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# Hydrophilic Microporous Membranes for Selective Ion Separation and Flow-Battery Energy Storage

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## Abstract

Membranes with fast and selective ion transport are widely used for water purification and devices for energy conversion and storage including fuel cells, redox flow batteries, and electrochemical reactors. However, it remains challenging to design cost-effective, easily processed ion-conductive membranes with well-defined pore architectures. Here, we report a new approach to designing membranes with narrow molecular-sized channels and hydrophilic functionality that enable fast transport of salt ions and high size-exclusion selectivity towards small organic molecules. These membranes, based on polymers of intrinsic microporosity (PIMs) containing Tröger's base or amidoxime groups, demonstrate that exquisite control over subnanometer pore structure, the introduction of hydrophilic functional groups, and thickness control all play important roles in achieving fast ion transport combined with high molecular selectivity. These membranes enable aqueous organic flow batteries with high energy efficiency and high capacity retention, suggesting their utility for a variety of energy-related devices and water purification processes.

In addition to conventional membrane separation processes<sup>1,2</sup>, there is a rapidly growing demand for ion-transport membranes in applications related to energy<sup>1-3</sup>. With greater reliance on renewable but intermittent energy sources such as solar and wind power, energy conversion and storage technologies are required to integrate low-carbon energy into the power grid. These include electrochemical water splitting and electrolysis for H<sub>2</sub> production<sup>4</sup>, proton-exchange membrane (PEMs) and alkaline fuel cells for energy conversion<sup>5</sup>, electrochemical reduction of CO<sub>2</sub> and N<sub>2</sub> to fuel and chemicals<sup>6</sup>, and scalable redox flow batteries (RFBs)<sup>3,7</sup>. In all of these established and emerging electrochemical processes, ion-selective membranes transport ions whilst isolating the electrochemical reactions in separate cells. In the new generation of RFBs<sup>8-14</sup>, low-cost and high-performance membranes need to have precise selectivity between ions and organic redox-active molecules<sup>15-18</sup>.

Whilst various new electrochemical processes have been developed, the use of expensive commercial ion-exchange membranes, such as the poly(perfluorosulfonic acid) (PFSA)-based Nafion

44 (~\$500 per m<sup>2</sup>), dominate, despite suffering from poor selectivity due to swelling in water. Intensive  
45 research efforts have developed low-cost hydrocarbon-based polymer electrolyte membranes<sup>5, 19,20,21</sup>, for  
46 example, polyaromatic ionomers with pendant ionic functional groups demonstrate promising  
47 performance in vanadium flow batteries<sup>22, 23</sup> and fuel cells<sup>24-26</sup>. Ion transport within these polymers  
48 depends on the formation of nanoscale interconnected water channels via microphase separation of the  
49 hydrophobic backbone and hydrophilic side chains,<sup>29</sup> which is a complex process that is difficult to  
50 control on a molecular level. Hence, the key scientific challenge for obtaining highly-selective ion-  
51 transport membranes is the design of processable materials that achieve precise control over pore  
52 architecture, pore size distribution, and ionic conductive functionality<sup>2, 27-35</sup>.

53 Here, we demonstrate a new approach for the design of ion-selective membranes based on  
54 hydrophilic polymers of intrinsic microporosity (PIMs)<sup>36-38</sup> that enable fast ion transport and high  
55 molecular selectivity (Fig. 1a). Our innovative strategy combines: (i) the use of PIMs to provide rigid and  
56 contorted polymer chains that pack inefficiently so as to generate microporosity with narrow pore size  
57 distribution; (ii) the incorporation of hydrophilic functional groups (including ionizable groups) that  
58 generate interconnected water channels for ion-conductivity; and (iii) solution processing to give thin  
59 films with submicron thickness that further reduces ion transport resistance and membrane production  
60 costs. We demonstrate the selective ion separation of these microporous membranes and their application  
61 within efficient and stable aqueous organic redox flow batteries.

## 62 **Synthesis and characterization of hydrophilic microporous membranes**

63 Figure 1b shows the conceptual diagram of the interconnected hydrophilic ionic channels in the  
64 microporous membranes fabricated from a hydrophilic PIM polymer (Fig. 1c). To realise our design  
65 strategy, we developed two types of hydrophilic PIMs firstly, PIMs derived from Tröger's base (TB-PIMs)  
66 and, secondly, dibenzodioxin-based PIMs with hydrophilic and ionizable amidoxime groups (AO-PIMs)  
67 (Fig. 1d). Details of PIM synthesis (Fig. S1) and spectroscopic characterisation (Fig. S2-S3) are provided  
68 in the Methods Section and the Supplementary Information. The three TB-containing polymers selected  
69 for investigation were based on ethanoanthracene (*i.e.*, PIM-EA-TB), benzo-methanoanthracene (*i.e.*,  
70 PIM-BzMA-TB) and dimethylbiphenyl (*i.e.*, DMBP-TB), which provide a range of microporosity (Fig.  
71 2a), as measured by gas adsorption, with apparent BET surface areas of 977, 808 and 325 m<sup>2</sup> g<sup>-1</sup>,

72 respectively. A simulation of the pore structure provided by the inefficient packing of polymer chains is  
73 shown in Fig. 1c for PIM-EA-TB. In addition, amidoxime-modified PIMs were prepared using a  
74 controlled reaction of the nitrile groups in PIM-1 with hydroxylamine<sup>39</sup>, to give 32, 56, 63, 83 and 100%  
75 conversions and PIM-SBF<sup>40, 41</sup> with 100% conversion. N<sub>2</sub> gas adsorption isotherms (Fig. 2d) show that  
76 the AO modification leads to a drop of BET surface area from 778 m<sup>2</sup> g<sup>-1</sup> (PIM-1) to 567 m<sup>2</sup> g<sup>-1</sup> (AO-  
77 PIM-1), likely due to hydrogen bonding interactions<sup>42</sup> that leads to tighter chain packing and the creation  
78 of more ultramicropores (i.e. of diameter <7 Å), whilst retaining overall high micropore volume (0.194  
79 cm<sup>3</sup> g<sup>-1</sup>). Pore size distributions derived from CO<sub>2</sub> adsorption isotherms confirm that the pores in PIM-  
80 EA-TB and AO-PIM-1 are predominately sub-nanometre in diameter (Extended Data Fig. 1). Atomistic  
81 molecular dynamics (MD) simulations suggest a narrow pore size distribution in the range of 2-8 Å (Fig.  
82 1e, Extended Data Fig. 2).

83 Thick self-supported PIM membranes were fabricated by solution-casting (Fig. 1f, Extended Data  
84 Fig. 3) and thin film composite membranes of PIM-EA-TB, PIM-BzMA-TB and DMBP-TB (~350 nm)  
85 were also prepared by spin-coating or blade-coating a dilute polymer solution onto a low-cost porous  
86 membrane support (Fig. 1g). The membranes were characterised using gas permeation (Table S1) and  
87 scanning electron microscopy (SEM), which confirms the defect-free cross-section of both thick films  
88 (Fig. 1f, Fig. S4-5) and thin film composite membranes (Fig. 1h, Fig. S6). The long-term chemical  
89 stability of PIM polymers towards strong alkaline solutions was confirmed by Fourier Transform-Infrared  
90 (FTIR) spectroscopy and gel permeation chromatography (GPC), which showed that the molecular  
91 weight distribution remained unchanged; the maintenance of microporosity was also confirmed by N<sub>2</sub>  
92 adsorption (Extended Data Fig. 4). Cyclic voltammetry (CV) indicated good electrochemical stability  
93 (Fig. S7). Thermogravimetric analysis (TGA) verified the good thermal stability with no obvious weight  
94 loss up to 150 °C (Fig. S8). The mechanical properties of the polymer membranes were measured by  
95 nanoindentation using atomic force microscopy (AFM) and tensile tests (Fig. S9-10). The Young's  
96 modulus and ultimate tensile strength (Table S2) of PIM-EA-TB and AO-PIM-1 films are as high as 2.0  
97 GPa and 40 MPa, respectively, both higher than those of Nafion membranes (0.3 GPa and 25 MPa).  
98 These results suggest that PIM membranes possess high chemical stability, electrochemical stability,  
99 thermal stability and mechanical strength.

