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Supplementary information:

Energy-efficient desalination by forward osmosis using responsive ionic liquid draw solutes

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Salt Rejection of Membrane Before and After Soaking in the Draw Solution

The measurement of membrane's salt rejection was conducted in a standard RO method. The feed was a 10 mM NaCl (C_f) solution and the hydraulic pressure was 5 bar. By measuring the permeate salinity C_p, the salt rejection can be calculated as:

$$R = (1 - C_p/C_f) * 100\%$$

Multiple and repeated salinity measurements were conducted at an interval of 30 minutes after stabilization was achieved. Data in Fig. S1 indicate high stability of membranes with the draw solutions.

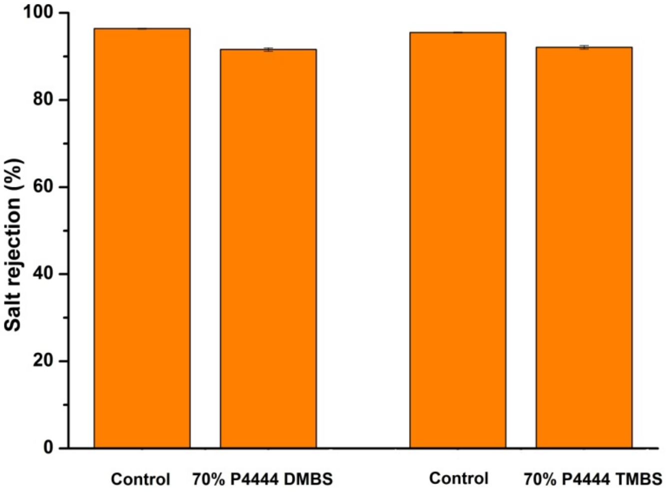


Fig.S1 Comparison of salt rejection of as-received membranes and those soaked for 7 days in 70 wt% P_{4444} DMBS or P_{4444} TMBS draw solution.

Schematics of the FO setup

FO was carried out using a laboratory membrane module operated in a continuous cross-flow configuration. The effective membrane size is 30 mm x 15 mm. Both the feed and the draw solutions were pumped at 240 ml/min. The

NF process was done using a dead-end membrane setup with mechanical agitation to reduce concentration polarization. The pressure in NF was generated by pressurized N_2 gas.

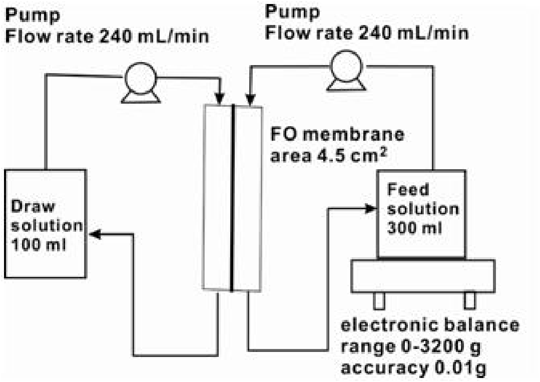


Fig.S2 Schematics of FO setups.

Differential Scanning Calorimetry (DSC) of Ionic Liquids

Fig.S3 shows the DSC results of the three ionic liquids. The temperature scan rate was 3℃/min under N_2 purge. The P_{4444}DMBS is colorless liquid at a wide temperature range from -50℃ to 150℃ with no transition observed. P_{4444}TMBS and P_{4448}Br are waxes at room temperature with melting points of ~80℃ and ~25℃, respectively. The exothermic peak on P_{4448}Br at around -3℃ is probably the crystallization peak, which is also observed in other ionic liquids[1, 2].

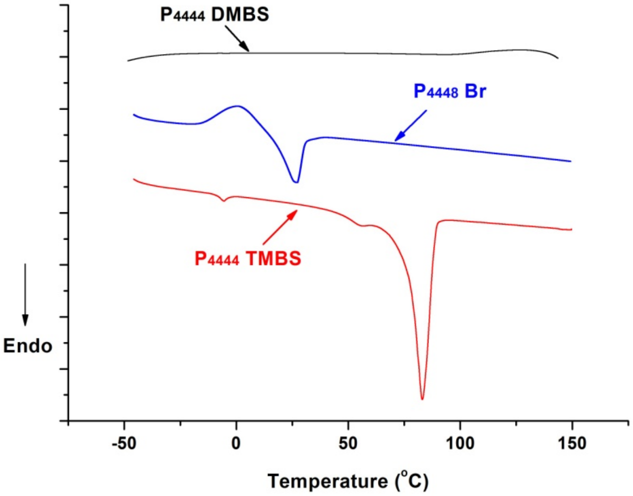


Fig.S3 DSC curves of the three ionic liquids.

