
Supplementary information

Diversity-oriented synthesis of polymer membranes with ion solvation cages

In the format provided by the
authors and unedited

Supplementary Methods

Materials

Paraformaldehyde, morpholine, pyrrolidine, diethylamine, hydroxylamine, magnesium perchlorate, sodium hydroxide, lithium hydroxide monohydrate, dimethyl sulfate, diethyl sulfate, di-*tert*-butyl dicarbonate, dimethyl sulfoxide (DMSO), *d*-chloroform, and *d*₄-*ortho*-dichlorobenzene were obtained from Sigma Aldrich. Hexanes, ethanol, toluene, methylene chloride (DCM), acetone, chloroform, methanol, dimethylformamide (DMF), tetrahydrofuran (THF), sodium chloride, magnesium sulfate, and potassium carbonate were obtained from Fisher Scientific. 3,3,3',3'-tetramethyl-1,1'-spirobisindane-5,5',6,6'-tetraol was obtained from Alfa Aesar, tetrafluoroterephthalonitrile was obtained from Oakwood Chemicals, *tert*-butyl piperazine-1-carboxylate was obtained from Ark Pharm, 2-methoxyethyl-piperazine was obtained from Matrix Scientific, and *d*₆-DMSO was obtained from Cambridge Isotope Laboratories. All chemicals were used as received without further purification. 9,10-dimethyl-9,10-dihydro-9,10-ethanoanthracene-2,3,6,7-tetraol was prepared according to literature procedure.¹

Instrumentation

¹H and ¹³C Nuclear Magnetic Resonance (NMR) Spectroscopy. ¹H and ¹³C NMR spectra were recorded on Bruker Avance II at 500 MHz and 125 MHz, respectively. Chemical shifts are reported in δ (ppm) relative to the residual solvent peak (CDCl₃: 7.26 for ¹H, 77.16 for ¹³C; *d*₆-DMSO: 2.50 for ¹H, 39.51 for ¹³C; *d*₄-*o*-C₆D₄Cl₂, 120 °C: 7.22 and 6.95 for ¹H). Splitting patterns are designated as s (singlet), br s (broad singlet), d (doublet), t (triplet), q (quartet), and m (multiplet).

Electrospray Ionization Mass Spectrometry (ESI-MS). Spectra for compounds **3–6** were acquired on a Synapt G2 Q-TOF spectrometer. Spectra for compounds **7–10** were acquired on a Bruker MicroTOF spectrometer. ESI-MS was performed by the University of California, Berkeley QB3/Chemistry Mass Spectrometry Facility.

Elemental Analysis (EA). EA was performed by the University of California, Berkeley College of Chemistry Microanalytical Facility.

Single-Crystal X-ray Diffraction (XRD). Single crystals for compounds **3–7**, **9**, and **10** were selected and mounted on Mitegen® loops with Paratone oil and placed in an Oxford Cryosystems Cryostream 700 plus at *T* = 100 K. Data were collected for **3–5** using a Bruker D8 diffractometer with APEXII CCD detector, with Mo K α (λ = 0.71073 Å), while for **6**, **7**, **9**, and **10** using beamline 12.2.1 at the Advanced Light Source with λ = 0.7288 Å using a Bruker D8 diffractometer with a Bruker PHOTONII CPAD detector. Data reduction was performed and corrected for Lorentz and polarization effects using SAINT² v8.38a and were corrected for absorption effects using SADABS v2016/2.³ Structure solutions were performed by SHELXT⁴ using the direct method and were refined by least-square refinement against F⁵¹ by SHELXL.⁵

Size-Exclusion Chromatography (SEC). SEC with THF as the mobile phase was carried out with a Malvern Viscotek TDA 302 system calibrated with a 99 kg mol⁻¹ monodisperse polystyrene standard. SEC using DMF (containing 0.2% w/v LiBr) as the mobile phase was carried out using a customized system consisting of a Shimadzu LC-20AD pump, Viscotek VE 3580 refractive index detector, and two mixed bed columns connected in series (Viscotek GMHHR-M). The system was operated at a temperature of 70 °C. Calibration on the system was performed with narrow poly(methyl methacrylate) standards (Polymer Laboratories) ranging from 620 g mol⁻¹ to 910,500 g mol⁻¹.

Gas Adsorption and Desorption. N₂ adsorption isotherms were collected at 77 K on a Micromeritics Tristar II 3020 gas sorption analyzer. CO₂ adsorption isotherms were collected on a Micromeritics ASAP 2020 gas sorption analyzer at 273 K. Nonlocal DFT (NLDFT) pore-size distributions from N₂ adsorption isotherms were calculated using SAIEUS software provided by Micromeritics using the 2D Heterogeneous Surface model. NLDFT pore-size distributions from CO₂ adsorption isotherms were calculated using the Micromeritics Carbon Slit model with high regularization. Samples were degassed under vacuum at 100–150 °C overnight prior to analysis.

Grazing Incidence Wide-Angle X-ray Scattering (GIWAXS). Samples for grazing-incidence wide-angle X-ray scattering (GIWAXS) were prepared by spin coating polymer inks onto silicon substrates. The substrates were previously cleaned by sonication at 40 °C in soap water, deionized water, acetone, and isopropyl alcohol before oven drying and UV/ozone treatment immediately prior to sample deposition. 11 through 16 were cast from chloroform solutions, and all other polymers were cast from solutions of NMP. Residual solvent was removed under vacuum at 90 °C for 24–48 h.

Scattering patterns were collected under a helium atmosphere at the Advanced Light Source beamline 7.3.3⁶ of the Lawrence Berkeley National Laboratory. A photon energy of 10 keV, a sample-to-detector distance of 275 mm, and incident angles between 0.05 and 0.20 were used. The beamline was equipped with a Pilatus 2M detector, samples were calibrated against a silver behenate standard, and the data was processed using the Nika package for Igor Pro.⁷

Each GIWAXS pattern exhibited two or more distinct, broad scattering features typical of microporous polymers. The scattering vectors of these features and the corresponding real-space distances are detailed in **Supplementary Table 2**.

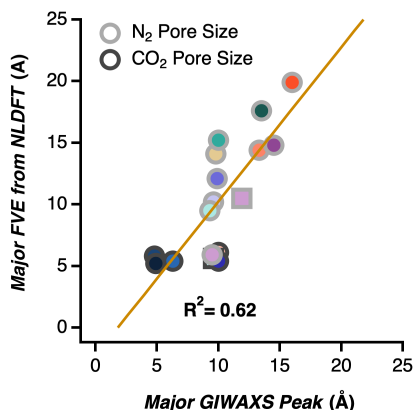
GIWAXS scattering patterns of microporous polymers are primarily informed by two types of structural features: 1) FVEs and concomitant semi-periodic regions of high and low electron density, which produce a broad feature whose peak intensity is at low q and spans much of the GIWAXS range, and 2) repeating chemical moieties along the polymer chain (e.g., spiro centers), which produce smaller features superimposed on the broader peak.⁸ In previously published scattering patterns of PIM-1 and variants thereof, four such peaks nominally associated with correlations among atoms in spiro centers are typically observed around 0.5, 0.9, 1.3, and 1.6 Å⁻¹, although not all polymers feature all these peaks.⁹ Both effects are evident in the scattering patterns reported here. Separately, aging in thin films of PIMs is known to influence the overall intensity

of the low- q feature; thermal annealing during thin film processing prior to the acquisition of scattering data can accelerate this aging effect.

In general, polymers in our DOS PIMs library present some combination of the smaller features previously observed in PIM-1 and related polymers, although with varying relative peak intensities and sometimes alongside additional peaks. A strong peak is observed at $q = 0.6\text{--}0.7\text{ \AA}^{-1}$ in the scattering patterns of many of the aminomethylated polymers, such as nitrile-containing PIMs **11**–**18**. Partially amplified by the broad low- q feature, this peak is similar to a signature observed in previously reported PIMs with bulky appended functional groups.⁸ A second feature in these PIMs at higher q -value ($\sim 1.3\text{ \AA}^{-1}$) is enhanced by scattering and conformational changes involving the appended group, as its intensity compared to the feature at $q = 0.6\text{--}0.7\text{ \AA}^{-1}$ qualitatively tracks with the size of the appended group. The lower- q peak in PIM **15** is slightly shifted and a third peak, enhanced by scattering and conformational changes associated with *tert*-butyl functionality, is present at $q = 0.95\text{ \AA}^{-1}$. These scattering patterns can be contrasted to those of polymers modified only at the nitrile group, such as PIMs **19**, **25**, **27**, and **29**. Capable of inter-chain hydrogen bonding, yet lacking a bulky aminomethylated functionalization, these generally do not exhibit a peak at $q = 0.6\text{--}0.7\text{ \AA}^{-1}$.

When multiple modifications are present along the polymer backbone, complementary and competing effects are observed in the scattering patterns. Some aminomethylated polymers also bearing amidoxime groups, such as PIMs **20** and **21**, exhibit the peak at $q = 0.6\text{--}0.7\text{ \AA}^{-1}$, perhaps because the added bulk around the polymer backbone inhibits interchain hydrogen bond formation. Amidoxime-bearing polymers with even bulkier chemical groups appended through the Mannich reaction exhibit complex GIWAXS patterns with many peaks, as seen with PIMs **22** and **23**. When the amidoxime groups on such polymers are alkylated, as in PIMs **26**, **30**, and **31**, the scattering patterns resemble those of PIMs **11**–**18**, although sometimes with shifted peak positions, highlighting the important role aminomethylation plays in dictating polymer chain packing in the condensed phase.

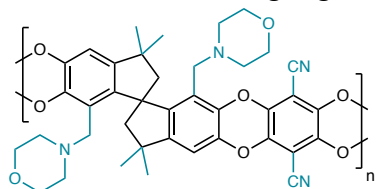
When plotted against NLDFT pore sizes obtained from N_2 and CO_2 isotherms, a good positive correlation ($R^2 = 0.62$) was achieved between the d -space value of the major GIWAXS peak and the maximum FVE obtained by gas porosimetry:



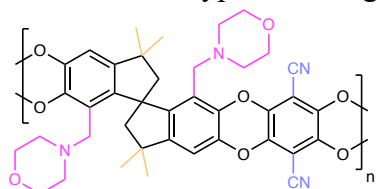
Collectively, these data suggest that the presence of complementary and competing effects in the scattering patterns of PIMs in our library showcase the library's diversity across multiple length scales, and that the major peak in the GIWAXS often provides an approximation of the size of accessible FVEs for PIMs in the condensed phase.

Principal Component Analysis. Principal component analysis was carried out in MATLAB[®] version R2015b using ten descriptors as defined below:

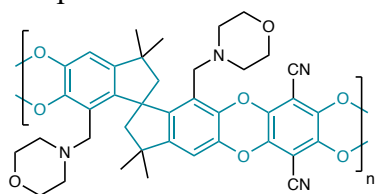
1. Molecular weight of side groups per repeat unit (M_s). The total molecular weight of components per repeat unit that do not comprise the polymer main chain. For example, in the case of **13**, the highlighted regions were designated as side groups:



2. BET surface area (A_{BET}). The BET surface area as calculated from nitrogen adsorption experiments (see **Gas Adsorption and Desorption** above), or as reported in References 10–12.
3. Number of oxygen atoms per repeat unit (N_O).
4. Number of nitrogen atoms per repeat unit (N_N).
5. Number of distinct types of side group per repeat unit (N_s). For example, in the case of **13**, there are three types of side group as highlighted below:



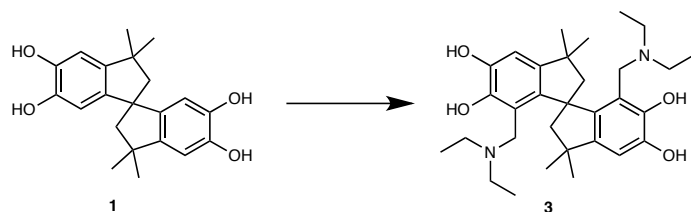
6. Molecular weight of polymer main chain per repeat unit (M_b). The total molecular weight of components per repeat unit that comprise the polymer main chain (backbone). For example, in the case of **13**, the highlighted regions were designated as main chain components:



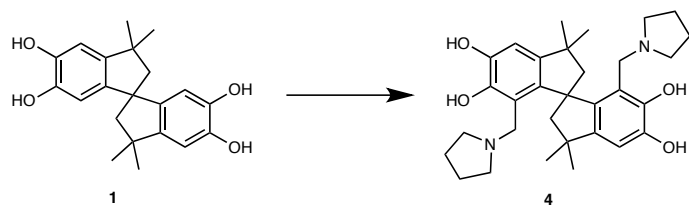
7. Number of sites of contortion along the polymer main chain per repeat unit (N_c).
8. Number of GIWAXS peaks (N_G).
9. d -space value of major GIWAXS peak (L_G).
10. Pore width of major FVE from NLDFT pore-size distributions based on N_2 isotherms (L_{N2}).