## 100 **Water uptake and ionic conductivity**

101 To demonstrate the effect of porosity on water sorption and transport,<sup>5, 15, 19, 43, 44</sup> we analysed a range of  
102 hydrophilic TB-PIMs with different microporosity using dynamic vapour sorption (DVS). For PIM-EA-  
103 TB, the combination of high porosity and hydrophilicity of the amine groups within the TB unit enables  
104 the polymer to adsorb up to 41.3 wt.% water vapor at 298 K and 30.0 mbar (Fig. 2b, Fig. S11), in contrast,  
105 the less porous DMBP-TB adsorbs only 11.3 wt%. Hydrophilicity also promotes the formation of water  
106 channels as demonstrated by a comparison of the microporous, hydrophobic PIM-1 with its hydrophilic  
107 derivative AO-PIM-1. Despite its high surface area of 778 m<sup>2</sup> g<sup>-1</sup> and micropore volume of 0.251 cm<sup>3</sup> g<sup>-1</sup>,  
108 PIM-1 adsorbs only 5.7 wt% of water vapour (Table. S3), whereas the uptake of water vapour in AO-  
109 PIM-1 increases linearly from 5.7 to 29.0 wt% on increasing the AO content from 0 to 100 %, (Fig. S11).  
110 AO-PIM-SBF with higher porosity (Fig. 2d) adsorbed water vapor up to 34.0 wt.% (Fig. S11). Bulk water  
111 uptake was also measured and showed a similar trend (Fig. 2e). Kinetic analyses suggest that water  
112 adsorption of PIM membranes follows the clustering mechanism<sup>44</sup> (Fig. S12). The microstructural  
113 changes of PIM membranes on hydration were investigated by wide-angle and small-angle X-ray  
114 scattering (Fig. S13-14), which suggest the presence of a continuous network of ultra-micropores in both  
115 dry and hydrated states.

116 Ionic conductivity of thick (50-80 μm) membranes of the three TB-PIM polymers was measured  
117 using electrochemical impedance spectroscopy (EIS) over a temperature range of 30-80°C (Fig. 2c and  
118 Fig. S15-16). At 30°C, PIM-EA-TB demonstrates an ionic conductivity of 4.4 × 10<sup>-4</sup> S cm<sup>-1</sup> in 1 M NaOH  
119 solution and a comparable value of 2.9 × 10<sup>-4</sup> S cm<sup>-1</sup> in 1 M NaCl solution. In contrast, lower  
120 conductivities in NaOH solution were obtained for PIM-BzMA-TB (4.1 × 10<sup>-5</sup> S cm<sup>-1</sup>) and less porous  
121 DMBP-TB (3.1 × 10<sup>-6</sup> S cm<sup>-1</sup>). The Arrhenius-type temperature dependence of ion-conductivity suggests  
122 it is controlled by thermally-activated confined water dynamics in the microporous and hydrophilic  
123 polymer. Although these intrinsic ionic conductivities are low relative to those of the benchmark ion-  
124 exchange membranes such as Nafion, the thin film composite membrane of PIM-EA-TB (300-400 nm)  
125 demonstrates a resistance of only 1.2 Ω cm<sup>2</sup> in 1 M NaOH solution at 25°C. EIS demonstrated that the  
126 fully converted 50-μm-thick AO-PIM-1 membranes achieve superior ionic conductivity (4.8 × 10<sup>-3</sup> S cm<sup>-1</sup>  
127 ). The more porous AO-PIM-SBF with a BET surface area of 618 cm<sup>2</sup> g<sup>-1</sup> achieves even higher ionic

128 conductivity of  $8.9 \times 10^{-3} \text{ S cm}^{-1}$  in 1 M NaOH solution at 30°C and  $2.1 \times 10^{-2} \text{ S cm}^{-1}$  at 80°C, which are  
129 comparable or superior to those of Nafion 212 ( $1.1 \times 10^{-2} \text{ S cm}^{-1}$  at 30°C and  $1.7 \times 10^{-2} \text{ S cm}^{-1}$  at 80°C)  
130 (Fig. 2f, S17, Extended Data Fig. 5a, Table S4). The high ionic conductivity of AO-PIMs in alkaline  
131 electrolytes can be ascribed to the introduction of negative charges due to the deprotonation of the  
132 amidoxime group ( $pK_a \sim 13.2$ ) at high  $pH^{45}$ , which facilitates the transport of positively charged cations  
133 (Extended Data Fig. 5, and Supplementary Information Section 3.1.1.). The incorporation of  $\text{Na}^+$  in AO-  
134 PIM-1 after NaOH treatment was confirmed by XPS spectra whereas NaCl treated AO-PIM-1 and NaOH  
135 treated PIM-EA-TB showed no evidence of  $\text{Na}^+$  uptake (Fig. S18). The high ionic conductivity in AO-  
136 PIMs suggests that the local mobility of water and ions in the micropores and channels is a collective  
137 property resulting from the combination of high micropore volume, a large amount of water adsorption  
138 due to hydrophilic functional groups, and interactions between charge-carrying ions with charged  
139 functional groups (*i.e.* deprotonated AO groups).

140 To gain direct experimental evidence of the interactions of water and ions with polymer membranes  
141 at a molecular level, *in situ* solid-state nuclear magnetic resonance (ssNMR) spectroscopy was used to  
142 investigate AO-PIMs membranes with hydrophilicity tuned by degree of conversion (0% to 100 %). Two  
143 distinct peaks can be identified in the  $^1\text{H}$  NMR spectra after the polymers are exposed to 20 wt% 1 M  
144 NaOH/ $\text{H}_2\text{O}$  solution: one centred at 3 ppm and the other at 4 ppm, both of which move towards higher  
145 chemical shifts on increasing membrane hydrophilicity (Fig. 2g and Extended Data Fig. 6). Time-  
146 resolved  $^1\text{H}$  and  $^{23}\text{Na}$  spectra (Fig. 2h, Extended Data Fig. 6 and Supplementary Information Section  
147 3.1.2.) reveal that water adsorption and the associated sodium ion diffusion into the pores occurs faster  
148 with higher AO modification. At only 32% conversion (Fig. 2i-j), the dynamic adsorption of water  
149 molecules and  $\text{Na}^+$  ions into the membrane channels and wetting of channel walls were captured in real  
150 time, whereas at 56% and 100%, these processes were complete before data acquisition. These  
151 unprecedented real-time experimental observations of water and ion uptake in intrinsically microporous  
152 membranes suggest that water adsorption in the confined three-dimensional interconnected micropores  
153 leads to the formation of water-facilitated ionic channels, enabling fast transport of water and ions.

#### 154 **Selective ionic and molecular transport**

155 Fast and selective ion transport in PIM membranes was demonstrated using concentration-driven  
156 dialysis diffusion tests (Fig. S19-20, Table S5-6). Free standing 300-nm-thick PIM-EA-TB membranes  
157 show a high permeation rate of hydrated  $K^+$  ions of up to  $10.8 \text{ mol m}^{-2} \text{ h}^{-1}$ , much higher than that of low-  
158 porosity DMBP-TB ( $0.2 \text{ mol m}^{-2} \text{ h}^{-1}$ ) of the same thickness (Fig. 3a) and surpassing values of recently  
159 reported ionic-sieving membranes including graphene oxide membranes<sup>2,27</sup>. TB-PIM membranes show a  
160 sharp size-exclusion cut-off of  $\sim 8.0 \text{ \AA}$ , allowing the transport of smaller hydrated ions ( $K^+$ ,  $Na^+$ ,  $Li^+$ ,  $Cl^-$ )  
161 while rejecting larger ions such as hydrated  $Mg^{2+}$  ( $8.56 \text{ \AA}$ ). The ideal selectivity of  $K^+$  over  $Mg^{2+}$  is up to  
162 30-40 for PIM-BzMA-TB and untreated AO-PIM-1 membranes. High selectivity is also observed for  
163 binary salt dialysis (Fig. 3b and Table S6), demonstrating the potential of these PIM membranes in ion  
164 separation applications. Similarly, the PIM-BzMA-TB membrane also shows a high ideal  $Li^+/Mg^{2+}$   
165 selectivity of 33, despite the small difference in hydrated diameter ( $7.6$  and  $8.56 \text{ \AA}$ ). Contra-dialysis  
166 diffusion tests with equal concentration of anion (*i.e.*,  $Cl^-$ ) on the feed and permeate sides (Fig. S20)  
167 confirmed the fast cation permeation and high selectivity. Ion transport in polymeric membranes is  
168 usually governed by the combination of Donnan exclusion, dielectric exclusion and steric hindrance (size-  
169 exclusion)<sup>43</sup>. Since the three TB-PIM polymers contain the same TB functional groups with similar  
170 charge properties, the high selectivity of monovalent ions over divalent ions suggests that a size-exclusion  
171 mechanism dominates resulting from narrow ionic channels. Fast ion permeation rates and high  
172 selectivity result in the performance of PIM membranes surpassing those of existing nanofiltration  
173 membranes and graphene oxide and MXene-based ion-sieving membranes<sup>2,28,46-48</sup> (Fig. 3b). The relative  
174 permeation rates of  $K^+$  ions over the larger  $Fe(CN)_6^{3-}$  anions ( $\sim 9.5 \text{ \AA}$ ), through both PIM-EA-TB and AO-  
175 PIM-1 show good selectivity of 48 and 82, respectively, comparable to that of Nafion (Fig. S19, Table  
176 S6). Hence these hydrophilic PIM membranes have potential for a range of applications such as ion  
177 separation, wastewater treatment, lithium ion extraction and recycling, and removal of heavy metal ions.