Estimation of Osmolality at High Concentrations via Curve Fitting/Extrapoltions

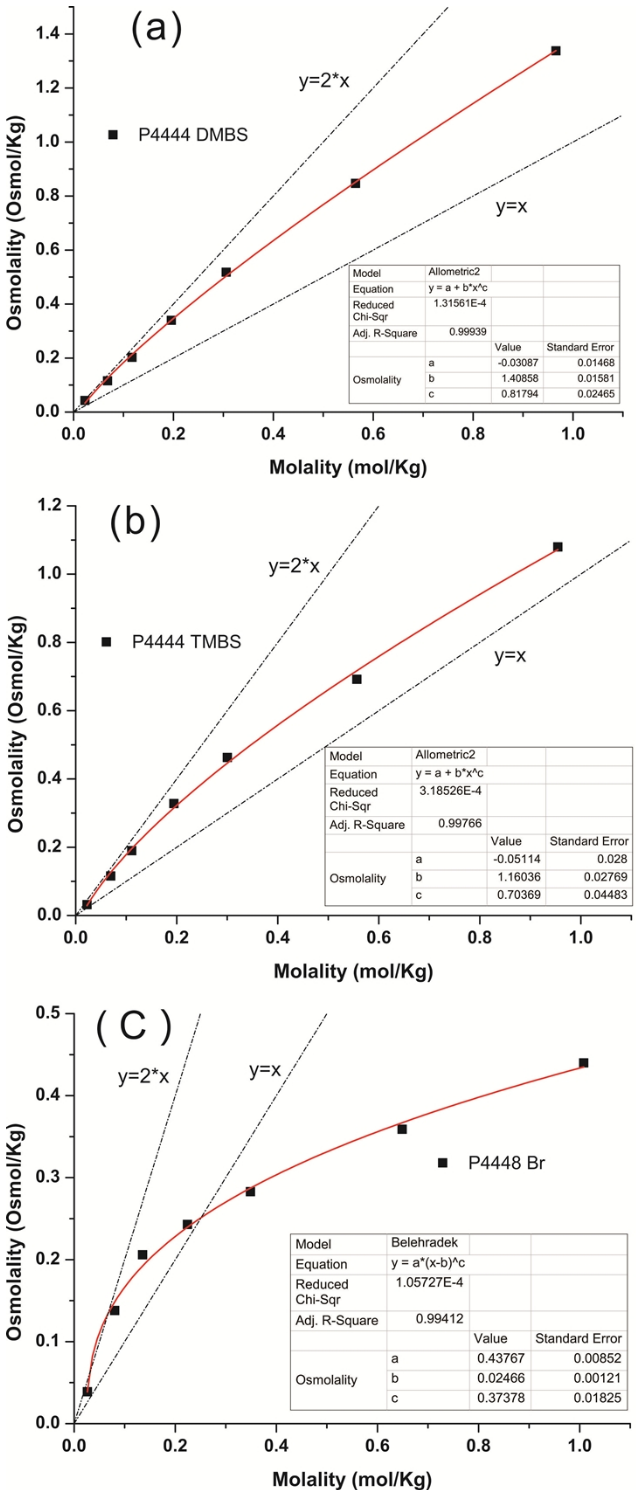
The measurement of osmolality was done by sensing the depression of freezing point. The principle of measuring osmomality by cryoscopic method can be found elsewhere.[3] The osmolalities of ionic liquid draw solutions with concentrations above 30 wt% cannot be obtained although the measuring limit has not been exceeded. This is probably due to the increased viscosity of draw solution as concentration increases. Therefore, in order to have a wider osmolality and concentration correlation, we applied the simulation of osmolality-molality correlation of the three draw solutes at low concentrations (< 1 mol/Kg, ~30 wt%) as shown in Fig.S4 to predict and estimate the osmolality-concentration correlation at high concentrations. The conversion formula between molality and weight concentration is:

$$\textbf{Wt\% concentration} = molality \times Mw/[(molality \times Mw) + 1000] \qquad \textbf{(S.1)}$$

where Mw is the draw solute molecular weight (g/mol). The conversion from weight concentration to molality is summarized in Table S1, and the correlation between molality and osmolality used the fittings shown in Fig.S4. From this prediction, a 70 wt% P_{4444}DMBS solution has an osmolality of about 5 osmol/Kg as shown in Fig.2b and Table S1. While we experimentally determined that a 70 wt% P_{4444}DMBS draw solution can generate a water flux of ~0.3 LMH from a 1.6 M NaCl solution feed solution at 14℃, which means that 70 wt% P_{4444}DMBS should have osmolality higher than 3.2 osmol/Kg (osmolility of 1.6 M NaCl solution) at 14℃. Considering that the osmolality was measured using cryoscopy at subzero degree and the osmolality is expected to increase with decreasing temperature for LCST-type draw solution, the prediction should be reasonable at least for showing the increasing trend of drawing ability.

