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# Supplementary Information

# An aquaporin-based vesicle-embedded polymeric membrane for low energy water filtration

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**Content**



## 1. Figures

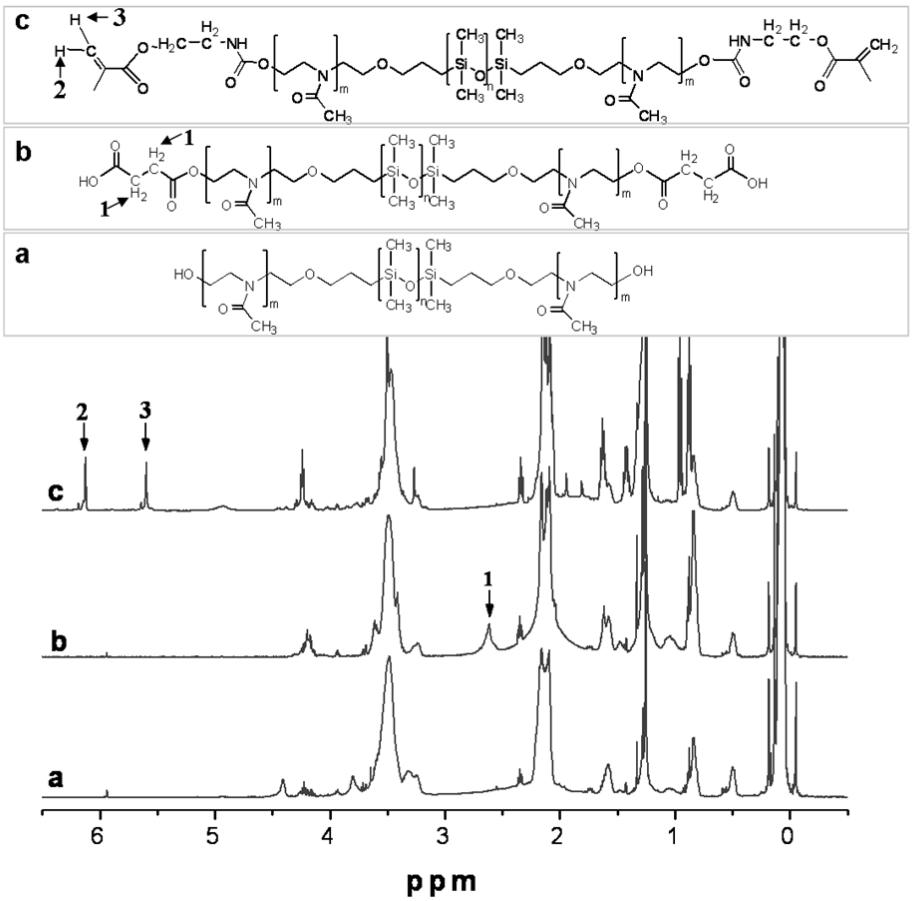


**Fig. S1.** $^{1}$H NMR spectrum of the triblock copolymers (a) hydroxyl terminated PMOXA-PDMS-PMOXA, (b) $P_1$: carboxyl terminated PMOXA-PDMS-PMOXA, and (c) $P_2$: methacrylate terminated PMOXA-PDMS-PMOX