Raw data were first normalized by calculating *Z* values based on the respective sample means and sample standard deviations for each of the seven descriptors described above. Principal component analysis (PCA) was then carried out on the normalized data (*Z* values) using the singular value decomposition algorithm. For the PCA comparing PIMs demonstrated in this work to archetypical literature PIMs (**Fig. 1b**), descriptors 1–7 were used. The first two principal components accounted for 43% and 21% of the total variance within the data set respectively. For the PCA carried out strictly on PIMs demonstrated in this work (**Supplementary Fig. 11**), descriptors 1–6 & 8–10 were used. The first two principal components accounted for 41% and 27% of the total variance within the data set respectively. Vectors for each descriptor were also calculated, the direction and length of which indicate how each descriptor contributes to the first two principal components. A complete summary of raw data used in these calculations is included in **Supplementary Tables 3 and 4**, respectively.

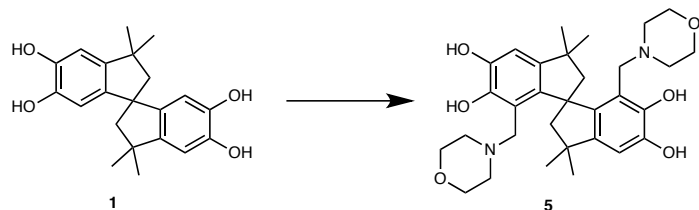
Synthetic Procedures



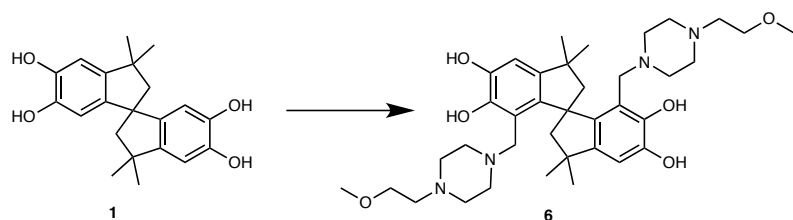
3: To a 500 mL round bottom flask was added toluene (250 mL), paraformaldehyde (4.50 g, 150 mmol), and diethylamine (15.51 mL, 150 mmol). The reaction was stirred for 10 min at reflux which point 3,3',3''-tetramethyl-1,1'-spirobisindane-5,5',6,6'-tetraol (10.21 g, 30 mmol) was added and the reaction was stirred at reflux overnight. After cooling to room temperature, the reaction mixture was washed with brine, dried over MgSO_4 , and concentrated by rotary evaporator. The resulting solid was washed with hexanes and dried under reduced pressure to give 12.00 g of **3** (78 %) as an orange powder. ^1H NMR (CDCl_3 , 500 MHz): δ (ppm) 6.66 (s, 2H), 3.25 (d, 2H, $J = 15.1$ Hz), 3.14 (d, 2H, $J = 15.1$ Hz), 2.55 (br s, 4H), 2.38 (br s, 4H), 2.27 (d, 2H, $J = 13.4$ Hz), 2.17 (d, 2H, $J = 13.4$ Hz), 1.34 (s, 6H), 1.29 (s, 6H), 0.95 (d, 12H, $J = 41.9$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 125 MHz): δ (ppm) 145.73, 144.67, 142.02, 137.91, 116.21, 106.56, 57.89, 56.71, 53.48, 53.24, 42.73, 32.83, 28.83, 13.45; HR-MS (m/z) [$\text{M}+\text{H}$] $^+$: Calculated: 507.3209, Found: 507.3210; Elemental Analysis for $\text{C}_{31}\text{H}_{46}\text{N}_2\text{O}_4$ Calculated: C 72.01, H 9.08, N 5.49; Found: C 72.66, H 9.37, N 5.28. Crystallographic data for compound **3** is available free of charge from the Cambridge Crystallographic Date Centre (www.ccdc.cam.ac.uk) under reference number 2061993.



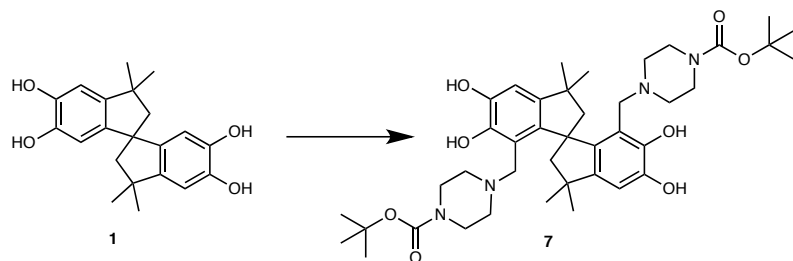
4: To a 500 mL round bottom flask was added ethanol (250 mL), paraformaldehyde (4.50 g, 150 mmol), and pyrrolidine (12.33 mL, 150 mmol). The reaction was stirred for 10 min at 70 °C which point 3,3,3',3'-tetramethyl-1,1'-spirobisindane-5,5',6,6'-tetraol 10.21 g (30 mmol) was added and the reaction was stirred at reflux overnight. After cooling to room temperature, the reaction mixture was concentrated by rotary evaporator and crude product washed with hexanes. The resulting solid was dried under reduced pressure to give 8.60 g of **4** (57 %) as a colorless solid. ^1H NMR (CDCl_3 , 500 MHz): δ (ppm) 6.60 (s, 2H), 3.27 (d, 4H, $J = 5.6$ Hz), 2.27 (d, 2H, $J = 13.4$ Hz), 2.20 (d, 2H, $J = 13.4$ Hz), 1.78 (br m, 8H), 1.52–1.02 (br m 8H), 1.34 (s, 6H), 1.29 (s, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 125 MHz): δ (ppm) 145.43, 144.28, 141.62, 137.92, 116.30, 106.76, 57.89, 56.71, 53.48, 53.24, 42.73, 32.83, 28.83, 23.45; HR-MS (m/z) [$\text{M}+\text{H}$] $^+$: Calculated: 507.3217, Found: 507.3277; Elemental Analysis for $\text{C}_{31}\text{H}_{42}\text{N}_2\text{O}_4$ Calculated: C 73.49, H 8.36, N 5.53; Found: C 73.31, H 8.33, N 5.69. Crystallographic data for compound **4** is available free of charge from the Cambridge Crystallographic Date Centre (www.ccdc.cam.ac.uk) under reference number 2061994.



5: To a 500 mL round bottom flask was added ethanol (250 mL), paraformaldehyde (4.50 g, 150 mmol), and morpholine (12.98 mL, 150 mmol). The reaction was stirred for 10 min at 70 °C which point 3,3,3',3'-tetramethyl-1,1'-spirobisindane-5,5',6,6'-tetraol (10.21 g, 30 mmol) was added and the reaction was stirred at reflux overnight. After cooling room temperature, 500 mL of hexanes was then added to the mixture, which was then cooled to 4 °C. The precipitate was filtered, washed with hexanes, and dried under reduced pressure to give a colorless solid (4.85 g, 30 % yield). ^1H NMR (CDCl_3 , 500 MHz): δ (ppm) 6.67 (s, 2H), 3.68 (br s, 8H), 3.15 (d, 2H, $J = 14.6$ Hz), 3.05 (d, 2H, $J = 14.6$ Hz), 2.60 (br s, 4H), 2.29 (d, 2H, $J = 13.5$ Hz), 2.16 (d, 2H, $J = 13.5$ Hz), 1.57 (br s, 8H), 1.36 (s, 6H), 1.27 (s, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 125 MHz): δ (ppm) 145.91, 145.16, 141.75, 138.26, 116.00, 108.75, 66.51, 57.86, 56.73, 55.90, 52.86, 42.53, 33.21, 30.05; HR-MS (m/z) [$\text{M}+\text{H}$] $^+$: Calculated: 539.3116, Found: 539.3117; Elemental Analysis for $\text{C}_{31}\text{H}_{42}\text{N}_2\text{O}_6$ Calculated: C 69.12, H 7.86, N 5.20; Found: C 69.14, H 7.97, N 5.11. Crystallographic data for compound **5** is available free of charge from the Cambridge Crystallographic Date Centre (www.ccdc.cam.ac.uk) under reference number 2061995.

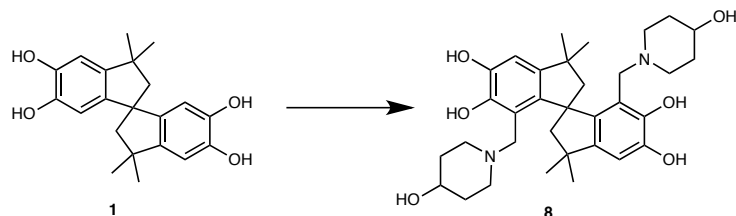


6: To a round bottom flask was added toluene (250 mL), paraformaldehyde (4.50 g, 150 mmol), and 2-methoxyethyl-piperazine (8.92 mL, 150 mmol). The reaction was stirred for 15 min at 70 °C which point 3,3,3',3'-tetramethyl-1,1'-spirobisindane-5,5',6,6'-tetraol (10.21 g, 30 mmol) was added and the reaction was stirred at reflux overnight. After cooling to room temperature, the reaction was washed with brine, dried over MgSO₄, then concentrated by rotary evaporator. The resulting solid was then washed with hexanes and dried under reduced pressure to give 12.30 g of **6** (63 %) as a colorless solid. ¹H NMR (CDCl₃, 500 MHz): δ (ppm) 6.65 (s, 2H), 3.48 (t, 4H, J = 5.5 Hz), 3.34 (s, 6H), 3.19 (d, 2H, J=14.8 Hz), 3.10 (d, 2H, J=14.8 Hz), 2.96–2.52 (br m, 12H), 2.33–2.00 (br m, 12H), 1.34 (s, 6H), 1.29 (s, 6H); ¹³C{¹H} NMR (CDCl₃, 125 MHz): δ (ppm) 146.11, 145.97, 140.35, 136.76, 116.00, 109.33, 69.94 66.51, 60.23 57.86, 56.73, 55.90, 52.86, 51.10 42.53, 33.21, 30.05; HR-MS (*m/z*) [M+H]⁺: Calculated: 653.4273, Found: 653.4271; Elemental Analysis for C₃₇H₅₆N₄O₆ Calculated: C 68.07, H 8.65, N 8.58; Found: C 67.83, H 8.79, N 8.59. Crystallographic data for compound **6** is available free of charge from the Cambridge Crystallographic Date Centre (www.ccdc.cam.ac.uk) under reference number 2061996.

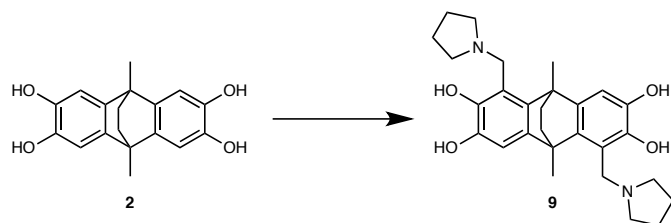


7: To a round bottom flask was added toluene (250 mL), paraformaldehyde (4.68 g, 156 mmol) and Boc-Piperazine (29.06 g, 156 mmol). The reaction was stirred for 10 min at 70 °C, at which point 3,3,3',3'-tetramethyl-1,1'-spirobisindane-5,5',6,6'-tetraol (10.21 g, 30 mmol) was added and the reaction was stirred at reflux overnight. After cooling to room temperature, the reaction mixture was washed with brine, dried over MgSO₄, and concentrated by rotary evaporator. The resulting solid was then washed with hexanes and dried under reduced pressure to give 14.70 g of **7** (67 %) as a colorless solid. ¹H NMR (CDCl₃, 500 MHz): δ (ppm) 6.68 (s, 2H), 3.15 (d, 2H, J = 15.0 Hz), 3.11 (d, 2H, J = 15.0 Hz), 3.00–2.54 (br m, 8H), 2.34–1.79 (br m, 12H), 1.46 (s, 18H), 1.36 (s, 6H), 1.29 (s, 6H); ¹³C{¹H} NMR (CDCl₃, 125 MHz): δ (ppm) 146.34, 145.16, 141.75, 138.26, 116.00, 108.75, 66.51, 57.86, 57.65, 54.93, 51.43, 44.63, 32.21, 30.15 28.41; HR-MS (*m/z*) [M+H]⁺: Calculated: 737.4484, Found: 737.4307; Elemental Analysis for C₄₁H₆₀N₄O₈ Calculated: C 66.82, H 8.21, N 7.60; Found: C 67.11, H 8.11, N 7.22. Crystallographic data for compound **7**

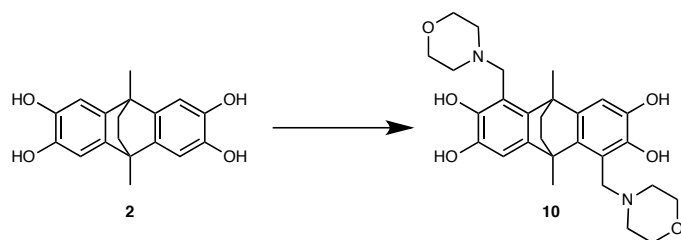
is available free of charge from the Cambridge Crystallographic Data Centre (www.ccdc.cam.ac.uk) under reference number 2061997.



