Electronic Supplementary Material (ESI) for ChemComm.
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Supporting Information

Screen printing directed synthesis of covalent organic framework membranes with water sieving property

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1. Experimental Section

1.1 Materials

1,3,5-Triformylphloroglucinol (Tp) was synthesized according to the reported protocol.[1] 2,5-Diaminohydroquinone dihydrochloride ($Pa(OH)_2 \cdot 2HCl$) and p-toluenesulfonic acid monohydrate ($PTSA \cdot H_2O$) were purchased from Jilin Chinese Academy of Sciences - Yanshen Technology Co., Ltd. and Alfa Aesar, respectively; and solvents of tetrahydrofuran (THF) and acetone (CH_3COCH_3) were commercially supplied. Salts of NaCl, KCl, $MgSO_4$ and $CaCl_2$ were all purchased from Beijing Chemical Reagent Company. Aqueous solutions of Na^+, K^+, Mg^{2+} and Ca^{2+} (1000 ppm) were prepared by dissolving the corresponding salts in deionized water.

1.2 Synthesis of the $TpPa(OH)_2$ membrane

0.375 mmol of 2,5-diaminohydroquinone dihydrochloride ($Pa(OH)_2$), 0.25 mmol of 1,3,5-triformylphloroglucinol (Tp), 2 mmol of p-toluenesulfonic acid monohydrate ($PTSA \cdot H_2O$) and 70 μl of water were well mixed to obtain a precursor. This precursor was then put on the top of 100 mesh screen and coated on the glass support by a squeegee to form a film at room temperature (conditions: T=25±2°C, RH=40±5%; screen printing machine: KV-SP-HY210, Zhuhai Kaivo Instruments and Equipments Co., Ltd., China). And then the resultant film was subjected to crystallisation using a stepwise heating mode (50 °C-90 °C-120 °C) for 18 h (6 h at each temperature). After the whole heating process, this membrane was cooled down at room temperature and then cautiously put into water bath to yield an integrated membrane. Finally, some residues of monomers or oligomers were washed with water, THF and acetone.

1.3 Characterisations

Powder X-ray diffraction (PXRD) was performed on a Rigaku D/Max-2550 diffractometer with Cu Kα radiation (λ=1.5418 Å). N_2 adsorption-desorption isotherm was collected at 77 K on Micromeritics ASAP 2020. Fourier-transform infrared (FT-IR) spectrum was acquired using a Nicolet iS50 Fourier transform infrared spectrometer. SEM images were observed from field emission scanning electron microscopy (FE-SEM) (Hitachi SU-8010 and JEOL JSM-7900F), equipped with energy-dispersive X-ray spectroscopy (Oxford, X-max 80). AFM image was taken on BioScope Resolve Atomic Force Microscopy (AFM), Bruker.

1.4 Water desalination

The reverse osmosis procedure for the $TpPa(OH)_2$ membrane was performed by using 1000 mg L^{-1} (1000 ppm) NaCl, KCl, $CaCl_2$ and $MgSO_4$ aqueous solutions in a lab-scale cross-flow filtration system with an available filtration membrane area of 5 cm^2 (Fig. S11). The detailed test conditions were: 25±2.0 °C in temperature, 0.8 MPa in transmembrane pressure and 1.0 L min^{-1} in feed cross-flow flux. The permeated solution was collected in a glass bottle. The ion concentrations of the feed and permeated solutions were analysed by inductively coupled plasma atomic emission spectrometer (ICP-AES, Leemanlabs Prodigy High Dispersion ICP Instrument). The separation characteristics were defined using the parameters of water flux (F, L m^{-2} h^{-1}) and ion rejection (R, %) in the following equations:

Equation (1)

$$F = \frac{V}{S \times t}$$

Equation (2)

$$R = \frac{C_{i,feed} - C_{i,permeate}}{C_{i,feed}} \times 100\%$$

where V is the permeate volume (L), S is the membrane area (m^2), t is the permeation time (h), i is the cation type, C_{feed} and $C_{permeate}$ are ion concentrations in the feed and permeated solution (ppm), respectively. After each test, the membrane was regenerated by washing with deionized water for three times.

