

Supporting Information

A Self-standing, Support-Free Membrane for Forward Osmosis with No Internal Concentration Polarization

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SUPPORTING DISCUSSION

Membrane Performance Testing. Membrane performance was examined on a lab-scale cross-flow FO module with an effective membrane area of 10 cm² at 25°C. DI water and Na₂SO₄ concentration of 1.5 M were used for feed solution and draw solution, respectively, with a fixed flow rate of 200 mL min⁻¹ (corresponding to crossflow velocity of 10.36 cm/s). Water flux (J_w , L m⁻² h⁻¹) was calculated from¹⁻³

$$J_w = \frac{\Delta m / \rho}{A \Delta t} \quad (S1)$$

where Δm is the weight change of feed solution (FS), ρ is the density of feed solution (assumed at 1 g cm⁻³), A is the effective membrane area, and Δt is the time interval. The reverse salt flux (J_s , mmol m⁻² h⁻¹) was determined using¹

$$J_s = \frac{C_f V_f - C_i V_i}{A \Delta t} \quad (S2)$$

where C_f and C_i are the final and initial salt concentrations of the feed solution, respectively, and V_f and V_i are the corresponding feed volumes, respectively. Each test was performed at least three times and the data were averaged.

Evaluation of Membrane Water and Salt Permeability Coefficients (A and B) and Structural Parameter (S)

Pure water permeability coefficient, A , solute permeability coefficient, B , and solute rejection, R , of the membranes were determined in a lab-scale cross-flow reverse osmosis (RO) cell with an effective membrane area of 12.56 cm². The flowrate was fixed at 0.9 L min⁻¹ (corresponding to a crossflow velocity of 39.0 cm/s), and the temperature was 25 °C. The membranes were compacted for 1 h with DI water at a pressure of 18 bar until steady state flux was observed. The pressure (ΔP) was then decreased and kept at 15 bar to measure the pure water flux (J_w^{RO}) and the salt rejection. The pure water permeability (A) was then calculated by

$$A = J_w^{RO} / \Delta P \quad (S3)$$

Similarly, the salt (Na₂SO₄) rejection was calculated by measuring the conductivity of the solution (DDS-307 Conductivity Meter, Shanghai, China) at 15 bar. The rejection values for the salt were calculated using

$$R = \left(1 - \frac{C_p}{C_f} \right) \times 100 \% \quad (S4)$$

where C_p and C_f are the concentrations of permeate and feed, respectively.

The salt permeability coefficient (B) was determined from

$$B = J_w^{RO} \frac{1-R}{R} \exp\left(-\frac{J_w^{RO}}{k}\right) \quad (S5)$$

27 where k is the mass transfer coefficient and is obtained from

$$k = \frac{ShD}{d_h} \quad (S6)$$

28 where D is the diffusion coefficient for Na_2SO_4 and was calculated based on previous literature
 29 for every concentration;^{4,5} d_h is the hydrodynamic diameter of the channel, and Sh is the
 30 Sherwood number. The latter is obtained from

$$Sh = 1.86 \left(Re Sc \frac{d_h}{L} \right)^{0.33} \quad (S7)$$

31 where L is the length of the flow channel, Re is the Reynolds number, and Sc is the Schmidt
 32 number. Re and Sc are obtained by

$$Re = \frac{u d_h \rho}{\mu} \quad (S8)$$

$$Sc = \frac{\mu}{\rho D} \quad (S9)$$

33 where ρ is the density of the liquid, μ is the dynamic viscosity of the liquid, u is the average
 34 crossflow velocity of the liquid, and D is the diffusivity of the solute in the liquid.

35 To calculate the predicted water flux J_w and salt flux J_s in FO mode, it is also necessary to
 36 calculate the mass transfer coefficient of the feed solution, k_F , and of the draw solution, k_D
 37 using equations S6 to S9.