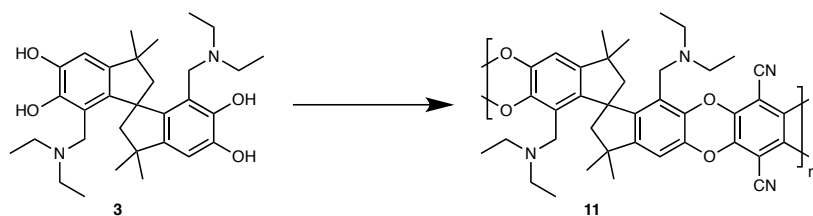
8: To a round bottom flask was added ethanol (250 mL), paraformaldehyde (4.41 mg, 147 mmol) and 4-hydroxypiperidine (15.17 g, 150 mmol). The reaction was stirred for 15 min at 70 °C, at which point 3,3',3',3'-tetramethyl-1,1'-spirobisindane-5,5',6,6'-tetraol (10.00 g, 29.4 mmol) was added and the reaction was stirred at reflux overnight. After cooling to room temperature, the reaction was concentrated by rotary evaporator. The resulting solid was then washed with hexanes and dried under reduced pressure to give 8.3 g of **8** (50%) as a colorless solid. ^1H NMR (d_6 -DMSO, 500 MHz): δ (ppm) 6.46 (br s, 2H), 4.63 (br s, 2H), 3.08 (d, 2H, 14.5 Hz), 3.02 (d, 2H, 14.5 Hz), 2.68–2.54 (br m, 4H), 2.15 (d, 2H, 13.1 Hz), 2.07 (d, 2H, 13.1 Hz), 2.01–1.56 (br m, 8H), 1.39–1.24 (br m, 10H), 1.18 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (d_6 -DMSO, 125 MHz): δ (ppm); 146.43, 145.11, 141.25, 137.99, 116.40, 108.56, 57.78, 56.69, 42.46, 33.17, 30.28; HR-MS (m/z) $[\text{M}+\text{H}]^+$: Calculated: 567.3429, Found: 567.3292.



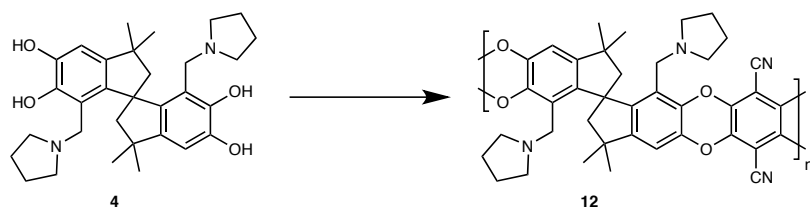
9: To a sealable reaction vial was added toluene (12.5 mL), paraformaldehyde (501 mg, 16.65 mmol), pyrrolidine (1.38 mL, 16.76 mmol), and 9,10-dimethyl-9,10-dihydro-9,10-ethanoanthracene-2,3,6,7-tetraol (501 mg, 1.68 mmol). After sealing, the vial was heated for 8 h at 120 °C while stirring. After cooling to room temperature, the reaction mixture was concentrated under reduced pressure, follow by the addition of hexanes (50 mL) to precipitate the product. The product was isolated by filtration, washed with ethanol (50 mL), and dried under reduced pressure to give **9** as a pale pink solid (219 mg) in 28% yield. ^1H NMR (CDCl_3 , 500 MHz): δ (ppm) 6.85 (s, 2H), 4.31 (d, 2H, $J = 14.1$ Hz), 4.26 (d, 2H, $J = 14.1$ Hz), 2.67 (br s, 8H), 2.03 (s, 6H), 1.85 (br s, 12H), 1.74 (s, 2H), 1.44 (s, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 125 MHz): δ (ppm) 143.98, 141.54, 139.71, 134.57, 117.90, 107.40, 54.77, 53.29, 43.94, 38.27, 27.04, 23.78; HR-MS (m/z) $[\text{M}+\text{H}]^+$: Calculated: 507.3217, Found: 507.3105. Crystallographic data for compound **9** is available free of charge from the Cambridge Crystallographic Data Centre (www.ccdc.cam.ac.uk) under reference number 2061999.



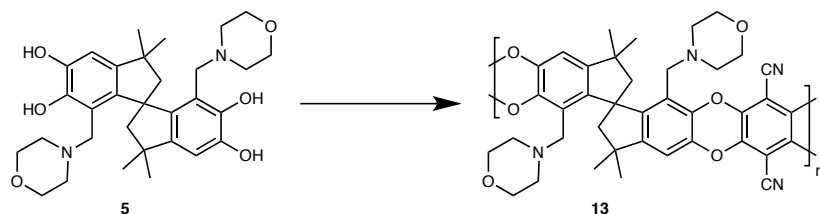
10: To a sealable reaction vial was added toluene (12.5 mL), paraformaldehyde (500 mg, 16.65 mmol), morpholine (1.45 mL, 16.76 mmol), and 9,10-dimethyl-9,10-dihydro-9,10-ethanoanthracene-2,3,6,7-tetraol (501 mg, 1.68 mmol). After sealing, the vial was heated for 8 h at 120 °C while stirring. After cooling to room temperature, the reaction mixture was concentrated under reduced pressure, followed by the addition of hexanes (50 mL) to precipitate the product. The product was isolated by filtration, washed with ethanol (50 mL), and dried under reduced pressure to give **10** as a nearly colorless solid (521 mg) in 62% yield. ^1H NMR (CDCl_3 , 500 MHz): δ (ppm) 6.87 (s, 2H), 4.18 (d, 2H, $J = 13.8$ Hz), 4.12 (d, 2H, $J = 13.8$ Hz), 3.72 (br s, 8H), 2.61 (br s, 8H), 2.05 (s, 6H), 1.74 (s, 2H), 1.46 (s, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 125 MHz): δ (ppm) 143.05, 141.72, 140.44, 135.41, 116.80, 108.07, 66.89, 57.08, 52.72, 43.94, 38.07; HR-MS (m/z) $[\text{M}+\text{H}]^+$: Calculated: 497.2646, Found: 497.2527. Crystallographic data for compound **10** is available free of charge from the Cambridge Crystallographic Data Centre (www.ccdc.cam.ac.uk) under reference number 2061998.



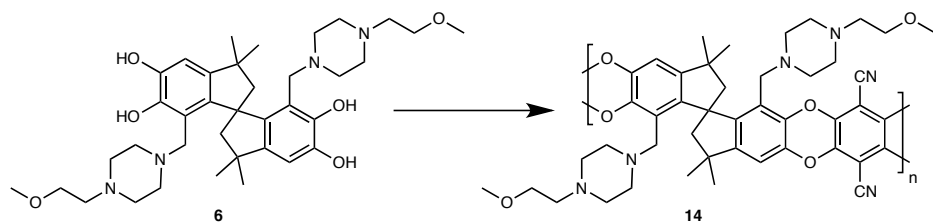
11: To a round bottom flask was added **3** (11.24 g, 22 mmol) and tetrafluoroterephthalonitrile (4.40 g, 22 mmol), which were dissolved in anhydrous DMF (100 mL) at 65 °C. Freshly ground potassium carbonate (12 g, 87 mmol) was slowly added and the mixture stirred for 48 h. The reaction mixture was then poured into water (500 mL) to precipitate the crude polymer as a yellow solid, which was then filtered and washed with an additional portion of water (250 mL). The crude polymer was dissolved in hot chloroform (200 mL) and subsequently precipitated into methanol (1.0 L), filtered, and washed with an additional portion of methanol (200 mL). This process was repeated. After drying *in vacuo* at 65 °C, **11** was isolated as a yellow solid (11.80 g) in 85% yield. ^1H NMR (CDCl_3 , 500 MHz): δ (ppm) 6.80 (br s, 2H), 3.53 (br s, 4H), 3.16 (br s, 2H), 2.99 (br s, 2H), 2.24 (br m, 8H), 1.39 (br s, 6H), 1.31 (br s, 6H), 0.69 (br m, 12H); Elemental Analysis for $\text{C}_{39}\text{H}_{42}\text{N}_4\text{O}_4$ Calculated: C 74.26, H 6.71, N 8.88; Found: C 69.91 H 5.90, N 8.16; SEC (THF): $M_n = 63.7 \text{ kg mol}^{-1}$, $M_w = 80.3 \text{ kg mol}^{-1}$, $D = 1.53$; BET Surface Area: $446 \text{ m}^2 \text{ g}^{-1}$.



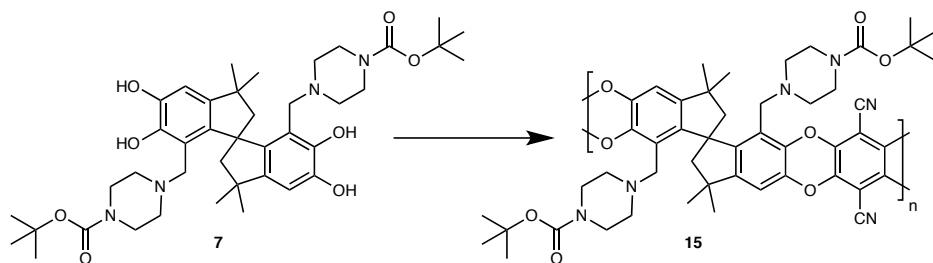
12: To a round bottom flask was added **4** (8.87 g, 17.5 mmol) and tetrafluoroterephthalonitrile (3.48 g, 17.4 mmol), which were dissolved in anhydrous DMF (50 mL) at 65 °C. Freshly ground potassium carbonate (9.67 g, 70 mmol) was slowly added and the mixture stirred for 48 h. The reaction mixture was poured into water (800 mL) to precipitate the crude polymer as a yellow solid, which was then filtered and washed with an additional portion of water (200 mL). The crude polymer was dissolved in hot THF (200 mL) and subsequently precipitated into acetone (1.0 L), filtered, and washed with an additional portion of methanol (200 mL). An additional precipitation of the polymer into methanol (1.0 L) was conducted from a solution **12** in hot chloroform (200 mL). After drying *in vacuo* at 65 °C, **12** was isolated as a yellow solid (10.03 g) in 92% yield. ¹H NMR (CDCl₃, 500 MHz): δ (ppm) 7.01 (s, 2H), 2.33 (br s, 4H), 1.99 (br m, 4H), 1.63 (br m, 16H), 1.42 (br m, 12H); Elemental Analysis for C₃₉H₃₈N₄O₄ Calculated: C 74.74, H 6.11, N 8.94; Found: C 73.91 H 5.90, N 8.16; SEC (THF): M_n = 126 kg mol⁻¹, M_w = 146 kg mol⁻¹, $\bar{D}$ = 1.16; BET Surface Area: 434 m² g⁻¹.



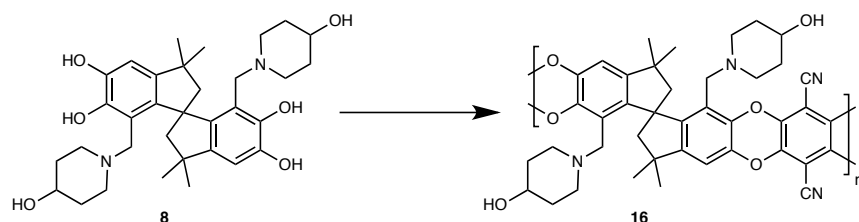
13: To a round bottom flask was added **5** (2.03 g, 3.77 mmol) and tetrafluoroterephthalonitrile (0.75 g, 3.77 mmol), which were dissolved in anhydrous DMF (38 mL) at 65 °C. Freshly ground potassium carbonate (2.08 g, 15.07 mmol) was slowly added and the mixture stirred for 48 h. The reaction mixture was poured into water (400 mL) to precipitate the crude polymer as a yellow solid, which was then filtered and washed with an additional portion of water (200 mL). The crude polymer was dissolved in hot THF (50 mL) and subsequently precipitated into methanol (500 mL), filtered, and washed with an additional portion of methanol (200 mL). This process was repeated in hot chloroform (50 mL) and methanol (500 mL). After drying *in vacuo* at 65 °C, **13** was isolated as a yellow-brown solid (1.94 g) in 78% yield. ¹H NMR (CDCl₃, 500 MHz): δ (ppm) 6.80 (br s, 2H), 4.08–3.42 (br m, 8H), 2.56–2.07 (br m, 8H), 2.24 (br m, 20H); Elemental Analysis for C₃₉H₃₈N₄O₆ Calculated: C 71.11, H 5.81, N 8.51; Found: C 69.91 H 5.90, N 8.16; SEC (THF): M_n = 66.7 kg mol⁻¹, M_w = 121 kg mol⁻¹, $\bar{D}$ = 1.81; BET Surface Area: 505 m² g⁻¹.