178 The size-selectivity was also demonstrated for recently reported redox active molecules with  
179 molecular weights in the range of 140-800 Da: 2,5-dihydroxy-1,4-benzoquinone (DHBQ)<sup>49</sup>, 2,6-  
180 dihydroxyanthraquinone (2,6-DHAQ)<sup>10</sup>,  $K_4Fe(CN)_6$ , riboflavin 5'-phosphate sodium salt (FMN-Na)<sup>13</sup>,  
181 and flavin adenine dinucleotide disodium salt hydrate (FAD). Nanofiltration studies in neutral-pH  
182 aqueous solutions showed that the PIM-EA-TB membrane achieved nearly 100% rejection of these



183 molecules with the exception of the relatively small DHBQ (Fig. 3c, Fig. S21-23). Dialysis diffusion  
184 experiments confirmed that the crossover of these redox molecules through PIM membranes is generally  
185 very slow over 100 h in alkaline solutions (Fig. 3d, S24, Extended Data Fig. 7, and Table S7).  
186 Importantly, the permeance of  $\text{K}_4\text{Fe}(\text{CN})_6$  through AO-PIM-1 ( $1.13 \times 10^{-3} \text{ mol m}^{-2} \text{ h}^{-1}$ ) and AO-PIM-SBF  
187 ( $3.41 \times 10^{-5} \text{ mol m}^{-2} \text{ h}^{-1}$ ), is at least an order of magnitude lower than that of commercial Nafion 212  
188 ( $1.17 \times 10^{-2} \text{ mol m}^{-2} \text{ h}^{-1}$ ). In addition, the diffusion of redox-active organic molecules including DHAQ and  
189 FMN are generally slower than that of  $\text{K}_4\text{Fe}(\text{CN})_6$ . Furthermore, in contra-diffusion crossover tests, the  
190 permeance of  $\text{K}_4\text{Fe}(\text{CN})_6$  through AO-PIM-1 dropped from  $1.13 \times 10^{-3} \text{ mol m}^{-2} \text{ h}^{-1}$  to around  $1.5 \times 10^{-4} \text{ mol}$   
191  $\text{m}^{-2} \text{ h}^{-1}$ , which is much lower than that of commercial Nafion 212 membranes ( $5.91 \times 10^{-3} \text{ mol m}^{-2} \text{ h}^{-1}$ )  
192 (Extended Data Fig. 7 and Table S8). Since these crossover tests were performed using alkaline solution,  
193 in which both the organic redox molecules and AO-PIM-1 membranes are negatively charged, charge  
194 exclusion may also contribute to the low crossover rates. Overall, these results confirm that PIM  
195 membranes effectively block large redox active molecules while enabling fast ion transport, which is  
196 crucial for the operation of organic RFBs.

### 197 **Ion-selective PIM membranes for efficient and stable aqueous redox flow batteries**

198 The hydrophilic PIM membranes were incorporated into aqueous redox flow batteries using recently  
199 reported organic redox couples (Fig. S25, Table S10), including DHBQ| $\text{K}_4\text{Fe}(\text{CN})_6$ <sup>49</sup> (Fig. S28), FMN-  
200 Na| $\text{K}_4\text{Fe}(\text{CN})_6$ <sup>13</sup> (Extended Data Fig. 8), and 2,6-DHAQ| $\text{K}_4\text{Fe}(\text{CN})_6$ <sup>10</sup> (Extended Data Fig. 9) for which  
201 the cyclic voltammetry curves are shown in Fig. 4b. EIS was used to investigate the area-specific  
202 resistance of TB-based and AO-functionalized PIM membranes (Fig. 4c, f, and Table S9). Crossover tests  
203 suggest that FMN-Na achieves near-100% rejection for all PIM membranes (Fig. 3d, Extended Data Fig.  
204 7I). Therefore, the FMN-Na| $\text{K}_4\text{Fe}(\text{CN})_6$  redox couple was used to determine the influence of the  
205 membrane area-specific resistance on battery performance. Microporous PIM-EA-TB and PIM-BzMA-  
206 TB were easily fabricated into nanoscale films, resulting in a significantly optimised area-specific  
207 resistance of 1.20 and 1.60  $\Omega \text{ cm}^2$ , respectively, lower than that of the less porous DMBP-TB (10.7  $\Omega$   
208  $\text{cm}^2$ ). Similarly, AO-PIM-1 membranes with the proportion of AO groups at 56, 63 and 100% have area-  
209 specific resistances of 10.4, 2.90 and 1.04  $\Omega \text{ cm}^2$ , respectively. The high-frequency area specific  
210 resistance of AO-PIM-1 measured in a flow cell is about 0.75  $\Omega \text{ cm}^2$  at 50% SOC, which is approximate



211 to  $0.97 \Omega \text{ cm}^2$  at 0% SOC (Fig. S27). The slight decrease in ASR at higher SOCs may be due to  
212 membrane activation during the charging process. Redox flow batteries assembled from membranes with  
213 lower resistance generally show a lower voltage gap in polarization tests (Fig. 4d, 4g), yielding a higher  
214 power density (Fig. S26) and higher energy efficiency (Fig. 4e, 4h). These results suggest that the  
215 hydrophilic ionizable groups in AO-PIMs play an important role in reducing ion transport resistance and  
216 achieving the efficient operation of RFBs.

217 A RFB based on the small quinone redox molecule DHBQ<sup>49</sup> paired with  $\text{K}_4\text{Fe}(\text{CN})_6$ , showed a  
218 swift battery capacity decay from 2.3 to 1.4 Ah  $\text{l}^{-1}$  over the initial 10 cycles (Fig. S28), consistent with  
219 rapid DHBQ crossover (Fig. 3c). In contrast, RFBs assembled with a redox couple of FMN-  
220  $\text{Na}|\text{K}_4\text{Fe}(\text{CN})_6$  using either a PIM-EA-TB thin film composite or an AO-PIM-1 membrane showed high  
221 cycling stability with electrochemical capacity retention of 86.5% and 84.5%, respectively, over 200  
222 cycles at  $80 \text{ mA cm}^{-2}$  (Fig. 4i, Extended Data Fig. 8). These values are comparable to that obtained from  
223 the equivalent RFB with a Nafion 212 membrane (85.1%). The area-specific resistance and conductivities  
224 of AO-PIM-1 in alkaline solution were unchanged during cycling (Fig. S29). Therefore, the slow decay of  
225 discharge capacity in these FMN-Na-based RFBs can be attributed to the known instability of FMN in  
226 strong alkaline solution<sup>12</sup>. Further experiments confirmed that degradation of FMN-Na leads to battery  
227 capacity decay (Fig. S30). RFBs based on the 2,6-DHAQ $|\text{K}_4\text{Fe}(\text{CN})_6$  redox couple operated in an argon-  
228 filled glovebox (Fig. 4j) achieved high coulombic efficiencies of >99.8 % with both PIM-EA-TB and  
229 AO-PIM-1 membranes at  $40 \text{ mA cm}^{-2}$ . The RFB using an AO-PIM-1 membrane exhibited the lowest  
230 capacity fade rate of 0.5% per day (0.006% per cycle), which is superior to the performance of Nafion  
231 212 membrane (2.3% per day, 0.025% per cycle) (Fig. 4j and Extended Data Fig. 10). The crossover rate  
232 of iron-containing species through AO-PIM-1 in an operating RFB was quantitatively determined by *ex-*  
233 *situ* ICP-OES to be  $1.48 \times 10^{-4} \text{ mol m}^{-2} \text{ h}^{-1}$ , which is significantly lower than that of an identical RFB using  
234 a Nafion 212 membrane ( $6.37 \times 10^{-4} \text{ mol m}^{-2} \text{ h}^{-1}$ ) (Fig. 3d and inset in Fig. 4j, Extended Data Fig. 10, and  
235 Fig. S32). Much more rapid decay of performance was observed by operating the 2,6-DHAQ- $\text{K}_4\text{Fe}(\text{CN})_6$   
236 battery in the open-air rather than an argon atmosphere (Fig. S31) suggests that oxygen causes  
237 degradation of the redox compounds. Although further work is required to fully understand the battery  
238 decay based on the degradation and crossover of organic molecules, it is clear that the highly conductive

239 and selective PIM membranes enable the battery to perform with significantly enhanced stability  
240 (Supplementary Information Section 4.4.). Indeed, based on the crossover of redox active species (*e.g.*  
241  $K_4Fe(CN)_6$ ), if we assume that the battery performs only one cycle per day with charging-discharging  
242 duration of 4 h, and the electrolytes are isolated from the membrane during the 20 hours when the battery  
243 isn't operating, we estimate that the lifetime of an RFB based on AO-PIM-1 (~6300 days) will be longer  
244 than that of a similar RFB based on Nafion 212 (~1464 days) (Table S11-12, and Supplementary  
245 Information Section 4.4.4).