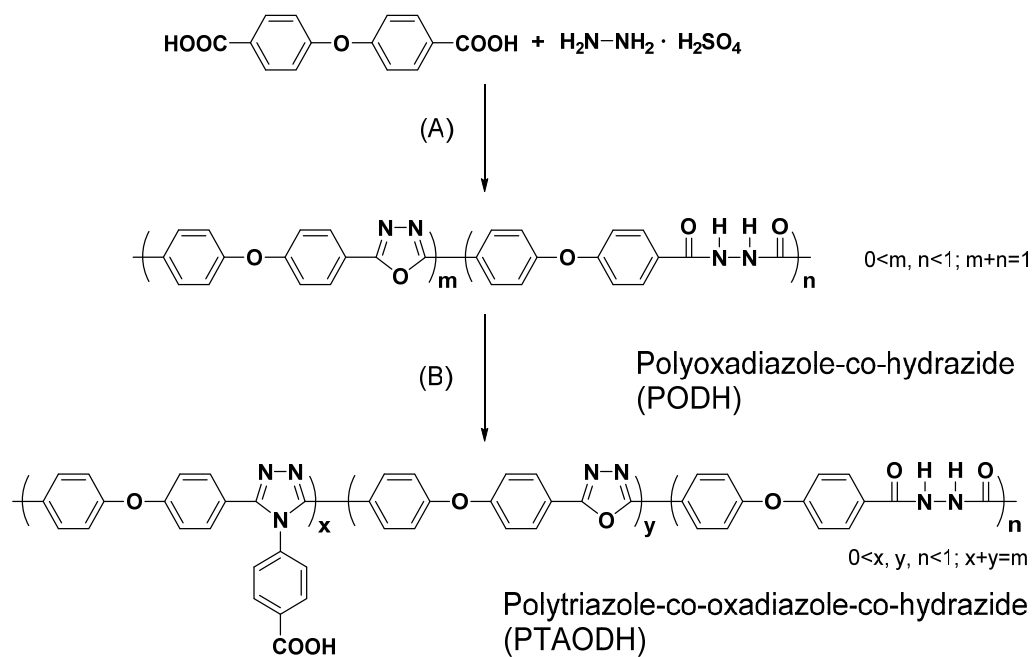
38 The membrane resistance to solute diffusion, K , is determined using⁶

$$K = \frac{1}{J_w^{FO}} \ln \frac{B + A\pi_d}{B + J_w^{FO} + A\pi_f} \quad (S10)$$

39 where π_d is the osmotic pressure of the draw solution and π_f is the osmotic pressure of the
 40 feed solution (0 bar for DI water).

41 Finally, the structural parameter (S) was calculated from⁶

$$S = KD \quad (S11)$$



Scheme S1. Synthetic route of polyoxadiazole-co-hydrazide (PODH) and polytriazole-co-oxadiazole-co-hydrazide (PTAODH). (A) PODH was synthesized from 4,4'-oxybis (benzoic acid) and hydrazine sulfate salt in polyphosphoric acid (PPA) at 160 °C for 3 h. (B) PTAODH was synthesized from PODH and 4-aminobenzoic acid in NMP at 195 °C for 12 h.

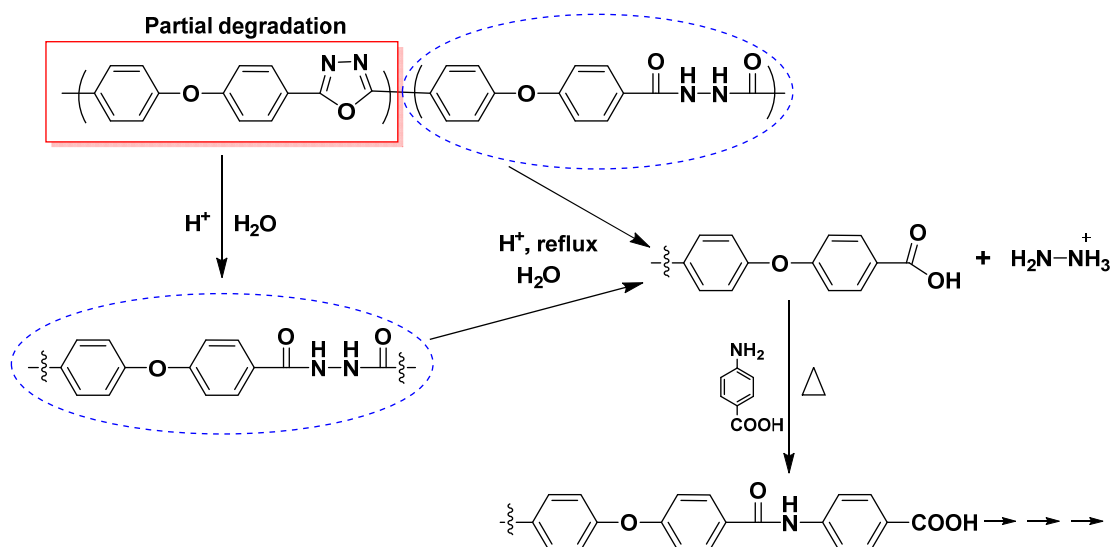
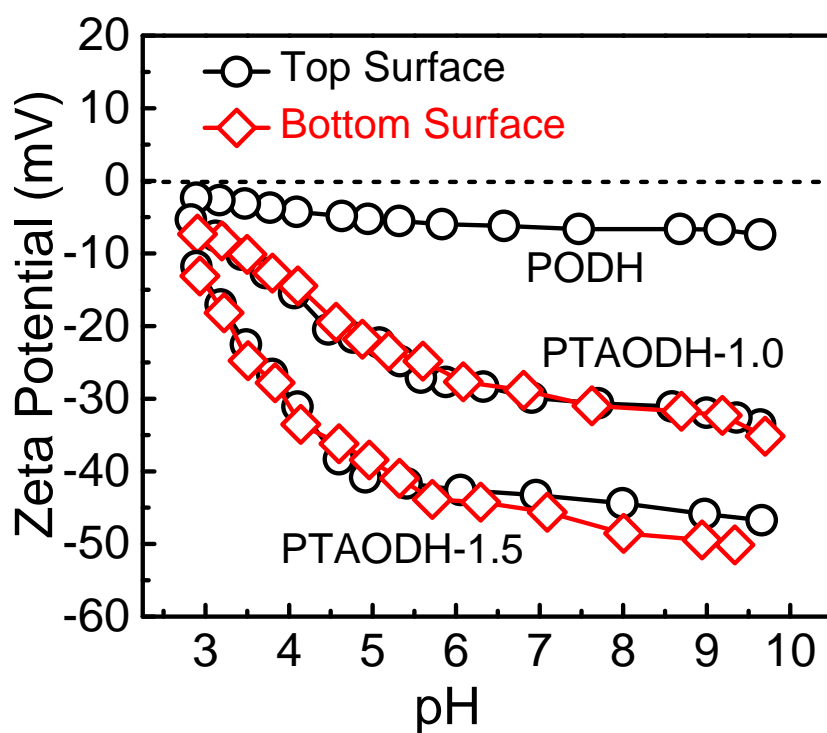