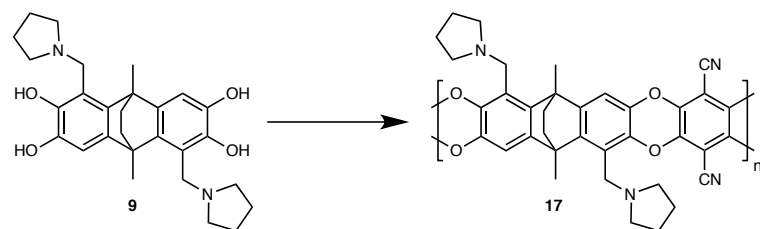
14: To a round bottom flask was added **6** (5.03 g, 7.7 mmol) and tetrafluoroterephthalonitrile (1.54 g, 7.7 mmol), which were dissolved in anhydrous DMF (50 mL) at 65 °C. Freshly ground potassium carbonate (4.28 g, 31 mmol) was then slowly added and the mixture stirred for 3 h. The reaction mixture was poured into water (200 mL) to precipitate the crude polymer as a yellow solid, which was then filtered and washed with an additional portion of water (200 mL). The crude polymer was dissolved in hot chloroform (75 mL) and subsequently precipitated into methanol (750 mL), filtered, and washed with an additional portion of methanol (200 mL). This process was repeated. After drying *in vacuo* at 65 °C, **14** was isolated as a yellow solid (3.21 g) in 54% yield. ¹H NMR (*d*₆-DMSO, 500 MHz): δ (ppm) 7.00 (br s, 2H), 3.36 (br s, 6H), 3.19 (br m, 12H), 2.57–2.13 (br m, 20H), 1.48 (br s, 6H), 1.38 (br s, 6H); Elemental Analysis for C₄₅H₅₂N₆O₆ Calculated: C 69.93, H 6.78, N 10.87; Found: C 69.77 H 6.75, N 10.53; SEC (THF): M_n = 26.1 kg mol⁻¹, M_w = 29.9 kg mol⁻¹, $\bar{D}$ = 1.15; BET Surface Area: 63 m² g⁻¹.



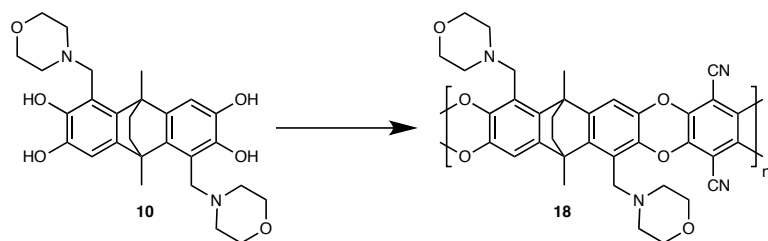
15: To a round bottom flask was added **7** (5.01 g, 6.8 mmol) and tetrafluoroterephthalonitrile (1.36 g, 6.8 mmol), which were dissolved in anhydrous DMF (60 mL) at 65 °C. Freshly ground potassium carbonate (3.73 g, 27 mmol) was then slowly added and the mixture stirred for 3 h. The reaction mixture was poured into water (200 mL) to precipitate the crude polymer as a yellow solid, which was then filtered and washed with an additional portion of water (200 mL). The crude polymer was dissolved in hot THF (100 mL) and subsequently precipitated into methanol (500 mL), filtered, and washed with an additional portion of methanol (200 mL). This process was repeated in hot chloroform (100 mL) and methanol (500 mL). After drying *in vacuo* at 65 °C, **15** was isolated as a yellow solid (4.78 g) in 82% yield. ¹H NMR (CDCl₃, 500 MHz): δ (ppm) 6.80 (br s, 2H), 3.53 (br s, 4H), 3.16 (br s, 2H), 2.99 (br s, 2H), 2.24 (br m, 16H), 1.45–1.31 (br m, 30H); Elemental Analysis for C₄₉H₅₆N₆O₈ Calculated: C 68.67, H 6.59, N 9.81; Found: C 71.10 H 6.54, N 8.25; SEC (THF): M_n = 46.9 kg mol⁻¹, M_w = 51.5 kg mol⁻¹, $\bar{D}$ = 1.11; BET Surface Area: 234 m² g⁻¹.



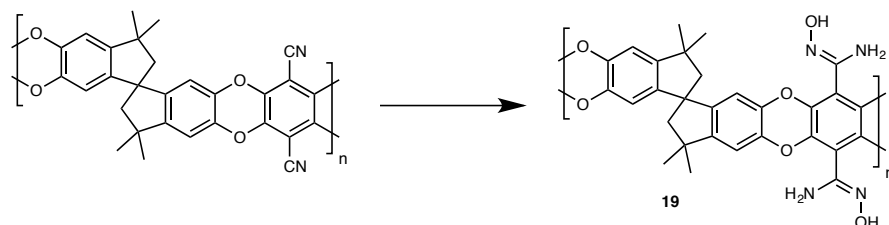
16: To a round bottom flask was added **8** (1.02 g, 1.8 mmol) and tetrafluoroterephthalonitrile (360 mg, 1.8 mmol), which were dissolved in anhydrous DMF (10 mL) at 65 °C. Freshly ground potassium carbonate 967 mg (7.0 mmol) was then slowly added and the mixture stirred for 48 h. The reaction mixture was poured into water (100 mL) to precipitate the crude polymer as a yellow solid, which was then filtered and washed with an additional portion of water (100 mL). The crude polymer was dissolved in hot chloroform (20 mL) and subsequently precipitated into methanol (200 mL), filtered, and washed with an additional portion of methanol (200 mL). This process was repeated. After drying *in vacuo* at 65 °C, **16** was isolated as a yellow solid (556 mg) in 45% yield. ¹H NMR (*d*₆-DMSO, 500 MHz): δ (ppm) 7.09 (br s, 2H), 4.53 (br s, 2H), 2.92 (br s, 4H), 2.03–2.45 (br m, 8H), 1.85 (br s, 4H), 1.56 (br m, 10H), 1.39 (br s, 6H), 1.29 (br s, 6H); SEC (DMF): $M_n = 11.9 \text{ kg mol}^{-1}$, $M_w = 19.2 \text{ kg mol}^{-1}$, $D = 1.61$; BET Surface Area: $11 \text{ m}^2 \text{ g}^{-1}$.



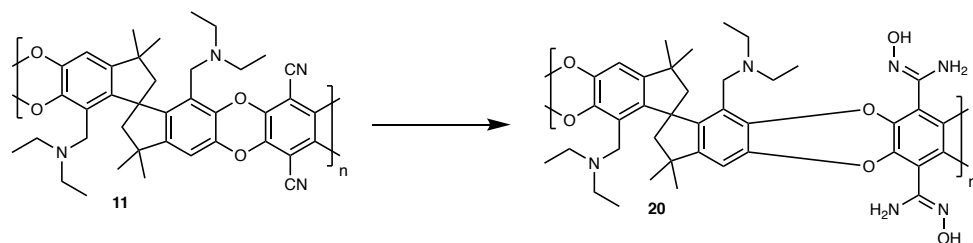
17: To a round bottom flask was added **9** (2.60 g, 5.6 mmol) and tetrafluoroterephthalonitrile (1.12 g, 5.6 mmol), which were dissolved in anhydrous DMF (20 mL) at 65 °C. Freshly ground potassium carbonate (3.10 g, 22.4 mmol) was then slowly added and the mixture stirred for 48 h. The reaction mixture was poured into water (50 mL) to precipitate the crude polymer as an orange solid, which was then filtered and washed with an additional portion of water (50 mL). The crude polymer was dissolved in hot THF (5 mL) and subsequently precipitated into methanol (50 mL), filtered, and washed with an additional portion of methanol (50 mL). This process was repeated from hot chloroform (5 mL) using methanol (50 mL). After drying *in vacuo* at 65 °C, **17** was isolated as an orange solid (2.95 g) in 90% yield. ¹H NMR (CDCl₃, 500 MHz): δ (ppm) 7.00 (br s, 2H), 3.89 (br d, 4H), 2.55 (br s, 8H), 2.32 (br s, 4H), 1.75 (br s, 6H), 1.58 (br s, 8H); Elemental Analysis for C₃₆H₃₂N₄O₄ Calculated: C 73.95, H 5.52, N 9.58; SEC (DMF): $M_n = 13.6 \text{ kg mol}^{-1}$, $M_w = 37.0 \text{ kg mol}^{-1}$, $D = 2.72$; BET Surface Area: $444 \text{ m}^2 \text{ g}^{-1}$.



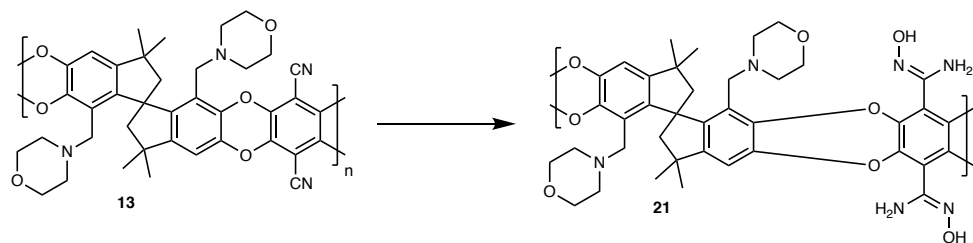
18: To a round bottom flask was added **10** (199 mg, 0.40 mmol) and tetrafluoroterephthalonitrile (82 mg, 0.41 mmol), which were dissolved in anhydrous DMF (3.4 mL) at 65 °C. Freshly ground potassium carbonate (229 mg, 1.66 mmol) was then slowly added and the mixture was stirred for 96 h. The reaction mixture was poured into water (50 mL) to precipitate the crude polymer as a yellow solid, which was then filtered and washed with an additional portion of water (50 mL). The crude polymer was dissolved in hot THF (5 mL) and subsequently precipitated into methanol (50 mL), filtered, and washed with an additional portion of methanol (50 mL). This process was repeated in hot chloroform (5 mL) and methanol (50 mL). After drying *in vacuo* at 65 °C, **18** was isolated as a yellow solid (211 mg) in 86% yield. ^1H NMR (CDCl_3 , 500 MHz): δ (ppm) 7.00 (br s, 2H), 3.66 (br m, 12H), 2.48 (br s, 8H), 2.29 (br s, 6H), 1.84–1.47 (br m, 4H); Elemental Analysis for $\text{C}_{36}\text{H}_{32}\text{N}_4\text{O}_6$ Calculated: C 70.12, H 5.23, N 9.09; SEC (DMF): $M_n = 90.5 \text{ kg mol}^{-1}$, $M_w = 206 \text{ kg mol}^{-1}$, $D = 2.28$; BET Surface Area: $19 \text{ m}^2 \text{ g}^{-1}$.



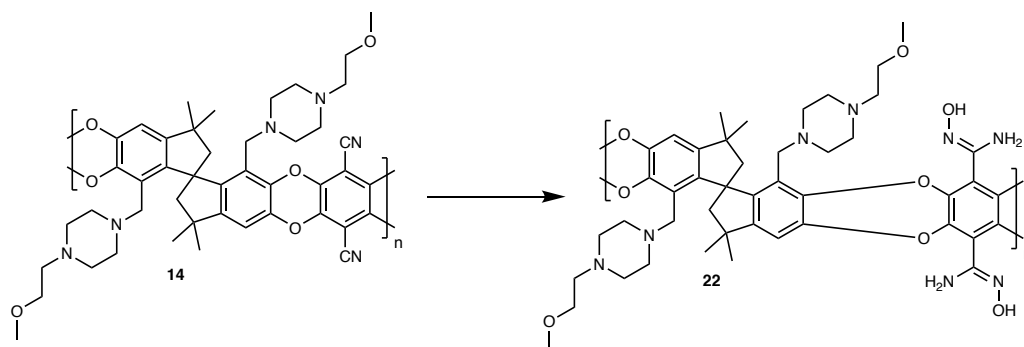
19: To a round bottom flask was added PIM-1 (5.00 g, 9.6 mmol) and THF (380 mL). The mixture was heated to at 60 °C to dissolve the polymer. A solution of 50 wt% aqueous hydroxylamine (50 mL, 816 mmol) was then added dropwise. The reaction mixture was stirred overnight and then cooled before precipitating the polymer into methanol (1320 mL). The solid was filtered and then rinsed twice with methanol (500 mL) before drying *in vacuo* at 50 °C to give **19** as a pale-yellow powder (3.93 g) in 69% yield. ^1H NMR (d_6 -DMSO, 500 MHz): δ (ppm) 9.47 (br t, 2H), 6.82 (br s, 2H), 6.16 (br s, 2H), 5.82 (br s, 4H), 2.17 (br d, 4H), 1.32 (br s, 6H), 1.25 (br s, 6H); Elemental Analysis for $\text{C}_{29}\text{H}_{26}\text{N}_4\text{O}_6$ Calculated: C 66.15, H 4.98, N 10.64; Found: C 64.62 H 5.09, N 10.17; SEC (DMF): $M_n = 42.7 \text{ kg mol}^{-1}$, $M_w = 119 \text{ kg mol}^{-1}$, $D = 2.78$; BET Surface Area: $454 \text{ m}^2 \text{ g}^{-1}$.