2. Supporting Figures

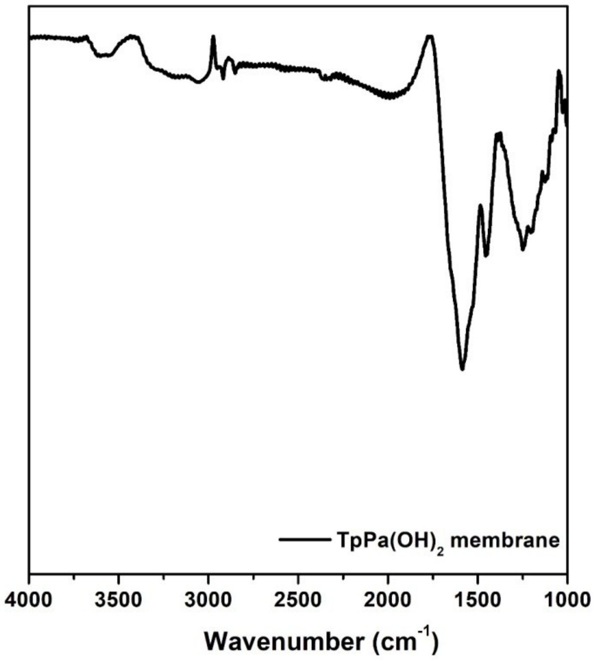

Fig. S1 FT-IR spectrum of the TpPa(OH)$_2$ membrane.

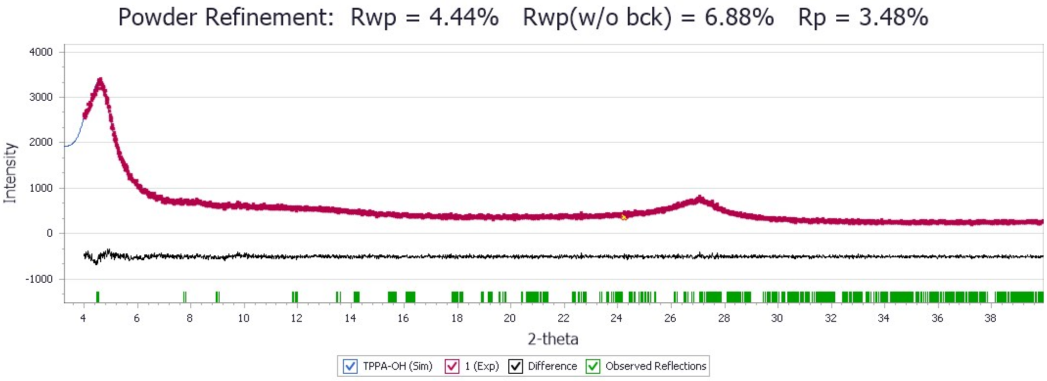

Fig. S2 Pawley refinement of XRD for the TpPa(OH)$_2$ membrane. Pawley refinement indicates the agreement between simulated and experimental PXRD patterns.

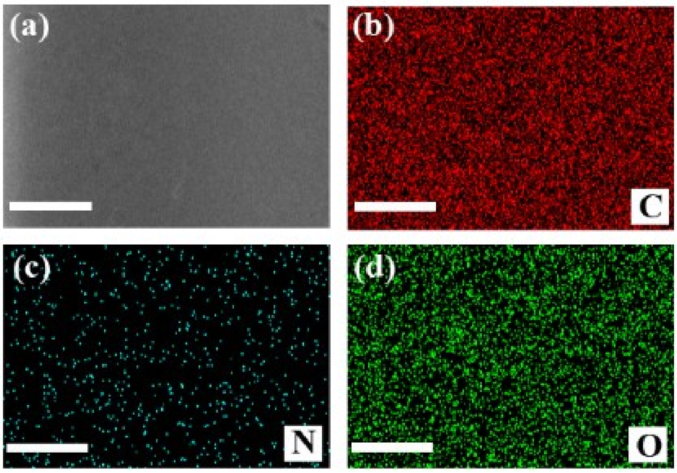

Fig. S3 (a) SEM image and (b-d) element mappings of the TpPa(OH)$_2$ membrane (scale bar: 10 μm).

