. The trinity coating of TA/PEI/Co²⁺ membrane was successfully fabricated.

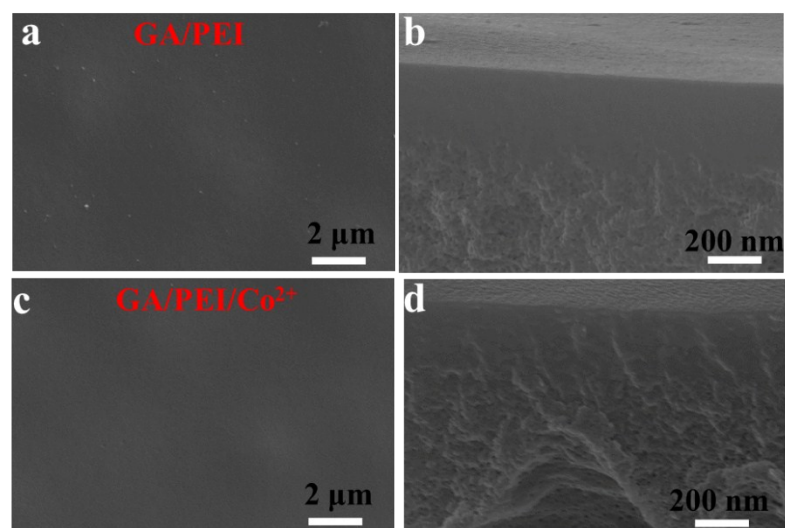


Figure S16. The SEM image and cross-sectional SEM image of the (a,b) GA/PEI and (c,d) GA/PEI/Co²⁺ coated membranes.

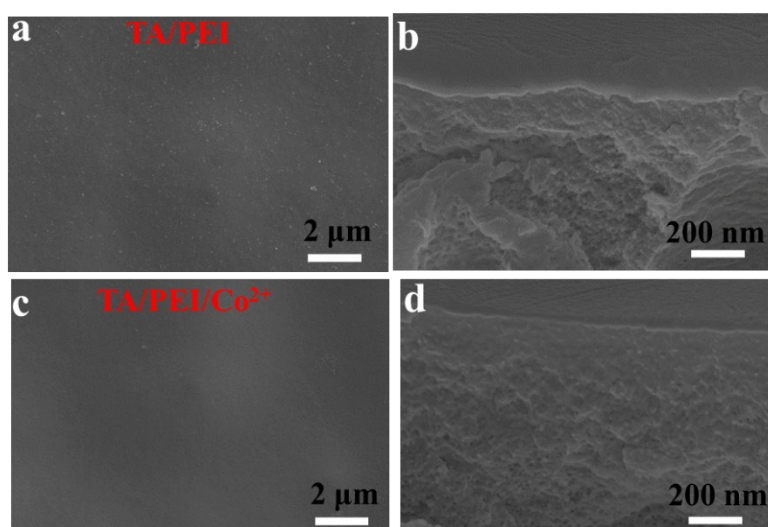


Figure S17. The SEM image and cross-sectional SEM image of the (a,b) TA/PEI and (c,d)TA/PEI/Co²⁺ coated membranes.