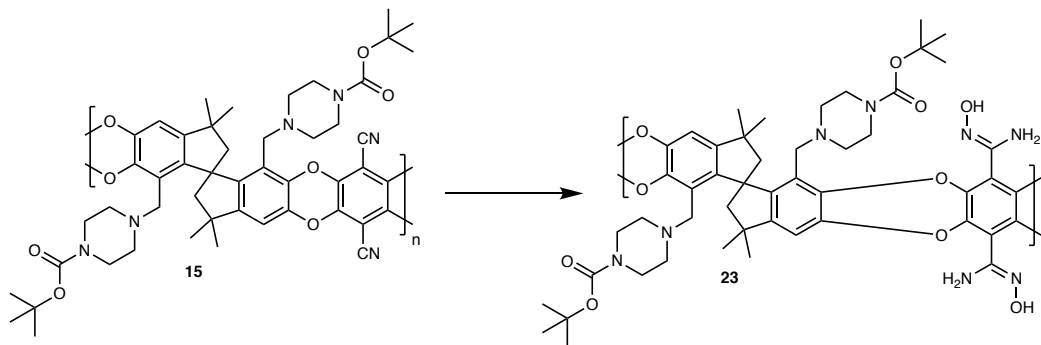
20: To a round bottom flask was added **11** (7.88 g, 12.5 mmol) and THF (375 mL). The mixture was heated to at 60 °C to dissolve the polymer. A solution of 50 wt% aqueous hydroxylamine (60 mL, 979 mmol) was then added dropwise. The reaction mixture was stirred overnight and then cooled before precipitating the polymer into a 1:1 (v/v) solution of water and methanol (1875 mL). The solid was filtered and then rinsed twice with methanol (500 mL) before drying *in vacuo* at 50 °C to give **20** as a white powder (1.45 g) in 17% yield. ^1H NMR (d_6 -DMSO, 500 MHz): δ (ppm) 9.48 (br s, 2H), 6.74 (br s, 2H), 5.81 (br s, 4H), 3.63 (br s, 4H), 2.91 (br s, 4H), 2.18 (br m, 8H), 1.31 (br s, 6H), 1.26 (br s, 6H), 0.69 (br m, 12H); SEC (DMF): $M_n = 5.0 \text{ kg mol}^{-1}$, $M_w = 14.2 \text{ kg mol}^{-1}$, $\bar{D} = 2.83$; BET Surface Area: $79 \text{ m}^2 \text{ g}^{-1}$.



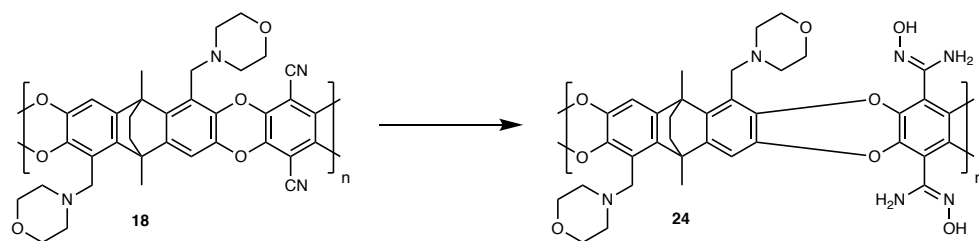
21: To a round bottom flask was added **13** (2.50 g, 3.8 mmol) and THF (120 mL). The mixture was heated to at 60 °C to dissolve the polymer. A solution of 50 wt% aqueous hydroxylamine (20 mL, 326 mmol) was then added dropwise. The reaction mixture was stirred overnight and then cooled before precipitating the polymer into methanol (400 mL). The solid was filtered and then rinsed twice with methanol (500 mL) before drying *in vacuo* at 50 °C to give **21** as a white powder (1.87 g) in 68% yield. ^1H NMR (d_6 -DMSO, 500 MHz): δ (ppm) 9.50 (br s, 2H), 6.79 (br s, 2H), 5.86 (br s, 4H), 3.43 (br s, 4H), 3.02 (br s, 2H), 2.84 (br s, 2H) 2.11 (br s, 16H), 1.36 (br s, 6H), 1.26 (br s, 6H); SEC (DMF): $M_n = 29.7 \text{ kg mol}^{-1}$, $M_w = 62.8 \text{ kg mol}^{-1}$, $\bar{D} = 2.12$; BET Surface Area: $152 \text{ m}^2 \text{ g}^{-1}$.



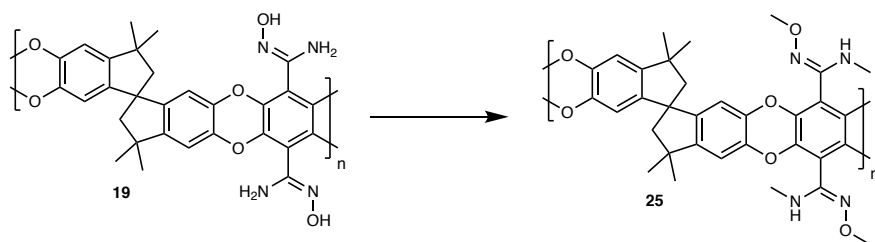
22: To a round bottom flask was added **14** (1.08 g, 1.4 mmol) and THF (75 mL). The mixture was heated to at 60 °C to dissolve the polymer. A solution of 50 wt% aqueous hydroxylamine (12 mL, 196 mmol) was then added dropwise. The reaction mixture was stirred overnight and then cooled before precipitating the polymer into a 1:1 (v/v) solution of water and methanol (450 mL). The solid was filtered and then rinsed twice with methanol (500 mL) before drying *in vacuo* at 50 °C to give **22** as a pale-yellow powder (0.87 g) in 74% yield. ¹H NMR (*d*₆-DMSO, 500 MHz): δ (ppm) 9.47 (br s, 2H), 6.77 (br s, 2H), 5.85 (br s, 4H), 3.17 (br m, 14H), 2.54–1.86 (br m, 24H), 1.37 (br s, 6H), 1.25 (br s, 6H); SEC (DMF): $M_n = 11.5 \text{ kg mol}^{-1}$, $M_w = 22.6 \text{ kg mol}^{-1}$, $\bar{D} = 1.96$; BET Surface Area: $10 \text{ m}^2 \text{ g}^{-1}$.



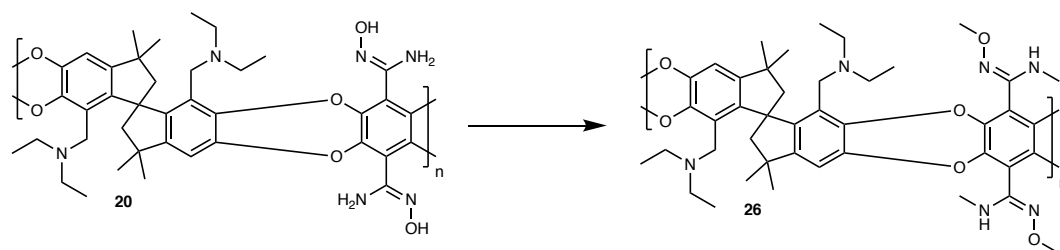
23: To a round bottom flask was added **15** (1.03 g, 1.2 mmol) and THF (60 mL). The mixture was heated to at 60 °C to dissolve the polymer. A solution of 50 wt% aqueous hydroxylamine (11 mL, 180 mmol) was then added dropwise. The reaction mixture was stirred overnight and then cooled before precipitating the polymer into water (600 mL). The solid was filtered and then rinsed twice with methanol (500 mL) before drying *in vacuo* at 50 °C to give **23** as a pale-yellow powder (0.95 g) in 86% yield. ¹H NMR (*d*₆-DMSO, 500 MHz): δ (ppm) 7.80 (br s, 2H), 6.81 (br s, 2H), 5.75 (br s, 4H), 3.12 (br m, 8H), 2.03 (br m, 16H), 1.46–1.18 (br m, 30H); SEC (DMF): $M_n = 8.0 \text{ kg mol}^{-1}$, $M_w = 12.4 \text{ kg mol}^{-1}$, $\bar{D} = 1.56$; BET Surface Area: $12 \text{ m}^2 \text{ g}^{-1}$.



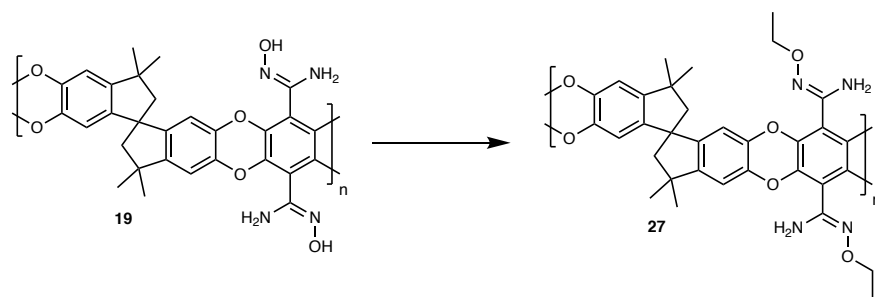
24: To a round bottom flask was added **18** (350 mg, 0.57 mmol) and THF (22 mL). The mixture was heated to 70 °C to dissolve the polymer. A solution of 50 wt% aqueous hydroxylamine (2.6 mL, 42 mmol) was then added dropwise. The reaction was stirred for 72 h and then cooled before precipitating the polymer in methanol (120 mL). The solid was filtered and rinsed twice with methanol (50 mL) before drying *in vacuo* 50 °C to give **24** as a white powder (323 mg) in 83% yield. ^1H NMR (d_6 -DMSO, 500 MHz): δ (ppm) 9.57 (br s, 2H), 6.77 (br s, 2H), 5.83 (br s, 4H), 3.49 (br t, 8H), 2.23–1.33 (broad m, 22H); SEC (DMF): $M_n = 22.7 \text{ kg mol}^{-1}$, $M_w = 36.7 \text{ kg mol}^{-1}$, $D = 1.52$; BET Surface Area: $10 \text{ m}^2 \text{ g}^{-1}$.



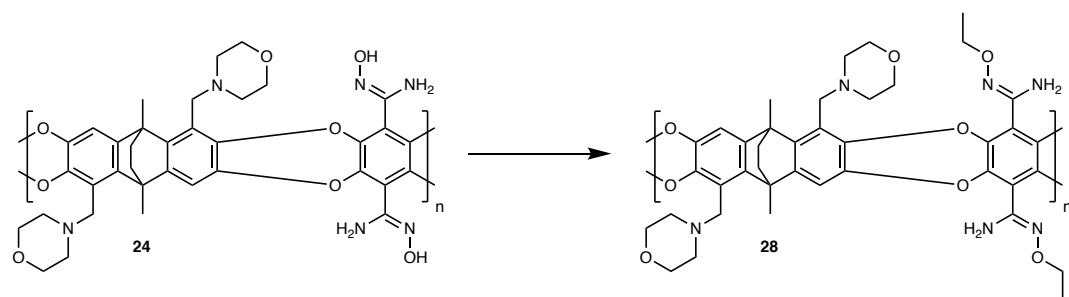
25: To a solution of **19** (1.50 g, 2.7 mmol) in dimethyl sulfoxide (57 mL) was added a solution of lithium hydroxide monohydrate (0.478 g, 11.4 mmol) in MilliQ water (5.75 mL) dropwise over 1 min. After stirring for 1 h under nitrogen, the reaction mixture was placed on ice, and dimethyl sulfate (1.08 mL, 11.4 mmol) was added in two portions. The reaction was allowed to reach room temperature and stirred for 72 h, before quenching with sufficient sodium hydroxide to increase the pH above 7. The product was precipitated in MilliQ water (400 mL), filtered and rinsed with two portions of MilliQ water (100 mL each), and then dried *in vacuo* at 60 °C to give **25** as a dark yellow solid (1.28 g) in 80% yield. ^1H NMR (d_6 -DMSO, 500 MHz): δ (ppm) 6.67 (br s, 2H), 6.28 (br s, 2H), 5.83 (br s, 2H), 4.08–3.42 (br m, 6H), 3.38–2.79 (br m, 6H), 2.20 (br d, 4H), 1.28 (br s, 6H), 1.33 (br s, 6H); Elemental Analysis for $\text{C}_{33}\text{H}_{34}\text{N}_4\text{O}_6$ Calculated: C 68.03, H 5.88, N 9.62; Found: C 65.21 H 5.76, N 8.93; SEC (DMF): $M_n = 17.5 \text{ kg mol}^{-1}$, $M_w = 102 \text{ kg mol}^{-1}$, $D = 5.85$; BET Surface Area: $7 \text{ m}^2 \text{ g}^{-1}$.