## 246 **Outlook**

247 The concept of generating intrinsic microporosity within solution processable polymers, via chain  
248 rigidity and contortion, combined with the incorporation of hydrophilic functional groups to optimise  
249 hydrophilicity and ion-conductivity has resulted in a new generation of ion selective membranes. For the  
250 fabrication of RFBs, these membranes show low area-specific resistance, fast ion permeation rate, and  
251 unprecedented selectivity towards redox couples, leading to RFB performance and stability that is  
252 comparable, and in some cases superior, to those based on benchmark Nafion membranes. PIMs, whose  
253 structural diversity can be controlled by monomer choice, polymerisation reaction and post-synthetic  
254 modification, allow for the rational optimisation of membranes for RFBs based on a wide variety of redox  
255 chemistries. For example, the more porous AO-PIM-SBF provided a membrane with enhanced ionic  
256 conductivity relative to AO-PIM-1 and our current effort is directed towards improving this polymer's  
257 robustness so as maintain its improved RFB performance. The modification of ultrapermeable PIMs with  
258 even greater intrinsic microporosity, such as those based on benzotriptycene<sup>50</sup>, may increase ionic  
259 conductivity further. Importantly, thin-film composite membranes can be prepared using roll-to-roll  
260 technology and low-cost supports. Hence, these innovative membranes could be cost-effective and  
261 applicable to a wide range of energy-related devices including fuel cells, redox flow batteries and  
262 electrochemical reactors in addition to water treatment processes such as electrodialysis, nanofiltration  
263 and desalination.

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### 385 Contributions

386 Q.S., R.T., and A.W. developed membranes and redox flow batteries. A.W. synthesised PIM-1, AO-PIMs, Amine-  
387 PIM-1 and DMBP-TB polymers, prepared membranes and performed characterizations. R.M. synthesized TB-  
388 PIMs and carried out characterizations. C.Y. synthesised PIM-SBF and performed modification and  
389 characterizations. R.T. and A.W. carried out the ion transport and diffusion measurements. X.Z. and Z.F. helped  
390 with the crossover measurements. R.T. and A.W. performed electrochemical and flow battery experiments. B.P.D  
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392 and C.P.G. contributed to solid state NMR measurements and interpretation and provided insights into the research.  
393 L.T., E. J., L.C., S.Y.C., K.E.J. and A.I.C. contributed to molecular simulations and analyses. T. Li contributed to  
394 the SAXS measurements. N.P.B. provided facility support and insights into flow battery systems. R.T., A.W.,  
395 N.B.M. and Q.S. wrote the manuscript with contribution from all co-authors. All of the authors participated in the  
396 discussion and commented on the manuscript. Q.S. conceived the project, designed the research, and directed the  
397 project with N.B.M.

398 **Competing interests**

399 The authors declare no competing interests.

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401

402 **Figure Caption**

403

404 **Figure 1 | Ion-selective microporous membranes.** **a**, Working principle of hydrophilic microporous membranes  
405 for fast ion transport and high ionic and molecular selectivity. **b**, Schematic diagram of interconnected sub-  
406 nanometer-sized cavities in microporous membranes for rapid and selective ion transport. **c**, Three-dimensional  
407 view of an amorphous cell of PIM-EA-TB polymer. Cell size: 66.8×66.8×66.8 Å. The grey surface indicates the van  
408 der Waals surface, and green surface is the Connolly surface with probe radius of 1.55 Å. **d**, Macromolecular  
409 structures of microporous polymers with size-selective ion separation function, and typical structures of hydrophilic  
410 microporous PIM polymers including PIM-EA-TB, PIM-BzMA-TB, DMBP-TB. Inset diagram shows the inefficient  
411 packing of rigid and contorted polymer chains. Macromolecular structures of microporous polymers with both size-  
412 exclusion and ion-conductive functionality, including typical examples of amidoxime-functionalized PIM-1 (AO-PIM-  
413 1) and deprotonated cation-exchange AO-PIM-1 in alkaline solutions at high pH, and AO-PIM-SBF studied in this  
414 work. Inset schematic diagram shows the inefficient packing of rigid and contorted polymer chains with negative  
415 charged functional groups located on the rigid backbone that facilitate the transport of cations. **e**, Normalized pore  
416 size distribution derived from molecular simulation as shown in (c). **f**, Cross-sectional SEM image of an AO-PIM-1  
417 membrane. **g**, Cross-sectional SEM image of a low-cost mesoporous polyacrylonitrile support membrane. **h**, Cross-  
418 sectional SEM image of a TFC membrane consisting of an ion-selective PIM polymer membrane (PIM-EA-TB)  
419 coated on the mesoporous polyacrylonitrile support.

420 **Figure 2 | Water adsorption, ionic conductivity and ionic dynamics of microporous membranes.** **a**, N<sub>2</sub>  
421 adsorption–desorption isotherms of Tröger-base containing PIM polymers (TB-PIMs) at 77 K. **b**, Water vapor  
422 sorption isotherms of thick self-supported TB-PIM membranes at 25°C measured by DVS. **c**, Temperature  
423 dependence of ionic conductivities of thick self-supported TB-PIM membranes measured in 1 M NaOH (filled  
424 symbol) or 1 M NaCl (open symbol) by electrochemical impedance spectroscopy. **d**, N<sub>2</sub> adsorption-desorption  
425 isotherms of PIM-1, AO-PIM-1 and AO-PIM-SBF polymers at 77 K. symbols in **a**, **b**, and **d**: filled, adsorption; open,  
426 desorption. **e**, Bulk water uptake and ionic conductivity as a function of amidoxime functional group ratio (from 32%  
427 to 100%) in amidoxime-functionalized PIM-1 (AO-PIMs). Error bars are standard deviations using at least three  
428 measurements from different samples. Ionic conductivity was measured in 1 M NaOH at 30°C. **f**, Temperature  
429 dependence of ionic conductivities of AO-PIMs and Nafion 212 membranes measured in 1 M NaOH (filled symbol)  
430 or 1 M NaCl (open symbol) by electrochemical impedance spectroscopy. **g–j**, Water and ionic dynamics in  
431 microporous membranes probed by in situ solid-state NMR spectroscopy: **g**, Equilibrated <sup>1</sup>H solid state nuclear  
432 magnetic resonance (ssNMR) spectra and, **h**, <sup>23</sup>Na ssNMR of 1M NaOH in H<sub>2</sub>O in AO-PIM membranes with varied  
433 portion of amidoxime groups (10 mg). **i**, Time-resolved <sup>1</sup>H ssNMR spectra showing the dynamic adsorption of  
434 H<sub>2</sub>O/OH<sup>-1</sup> in micropores of AO-PIM-1 membrane with 32% of amidoxime groups. **j**, Time-resolved <sup>23</sup>Na ssNMR  
435 spectra showing the dynamic adsorption of Na ions in micropores of AO-PIM-1 membrane with 32% of amidoxime  
436 groups.