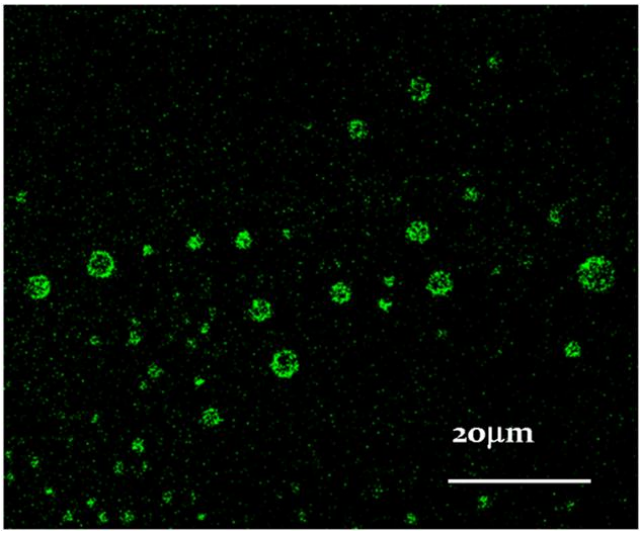


**Fig. S2** Morphologies of non-extruded polymersomes with fluorescent dye Coumarin-6 by confocal microscopy.

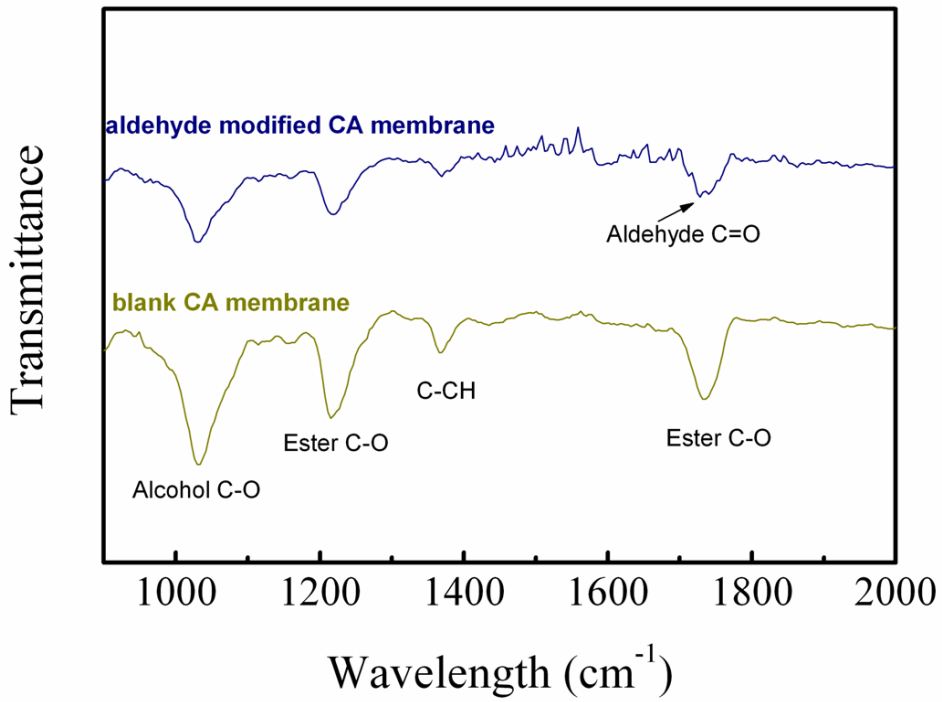


**Fig. S3** FTIR transmission spectra of the original CA and aldehyde functionalized CA membranes: a) Original CA, b) Aldehyde functionalization.

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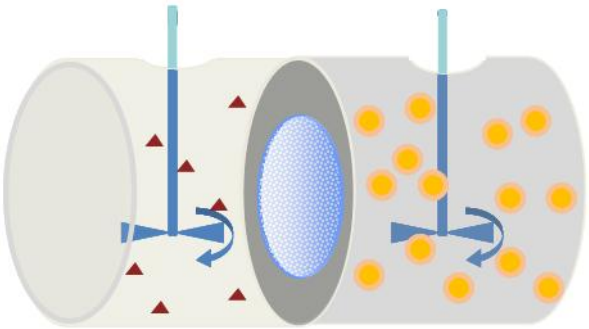

**Fig. S4** Scheme of dialysis permeation cell for membrane forward osmosis testing. The permeation cell contains two chambers. The biomimetic membrane was clamped between two chambers. 200 ppm sodium chloride solution was used as feed solution, and 0.3 mol/L sucrose solution was used as draw solution.