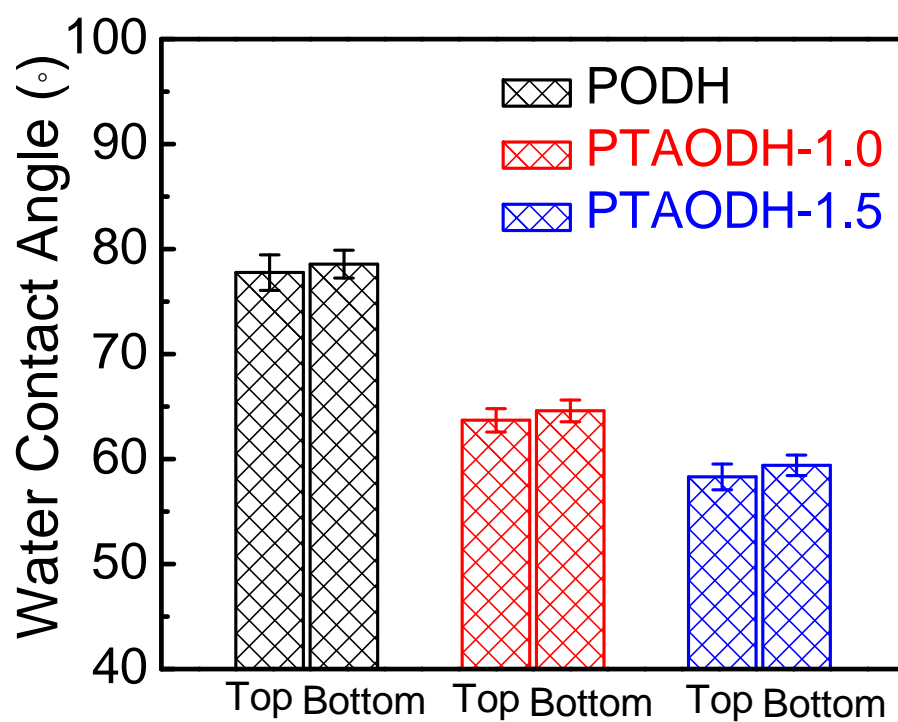
Figure S1. Possible degradation mechanism during the synthesis of PTAODH. The oxadiazole ring may undergo a ring-opening reaction in the acid medium to form the hydrazine unit, while the formed hydrazine group can be further hydrolyzed in the presence of H^+ and water (or even moisture). In this manner, 4-aminobenzoic acid may not only react with oxadiazole ring to form the triazole ring, but also react with the end-capped carboxyl acid groups.