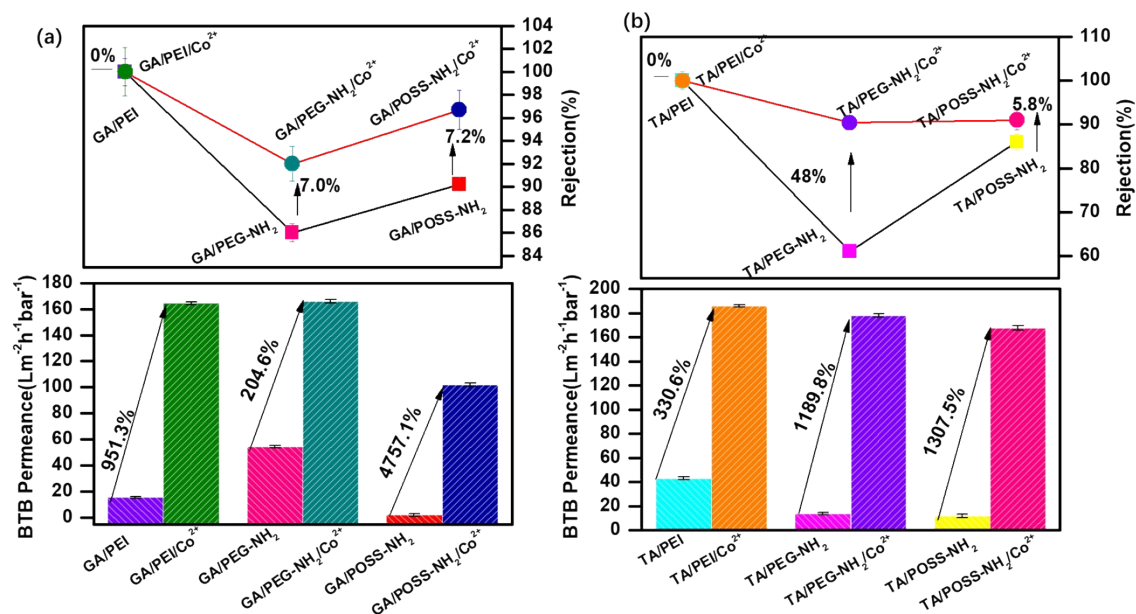


Figure S18. Nanofiltration performance of ternary competitive GA and TA systems consisting of different structural AS (linear polymer PEG-NH₂ and cage-like POSS-NH₂).

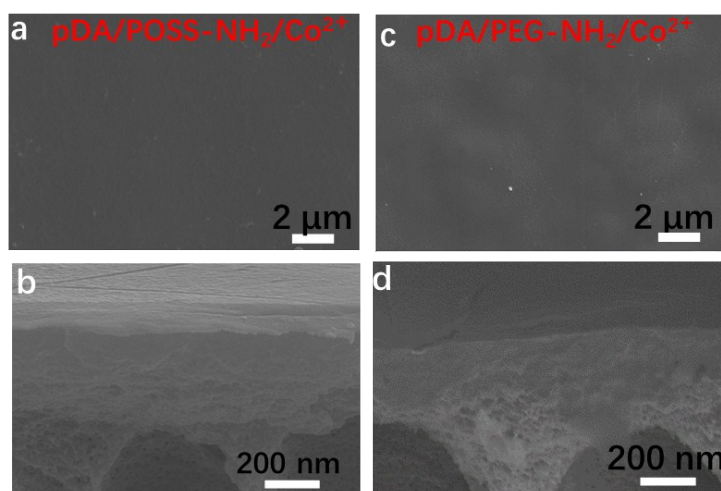


Figure S19. The SEM image and cross-sectional SEM image of the (a,b) pDA/POSS-NH₂/Co²⁺ and (c,d)pDA/PEG-NH₂/Co²⁺ coated membranes.

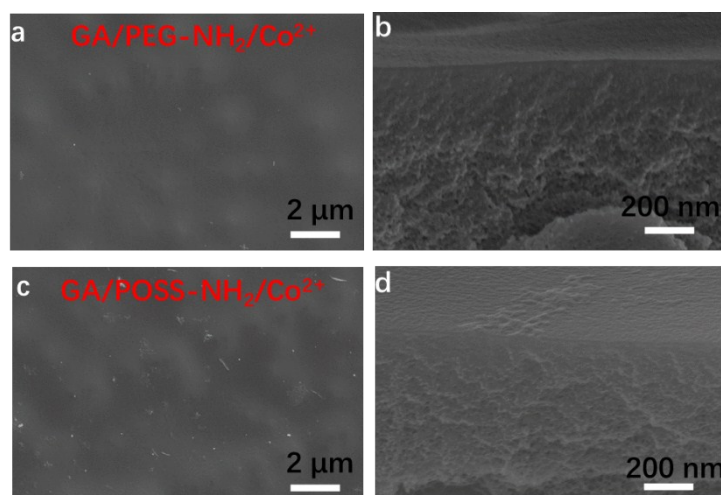


Figure S20. The SEM image and cross-sectional SEM image of the (a,b) GA/PEG-NH₂/Co²⁺ and (c,d) GA/POSS-NH₂/Co²⁺ coated membranes.