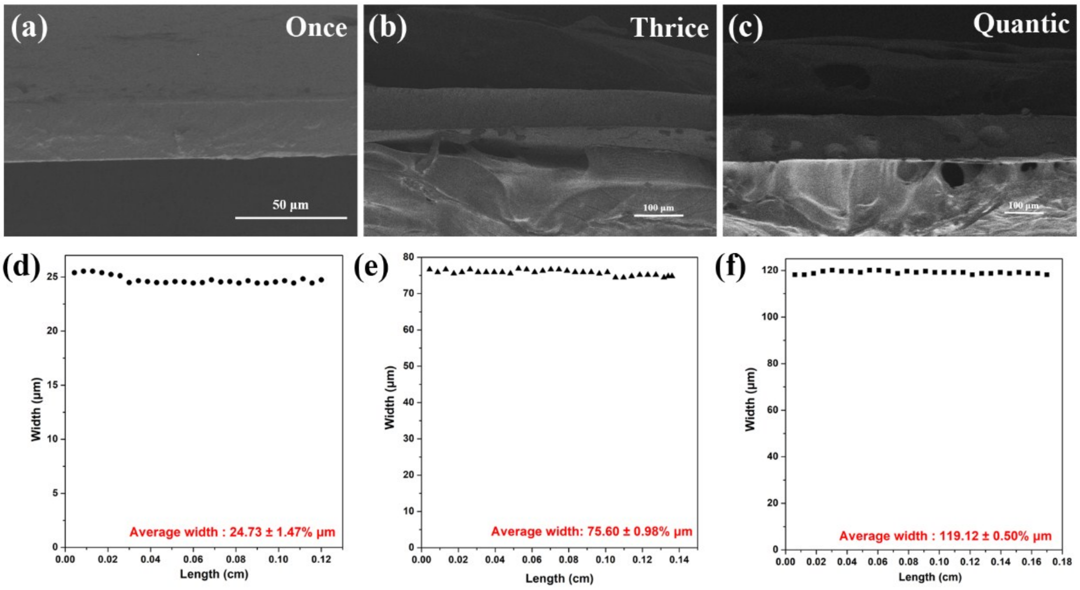

Fig. S4 (a, b, c) Cross-section SEM images of TpPa(OH)$_2$ membranes with 25 μm (once), 76 μm (thrice) and 119 μm (quantic) in thickness, respectively; (d, e, f) the corresponding thicknesses at different positions along the length of the TpPa(OH)$_2$ membrane (the thickness is reported in average width with relative standard deviation).

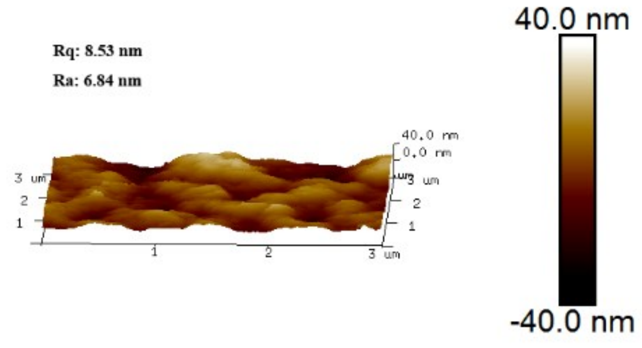

Fig. S5 AFM image of the TpPa(OH)$_2$ membrane.