437 **Figure 3 | Ionic and molecular sieving.** **a**, Selective ion permeation of common salts through freestanding  
438 microporous PIM membranes with a thickness of about 300 nm. Dashed lines are added to guide the eyes. The  
439 feed solution: 1 M salt solution in high-purity deionized water, including KCl, NaCl, LiCl, CaCl<sub>2</sub>, MgCl<sub>2</sub> and  
440 K<sub>3</sub>Fe(CN)<sub>6</sub> with varied hydrated diameter of cations or anions<sup>2, 28</sup>. The permeate side: high-purity deionized water. **b**,  
441 K<sup>+</sup> permeation rate versus K<sup>+</sup>/Mg<sup>2+</sup> selectivity for PIMs membranes. Solid symbols: ideal selectivity; Open symbols:  
442 binary salt selectivity. Typical ion separation data of ion-exchange membrane, nanofiltration membranes, and state-  
443 of-the-art ion-sieving membranes such as graphene-oxide and MXene membranes reported in the literature<sup>2, 28, 46-48</sup>  
444 are included. The line is added manually to show the trade-off between the ion permeation and selectivity towards  
445 large ions. **c**, Rejection of redox materials measured by nanofiltration using thin film composite membranes  
446 consisting a PIM-EA-TB thin film supported on a porous polyacrylonitrile substrate. Typical commercially available  
447 redox active materials with varied molecular size for redox flow batteries, including 2,5-dihydroxy-1,4-benzoquinone  
448 (DHBQ), 2,6-dihydroxyanthraquinone (2,6-DHAQ), K<sub>4</sub>Fe(CN)<sub>6</sub>, riboflavin 5'-phosphate sodium salt (FMN-Na),  
449 and flavin adenine dinucleotide (FAD-Na). The feed aqueous solution (20 ppm) was pressurised in a nanofiltration  
450 stirred cell under a feed pressure of 10 bar at room temperature. Inset photo shows the colours of retentate (R) and  
451 permeate (P) solutions for typical redox molecules. Error bars are standard deviations using at least three  
452 measurements from different samples. **d**, Permeance of NaOH, FMN-Na, 2,6-DHAQ, K<sub>4</sub>Fe(CN)<sub>6</sub> through PIM-EA-  
453 TB TFC, AO-PIM-1 and Nafion 212 measured by single redox-specie /salt dialysis diffusion tests in H-cells and  
454 operating RFBs (labelled above the columns).

455 **Figure 4 | Hydrophilic microporous membranes enable efficient and stable operation of aqueous redox flow**  
456 **batteries.** **a**, Schematic diagram of a redox flow battery system for grid scale energy storage. Redox materials are  
457 visualized using the 3D molecular models of 2,6-DHAQ and Fe(CN)<sub>6</sub> couple. **b**, Cyclic voltammogram of 2mM 2,6-  
458 DHAQ, FMN-Na (red curve) and ferrocyanide (blue curve) at a scanning rate of 10 mV/s on glassy carbon  
459 electrode. The theoretical potentials were marked in this figure. **c**, EIS spectra of TB-PIM membranes and Nafion  
460 212 in 1 M NaOH. **d**, Voltage versus capacity for TB-PIM membranes with FMN-Na (0.1 M) | K<sub>4</sub>Fe(CN)<sub>6</sub> (0.1 M)

461 redox couple in 1M NaOH solution at a charging-discharging rate of 20 mA cm<sup>-2</sup>. **e**, Battery energy efficiency and  
462 membrane area-specific resistance versus the BET surface areas of TB-PIM polymers. PIM-BzMA-TB and DMBP-  
463 TB were blended at a certain ratio (*i.e.*, 1:2 and 2:1 by weight) to yield blend polymers with the BET surface area of  
464 509 and 674 m<sup>2</sup> g<sup>-1</sup>, respectively, as measured by N<sub>2</sub> adsorption. **f**, EIS spectra of Nafion 212 and AO-PIM-1  
465 membranes with a varied proportion of AO groups in 1 M NaOH. **g**, Voltage versus capacity for AO-PIM-1  
466 membranes with FMN-Na(0.1 M) | K<sub>4</sub>Fe(CN)<sub>6</sub> (0.1 M) redox couple in 1M NaOH solution at a charging-discharging  
467 rate of 20 mA cm<sup>-2</sup>. **h**, Battery energy efficiency and membrane area-specific resistance versus conversion degree  
468 of AO functional groups. Lines in (**e**) and (**h**) are added to guide the eyes. **i**, Cycling stability of FMN-Na|K<sub>4</sub>Fe(CN)<sub>6</sub>  
469 battery assembled with PIM-EA-TB TFC, AO-PIM-1 and Nafion 212 membranes. Mesoporous PAN membrane is  
470 included for comparison. **j**, Cycling performance of RFBs assembled with PIM-EA-TB TFC, AO-PIM-1 and Nafion  
471 212 membranes in an Argon-filled glove box with 2,6-DHAQ | K<sub>4</sub>Fe(CN)<sub>6</sub> redox couple in 1M NaOH solution under  
472 a current density of 40 mA cm<sup>-2</sup>. To evaluate cycling stability, discharge capacity is normalized by the fully-  
473 discharged capacity. The cyclic capacity decay rates labelled for different membranes correspond to the total  
474 percentage loss of capacity divided by the total operation time. Inset figure shows the crossover rates of iron-  
475 containing species through membranes in the operating batteries.



476 **Methods**

477 **Materials.** Most of chemicals were commercially purchased from Sigma-Aldrich and TCI without further  
478 purification, including potassium ferrocyanide ( $K_4Fe(CN)_6$ , >99%), sodium ferrocyanide ( $Na_4Fe(CN)_6$ , >99%),  
479 riboflavin-5'-phosphate sodium salt (FMN-Na, >93%), flavin adenine dinucleotide disodium salt hydrate (FAD-  
480 Na, >95%), 2,6-dihydroxy-antraquinone (2,6-DHAQ, >90%), 2,5-Dihydroxy-1,4-benzoquinone (DHBQ, >98%),  
481 anhydrous zinc chloride ( $ZnCl_2$ , >99%), anhydrous potassium chloride (KCl, >99%), anhydrous sodium chloride  
482 ( $NaCl$ , >99%), anhydrous lithium chloride (>98%), anhydrous calcium chloride ( $CaCl_2$ , >97%), anhydrous  
483 magnesium chloride ( $MgCl_2$ , >98%), potassium hexacyanoferrate ( $K_3Fe(CN)_6$ , >99%), potassium hydroxide  
484 (anhydrous, >99%), sodium hydroxide (NaOH, >99%), and superconductive carbon (KJ-black).

485 Membranes and substrates: Nafion<sup>®</sup>212 (Dupont) membranes were purchased from Sigma-Aldrich. PTFE  
486 substrates were purchased from Cole-Parmer.

487 **Synthesis of PIM-1.** PIM-1 polymer was synthesised following the published method<sup>51</sup>. 3,3,3',3'-tetramethyl-1,1'-  
488 spirobisindane-5,5',6,6'-tetrol (TTSBI) was purified by recrystallization in methanol/dichloromethane. 2,3,5,6-  
489 tetrafluoroterephthalonitrile (TFTPN) was purified by recrystallization in methanol, followed by vacuum  
490 sublimation at 155°C. Purified monomers TTSBI (10.21 g, 30 mmol) and TFTPN (6.00 g, 30 mmol) were dissolved  
491 in anhydrous DMF (200 ml). Anhydrous  $K_2CO_3$  (8.40g, 60.8 mmol) was added to this solution and the mixture was  
492 heated to 70°C for 72 h under  $N_2$ . The reaction mixture was poured into 1 L water and the solid collected by  
493 filtration then washed with water, acetone and methanol. The polymer was purified by repeated precipitation from  
494 chloroform solution by adding methanol drop-wise until the solution became turbid. The purified polymer was  
495 collected by filtration and dried at 110°C under vacuum to yield yellow powders.

496 **Synthesis of AO-PIM-1 and AO-PIM-SBF.** AO-PIM-1 was synthesised by modifying PIM-1 polymer following  
497 a published protocol<sup>39</sup>. PIM-1 (4.80 g) was dissolved in THF (300 ml) and heated to 65°C. To this, hydroxylamine  
498 solution (50 ml, 50 wt.% in  $H_2O$ ) was added dropwise and the mixture was allowed to reflux for 20 h under  $N_2$ . The  
499 reaction mixture was poured into 1 L ethanol and the solid collected by filtration then washed with ethanol. The  
500 product was dried at 100°C under vacuum to yield off-white powders. AO-PIM-1 with varied contents of  
501 amidoxime functionality (32%, 56%, 63% and 83% as confirmed by ssNMR) were obtained by shortening the  
502 reaction time to 30 min, 1 h, 2.5 h and 5 h, respectively. For simplicity, fully converted AO-PIM-1 was named as  
503 AO-PIM-1, while partially converted AO-PIM-1 polymers with varied degree of AO groups were named as AO-  
504 PIM-1 32%, AO-PIM-1 56%, AO-PIM-1 63% and AO-PIM-1 83%. AO-PIM-SBF with 100% conversion of nitrile  
505 group was prepared similarly from PIM-SBF<sup>40, 41</sup>.