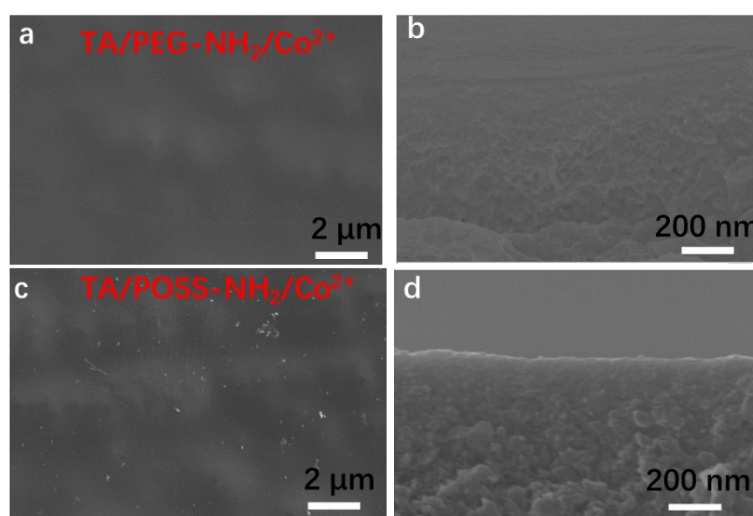


Figure S21. The SEM image and cross-sectional SEM image of the (a,b)TA/PEG-NH₂/Co²⁺ and (c,d) TA/POSS-NH₂/Co²⁺ coated membranes.

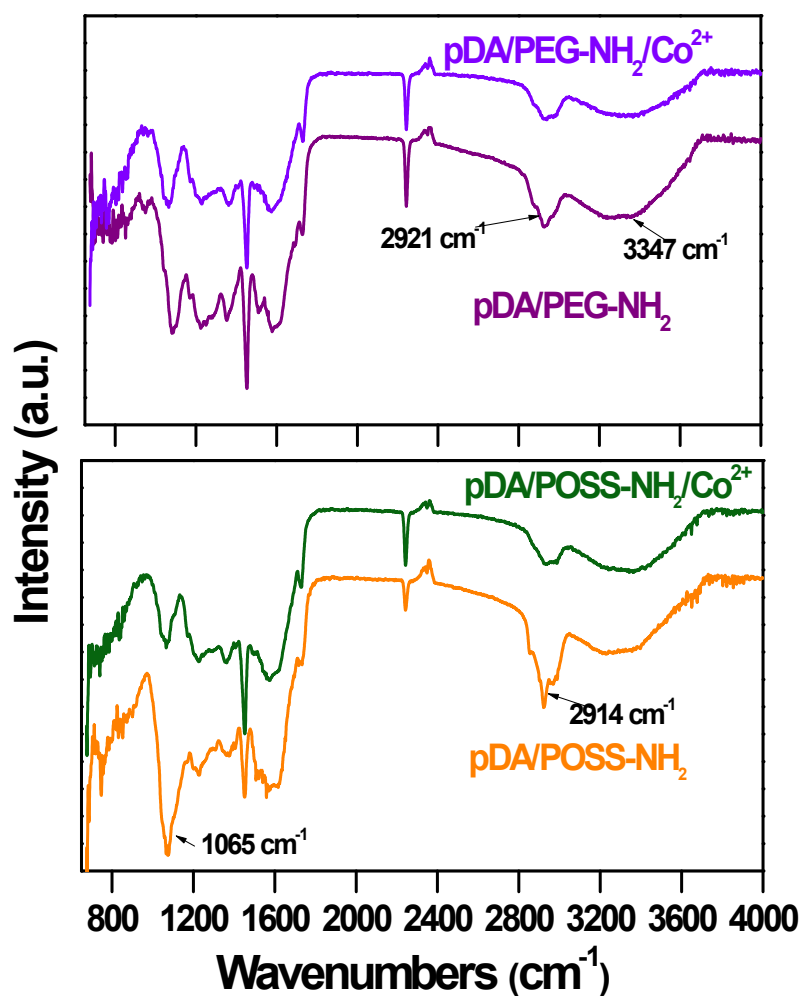


Figure S22. The FT-IR image of pDA/PEG-NH₂, pDA/PEG-NH₂/Co²⁺, pDA/POSS-NH₂, pDA/POSS-NH₂/Co²⁺ membranes.