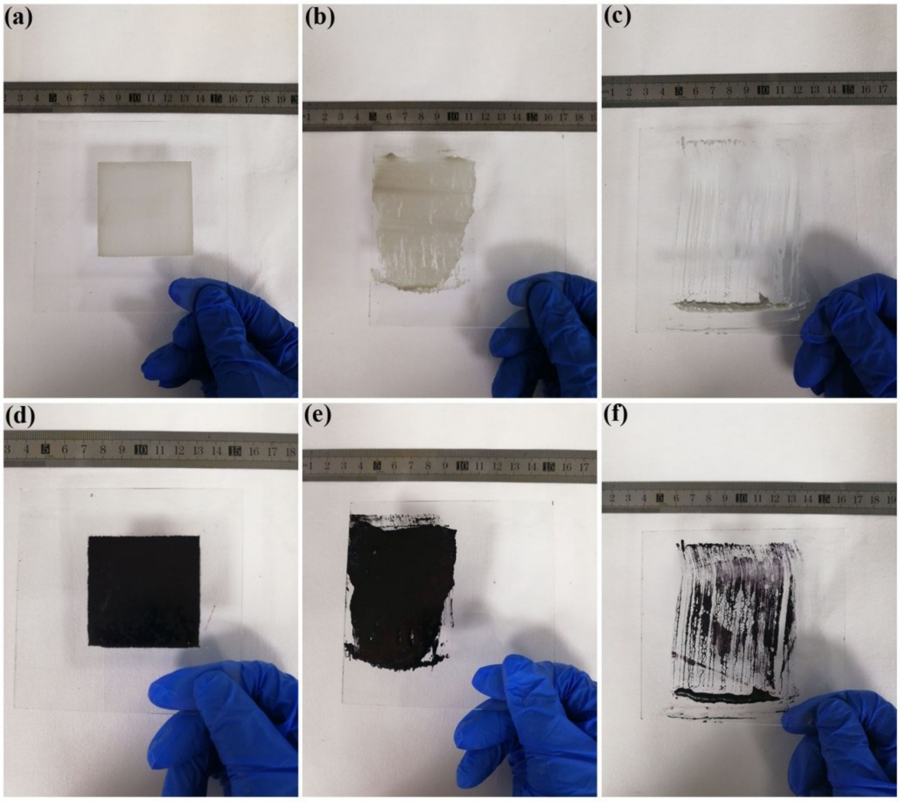

Fig. S6 (a-c) Optical photos of the TpPa(OH)$_2$ precursors prepared by different methods (a: screen printing, b: glass casting, c: knife casting), and (d-f) optical photos of correspondingly obtained membranes after heating (50 ^{o}C-90 ^{o}C-120 ^{o}C).

Fig. S7 (a, b, c) Optical photos of the synthesised TpPa$(OH)_2$ membranes with different shapes (scale bar: 1 cm).

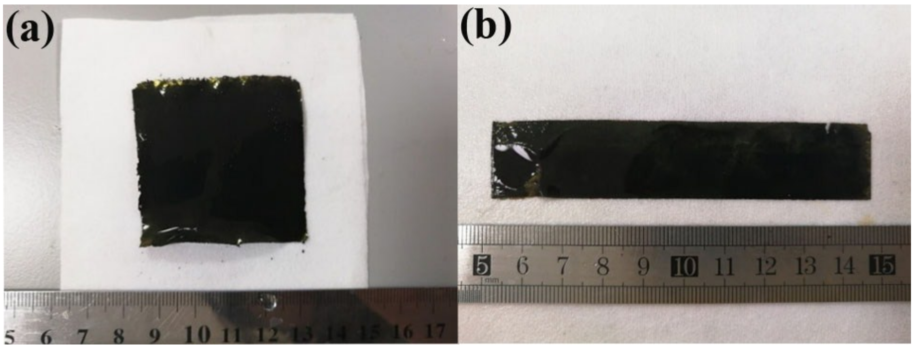

Fig. S8 (a, b) Optical photos of the synthesised TpPa$(OH)_2$ membranes with two different sizes.