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58 **Figure S2.** Zeta potential of the PODH (top surface), PTAODH-1.0 (top and bottom
 59 surfaces), and PTAODH-1.5 (top and bottom surfaces) FO membranes as a function of
 60 pH in the presence of 0.1 M KCl as a background electrolyte solution.

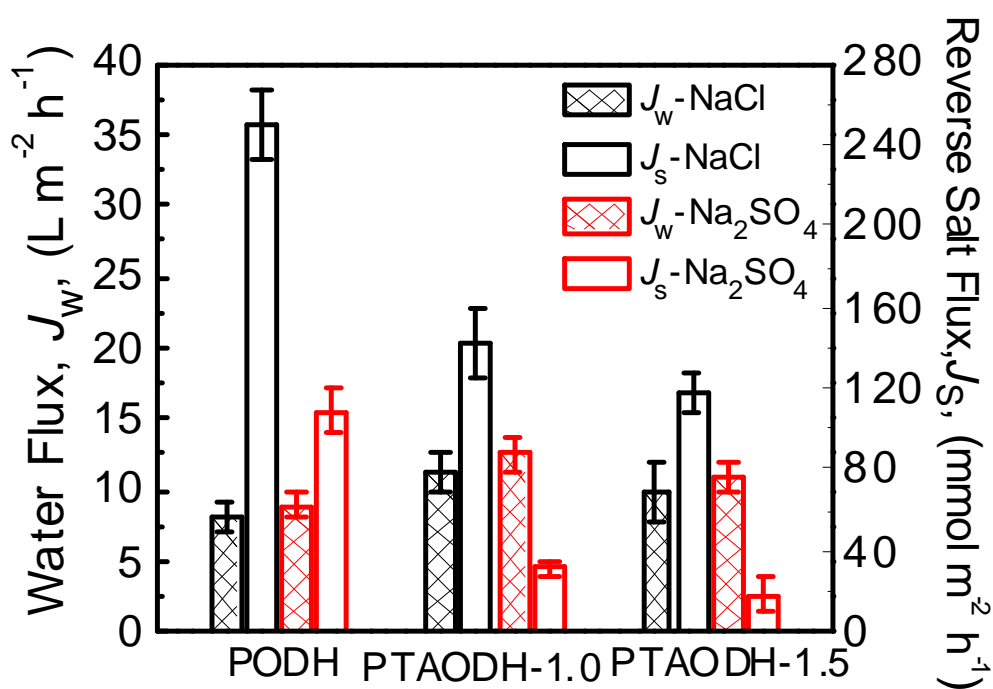
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64 **Figure S3.** Static water contact angles of different FO membranes (PODH, PTAODH-
 65 1.0, and PTAODH-1.5) measured with DI water. A 3- μ L liquid droplet was dropped on
 66 the membrane surfaces (top and bottom) with 5 s of contact time. At least three
 67 measurements were made at different locations for each membrane surface. Average
 68 values and error bars are presented.

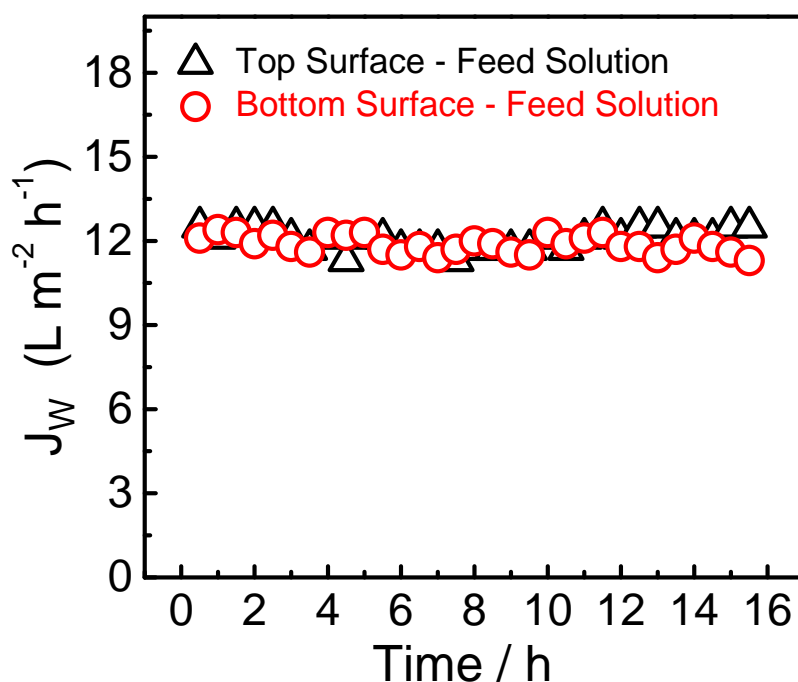
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72 **Figure S4.** FO performance of PODH, PTAODH-1.0 and PTAODH-1.5 membranes as
 73 a function of different type of draw solutes (Na_2SO_4 and NaCl). 1.5 M Na_2SO_4 and 2
 74 M NaCl solution were used as draw solution, respectively. The thicknesses for all three
 75 membranes was approximately 8 μm .