For pDA/PEG-NH₂ membrane, peaks at 3347 cm⁻¹ is belong to stretching peaks of -NH₂ and -OH. Furthermore, the peak around 3347 cm⁻¹ became weaker after adding Co²⁺. Coordination reaction of Co²⁺ with pDA and PEG-NH₂ occurred. The ternary system pDA/PEG-NH₂/Co²⁺ membranes was fabricated. For pDA/POSS-NH₂ membrane, peaks at 1065 cm⁻¹ is belong to stretching peaks of -Si-O-, indicating the formation of the pDA/POSS-NH₂ coatings. Furthermore, the peak around 1065 cm⁻¹ and 2914 cm⁻¹ became weaker after adding Co²⁺.

Coordination reaction of Co^{2+} with pDA and POSS-NH₂ occurred. The ternary system pDA/POSS/ Co^{2+} membranes was fabricated.

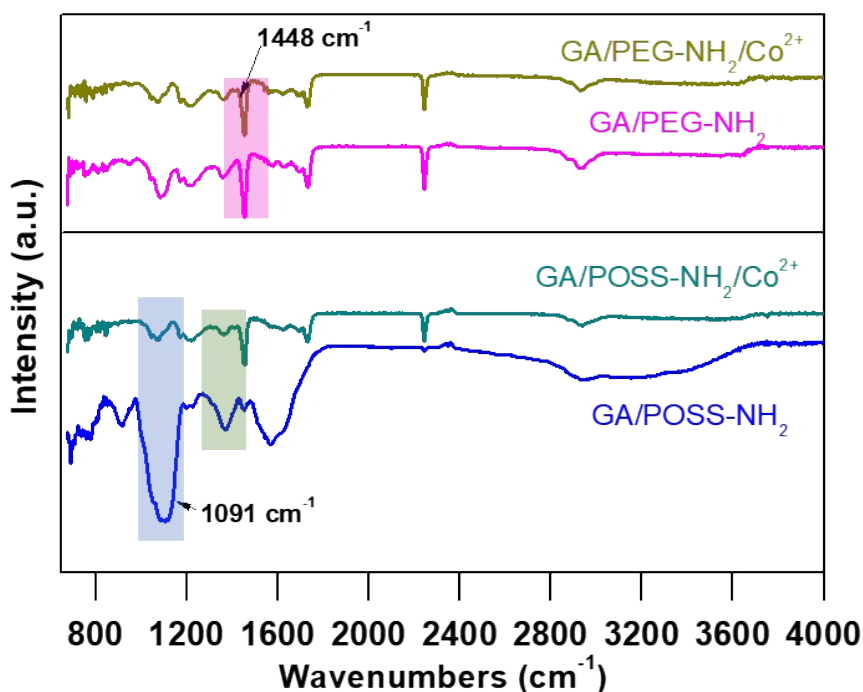


Figure S23. The FT-IR image of GA/PEG-NH₂, GA/PEG-NH₂/Co²⁺, GA/POSS-NH₂, GA/POSS-NH₂/Co²⁺ membranes.

For GA/PEG-NH₂ membrane, peaks at 1448 cm⁻¹ is belong to stretching peaks of C=O. Furthermore, the peak around 1448 cm⁻¹ became weaker after adding Co²⁺. Coordination reaction of Co²⁺ with GA and PEG-NH₂ occurred. The ternary system GA/PEG-NH₂/Co²⁺ membranes was fabricated. For GA/POSS-NH₂ membrane, peaks at 1091 cm⁻¹ is belong to stretching peaks of -Si-O-, indicating the formation of the GA/POSS-NH₂ coatings. Furthermore, the peak around 1091 cm⁻¹ became weaker after adding Co²⁺. Coordination reaction of Co²⁺ with GA and POSS-NH₂ occurred. The ternary system GA/POSS/Co²⁺ membranes was fabricated.