506 **Synthesis of Tröger's base PIM polymers.** Tröger's base PIM polymers were synthesised following a previously  
507 reported method, including PIM-EA-TB, PIM-BzMA-TB and DMBP-TB<sup>52</sup>. Detailed synthetic methods of  
508 monomers for PIM-BzMA-TB are given in the Supplementary information. In general, a certain aromatic diamine  
509 monomer (1 mol eq.) was dissolved in dimethoxymethane (5 mol eq.) under nitrogen and the solution cooled to  
510 0 °C. To this, trifluoroacetic acid (120 mol eq.) was added dropwise over 30 min and the solution was stirred for an  
511 appropriate time at room temperature. The viscous reaction solution was slowly poured into aqueous ammonium  
512 hydroxide solution and the mixture stirred vigorously for 2 h during which time an off-white solid was formed. The  
513 solid was filtered, washed with water and then acetone until the washings were clear. The polymer was purified by  
514 repeated precipitation from chloroform solution by adding methanol drop-wise until the solution became turbid.  
515 The purified polymer was collected by filtration and dried at 110°C under vacuum to polymer powders. In some  
516 cases, PIM-BzMA-TB and DMBP-TB were blended to achieve polymer samples with tuned surface area and free  
517 volume. The two polymers were dissolved in chloroform with certain weight ratio to form a homogeneous solution,  
518 and then precipitated in hexane, and further dried at 110°C under vacuum before adsorption analysis.

519 **Fabrication of membranes.** Thick symmetric membranes were fabricated by casting polymer solutions on clean  
520 glass plates using a doctor blade. Chloroform, THF or DMF was used as the solvent to prepare polymer solutions  
521 depending on the solubility of PIMs (chloroform for PIM-1 and TB-based PIMs, THF for AO-PIM-1 32%, and  
522 DMF for AO-PIM-1 56%, 63%, 83% and 100%, respectively); polymer solutions were centrifuged at 12000 rpm  
523 for 5 mins to remove undissolved impurities. After blade casting, the polymer solution films were kept in a  
524 desiccator for two days at a certain temperature (room temperature for chloroform and THF and 60°C for DMF) in  
525 order for slow evaporation of the solvent. Dry polymer membranes were then peeled off from the glass plates and  
526 soaked in methanol overnight. Afterwards, the membranes were dried in air for 12 h and annealed at 110°C for  
527 another 12 h. The thickness of symmetric membranes was controlled by varying the gap thickness of doctor blade  
528 and the concentration of polymer dope solutions.

529 Thin films were fabricated by spin coating dilute polymer solutions onto a substrate.<sup>53</sup> Polymer solutions were  
530 filtered through syringe filters (PTFE, 0.45  $\mu m$ ) and dropped onto the substrate which was kept static. Then the  
531 substrate was rotated at a speed of 2000 rpm with an acceleration speed of 1500 rpm for 1 min. Thin film  
532 composite (TFC) membranes were prepared by using porous hydrophilic polytetrafluoroethylene (PTFE)  
533 membranes, porous anodized aluminum oxide (AAO) membranes, or porous polyacrylonitrile (PAN) ultrafiltration  
534 membranes prepared following previous protocol<sup>54</sup> as the substrate. In some cases, polymer blend films were

535 prepared from PIM-BzMA-TB and DMBP-TB by mixing the two polymers at certain weight ratio. Free standing  
536 thin films were prepared by using glass plates as the substrate, followed by floating them off onto a water surface.  
537 The thickness of the thin film was controlled by varying the concentration of polymer solutions in the range of 1.0 -  
538 4.0 wt%.

539 **Characterization techniques.** Scanning electron microscopy (SEM) was performed using a Hitachi S5500  
540 microscope. Before testing, the membranes were manually fractured in liquid nitrogen and coated with a thin layer  
541 of Au/Pd. The surfaces and cross-sectional morphologies of membranes were observed. Infrared spectroscopy was  
542 performed on a Perkin-Elmer Spectrum 100 FTIR spectrometer with polymer membrane samples mounted on a  
543 zinc-selenium/diamond plate. Thermal analyses were performed using a NETZSCH STA 449 F5 Jupiter  
544 thermogravimetric analyser. Polymer samples were heated from room temperature to 900 °C under flowing  
545 nitrogen at a heating rate of 10°C min<sup>-1</sup>. Tensile tests were carried out using a Lloyd-Ametek EZ50 Material  
546 Testing Machine at room temperature and a relative humidity of around 50% with a strain rate of 10% min<sup>-1</sup>.  
547 Nanomechanical properties were determined using Atomic Force Microscopy (AFM, Asylum Instruments MFP-3D)  
548 with a dual frequency technique (AM-FM) and nanosensor probes (PPP-NCHR, tip radius < 7nm, nom. Spring  
549 constant 42 N m<sup>-1</sup>). Probes were calibrated before use using the built-in 'Get-Real' software. Typical parameters  
550 used were tapping amplitude, set point 0.8 V with a 256 points per line, 1 Hz scan rate. X-ray scattering tests were  
551 performed using a PANalytical X'Pert Pro diffractometer with Cu-K<sub>α</sub> radiation at room temperature. X-ray  
552 photoemission spectra (XPS) were measured with an X-ray photoemission spectroscopy instrument (ESCALAB  
553 250Xi, Cavendish Laboratory). The polymer films were evacuated under vacuum of 10<sup>-10</sup> mbar for one hour prior  
554 to moving to the chamber for measurement. The C-C peak at 284.8 eV was used as a charge correction reference.  
555 Gel permeation chromatography (GPC) analyses were performed either on chloroform solutions (2 mg ml<sup>-1</sup>) using a  
556 GPC MAX variable loop equipped with two KF-805L SHODEX columns and a RI(VE3580) detector, operating at  
557 a flow rate of 1 ml min<sup>-1</sup>, or on DMF solutions containing 0.1 wt% lithium bromide (5 mg ml<sup>-1</sup>) using a high  
558 performance liquid chromatography system (Shimadzu, Prominence system) equipped with a pump (Shimadzu,  
559 LC-20AD), 3 columns including a guard column (Agilent Technologies, guard column: 1xPolarGel-M, separation  
560 columns: 1xPolarGel-M and 1xPolarGel-L) and a photodiode array detector (Shimadzu, SPD-M20A) at 60°C.  
561 Calibration was achieved using Viscotek polystyrene standards (*M<sub>w</sub>* 1000 – 1,000,000 g mol<sup>-1</sup>). Skeletal densities of  
562 polymer powders were measured using a Micromeritics Accupyc II 1340 helium pycnometer equipped with a 3.5  
563 cm<sup>3</sup> sample chamber at 25°C. Each sample was degassed at 110°C under vacuum for 12 h before measurement. A  
564 cycle of 10 measurements was performed to derive the mean value and standard deviation. Low-pressure gas  
565 physisorption was performed using a Micromeritics 3Flex surface characterization analyser. Each sample was  
566 degassed at 110°C under vacuum for 12 h, and then loaded into the apparatus and in-situ degassed at 110°C for  
567 another 12 h. Nitrogen adsorption isotherms were measured at 77 K and CO<sub>2</sub> adsorption isotherms measured at  
568 273 K. Dynamic water vapor sorption was performed using a DVS Endeavour gravimetric sorption analyser  
569 (Surface Measurement Systems, UK) at 25°C. Polymer films (20-30 mg, about 50 μm thick) were dried *in vacuo* at  
570 110°C for 12 h, and *in situ* dried under flowing dry air at room temperature for at least 24 h and when the mass  
571 became constant Water uptake (WU) was determined by measuring the weight changes of polymer membranes in  
572 dry and fully hydrated states. Membrane samples were dried at 110 °C under vacuum for 12 h, and then quickly  
573 weighed with a high-precision analytical balance to obtain the dry mass. These samples were immersed in  
574 deionized water at room temperature for 24 h. The mass of fully hydrated samples was measured after the excess  
575 surface water was quickly wiped off with tissue paper. WU was calculated according to the following equation:  
576  $WU(\%) = (W_{\text{hydrated}} - W_{\text{dry}}) / W_{\text{dry}} \times 100\%$  Where  $W_{\text{hydrated}}$  and  $W_{\text{dry}}$  are the masses of fully hydrated and dry membrane  
577 samples, respectively. The concentration of metal-ions in ion diffusion measurements were detected by inductively  
578 coupled plasma - optical emission spectrometry (ICP-OES). Before testing, the permeate aliquots were diluted in 2  
579 wt% HNO<sub>3</sub>. Ultraviolet-Vis spectra were measured using a UV-VIS spectrometer UV-1800 (Shimadzu) with a  
580 wavelength range of 190–800 nm at an interval of 0.5 nm. High powered decoupling (Hpdéc) magic angle spinning  
581 (MAS) solid state <sup>13</sup>C nuclear magnetic resonance (NMR) spectra were collected using a Bruker Avance III 600  
582 MHz instrument using an adamantane reference. A spinning rate of 15 000 Hz was used with powder samples  
583 packed into a 3.2 mm zirconium rotor. Spectra were typically compiled from 4000 scans with a 6 s recycle delay.

