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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^{1,2}, there is a rapidly growing demand for ion-transport membranes in applications related to energy¹⁻³. 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 H₂ production⁴, proton-exchange membrane (PEMs) and alkaline fuel cells for energy conversion⁵, electrochemical reduction of CO₂ and N₂ to fuel and chemicals⁶, and scalable redox flow batteries (RFBs)^{3,7}. 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 RFBs⁸⁻¹⁴, low-cost and high-performance membranes need to have precise selectivity between ions and organic redox-active molecules¹⁵⁻¹⁸.

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 m²), dominate, despite suffering from poor selectivity due to swelling in water. Intensive
45 research efforts have developed low-cost hydrocarbon-based polymer electrolyte membranes^{5, 19,20,21}, for
46 example, polyaromatic ionomers with pendant ionic functional groups demonstrate promising
47 performance in vanadium flow batteries^{22, 23} and fuel cells²⁴⁻²⁶. 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,²⁹ 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^{2, 27-35}.

53 Here, we demonstrate a new approach for the design of ion-selective membranes based on
54 hydrophilic polymers of intrinsic microporosity (PIMs)³⁶⁻³⁸ 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 m² g⁻¹,

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 hydroxylamine³⁹, to give 32, 56, 63, 83 and 100%
75 conversions and PIM-SBF^{40, 41} with 100% conversion. N₂ gas adsorption isotherms (Fig. 2d) show that
76 the AO modification leads to a drop of BET surface area from 778 m² g⁻¹ (PIM-1) to 567 m² g⁻¹ (AO-
77 PIM-1), likely due to hydrogen bonding interactions⁴² 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 cm³ g⁻¹). Pore size distributions derived from CO₂ 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 N₂
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,^{5, 15, 19, 43, 44} 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 m² g⁻¹ and micropore volume of 0.251 cm³ g⁻¹,
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 mechanism⁴⁴ (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 × 10⁻⁴ S cm⁻¹ in 1 M NaOH
119 solution and a comparable value of 2.9 × 10⁻⁴ S cm⁻¹ in 1 M NaCl solution. In contrast, lower
120 conductivities in NaOH solution were obtained for PIM-BzMA-TB (4.1 × 10⁻⁵ S cm⁻¹) and less porous
121 DMBP-TB (3.1 × 10⁻⁶ S cm⁻¹). 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 cm² 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 × 10⁻³ S cm⁻¹
127). The more porous AO-PIM-SBF with a BET surface area of 618 cm² g⁻¹ 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 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 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 ^1H NMR spectra after the polymers are exposed to 20 wt% 1 M
144 NaOH/ H_2O 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 ^1H and ^{23}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 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^{2,27}. 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 \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 \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)⁴³. 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^{2,28,46-48} (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)⁴⁹, 2,6-
180 dihydroxyanthraquinone (2,6-DHAQ)¹⁰, $K_4Fe(CN)_6$, riboflavin 5'-phosphate sodium salt (FMN-Na)¹³,
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| $\text{K}_4\text{Fe}(\text{CN})_6$ ⁴⁹ (Fig. S28), FMN-
200 Na| $\text{K}_4\text{Fe}(\text{CN})_6$ ¹³ (Extended Data Fig. 8), and 2,6-DHAQ| $\text{K}_4\text{Fe}(\text{CN})_6$ ¹⁰ (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 Ω
208 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 DHBQ⁴⁹ paired with $\text{K}_4\text{Fe}(\text{CN})_6$, showed a
218 swift battery capacity decay from 2.3 to 1.4 Ah 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 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 solution¹². 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 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 benzotriptycene⁵⁰, 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.
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395 N.B.M. and Q.S. wrote the manuscript with contribution from all co-authors. All of the authors participated in the
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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**, N₂
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**, N₂ 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 ¹H solid state nuclear
432 magnetic resonance (ssNMR) spectra and, **h**, ²³Na ssNMR of 1M NaOH in H₂O in AO-PIM membranes with varied
433 portion of amidoxime groups (10 mg). **i**, Time-resolved ¹H ssNMR spectra showing the dynamic adsorption of
434 H₂O/OH⁻¹ in micropores of AO-PIM-1 membrane with 32% of amidoxime groups. **j**, Time-resolved ²³Na 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, CaCl₂, MgCl₂ and
440 K₃Fe(CN)₆ with varied hydrated diameter of cations or anions^{2, 28}. The permeate side: high-purity deionized water. **b**,
441 K⁺ permeation rate versus K⁺/Mg²⁺ 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^{2, 28, 46-48}
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), K₄Fe(CN)₆, 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, K₄Fe(CN)₆ 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)₆ 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) | K₄Fe(CN)₆ (0.1 M)