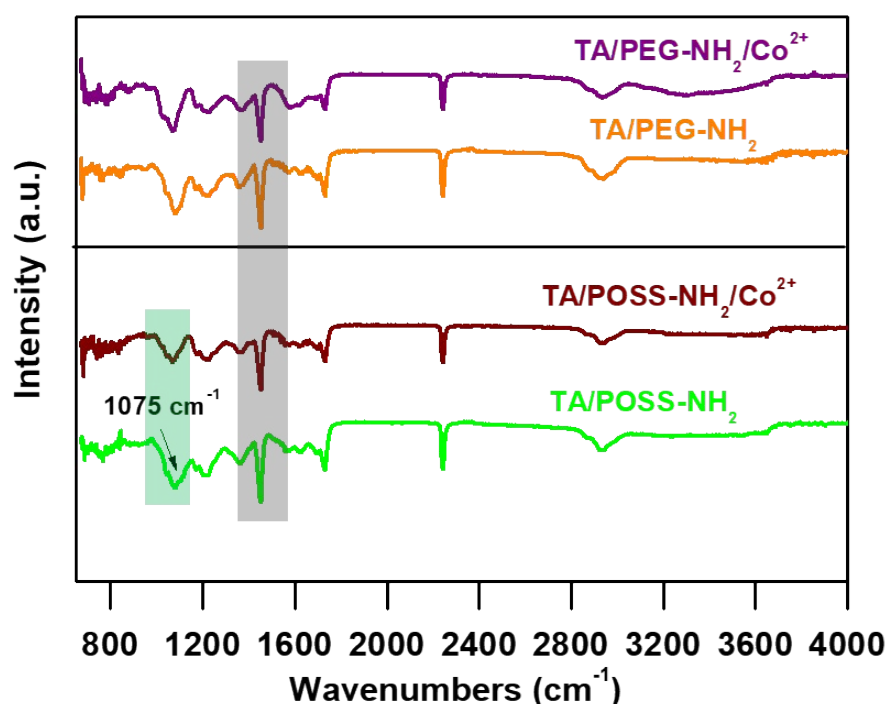


Figure S24. The FT-IR image of TA/PEG-NH₂, TA/PEG-NH₂/Co²⁺, TA/POSS-NH₂, TA/POSS-NH₂/Co²⁺ membranes.

For TA/PEG-NH₂ membrane, peaks at 1502 cm⁻¹ is belong to stretching peaks of C=O. Furthermore, the peak around 1502 cm⁻¹ became weaker after adding Co²⁺. Coordination reaction of Co²⁺ with TA and PEG-NH₂ occurred. The ternary system TA/PEG-NH₂/Co²⁺ membranes was fabricated. For TA/POSS-NH₂ membrane, peaks at 1075 cm⁻¹ is belong to stretching peaks of -Si-O-, indicating the formation of the TA/POSS-NH₂ coatings. Furthermore, the peak around 1075 cm⁻¹ became weaker after adding Co²⁺. Coordination reaction of Co²⁺ with TA and POSS-NH₂ occurred. The ternary system TA/POSS/Co²⁺ membranes was fabricated.

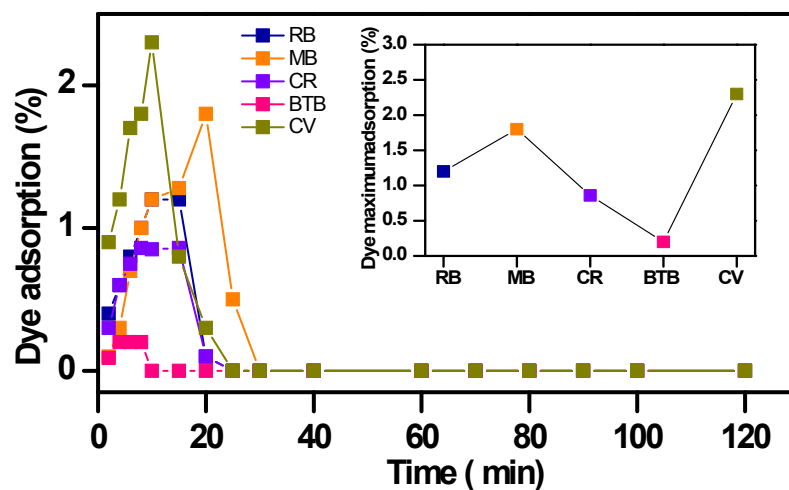


Figure S25. The dyes adsorption of pDA/PEI/Co²⁺ membrane with time. Inset: Dye maximum adsorption.