584 **SAXS/WAXS characterization.** SAXS/WAXS experiments were performed at the APS 12ID-B and C station.  
585 The 2D SAXS/WAXS data were collected on a Pilatus 2 M and 300 K area detector (DECTRIS Ltd) with an  
586 incident energy of 12 KeV. The scattering vector, *q*, was calibrated using silver behenate.

587 **Gas permeation tests.** Pure gas permeation tests were carried out with H<sub>2</sub>, CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub> and CH<sub>4</sub> (research grade,  
588 BOC, UK) under a feed pressure of 4 bar at 22°C, using a constant-volume pressure-increase apparatus. The  
589 detailed procedure and analysis methods were reported in previous work.<sup>55</sup> The membrane was evacuated  
590 thoroughly with a vacuum pump before measurements. The gas permeability is derived from the volume of gas  
591 flowing across the membrane. Permeability (*P*) is expressed in Barrer (1 Barrer = 10<sup>-10</sup> cm<sup>3</sup> (STP) cm cm<sup>-2</sup> s<sup>-1</sup> cm  
592 Hg<sup>-1</sup>). The ideal selectivity for a gas pair (A/B) is calculated from the ratio of their permeability.

593 **Diffusion and crossover experiments.** Ion diffusion and redox molecule crossover tests were carried out using  
594 stirred H-shaped cells. Membrane samples were sandwiched between two polydimethylsiloxane (PDMS) O-rings  
595 and sealed in the middle of H-cells using clips or screw claps. The effective area of membrane samples in the H-  
596 cell was 1.54 cm<sup>2</sup>. We used magnetic stirring in both feed and permeate solutions to alleviate concentration  
597 polarization near the membranes. In single salt dialysis diffusion tests, 50 ml 1 M salt solution (KCl, NaCl, LiCl,  
598 CaCl<sub>2</sub>, MgCl<sub>2</sub>, K<sub>3</sub>Fe(CN)<sub>6</sub>, K<sub>4</sub>Fe(CN)<sub>6</sub>, KOH, NaOH or LiOH) was used as the feed solution, and the permeate side  
599 was filled with 50 ml deionised water. The ionic conductivity of permeate solution was continuously recorded  
600 using an ionic conductivity meter (Thermo Scientific Orion Star A210) at a recording interval of 20 s. Afterwards,  
601 the concentration change of permeate solution over time was obtained based on the linear relationship between the  
602 conductivity and concentration of salt solutions. A series of salt solutions with various concentrations were  
603 prepared and their conductivities measured by conductivity meter to derive the calibration curves. The reliability of  
604 this conductivity method was confirmed by ICP-OES measurements. In the permeation measurements of  
605 interchanged cations, 1 M KCl solution was used as the feed with 1M NaCl, 1M LiCl, or 0.5 M MgCl<sub>2</sub> solution as  
606 the permeate, and PIM-EA-TB thin film as the membrane. In binary ion diffusion tests, 50 ml salt solution  
607 containing 0.5 M KCl and 0.5 M MgCl<sub>2</sub> was used as the feed solution, and the permeate side was filled with 50 ml  
608 deionised water. The concentrations of K<sup>+</sup> and Mg<sup>2+</sup> in permeate side were measured by ICP-OES. In single redox-  
609 specie crossover tests of redox molecules, redox active materials (2,6-DHAQ, FMN-Na or K<sub>4</sub>Fe(CN)<sub>6</sub>) dissolved in  
610 1M NaOH aqueous solution were used as the feed solution and the volume was 50 ml; 50 ml 1M NaOH aqueous  
611 solution was used in the permeate side. The concentration change of the permeate solution was monitored and  
612 quantitatively measured by a calibrated UV-Vis spectrometer or ICP-OES. In contra-diffusion crossover tests of  
613 redox molecules, redox active materials (K<sub>4</sub>Fe(CN)<sub>6</sub>) dissolved in 1M NaOH aqueous solution were used as the  
614 feed solution and the volume was 50 ml; redox species (2,6-DHAQ) dissolved in 50 ml 1M NaOH aqueous  
615 solution was used in the permeate side. The concentration change of Fe in the permeate solution was monitored by  
616 ICP-OES, and the concentration change of 2,6-DHAQ in feed solution was quantitatively measured by a calibrated  
617 UV-Vis spectrometer. The concentration of these redox couples are same as those of redox solutions for battery  
618 tests.

619  
620 In these concentration-driven diffusion and crossover tests, the increase of concentration in permeate solution over  
621 the initial period without any volume change follows Fick's first law. The permeation rates (i.e., flux) of ions and  
622 redox species across a membrane are calculated from:

623 
$$J = \frac{V}{A} \left( \frac{\partial C}{\partial t} \right)$$

624 Where  $J$  is the flux,  $V$  is the volume of solution and  $A$  is the effective area of membranes.  $C$  and  $t$  are the  
625 concentration of permeate and diffusion time, respectively.

626 During the process with a constant flux, Fick's first law can be simplified as:

627 
$$J = D \frac{C_1 - C_2}{l} = P(C_1 - C_2)$$

628 Where  $D$  is the permeability;  $C_1$  and  $C_2$  are the concentrations of feed and permeate solutions, respectively;  $l$  is the  
629 thickness of membranes;  $P$  is the permeance.

630 **Nanofiltration experiments.** In order to evaluate the transport properties of PIM membranes towards ions and  
631 redox species with varied sizes, nanofiltration tests were performed using a dead-end stirred cell (300 – 400 rpm)  
632 under a feed pressure of 5-10 bar at room temperature. The effective membrane area was 14.6 cm<sup>2</sup>. Feed solution  
633 concentration was 500 mg L<sup>-1</sup> in deionised water for salt rejection tests, and 20 and 500 mg L<sup>-1</sup> in deionised water  
634 for redox species nanofiltration tests. Feed volume was 200 ml. Concentration of the feed and permeate solutions  
635 was analysed using a conductivity meter or a UV-Vis spectrometer. The water permeance ( $J$ , L m<sup>-2</sup> h<sup>-1</sup> bar<sup>-1</sup>) was  
636 determined by the following equation:  $J = V/(A \times t \times p)$ , where  $V$  is the volume of permeate solutions;  $A$  is the  
637 effective area of membranes using in nanofiltration cells;  $t$  is the testing time;  $P$  is the applied pressure. The  
638 rejection ( $R_i$ ) was calculated from  $R_i = (1 - (C_{P,i}/C_{F,i})) \times 100\%$ , where  $C_{P,i}$  and  $C_{F,i}$  correspond to the concentrations in  
639 the permeate and the feed, respectively.

640 **Ionic conductivity measurements.** Ionic conductivity of polymer membranes was measured by the  
641 electrochemical impedance spectra (EIS) using the potentiostat mode with an AC bias of 10 mV and a frequency  
642 range of 0.2 MHz - 10 Hz. Membrane samples were soaked in 1 M NaOH or NaCl aqueous solutions for 24 h prior  
643 to measurements. The membranes were then sandwiched between two stainless steel electrodes and sealed with  
644 coin cells (Type 2032). The assembly process was carried out in 1M NaOH or NaCl aqueous solution in order to  
645 avoid any air bubbles from being trapped in the cells. The ionic conductivity was calculated according to the  
646 following equation:  $\sigma = L/(R_m \times A)$ , where  $R_m$  is the ionic resistance,  $L$  is the membrane thickness,  $A$  is the active  
647 membrane area (2.00 cm<sup>2</sup>), respectively. Nyquist plots were fitted by an equivalent circuit (Z-view, Fig S21) to  
648 derive  $R_m$ . Membrane thickness was measured by a micrometer.

649 **Cyclic Voltammetry.** CV measurements were carried out using a Biologic SP-150 potentiostat. CV measurements  
650 of redox species were performed using a three-electrode configuration composed of a glassy carbon working  
651 electrode, a Pt counter electrode and a Ag/AgCl reference electrode (pre-soaked in 3 M KCl solution). A two-  
652 electrode configuration was used to study the electrochemical stability of polymers; lithium metal was used as  
653 reference and counter electrodes, and PIM/conductive carbon/PVDF composite (6: 3: 1 by weight) was used as the  
654 working electrode. Lithium metal and PIM composite electrodes were assembled in coin cells (Type 2032) with  
655 lithium salt electrolytes. The scanning rate for both configuration was 10 mV s<sup>-1</sup>.