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79 **Figure S5.** Stability test of water flux (J_w) for PTAODH-1.0 membrane with a thickness
80 of nearly 8 μm at 25°C for 16 h. The concentration of Na_2SO_4 solution was monitored
81 every ~ 2 h, and additional Na_2SO_4 was added to the draw solution to keep the salt
82 concentration constant at 1.5 M. The FO performance of the membrane on both sides
83 was also studied here. The black and red symbols represent data collected when the
84 membrane top surface or bottom surface faced the feed solution.

85

86 Figure S5 shows the stability test of PTAODH-1.0 membrane with a thickness of 8 μm .
87 Both the top and bottom surfaces were measured and compared. The osmotic pressure
88 was controlled by the concentration of the draw solution, and constant water flux of
89 $\sim 12.3 L m^{-2} h^{-1}$ was obtained over the entire test period. It should be noted that no
90 significant difference existed between flux results for the two sides of the membrane,
91 which indicates the symmetric nature of the membrane.

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Table S1 GPC data of all polymers (PODH, PTAODH-1.0, and PTAODH-1.5).

	M_n (kDa)	M_w (kDa)	PDI
PODH	147	295	2.01
PTAODH-1.0	121	252	2.08
PTAODH-1.5	79	178	2.55

The degradation of polymer chains was further validated by the change in molecular weight, as listed in Table S1. PODH was obtained with the highest M_n of 147 kDa, whereas 121 and 79 kDa were determined for PTAODH-1.0 and PTAODH-1.5, respectively. The highest polydispersity index (PDI) value of 2.55 for PTAODH-1.5 also indicates the wide distribution due to the existence of more hydrolyzed polymer chains.

Table S2 Mechanical properties of PODH, PTAODH-1.0, and PTAODH-1.5 membranes with the same thickness of $\sim 8 \mu\text{m}$.

	Elongation (%)	Young's Modulus (GPa)	Maximum Stress (MPa)
PODH	43.5	0.82	64.4
PTAODH-1.0	6.7	1.31	71.2
PTAODH-1.5	4.1	1.35	59.1

Table S3 Values of parameters for PTAODH-1.0 membrane with different thicknesses (RO and FO performance).

Membrane	A $\text{L m}^{-2} \text{h}^{-1}$	B $\text{L m}^{-2} \text{h}^{-1}$	$J_{\text{RO}}^{\text{c)}$ $\text{L m}^{-2} \text{h}^{-1}$	$R^{\text{c)}$ %	$J_{\text{FO}}^{\text{d)}$ $\text{L m}^{-2} \text{h}^{-1}$	S μm	J_w/J_s L mol^{-1}
5 $\mu\text{m}^{\text{a)}$	0.170	0.054	2.55	98.1	18.1	4.5 \pm 2.0	304.0 \pm 18.0
8 $\mu\text{m}^{\text{a)}$	0.118	0.026	1.77	98.5	12.9	3.5 \pm 5.7	412.0 \pm 30.9
15 $\mu\text{m}^{\text{a)}$	0.049	0.010	0.74	98.7	5.5	1.0 \pm 5.5	361.1 \pm 28.3
HTI-CTA ^{b)}	0.375	0.075	5.63	98.6	7.4	490.1 \pm 29.5	375.7 \pm 14.4

a) PTAODH-1.0 membrane with different thicknesses.

b) Commercial HTI-cellulose triacetate asymmetric membrane.

c) 1.0 g L⁻¹ of Na₂SO₄ was used for the RO performance test. The flowrate was fixed at 0.9 L min⁻¹ (corresponding to a crossflow velocity of 39.0 cm/s), and temperature was fixed at 25 °C. The membranes were compacted for 1 h with DI water at a pressure of 18 bar until a steady state flux was observed. The operating pressure (ΔP) was then decreased and kept constant at 15 bar to measure pure water flux and salt rejection.

d) 1.5 M of Na₂SO₄ was used as the draw solution and DI water was used as the feed solution.

References

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