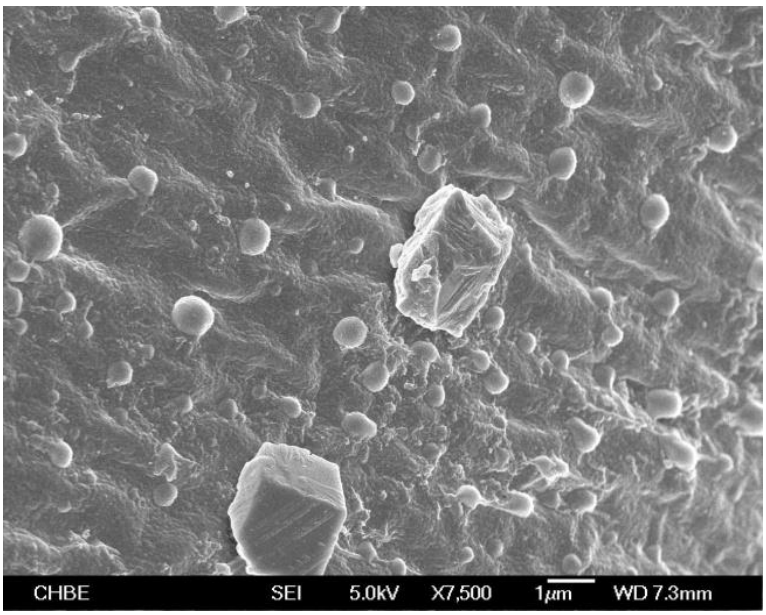


**Fig. S5** Morphology of AQPz-vesicle-imprinted membrane after nanofiltration test by SEM.

Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A

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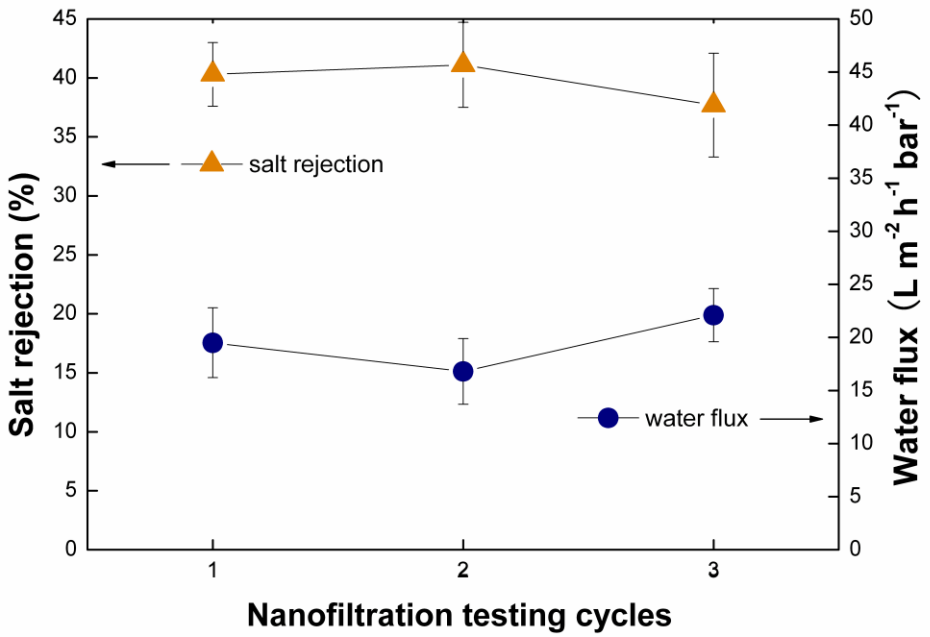