Table S1 Correlation between the predicted osmolality and weight concentration of draw solutions. The conversion from weight concentration to molality is done using equation S1, and the correlation between molality and osmolality was based on extrapolation with equations obtained in Fig. S4

		40 wt%	**50 wt%**	**60 wt%**	**70 wt%**	**80 wt%**
P_{4444} DMBS	**Molality (mol/Kg)**	1.5015	2.2523	3.3784	5.2553	9.0090
	Osmolality(osmol/kg)	1.9333	2.7057	3.7818	5.4416	8.4737
P_{4444} TMBS	**Molality (mol/Kg)**	1.4556	2.1834	3.2751	5.0946	8.7336
	Osmolality(osmol/kg)	1.4647	1.9653	2.6311	3.6092	5.2975
P_{4448} Br	**Molality (mol/Kg)**	1.6835	2.5253	3.7975	N.A.	N.A.
	Osmolality(osmol/kg)	0.5293	0.6171	0.7189	N.A.	N.A.



Model	Allometric2		
Equation	y = a + b*x^c		
Reduced Chi-Sqr	1.31561E-4		
Adj. R-Square	0.99939		
		Value	Standard Error
Osmolality	a	-0.03087	0.01468
	b	1.40858	0.01581
	c	0.81794	0.02465

Model	Allometric2		
Equation	y = a + b*x^c		
Reduced Chi-Sqr	3.18526E-4		
Adj. R-Square	0.99766		
		Value	Standard Error
Osmolality	a	-0.05114	0.028
	b	1.16036	0.02769
	c	0.70369	0.04483

Model	Belehradek		
Equation	y = a*(x-b)^c		
Reduced Chi-Sqr	1.05727E-4		
Adj. R-Square	0.99412		
		Value	Standard Error
Osmolality	a	0.43767	0.00852
	b	0.02466	0.00121
	c	0.37378	0.01825

Fig.S4 Osmolality-molality fitting for the three draw solutes using expereimental data.

Water Flux Generated by the IL Draw Solutions at Different Concentrations against Different Feed Solutions

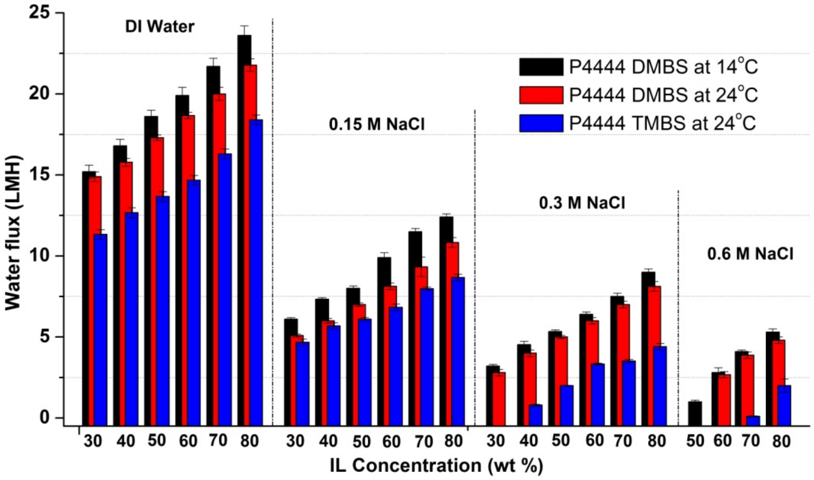


Fig.S5 Water flux profile of P_{4444}DMBS and P_{4444}TMBS draw solutions with various concentrations against feed solutions with different salinities at different temperatures.