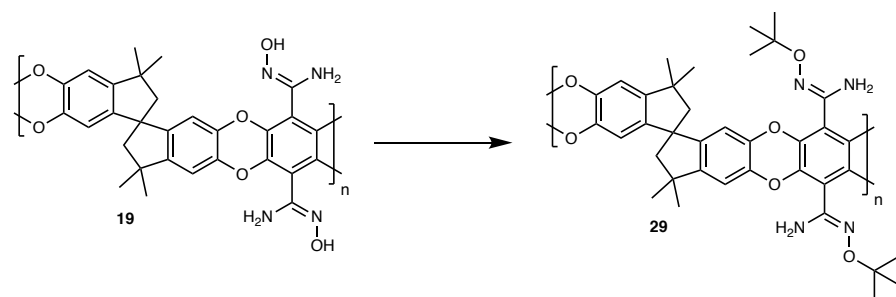
26: To a solution of **20** (1.50 g, 2.2 mmol) in dimethyl sulfoxide (43 mL) was added a solution of lithium hydroxide monohydrate (0.36 g, 8.6 mmol) in MilliQ water (4 mL) dropwise over 1 min. After stirring for 1 h under nitrogen, the reaction mixture was placed on ice, and dimethyl sulfate (820 μ L, 8.6 mmol) was added in two portions. The reaction was allowed to reach room temperature and stirred for 72 h, before quenching with 5.0 N sodium hydroxide (2 mL). The product was precipitated in MilliQ water (500 mL), filtered and rinsed with two portions of MilliQ water (100 mL each), followed by an additional precipitation from dimethyl sulfoxide into MilliQ water, and then dried *in vacuo* at 60 $^{\circ}$ C to give **26** as a dark yellow solid (0.94 g) in 57% yield. ^1H NMR (d_6 -DMSO, 500 MHz): δ (ppm) 6.76 (br s, 2H), 5.82 (br s, 2H), 3.64 (br s, 4H), 2.91 (br s, 4H), 2.18 (br m, 20H), 1.32 (br s, 6H), 1.27 (br s, 6H), 0.69 (br m, 12H); SEC (DMF): M_n = 6.9 kg mol $^{-1}$, M_w = 13.8 kg mol $^{-1}$, D = 1.99; BET Surface Area: 8 m 2 g $^{-1}$.



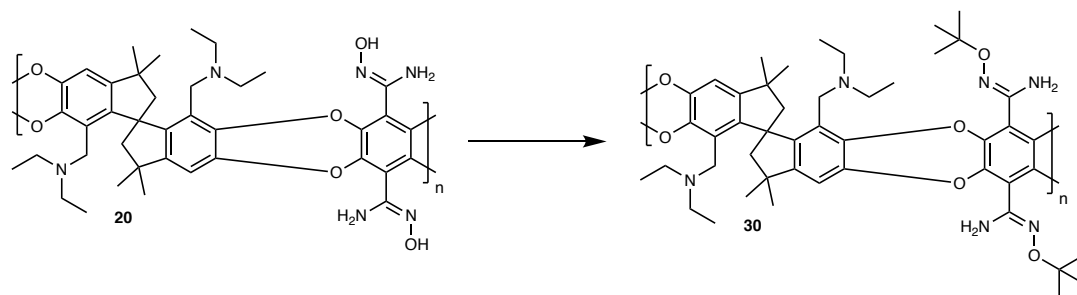
27: To a solution of **19** (1.37 g, 2.6 mmol) in dimethyl sulfoxide (57 mL) was added a solution of lithium hydroxide monohydrate (0.48 g, 11.4 mmol) in MilliQ water (5.75 mL) dropwise over 1 min. After stirring for 1 h under nitrogen, the reaction mixture was placed on ice, and diethyl sulfate (1.76 g, 11.4 mmol) was added in two portions. The reaction was allowed to reach room temperature and stirred for 72 h, before quenching with sufficient sodium hydroxide to increase the pH above 7. The product was precipitated in MilliQ water (400 mL), then filtered and rinsed with two portions of MilliQ water (100 mL each), and then dried *in vacuo* at 60 $^{\circ}$ C to give **27** as a dark yellow solid (1.34 g) in 88% yield. ^1H NMR (d_6 -DMSO, 500 MHz): δ (ppm) 6.82 (br s, 2H), 6.18 (br s, 2H), 5.82 (br s, 4H), 3.88 (br t, 4H), 2.17 (br d, 4H), 1.72–0.76 (br m, 18H); Elemental Analysis for C $_{33}$ H $_{34}$ N $_4$ O $_6$ Calculated: C 68.03, H 5.88, N 9.62; Found: C 66.17 H 6.08, N 8.85; SEC (DMF): M_n = 45.4 kg mol $^{-1}$, M_w = 222 kg mol $^{-1}$, D = 4.87; BET Surface Area: 10 m 2 g $^{-1}$.



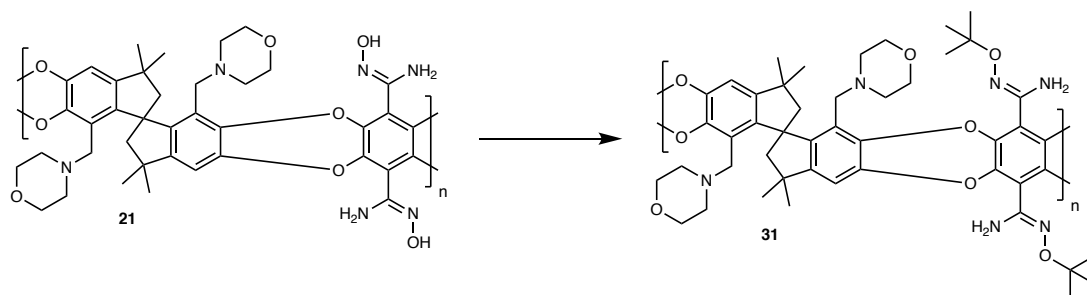
28: To a solution of **24** (0.21 g, 0.32 mmol) in dimethyl sulfoxide was added lithium hydroxide monohydrate (0.05 g, 1.3 mmol) in water (0.6 mL). The mixture was stirred for 1 h on ice before adding diethyl sulfate (0.20 g, 1.3 mmol) and warming to room temperature. Reaction was stirred for two days, and then quenched by adding sufficient 5.0 N sodium hydroxide to increase the pH of the solution above 7. The polymer was precipitated in MilliQ water (100 mL) and then filtered, rinsed with an additional two portions of water (20 mL), and dried *in vacuo* at 50 °C to give **28** as a light-yellow powder (0.23 g) in 98% yield. ^1H NMR (d_6 -DMSO, 500 MHz): δ (ppm), 6.77 (br s, 2H), 6.05 (br s, 4H), 3.94 (br d, 4H), 3.48 (br m, 8H) 2.23–1.25 (broad m, 28H); SEC (DMF): M_n = 16.6 kg mol $^{-1}$, M_w = 41.9 kg mol $^{-1}$, D = 2.54; BET Surface Area: 24 m 2 g $^{-1}$.



29: To a solution of **19** (1.00 g, 1.9 mmol) in dimethyl sulfoxide (38 mL) was added magnesium perchlorate (0.08g, 0.38 mmol) and di-*tert*-butyl dicarbonate (2.14 g, 9.8 mmol). The reaction was stirred for 24 h at 40 °C, then cooled and precipitated in MilliQ water (400 mL) with 4 drops of 5.0 N sodium hydroxide and then filtered. The solid was rinsed with three portions of MilliQ water (50 mL each), and then two portions of chloroform (50 mL each) to remove excess di-*tert*-butyl dicarbonate, and then dried *in vacuo* at 60 °C to give **29** as a dark yellow solid (0.90 g) in 74% yield. ^1H NMR (d_6 -DMSO, 500 MHz): δ (ppm) 6.87 (br s, 6H), 6.25 (br s, 2H), 2.18 (br m, 4H), 1.73–0.93 (br m, 34H); Elemental Analysis for C $_{37}$ H $_{42}$ N $_4$ O $_6$ Calculated: C 69.57, H 6.63, N 8.77; Found: C 61.29 H 5.47, N 8.09; SEC (DMF): M_n = 43.2 kg mol $^{-1}$, M_w = 154 kg mol $^{-1}$, D = 3.56; BET Surface Area: 11 m 2 g $^{-1}$.



30: To a solution of **20** (1.53 g, 2.2 mmol) in dimethyl sulfoxide (43 mL) was added magnesium perchlorate (0.1 g, 0.43 mmol) and di-*tert*-butyl dicarbonate (1.88 g, 8.6 mmol). The reaction was stirred for 24 h at 40 °C, then cooled and precipitated in MilliQ water (430 mL) with 4 drops of 5.0 N sodium hydroxide and then filtered. The solid was rinsed with three portions of MilliQ water (50 mL each), and then two portions of chloroform (50 mL each) to remove excess di-*tert*-butyl dicarbonate, and then dried *in vacuo* at 60 °C to give **30** as a dark yellow solid (0.98 g) in 55% yield. ¹H NMR (*d*₆-DMSO, 500 MHz): δ (ppm) 6.80 (br m, 6H), 3.27 (br s, 4H), 2.93 (br s, 4H), 2.14 (br m, 8H), 1.37 (br m, 30H), 0.67 (br s, 12H); SEC (DMF): $M_n = 10.9 \text{ kg mol}^{-1}$, $M_w = 15.2 \text{ kg mol}^{-1}$, $\bar{D} = 1.39$; BET Surface Area: $48 \text{ m}^2 \text{ g}^{-1}$.



31: To a solution of **21** (1.59 g, 2.2 mmol) in dimethyl sulfoxide (43 mL) was added magnesium perchlorate (0.1 mg, 0.43 mmol) and di-*tert*-butyl dicarbonate (1.88 g, 8.6 mmol). The reaction was stirred for 24 h at 40 °C, then cooled and precipitated in MilliQ water (400 mL) with 4 drops of 5.0 N sodium hydroxide and then filtered. The solid was rinsed with three portions of MilliQ water (50 mL each), and then two portions of chloroform (50 mL each) to remove excess di-*tert*-butyl dicarbonate, and then dried *in vacuo* at 60 °C to give **31** as a dark yellow solid (1.03 g) in 56% yield. ¹H NMR (*d*₆-DMSO, 500 MHz): δ (ppm) 6.84 (br m, 6H), 2.34–1.79 (br m, 12H), 1.57–0.98 (br m, 42H); SEC (DMF): $M_n = 43.0 \text{ kg mol}^{-1}$, $M_w = 137 \text{ kg mol}^{-1}$, $\bar{D} = 3.19$; BET Surface Area: $31 \text{ m}^2 \text{ g}^{-1}$.

Polymer solubility. Qualitative solubility tests were determined by stirring 5 mg of polymer and 2 mL of solvent in a test tube for 12 h. Complete solubility is indicated with “+++”, partial solubility with “+”, and poor solubility with “–” as indicated in **Supplementary Table 1**.

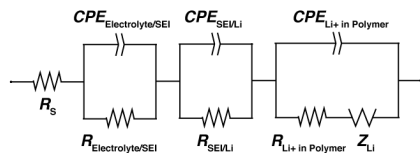
Electrochemical Methods

Electrochemical Cell Assembly. All electrochemical studies were performed using CR2032 coin cells with a single spacer and spring pressed at 1000 psi, Celgard 2325 separators, 70 μL of liquid electrolyte (1.0 M LiPF_6 in EC:DEC (1:1 v/v) with fluoroethylene carbonate (FEC, 10% w/w) and vinylene carbonate (VC, 1% w/w) and 750- μm thick Li electrodes, onto which PIMs were drop cast as inks in THF and dried overnight before cell assembly.

Symmetric Lithium (Li–Li) Cells for Rapid Screens of Conductivity, Activation Energy, and Steady-State Cation Transference Number. Li–Li cells were assembled with PIM interlayers cast on both Li electrodes (loading and interlayer thickness given below), with coating facing toward the separator. Cells were allowed to equilibrate at ambient temperature at least 24 h before testing.

Polymers	Total polymer thickness in cell (μm)
PIM-1, 11–15	15
17	2
18, 21, 23–26, 28, 30, 31	6

Electrochemical impedance spectroscopy (EIS) was conducted at open-circuit voltage (OCV) with a Biologic VMP3 potentiostat from 1 MHz to 1 Hz with AC voltage amplitude of 10 mV. Conductivity measurements were taken in a temperature control oven, which was allowed to equilibrate to 25, 40, 55, and 70 $^{\circ}\text{C}$ for 2.5 h before acquiring impedance spectra at each temperature. Spectra were modelled using the equivalent circuit below.



The resistance for a given polymer was determined by subtracting the solution resistance (R_s) of a cell with no interlayer (Celgard only) at the same temperature from the solution resistance of the given cell. Conductivity was then determined from the interlayer thickness (l), resistance (R_{Polymer}), and electrode area (A , 1.267 cm^2).

$$R_{\text{Polymer}} = R_{\text{S Polymer}} - R_{\text{S Celgard}}$$

$$C_{\text{Polymer}} = \frac{l}{R_{\text{Polymer}} A}$$

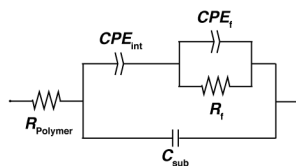
Conductivity values at 25 $^{\circ}\text{C}$ are reported in **Fig. 2**. Activation energy values were determined from the slope of a plot of $\ln(CT)$ vs. $1/T$, shown in **Supplementary Figs. 12–28**.