**Fig. S6** Nanofiltration performance of AQPz-vesicle-imprinted membrane for reusability

## 2. Methods and protocols:

### 1.1 Polymer structure characterization

The vesicles used in this work were formed from a ABA triblock copolymer mixture of poly(2-methyloxazoline)-*block*-poly(dimethylsiloxane)-*block*-poly(2-methyloxazoline) with carboxyl acid functional end groups ($P_1$) and poly(2-methyloxazoline)-*block*-poly(dimethylsiloxane)-*block*-poly(2-methyloxazoline) with methacrylate functional end groups ($P_2$). ABA copolymers with functional groups were prepared by end group modification. The structure of the synthesized block copolymer $P_1$ and $P_2$ was monitored using a proton nuclear magnetic resonance spectrometer ($^1$H-NMR, Bruker Avance 500) in $CDCl_3$, as shown in Figure S1. (a) hydroxyl-terminated PMOXA-PDMS-PMOXA: 0 (s, 3H, Si-$CH_3$), 0.5 ppm (t, 2H, -$CH_2$-Si), 2.0-2.2 ppm (s, 3H, $CH_3$-CO), 3.3-3.5 ppm (t, 4H, >N-$CH_2$-$CH_2$-N<); (b) $P_1$: 0 ppm (s, 3H, Si-$CH_3$), 0.5 ppm (t, 4H, -$CH_2$-Si), 2.0-2.2 ppm (s, 3H, $CH_3$-CO), 3.3-3.5 ppm (t, 4H, >N-$CH_2$-$CH_2$-N<), 2.6 ppm (t, 4H, CO-$CH_2$-$CH_2$-CO); (c) $P_2$: 0 ppm (s, 6H, Si-$CH_3$), 0.5 ppm (t, 2H, -$CH_2$-Si), 2.0-2.2 ppm (s, 3H, $CH_3$-CO), 3.3-3.5 ppm (t, 4H, >N-$CH_2$-$CH_2$-N<), 5.5 ppm (s, 1H, $CH_2$=), 6.1 ppm (s, 1H, $CH_2$=). The presence of a chemical shift peak at 2.6 ppm (peak 1) proved that the carboxyl groups were successfully introduced into the PMOXA-b-PDMS-b-PMOXA end groups. The presence of chemical shift peaks at 5.6 ppm and 6.1 ppm (peak 2 and peak 3) proved that the methacrylate groups were successfully introduced into the PMOXA-b-PDMS-b-PMOXA end groups. The functionality was >95% according to $^1$H NMR.

### 1.2 Vesicle size Characterization

Morphology of Non-extruded vesicles was measured by a confocal laser scanning microscope (Nikon, A1R, Tokyo, Japan). The excitation wavelength used was 495 nm and the emitted fluorescence was detected at a wavelength of 520 nm. For evaluation of the images, the EZ-C1 3.60 software (Nikon, Tokyo, USA) was used. The self-assembled polymersomes were incubated with a hydrophobic green fluorescence dye Coumarin-6 (Sigma Aldrich) for 24 h before observation. Vesicle size was measured by a dynamic light scattering unit (Zetasizer 3000 HAS equipped with a He–Ne laser beam at 658 nm, Malvern Instrument Ltd., Malvern, UK; scattering angle: 90$^o$). An average

value was obtained from three measurements. Table S1 shows that the average diameters of the extruded vesicles have been regulated by the pore size of the polycarbonate membrane used for the extrusion while the vesicle sizes remained the same before and after UV-crosslinking.

### 1.3 Vesicles Permeability Characterization

The permeability of the polymer vesicles was characterized using the stopped-flow (Chirascan Circular Dichroism Spectrometer, Applied Photophysics, UK) method. Polymersomes with unilamellar structure and an average diameter of 130 nm were quickly mixed with a sucrose buffer (0.6 osmol/L), which caused water efflux from vesicles that resulted in vesicle shrinkage. The vesicle size changes were monitored and recorded in the form of an increasing signal in the light scattering analysis. The initial rise of the signal curve was fitted to equation (S1).

$$Y = A\exp(-kt) \tag{S1}$$

Where $Y$ is the signal intensity, $A$ is the negative constant, $k$ is the initial rate constant ($s^{-1}$), and $t$ is the recording time. The osmotic water permeability was calculated using Equation (S2).

$$P_f = \frac{k}{(S/V_0)V_w\Delta_{osm}} \tag{S2}$$

Where $P_f$ is the osmotic water permeability (m/s), $S$ is the vesicle surface area ($m^2$), $V_0$ is the initial vesicle volume ($m^3$), $V_w$ is the partial molar volume of water (0.018 L/mol), and $\Delta osm$ is the osmolarity difference that drives the shrinkage of the vesicles (osmol/L).