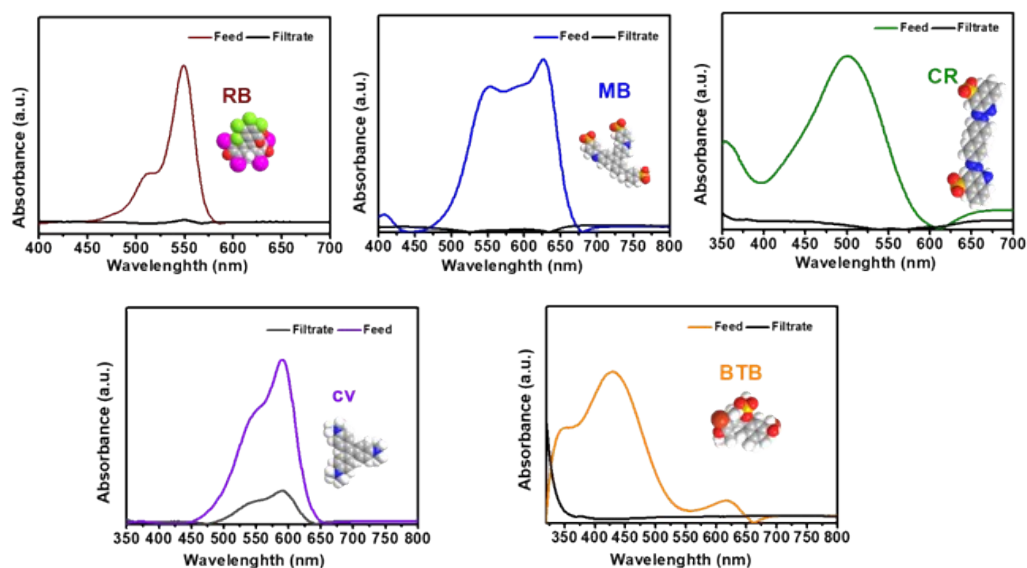


Figure S26. Ultraviolet-visible absorption spectra of RB, MB, CR, CV and BTB in feed and filtrate of pDA/PEI/Co²⁺ membrane.

Table S1. The elemental compositions of the pDA/PEI/Co²⁺ membrane with different amounts of PEI.

Samples	Element content (At. %)			
	C	N	O	Co
pDA/PEI_{0.2}/Co²⁺	74.2	17.92	7.48	0.4
pDA/PEI_{0.4}/Co²⁺	75.56	16.77	7.4	0.27
pDA/PEI_{0.6}/Co²⁺	74.22	20.13	5.29	0.35
pDA/PEI_{0.8}/Co²⁺	75.61	16.96	7.16	0.27

Table S2. Comparison of the separation performance of different membranes in the literatures.⁷⁻¹²

Membrane type	Dye molecule	Permeance (L m ⁻² h ⁻¹ bar ⁻¹)	Rejection (%)	Ref
COF-LZU1	Congo red	53.4	98.6	S7
ZIF-8/PSS	Methyl blue	26.5	98.6	S8
ZIF-8/PEI	Congo red	75.1	99.2	S9
PDA/PEI	Direct red	26.2	99.4	S10
CNT-GO	Direct yellow	11.3	99	S11
Sepro/NF-6	Congo red	13.7	99.93	S12
Sepro/NF-2A	Congo red	10.5	99.96	S12
pDA/PEI/Co ²⁺	Congo red	104	100	This work
	Bromothymol blue	114	100	This work

Table S3. The elemental compositions of the pDA/PEI/TMIs membranes

Samples	Element content (At. %)						
	C	N	O	Ni	Cu	Fe	Co
pDA/PEI/Ni²⁺	72.25	17.7	9.56	0.49			
pDA/PEI/Cu²⁺	68.23	10.09	20.43		1.25		
pDA/PEI/Fe³⁺	70.39	9.35	19.37			0.89	
pDA/PEI/Co²⁺	74.22	20.13	5.29				0.35

Table S4. The elemental compositions of the GA/PEI/Co²⁺ and TA/PEI/Co²⁺ coated membranes.

Samples	Element content (At. %)			
	C	N	O	Co
GA/PEI/Co²⁺	73.87	15.89	9.84	0.40
TA/PEI/Co²⁺	73.52	16.74	9.29	0.45

Table S5. The concentration of TMIs in the filtrate were test by ICP.

Samples	TMI content (ppb)			
	Fe	Co	Ni	Cu
pDA/PEI/TMI	none	none	none	none

Table S6. The elemental compositions of the pDA/PEI/Co²⁺ ternary coated membrane after NaOH and HCl treatment

Samples	Element content (At. %)			
	C	N	O	Co
After NaOH	74.31	19.91	5.46	0.32
After HCl	74.14	20.20	5.29	0.37

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