461 redox couple in 1M NaOH solution at a charging-discharging rate of 20 mA cm⁻². **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 m² g⁻¹, respectively, as measured by N₂ 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) | K₄Fe(CN)₆ (0.1 M) redox couple in 1M NaOH solution at a charging-discharging
467 rate of 20 mA cm⁻². **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|K₄Fe(CN)₆
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 | K₄Fe(CN)₆ redox couple in 1M NaOH solution under
472 a current density of 40 mA cm⁻². 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[®]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 method⁵¹. 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 protocol³⁹. 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^{40, 41}.

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-TB⁵². 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.⁵³ Polymer solutions were
530 filtered through syringe filters (PTFE, 0.45 μm) 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 protocol⁵⁴ 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⁻¹. 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⁻¹.
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⁻¹). 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_α 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 10⁻¹⁰ 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⁻¹) 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⁻¹, or on DMF solutions containing 0.1 wt% lithium bromide (5 mg ml⁻¹) 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_w* 1000 – 1,000,000 g mol⁻¹). Skeletal densities of
562 polymer powders were measured using a Micromeritics Accupyc II 1340 helium pycnometer equipped with a 3.5
563 cm³ 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 CO₂ 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*
570 at 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_{hydrated}* and *W_{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% HNO₃. 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 ¹³C 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 H₂, CO₂, O₂, N₂ and CH₄ (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.⁵⁵ 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 = 10⁻¹⁰ cm³ (STP) cm cm⁻² s⁻¹ cm
592 Hg⁻¹). 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 cm². 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 CaCl₂, MgCl₂, K₃Fe(CN)₆, K₄Fe(CN)₆, 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 base 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 MgCl₂ 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 MgCl₂ was used as the feed solution, and the permeate side was filled with 50 ml
608 deionised water. The concentrations of K⁺ and Mg²⁺ 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 K₄Fe(CN)₆) 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 (K₄Fe(CN)₆) 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:

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

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:

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

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 cm². Feed solution
633 concentration was 500 mg L⁻¹ in deionised water for salt rejection tests, and 20 and 500 mg L⁻¹ 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⁻² h⁻¹ bar⁻¹) 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 cm²), 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⁻¹.

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 cm². Electrolytes were fed into the cell at a flow rate of 100 ml
660 min⁻¹ controlled by a peristaltic pump (Cole-Parmer).

661 Membranes were pretreated prior to full cell tests. Nafion[®] 212 membranes were heated to 80 °C in deionized water
662 for 20 minutes and then soaked in 6% hydrogen peroxide solution for 35 minutes¹⁰. After pretreatment, Nafion[®]
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 K₄Fe(CN)₆|2,6-DHAQ, K₄Fe(CN)₆|FMN and K₄Fe(CN)₆|ZnCl₂ 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⁻². In long-term cycling tests, current density was 80 mA cm⁻² for
671 K₄Fe(CN)₆|2,6-DHAQ and K₄Fe(CN)₆|FMN systems, and 20 mA cm⁻² for K₄Fe(CN)₆|ZnCl₂ 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|K₄Fe(CN)₆ system with a scanning rate of 10
676 mA s⁻¹ 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 efficiency⁷. 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⁻¹. The crossover rates of K₄Fe(CN)₆ 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% HNO₃ 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 K₄Fe(CN)₆ 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⁻¹, determined
689 by the limiting electrolyte, *i.e.*, the catholyte. For the high-concentration 2,6-DHAQ cycling experiment, 0.4 M
690 K₄Fe(CN)₆ and 0.25 M DHAQ were used as the electrolytes and gave a theoretical specific capacity of 10.7 Ah L⁻¹.
691 In neutral RFBs, 0.1 M ZnCl₂ or 0.1 M MV dissolved in 1M KCl solution was used as the anolyte, and 0.1 M
692 K₄Fe(CN)₆ 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 elsewhere⁵⁶. 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 N₂, 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 ^1H and ^{23}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 ^1H and ^{23}Na , respectively), and radiofrequency (rf) field strengths of 142 kHz and 385 kHz,
714 respectively. ^1H and ^{23}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 H_2O and Na^+ , automated multiple single pulse experiments were performed
716 with a time interval of 10 s. Spin-lattice relaxation (T_1) measurements of ^1H 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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