Vesicles permeability results were shown in Figure 3. Single AQPz channel permeability was calculated using Equation (S3).[12]

$$P_a = \frac{P_{f,proteopolymersome} - P_{f,polymersome}}{Mon/A} \tag{S3}$$

$P_{f,proteopolymersome}$ is the permeability of the AQPz-vesicles, $P_{f,polymersome}$ is the permeability of the polymersomes without AQPz incorporation, and $Mon/A$ is the number of AQPz monomers per unit area in the proteopolymersomes.

### 1.4 Preparation and modification of the porous substrate membranes

The porous substrate membranes were prepared by the phase inversion method. A 15 wt % of cellulose acetate solution was prepared by dissolving dried cellulose acetate (CA CA-389-30, Eastman Chemical Company, USA) powder in N-methyl-2-pyrrolidone (NMP, 99.5 %, Merck, USA) with constant mechanical stirring (100 rpm) in a flask for 14 h at 40°C. The obtained homogeneous solution was allowed to stand at room temperature for a day to remove any bubbles. The polymer solution was then poured onto a glass plate at ambient temperature and cast with a casting knife to obtain the desired thickness of 250 μm. The glass plate was then immediately immersed in a water bath at ambient temperature for 48 h for precipitation and solvent exchange. The pore size of the substrate CA membrane was characterized via neutral solute rejection by using a dead-end permeation cell. Polyethylene glycol (PEG) with Mws of 20 and 35 kDa and polyethylene oxide (PEO) with Mws of 100, 200, 300, 600 kDa were used as neutral solutes for the preparation of feed solutions. The concentrations of the feed and permeate solutions were determined using total organic carbon analyzer (Shimadzu ASI-5000A). The single solute rejection was calculated as follows:

$$R = \left(\frac{C_f - C_p}{C_f}\right) \times 100\% \tag{S4}$$

The average pore size of the substrate membrane is 25±3 nm which is much larger than the radius of the magnesium ion (1.08 nm). The CA substrate membrane is ultrafiltration membrane.

The CA membrane surface was further modified with aldehyde followed by amino groups. Briefly, a CA membrane with an area of 20 $cm^2$ was fixed onto a Petri dish and incubated with 15 ml of sodium periodate (Sigma Aldrich) (7.0 wt% in de-ionized water) solution for 6 h in darkness. The reaction was stopped by flushing the membrane surface with a large amount of de-ionized water. The CA membrane with aldehyde groups on the surface was then further fixed onto a petri dish and incubated with 15 ml of ethylene diamine (Sigma Aldrich) (0.5 wt% in de-ionized water) solution for 3 h. The reaction was stopped by flushing the membrane surface with a large amount of de-ionized water.

The modification of the membranes after aldehyde functionalization was monitored using an FTIR Spectrum 2000 (Perkin-Elmer) with an attenuated total reflection (ATR-FTIR) technique. X-ray photoelectron spectroscopy (XPS) (AXIS Hi-S, 165 Ultra, Shimadzu) was employed to determine the surface elemental composition of the membranes after each surface modification step.

As shown in Figure S4, the appearance of the characteristic peak of aldehyde group at 1720 $cm^{-1}$ in the FTIR spectrum demonstrates that the modification of CA membrane using $NaIO_4$ generated aldehyde groups from the hydroxyl groups of the CA polymer. These aldehyde groups could then be used as binding sites for subsequent amine modification.

## 3. Table

**Table S1**. Diameter of vesicles by DLS. Values represent the mean ± standard deviation (error bars) with n=3.

| Pore size of filter membrane (nm in diameter) | Average diameter of uncrosslinked vesicles (nm) | Average diameter of crosslinked vesicles (nm) |
|---|---|---|
| 100 | 132±3 | 128±3 |
| 200 | 264±5 | 260±6 |