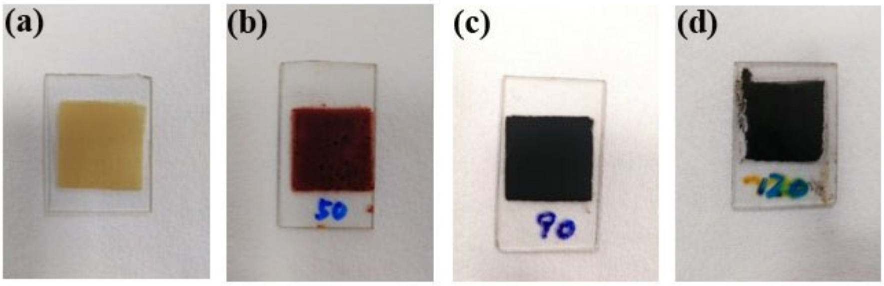

Fig. S9 (a-d) Optical photos of the TpPa$(OH)_2$ membrane at each temperature during the growth process.

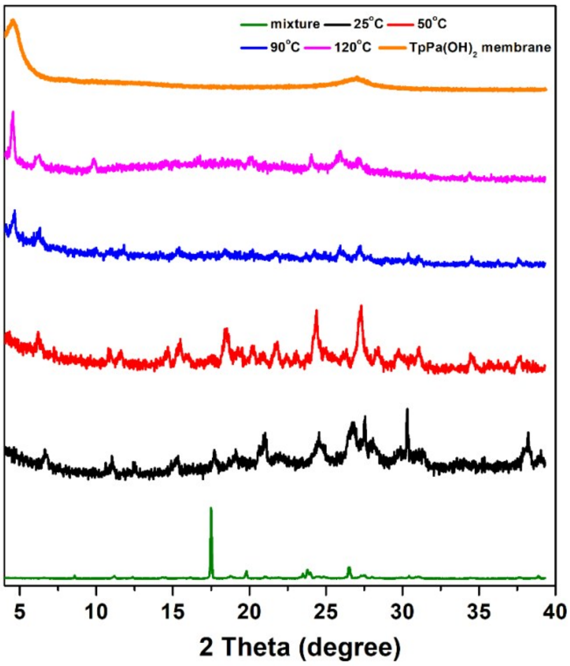

Fig. S10 PXRD patterns of the TpPa(OH)$_2$ membrane during the growth process (green: mixture of Tp, Pa(OH)$_2$ and PTSA, black: precursor (the above mixture after homogenisation with water), red: precursor after heating for 6 h at 50 °C, blue: precursor after another heating for 6 h at 90 °C, purple: precursor after additional heating for 6 h at 120 °C, orange: membrane after washing with water, THF, acetone).

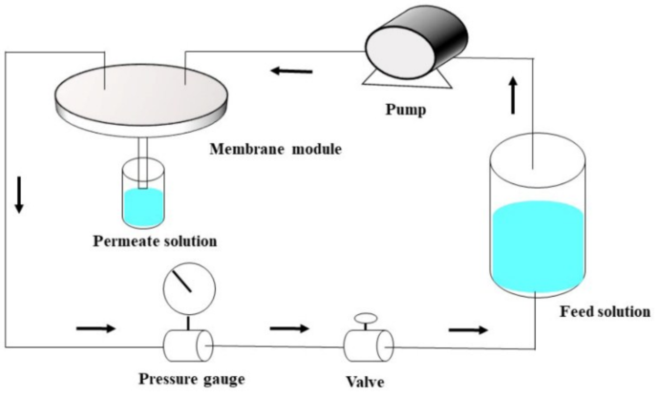

Fig. S11 A scheme for the setup of RO separation for water desalination.

3. References

1. J. H. Chong, M. Sauer, B. O. Patrick and M. J. MacLachlan, *Org. Lett.*, 2003, **5**, 3823-3826.