#### 656 **Battery tests and crossover measurements of operating batteries**

657 Full-cell tests were carried out using a cell hardware (Scribner Associates) consisting of poly(tetrafluoroethylene)  
658 (PTFE) frames, conductive graphite plates with flow fields, copper current collectors, and graphite felt electrodes  
659 (GFA6, SGL) with an effective geometric area of 5 cm<sup>2</sup>. Electrolytes were fed into the cell at a flow rate of 100 ml  
660 min<sup>-1</sup> controlled by a peristaltic pump (Cole-Parmer).

661 Membranes were pretreated prior to full cell tests. Nafion<sup>®</sup> 212 membranes were heated to 80 °C in deionized water  
662 for 20 minutes and then soaked in 6% hydrogen peroxide solution for 35 minutes<sup>10</sup>. After pretreatment, Nafion<sup>®</sup>  
663 212 membranes were stored in 0.1 M NaOH solution. Thin film composite membranes were pretreated in 1 M  
664 NaOH water/ethanol (50: 50 by weight) for 18 h and then washed thoroughly with deionized water. Thick self-  
665 supported PIM membranes were soaked in 1 M NaOH solution for 24 h.

666 Charging-discharging measurements were performed using an electrochemical station (Biologic SP-150  
667 potentiostat) with a constant current density at room temperature. Depending on the electrochemical properties of  
668 redox species, cut-off voltages for K<sub>4</sub>Fe(CN)<sub>6</sub>|2,6-DHAQ, K<sub>4</sub>Fe(CN)<sub>6</sub>|FMN and K<sub>4</sub>Fe(CN)<sub>6</sub>|ZnCl<sub>2</sub> species were set  
669 as 0.5-2.0, 0.6-1.7, and 0.8-1.7 V, respectively. Electrochemical rate tests were performed at varied current  
670 densities of 20, 40, 60, 80 and 100 mA cm<sup>-2</sup>. In long-term cycling tests, current density was 80 mA cm<sup>-2</sup> for  
671 K<sub>4</sub>Fe(CN)<sub>6</sub>|2,6-DHAQ and K<sub>4</sub>Fe(CN)<sub>6</sub>|FMN systems, and 20 mA cm<sup>-2</sup> for K<sub>4</sub>Fe(CN)<sub>6</sub>|ZnCl<sub>2</sub> system. Coulombic  
672 efficiency was calculated by ratio of the discharge capacity to the charge capacity. Energy efficiency was  
673 calculated by the ratio of average discharge energy to the average charge energy. Voltage efficiency was calculated  
674 by the ratio of average discharge voltage to the average charge voltage. In electrochemical polarization tests, linear  
675 galvanic sweep measurements were carried out using the FMN-Na|K<sub>4</sub>Fe(CN)<sub>6</sub> system with a scanning rate of 10  
676 mA s<sup>-1</sup> from -400 to 800 mA. Specific power density was derived from i-v curves.

677 We found that carbon electrodes have critical effects on the energy efficiency, for example, thermal treatment could  
678 enhance the redox reactions and increase the energy efficiency<sup>7</sup>. However, the batch thermal treatment processing  
679 can be slightly different resulting in different performance. Therefore, for consistent comparison of membrane  
680 performance, we used the same batch of fresh graphite felt electrodes without thermal treatment throughout this  
681 study.

682 Crossover rates in the operating batteries: the crossover rates of 2,6-DHAQ through separators to catholytes were  
683 measured by Cyclic Voltammetry with a scanning rate of 10 mV s<sup>-1</sup>. The crossover rates of K<sub>4</sub>Fe(CN)<sub>6</sub> through  
684 separators to anolytes were measured by ICP-OES. The samples for ICP-OES tests were collected after a certain  
685 time and diluted for 200 times in 2.0 wt% HNO<sub>3</sub> solutions.

686 **Electrolyte preparation.** In alkaline RFBs, 0.1 M 2,6-DHAQ, 0.1 M DHBQ, or 0.06 M FMN-Na dissolved in 1M  
687 NaOH solution was used as the anolyte; 0.1 M K<sub>4</sub>Fe(CN)<sub>6</sub> dissolved in 1M NaOH was used as the catholyte.  
688 Electrolyte volume was 10 ml. The theoretical specific capacity of these redox couples was 2.68 Ah L<sup>-1</sup>, determined  
689 by the limiting electrolyte, *i.e.*, the catholyte. For the high-concentration 2,6-DHAQ cycling experiment, 0.4 M  
690 K<sub>4</sub>Fe(CN)<sub>6</sub> and 0.25 M DHAQ were used as the electrolytes and gave a theoretical specific capacity of 10.7 Ah L<sup>-1</sup>.  
691 In neutral RFBs, 0.1 M ZnCl<sub>2</sub> or 0.1 M MV dissolved in 1M KCl solution was used as the anolyte, and 0.1 M  
692 K<sub>4</sub>Fe(CN)<sub>6</sub> or 0.1 M TEMPO dissolved in 1M KCl solutions was used as catholytes. For zinc semi-solid systems, a  
693 zinc plate was placed into the carbon electrodes in the anode side.

694 **Molecular simulation.** We generated three amorphous models of PIM-1, AO-PIM-1 and PIM-EA-TB polymers,  
695 using the Amorphous Cell module in Materials Studio 2018 (Dassault Systèmes BIOVIA). All polymer chains  
696 consisted of 30 monomer units and amorphous models were constructed with 20 polymer chains per simulation box,  
697 with all interactions defined by the polymer consistent forcefield (PCFF). The procedure for packing and  
698 equilibration are described in detail elsewhere<sup>56</sup>. Void analysis was carried out using the software zeo++. This  
699 software uses a Voronoi decomposition to calculate the interconnectivity of a porous material's pore network with  
700 respect to a probe of a given size, and for that probe can also calculate the surface area, accessible volume, largest  
701 included sphere, pore limiting diameter and a distribution of pore sizes. In this work, a probe size of 1.55 Å,  
702 equivalent to the Van der Waals radius of N<sub>2</sub>, was used to acquire all quantities except the pore size distribution.  
703 Furthermore, 0.85 Å probe was also used to probe all three polymers, due to the presence of ultramicropores and  
704 smaller channels.

705 **In situ solid-state NMR tests.** All polymer membranes were dried *in vacuo* at 120°C before transferring into an Ar  
706 glove box. The membranes were not exposed to air during transfer. The membranes were then fractured into small  
707 pieces and packed into 3.2 mm solid state NMR rotors in the glove box. The mass loadings of PIM-1, AO-PIM-1

708 32%, AO-PIM-1 56% and AO-PIM-1 100% membranes were 8.0, 11.6 mg, 13.0 and 13.8 mg, respectively. 20 wt%  
709 1M NaOH aqueous solution was added into each of the above polymer membranes inside a rotor; these soaked  
710 membrane samples were then subjected to NMR measurements immediately. All solid-state  $^1\text{H}$  and  $^{23}\text{Na}$  NMR  
711 spectra were acquired on a 16.4 T Bruker Avance III spectrometer using a 3.2 mm HXY probe head. A single-pulse  
712 sequence was used to acquire magic-angle spinning (MAS) spectra with spinning frequencies of 15 kHz, recycle  
713 delays of 5 and 3 s (for  $^1\text{H}$  and  $^{23}\text{Na}$ , respectively), and radiofrequency (rf) field strengths of 142 kHz and 385 kHz,  
714 respectively.  $^1\text{H}$  and  $^{23}\text{Na}$  shifts were externally referenced to solid adamantane at 1.87 ppm and  $\text{Na}_2\text{Ti}_3\text{O}_7$  at 3 ppm.  
715 To monitor the adsorption dynamics of  $\text{H}_2\text{O}$  and  $\text{Na}^+$ , automated multiple single pulse experiments were performed  
716 with a time interval of 10 s. Spin-lattice relaxation ( $T_1$ ) measurements of  $^1\text{H}$  were performed using the saturation  
717 recovery technique with 25 spectra with incremental  $t$  in the second-dimension and 50 saturation pulses. The  
718 integrated peak areas were fitted to  $f(t)=I_0 \times [1-\exp(-t/T_1)]$  to obtain relaxation constant  $T_1$ .  
719

720 **Data availability.** The data shown in the plots and that support the findings of this study are available from the  
721 corresponding authors on reasonable request.

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