The Bruce–Vincent steady-state cation transference number was determined by EIS before and after potentiostatic polarization at 10 mV for 2 h, shown in **Supplementary Figs. 29–44**. The applied voltage (ΔV) initial current (I_0), steady state current (I_{ss}), and solution resistance values before (R_0), and after polarization (R_{ss}) were used to calculate cation transference number (t_+).

$$t_+ = \frac{I_{ss} (\Delta V - I_0 R_0)}{I_0 (\Delta V - I_{ss} R_{ss})}$$

Determinations of t_+ using the Bruce–Vincent method^{13,14} are relatively high-throughput, highly differentiating for the PIMs reported here in our library, and ultimately comparable to other work in the field on that basis. Nevertheless, there are emerging insights from Balsara and Newman that advise reconsidering the electroanalytical methods needed to more precisely quantify cation transference numbers in electrolytes for Li metal batteries at battery relevant salt concentrations, e.g., from Newman’s concentrated solution theory and the associated Stefan–Maxwell diffusion coefficients for all interacting species.¹⁵ Such a treatment, even in simple systems, requires multi-pronged experiments in a variety of cell configurations using different testing protocols. Such pursuits are therefore intrinsically lower-throughput than the more common Bruce–Vincent method. A further consideration is that these emerging methodologies have not yet been developed or validated for Li metal batteries with thin polymer interlayers, particularly those featuring nanoconfined electrolytes and solid-solvation cages, where double layer effects manifest and are typically dominant contributors to the transport behaviors. We qualify our screens of t_+ in light of these important considerations.

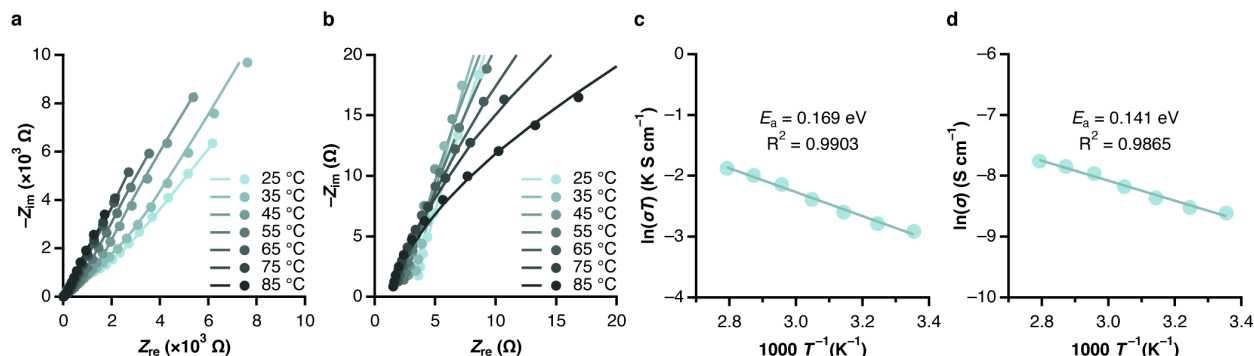
Symmetric Stainless Steel (SS|SS) Cells for Validating Screens for Conductivity and Activation Energy. SS|SS symmetric cells were assembled with an 8- μ m thick polymer layer cast onto a stainless-steel spacer ($A = 1.979 \text{ cm}^2$) from THF and infiltrated with 1.0 M LiPF₆ in EC:DEC (1:1 v/v) containing FEC (10% w/w) and VC (1% w/w) prior to assembly into a coin cell. Electrochemical impedance spectroscopy (EIS) was measured at open-circuit voltage (OCV) with a Biologic VMP3 potentiostat from 1 MHz to 1 Hz with AC voltage amplitude of 10 mV. Conductivity measurements were taken in a temperature-controlled oven, which was allowed to equilibrate to $T = 25, 35, 45, 55, 65, 75$, and 85°C for 2.5 h before acquiring impedance spectra at each temperature. Spectra were modelled using the equivalent circuit below.



The resistance from each polymer was taken as R_p based on the above model, and conductivity was then determined from the interlayer thickness (l), resistance (R_p), and electrode area.

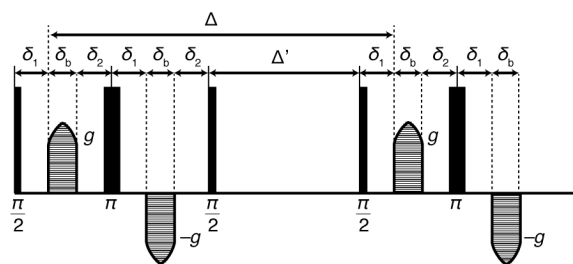
$$\sigma_{\text{Polymer}} = \frac{l}{R_p A}$$

The activation energy could be extracted from either Arrhenius ($\ln(\sigma T)$ vs. $1/T$) or Volger–Fulcher–Tamman (VFT) ($\ln(\sigma)$ vs. $1/T$) plots.



Variable-Temperature EIS for electrolyte-infiltrated PIM 13 with stainless steel blocking electrodes. **a**, Nyquist plot and **b**, High-frequency region, **c**, Arrhenius plot, and **d**, Volger–Fulcher–Tamman (VFT) plot at 25 °C, 35 °C, 45 °C, 55 °C, 65 °C, 75 °C, and 85 °C.

Quantifying Self-Diffusion of Ions and Solvent in the Bulk and Under Confinement in PIMs by Using Pulsed-Field Gradient NMR (PFG-NMR). Self-diffusion coefficients of Li^+ at 25 °C in the electrolyte and in electrolyte-infiltrated PIMs were determined by ^7Li PFG-NMR at Larmor frequency of $2\pi \cdot 232.954$ rad·MHz. The diffusion coefficients of fluorine containing species, PF_6^- and FEC, at 25 °C were determined by ^{19}F PFG-NMR at Larmor frequencies of $2\pi \cdot 563.954$ and $2\pi \cdot 563.926$ rad·MHz, respectively. All measurements were carried out on a 600 MHz NMR spectrometer (Agilent, USA) equipped with a 5-mm z-gradient probe (Doty Scientific, USA), that can generate the maximum gradient strength of $\sim 31 \text{ T m}^{-1}$. PFG echo profiles with 16 equal steps as a function of gradient strength (g) were obtained using the bipolar gradients PFG sequence (Dbpppste, vender supplied sequence in VNMRJ, Agilent, USA) represented below (where gradient length $\delta = 2\delta_b$). Maximum gradient strengths were carefully chosen for observing a sufficient decay of the echo profiles.

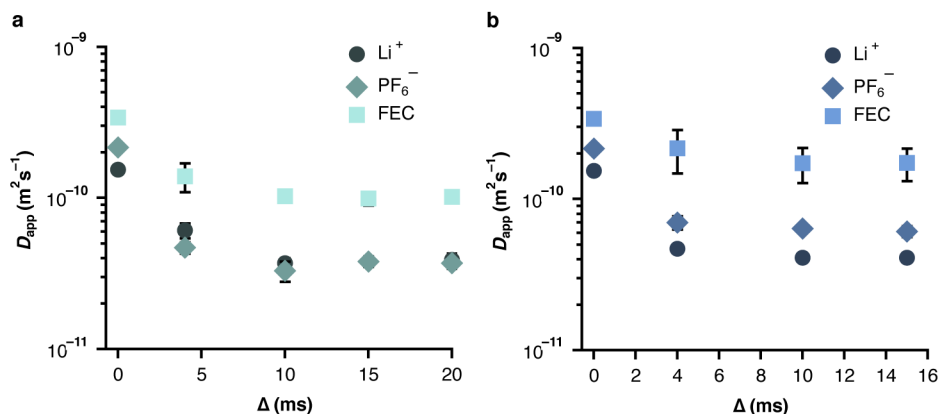


Diffusion coefficients were determined from the echo profiles fitted with the Stejskal–Tanner equation.¹⁶

$$S(g) = S(0) \exp \left[-D (\gamma \delta g)^2 \left(\Delta - \frac{\delta}{3} \right) \right]$$

where, $S(g)$ and $S(0)$ are the echo height at the gradient strength of g and 0, respectively, D is diffusion coefficient, γ is the gyromagnetic ratio of nucleus observed (^7Li or ^{19}F), δ is the gradient length, and Δ is the diffusion delay. The 90° pulse lengths for ^7Li and ^{19}F were 8 and 11 μs , respectively. Unrestricted diffusion in an unbounded medium is time independent; $D_{\text{app}}(0)$ (i.e., D_0) for Li^+ , PF_6^- , and FEC are therefore estimated as the diffusion coefficient in the bulk solution of 1.0 M LiPF_6 in EC:DEC (1:1 v/v) with FEC (10% w/w) and VC (1% w/w) electrolyte. Apparent diffusion coefficients, D_{app} , of Li^+ , PF_6^- , and FEC confined in PIMs were obtained as a function of diffusion delay $\Delta = 4, 10, 15$, and 20 ms with a fixed gradient length (δ) of 2 ms.

Restricted diffusion in a connected porous medium is characterized by a time-dependent diffusion D_{app} , where $D_{\text{app}}(\Delta)$ decreases with increasing of diffusion delay, eventually reaching a steady-state ($D_{\text{app},\infty}$). The shape of the D_{app}/D_0 vs. Δ curve is dictated by pore architecture, where pore size and surface-to-pore volume ratio can sometimes be extracted from the initial slope; the plateau in the curve is determined by the tortuosity (i.e., blocking factor) of the pore network, as experienced by a given species under observation.^{17,18} Determination of pore size and surface-to-pore volume ratio is limited by the minimum Δ that can be measured during the experiment. For very high surface-to-pore volume materials, including PIMs, the initial slope is too steep to measure reliably with currently available instrumentation; therefore, it is not possible to measure D_{app} at sufficiently short Δ to determine the pore dimensions in PIMs without unacceptable degrees of uncertainty. On the other hand, from the plateaus in the time-dependent diffusion measurements, $D_{\text{app},\infty}$ values are reliably extracted for each species and informative of the blocking factor on that basis.



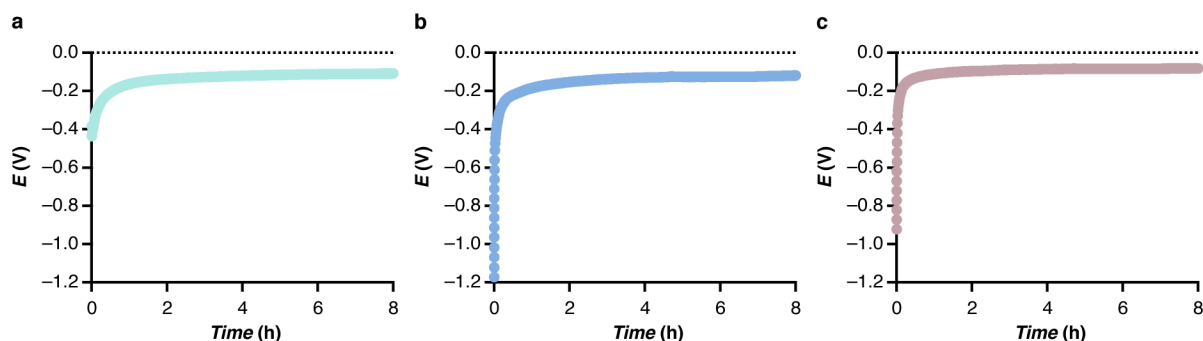
Time-dependent diffusion of electrolyte components in PIM membranes. Delay-dependent diffusion of Li^+ , PF_6^- , and FEC in **a**, PIM 13 and **b**, PIM-1. Error bars represent fitting error from the application of the Stejskal–Tanner equation.

Relative values for the self-diffusion of Li^+ and PF_6^- in the bulk or under nanoconfinement in PIMs may not be directly compared with the cation transference number, as the latter also takes into account mutual diffusion and changes in the chemical potential for each species due to an electric field, etc. and cannot be disentangled therefrom.¹⁵

Li–Cu Cells for Determining the Limiting Current. Chronopotentiometry was performed on Li–Cu cells to determine the limiting current density of PIM 13, PIM-1, and the bulk carbonate

electrolyte. Cu foil was treated with 1.0 M HCl to remove the native oxide layer, then washed the foil with excess water and acetone. For Li–Cu cells featuring a PIM interlayer, inks of PIMs in THF (50 mg mL⁻¹) were coated onto Cu foil using a blade coater and the working electrodes punched therefrom after drying. Each coin cell was assembled with a thick Li counter electrode, either a coated or uncoated Cu working electrode, two Celgard separators, and 30 μ L of electrolyte. Cells were equilibrated at 25 °C for at least 12 h to ensure effective wetting and partitioning of the electrolyte in the separator and PIM interlayers, respectively. Prior to cycling, two cycles of plating at 0.20 mA cm⁻² for 5 h and stripping at 0.20 mA cm⁻² for 2 h were carried out to deposit a layer of fresh Li onto the working electrode. Li was galvanostatically plated onto either the coated or uncoated working electrode at current densities of 0.10–1.3 mA cm⁻² for 0.5 h while monitoring the potential; a 0.5 h rest was implemented between step increases in current density in increments of 0.10 mA cm⁻².