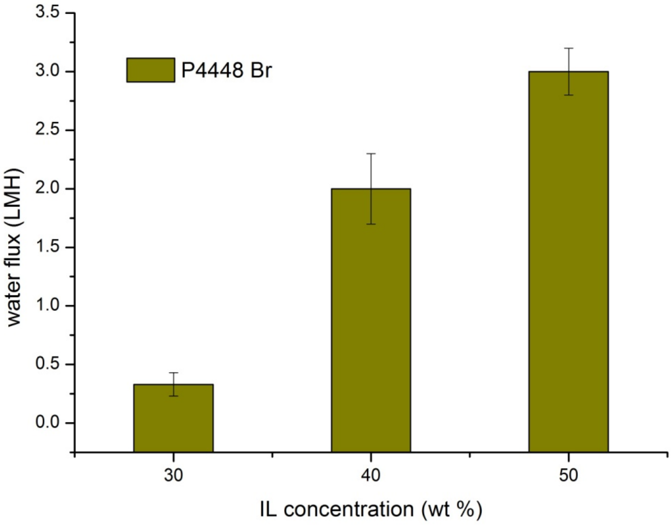


Fig.S6 Water flux profile of P4448Br with different concentrations. Feed solution is 2000 ppm (or 0.03 M) NaCl and the temperature is 14±1 ℃. Note that P4448Br has a poorer solubility.

Draw Solute Back-diffusion

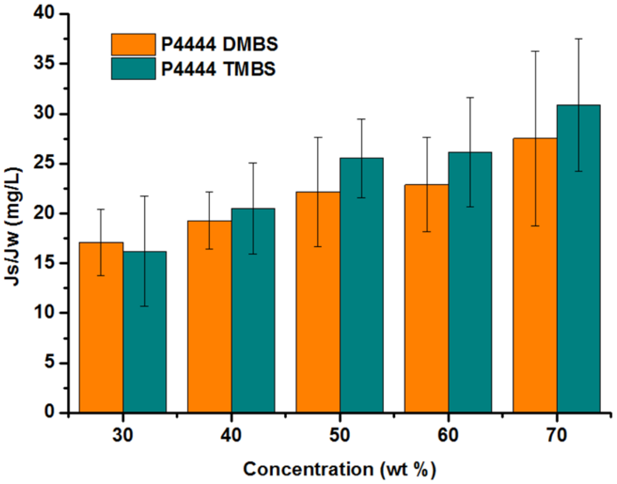


Fig.S7 Relationship of back-diffusion flux J_s and water flux J_w ratio with draw solution concentration. The ratio measures the draw solute back diffusion in mg per liter of water obtained. DI water was used as the feed solution.

The draw solute reverse diffusion (J_s) was measured by monitoring the change of total organic carbon (ΔTOC) in the feed solution

$$J_s = \Delta TOC * V_{feed} / (A*t*C),$$

where V_{feed} is the feed solution volume before sampling for TOC measurement, C is the weight concentration of carbon atoms in draw solute molecules, which is 64.86% for P4444 DMBS and 65.50% for P4444 TMBS. A is the membrane area and t is the FO testing time. J_w is the water flux generated by draw solution.

Enthalpy of Phase Separation of Draw Solution

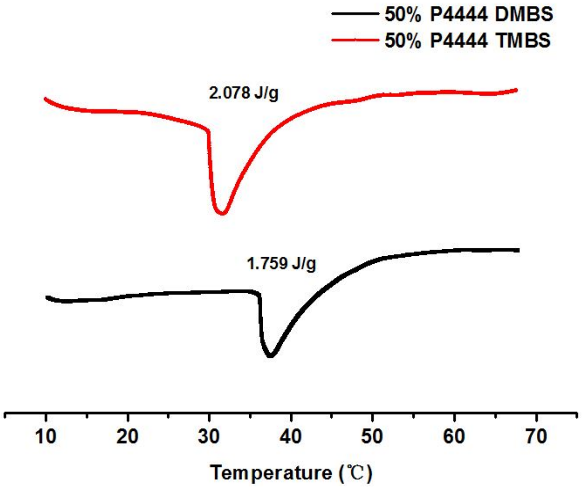


Fig. S8 DSC curves of draw solutions showing the endothermic phase separation. Downward is endothermic and the latent heat of each draw solution is also determined.

Viscosity of Draw Solutions at Various Concentrations

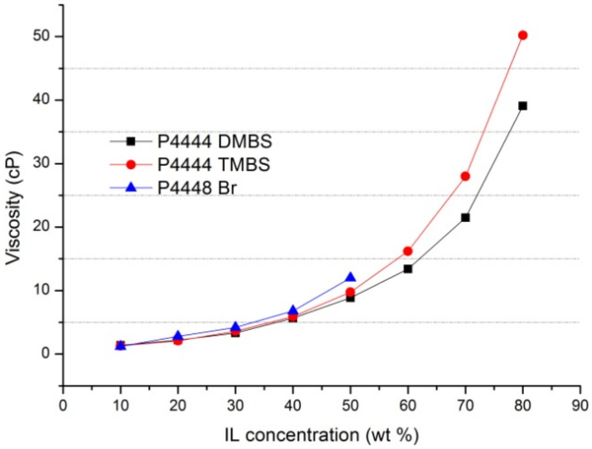


Fig.S9 The viscosity profiles of the three draw solutions. P_{4448} Br was measured at 16℃ while others were measured at 23℃.

Visual Observation during Phase Separation

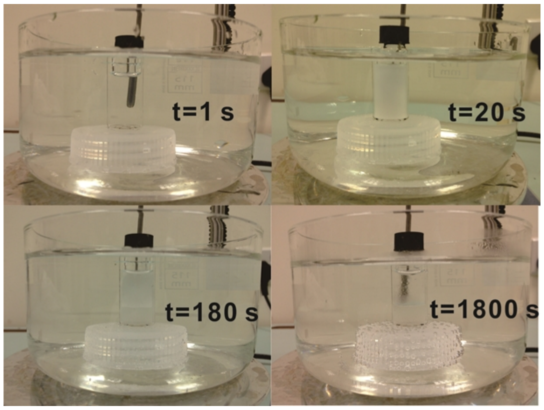


Fig.S10 Visual observation of phase separation in a 40 wt% P4444 DMBS draw solution above its LCST. The water bath temperature is 50℃. The white plastic cover under the vial was used for avoiding direct contact with the hot plate. Phase separation occurred as indicated by turbidity after 20 second at 50℃.

FO Seawater Desalination Economy/Energy Analysis

Generally the cost analysis and comparison of desalination is a complex issue no matter what method (FO, RO or MD) is used. The task is by no means trivial and requires a rather major undertaking because desalination cost depends on a number of factors. However, it is known that the energy cost would accounts for larger portion in total costs and it also increases when the salinity of the feed stream increases. For seawater desalination by RO, electrical energy cost already accounts for half of total costs.[4] We believe that by replacing high grade and more expensive electric energy with low grade and less expensive thermal energy, the total cost will be reduced. In this study, we clearly demonstrated that the electric energy requirement is at about 16% of that needed for the standard RO. One reason is that the regeneration of the draw solute and recovery of water can now be done via an NF process at only 6 bar pressure which is substantially lower than that for RO. Thermodynamically, the new draw solutes allow the balance of the energy required for desalination to be provided by lower cost thermal energy (preferably waste heat). Furthermore, it is suggested that the use of low grade waste heat would make even better economical sense than using heat generated by fossil fuel. Another very important factor is that the use of waste heat or heat from renewable sources will lead to a significant reduction of carbon footprint even though there may be an initial capital investment.

Finally we further estimated the theoretical thermal energy requirement based on the experimentally measured enthalpy of phase separation of the diluted draw solution (50% P_{4444}DMBS, Fig. S8). The following is the basis of our estimation. The enthalpy of phase separation for a diluted draw solution (50% P_{4444}DMBS) was determined to be around 1.759 J/g via DSC measurement. Based on our experimental data, 1 g of the diluted draw solution phase separates into 0.34 g of 7.5% water-rich supernatant and 0.66 g of 70% IL-rich sediment during the liquid-liquid phase separation. While the latter can be reused directly as draw solution, the 7.5% water-rich supernatant was treated with NF which yields 0.30 g water after NF from our experiment. Therefore, the theoretical thermal energy required to produce a unit weight of water would be 5.86 J/g (1.759 J/g divided by 0.3) or 5.86 MJ/m^3, which is equivalent to 1.63 kWh/m^3. Together with the electric energy of 0.17 kWh/m^3 needed for NF, the theoretical total energy requirement would be 1.80 kWh/m^3 (heat needed for phase separation plus the electricity needed for NF). This estimation is higher than but of the same order as the theoretical limit of 1.09 kWh/m^3 earlier reported for RO desalination.

Toxicity of the New Draw Solutes

The phosphonium ionic liquid compounds are not considered to be very toxic because phosphonium compounds are often used in cleaning agents and surfactants. We have initiated a cytotoxicity study of P4444 DMBS and P4444 TMBS using human fibroblast cell model, and the preliminary findings indicate that they have very low cytotoxicity. Virtually no change in cell viability was observed below the concentration of 100 µg/ml for both P_{4444} DMBS and P_{4444} TMBS. In fact we are not surprised because the amphiphilic phosphonium IL draw solutes have molecular structures analogous to phosphonium-containing lipids and polyelectrolytes. The latter have been widely used as vectors for gene delivery to living cells in biomedical research due to their low cytotoxicity.[5, 6] While more systematic toxicity study would take much longer time to complete, the above evidence shows that such level of toxicity should at least be acceptable for treating water for industrial applications.

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