Li–Li Cells for Synchrotron Hard X-ray Microtomography. Li–Li symmetric cells were assembled with either bare lithium electrodes, or PIM interlayers coated on both Li electrodes (PIM 13 or PIM-1 drop-cast from 40 μ L of 12.5 mg mL⁻¹ ink to yield $\sim$ 15 μ m interlayers) with coating facing toward the separator. Cells were allowed to equilibrate at ambient temperature at least 24 h before polarization for 8 h at 1 mA cm⁻² on an Arbin BT-2043 System.



Li–Li cell polarization showed no evidence of shorting behavior in advance of hard X-ray microtomography characterization. a–c, Polarization curves for PIM 13, PIM-1, and Celgard Li–Li symmetric cells at 1 mA cm⁻².

After polarization, cells were disassembled and the electrode stack was placed on a 3 mm polystyrene disc + side down before vacuum sealing in a Mylar pouch. Pouches were allowed at least 1 h to equilibrate to hutch temperature at Beamline 8.3.2 at the Advanced Light Source at Lawrence Berkeley National Laboratory¹⁹ before analysis. Monochromatic hard X-ray (17 keV) microtomography was carried out with cells + side down, rotating samples 180° under the X-ray beam and reconstructing the resulting shadows to image stacks of $\sim$ 1000 images each using Xi-Cam software. Brightness and contrast were adjusted to the same level across all image stacks in ImageJ before compressing from 32-bit to 8-bit images. Image stacks were visualized in Avizo, where volume rendering and cross-sectional images of a representative 320 x 640 x 210 μ m section of each cell was obtained.

Li–NMC622 Battery Cells. Lithium metal anodes left bare, or optionally coated with either PIM-1 or **13** (~ 3 μm -thick overlayers), were paired with $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$ (NMC622) composite cathodes with an areal capacity of 1.44 mAh cm^{-2} (supplied by the CAMP facility at Argonne National Lab); the cathodes were 12 mm in diameter. Celgard 2325, 19 mm in diameter, and used as separator. The electrolyte was 1.0 M LiPF_6 in EC:DEC (1:1 v/v) with FEC (10% w/w) and VC (1% w/w); 70 μL was used in each cell. Cycling was carried out at 25 $^\circ\text{C}$ on an Arbin BT-2043 System with three initialization cycles at 0.1 mA cm^{-2} before cycling at a current density of 1 mA cm^{-2} ; alternatively, we performed rate tests at variable current density ($0.10\text{--}5.0 \text{ mA cm}^{-2}$).

Computational Methods

General Methodology. To explore the functional role of Li^+ solid solvation cages we use a multiscale computational approach with the main focus on the study of Li^+ ion transport between cages when in contact with the liquid electrolyte. Specifically, we analyze the structural properties and thermodynamics of Li^+ in solid solvation cages of PIM **13** in dimethyl carbonate (DMC). The processes of dissociation of the cation from a cage and its solvation/desolvation was performed in three steps.

In the first step, we used quantum mechanical (density functional theory, DFT) calculations (ignoring finite temperature effects) of small molecular clusters, involving the PIM **13** unit, the solvated Li^+ ion and DMC molecules. We calculated the equilibrium configurations of polymer units with and without the Li^+ ion. Long-range solvent effects are included in these quantum chemical calculations using the polarizable continuum model (PCM). These calculations not only provide structural and electronic details (the equilibrium configurations and atomic partial charges, based on natural bond orbitals) but also their sensitivity to dielectric screening from the electrolyte solvent. Using thermodynamic cycles we evaluated the cation solvation energies and relative stability of different configurations (e.g., contrasting Li^+ in the cage versus in the solvent) by reference to the corresponding condensed phases.

In the second step, sampling of the ensemble of molecular configurations accessible at finite temperature, with inclusion of explicit solvent molecules, was provided by classical molecular dynamics (MD) simulations. We tested a various force fields and different charge schemes. Special attention was paid to partial charges of the lithium ion, as well as the coordinating oxygen and nitrogen moieties in the cages.

In the third step, we employed metadynamics to explore the free-energy landscape associated with Li^+ transport: the kinetic barriers and the relative free energy differences of various states of the Li^+ cation, on its path from solid solvation cage to bulk solvent or to another cage. The metadynamics approach also incorporates the entropy of all the thermodynamically accessible configurations of the polymer, cation and solvent molecules. We used 1D and 2D free energy analyses with particular choices of collective variables that reflect the transport processes of interest (see below).

Quantum Chemistry Calculations. Optimized geometries, relative energies, and molecular orbitals were calculated using DFT, with the GPU-based TeraChem package.²⁰ As suggested in previous extensive computational studies of aprotic ionic liquids, we used the B3LYP5-D3 functional with the 6-311++G** basis set,²¹ employing the third version of Grimme’s empirical dispersion correction.²² We used the L-BFGS geometry optimization method²³ with the termination criterion for the maximum energy gradient component of 4.5×10^{-4} au. The wave function convergence threshold was set as 3.0×10^{-5} . The two-electron integral threshold was set as 1.0×10^{-12} , and the basis set linear dependency threshold was 1.0×10^{-4} . The numerical accuracy was set to double precision. Partial charges were computed using the full natural bond orbital²⁴ (NBO) and Mulliken analysis. The structure of an isolated DMC molecule is shown in **Supplementary Fig. 46**. The analysis of the stability of the Li⁺-ion in DMC revealed that the most stable configuration is the 4-fold coordinated cation, shown in **Supplementary Fig. 47**, as previously found.^{25–28} The equilibrium configuration of the PIM **13** fragment is shown in **Supplementary Fig. 48**. Note the “chair” configuration of morpholine. When Li⁺ is added to the polymer, it finds the most stable configuration in the cage indicated by indices in **Supplementary Fig. 49**; the “boat” configuration of morpholine has been adopted, which provides both nitrogen and oxygen atoms to coordinate the cation. NBO charges for nitrogen and oxygen atoms of the cages are shown in table **Supplementary Table 6**.

Next we used nudged elastic band²⁹ (NEB) calculations to evaluate the kinetic barrier for transition of the Li⁺ ion between neighboring cages (the PIM **13** unit contains two adjacent though not fully identical cages). No continuum dielectric media or explicit solvent molecules were used. NEB energies are shown in **Supplementary Fig. 50**. Since the cages are not fully identical, the minima have slightly different energies, and the left minimum corresponds to the cage shown in **Supplementary Fig. 48**. As **Supplementary Fig. 51** suggests, the kinetic barrier of 4.51 eV for motion of the Li⁺ ion is unsurmountable for the transport between cages. Note that these are energies at $T = 0$ K, and no entropy effects are considered. Moreover, since the ends of the polymer unit are not fixed, one may expect higher energies as the molecular configuration could be more compact because of the finite size effect.

Hybrid Cluster/Continuum Quantum Mechanical Calculations: Ion Solvation Free Energies. Quantum mechanical calculations (B3LYP5-D3/6-311++G**) with polarizable continuum media (PCM) calculations with COSMO³⁰ model were used to account for the effects of the solvent and to calculate the solvation energies of species of interest. The dielectric constant of DMC was set as 3.087, and atomic radii as suggested by Bondi.³¹ To evaluate the free energy of dissociation of the Li⁺ ion from the cage to the bulk solvent we use the thermodynamic cycle shown in **Supplementary Fig. 51**.

From this cycle, $\Delta G_{diss}^* = \Delta G_1 + \Delta G_2 + \Delta G_3 + \Delta G_{sol}^*(Li^+)$, with ΔG_1 denoting the free energy of desolvation of the polymer (PIM **13**) unit with the Li⁺ ion inside the cage, ΔG_2 denoting the dissociation energy into a free unit and an isolated cation in vacuum, ΔG_3 denoting the free energy of solvation of the polymer unit, and finally, $\Delta G_{sol}^*(Li^+)$ denoting the Li⁺ ion absolute solvation free energy. Since we ignore the concentration of PIM, no thermodynamic correction terms for the standard 1.0 M state were applied. Moreover, due to the large size of the polymer unit and low

dielectric constant of DMC, we assume $\Delta G_3 = 0$. To evaluate $\Delta G_{sol}^*(Li^+)$ we employed the “monomer” thermodynamic cycle³² shown in **Supplementary Fig. 52**.

Using this cycle, the ion solvation energy can be calculated as follows:

$$\Delta G_{solv}^*(Li^+) = \Delta G_{g,bind}^o(I) + \Delta G_{solv}^*([Li(DMC)_n]^+) - n\Delta G_{solv}^*(DMC) - nRT\ln[DMC] - n\Delta G^{o-*}$$

Where,

$\Delta G_{g,bind}^o(I)$ is the cluster $Li^+(DMC)_n$ formation energy referenced to the dissociated state in vacuum;

$\Delta G_{solv}^*([Li(DMC)_n]^+) = G([Li(DMC)_n]^+)_{DMC} - G([Li(DMC)_n]^+)_{gas}$ is the solvation energy of the cluster (calculated with the COSMO model);

$\Delta G_{solv}^*(DMC)$ is the free energy of self-solvation of DMC in DMC (i.e., the negative vaporization energy), which could be obtained either from the pressure of the saturated vapor at $T = 298.15$ K in equilibrium with the liquid DMC: $\Delta G_{solv}^*(DMC) = RT\ln\left(\frac{[DMC_g]}{[DMC_{liq}]}\right)$ or from PCM calculations: $\Delta G_{solv}^*(DMC) = G(DMC)_{THF} - G(DMC)_{gas}$;

$RT\ln[DMC] = 1.4654 \text{ kcal/mol}$ is the thermodynamic correction for the standard state (1 M) of the solvent, i.e., the free energy cost of transferring of a compound from a hypothetical ideal gas at 1.0 M into a hypothetical ideal 1.0 M solution. Molar concentration of DMC $[DMC(l)] = 11.879$ M;

$\Delta G^{o-*} = 1.89 \text{ kcal/mol}$ is the thermodynamic correction of conversion of an ideal gas standard state of 1.0 atm to a standard state of 1.0 M.

Note that the formation of a cluster of a solvated ion in liquid DMC does not involve any change in free energy, so the lower cycle leg has only $RT\ln[DMC]$ correction. As suggested from our previous calculations, the first solvation sphere contains four DMC molecules (**Supplementary Fig. 47**), so we put $n = 4$. The results of quantum mechanical calculations are summarized in **Supplementary Tables 7 and 8**.

As follows from these calculations, solvation energy of the Li^+ ion in DMC (-6.86 eV) is on par with that in water (-5.49 eV)³³ despite the difference in dielectric constants. It is also close to the values of solvation energies of other monovalent cations (e.g., Na^+) in methanol and acetonitrile³⁴ (-7.043 eV and -6.90 eV , respectively). These calculations suggest that the dissociation of Li^+ from the cage in the bulk solvent is significantly renormalized ($+0.457 \text{ eV}$) as compared to that in vacuum ($+5.827 \text{ eV}$), and remains thermodynamically unfavorable: the equilibrium $Li_{sol}^+ + cage \leftrightarrow Li_{cage}^+$ is then expected to be strongly shifted to the right. The explicit free energy sampling

(see below) shows even further renormalization of the dissociation energy, up to 0.14–0.15 eV (see Main Text).

Classical Molecular Dynamics Calculations. Classical molecular dynamics (MD) simulations were conducted using the LAMMPS simulation package.³⁵ Long-range electrostatic interactions were treated within the particle-mesh Ewald (PME) method with a cutoff distance 1.0 nm with grid spacing in k -space of 10^{-5} . A cut-off of 1.0 nm with a spline from 0.9 to 1.0 nm was used for Lennard-Jones interactions. The relaxation of the initial structures was performed in two steps, first using steepest descent with a convergence criterion of 10^{-4} kcal mol⁻¹ for energies and 10^{-4} kcal mol⁻¹ Å⁻¹ for forces. The systems were first heated to 298 K in the canonical ensemble (NVT). To remove any “memory” effects, the systems were first melted at 400 K and then annealed back to 298 K three times (evolving the trajectory 2 ns for annealing each step). Then, isothermal-isobaric (NPT, isotropic $P = 1$ atm, $T = 298$ K) simulations were performed for 2 ns (2 fs time step) to obtain the correct density using a Nose/Hoover thermostat³⁶ and Nose/Hoover barostat.³⁷ The temperature coupling constant was 0.1 ps, the pressure piston constant was 2.0 ps. Afterwards, NVT simulations were performed ($T = 298$ K) for 1 ns (1 fs time step) to equilibrate. Structural properties were obtained from 5 ns MD simulation runs with an integration time step 1 fs in NVT ensemble with coordinates and velocities saved every 5 ps for post-trajectory analysis.

Throughout all classical MD calculations (regular and metadynamics protocols) the Generalized Amber force field³⁸ (GAFF) was used for ions and solvent molecules. The diagonal vdW parameters of the Lennard-Jones potential for the Li⁺ ion are: 2.050 and 0.028 for σ and ϵ , respectively, as suggested by Aqvist.³⁹ The charge of the Li⁺ ion is fixed as +1 (NBO charge of Li in the $[Li(DMC)_4]^+$ complex is ca. 0.91). For the anion PF₆ we used the harmonic potential for the P – F bond ($k = 507.6$ kcal mol⁻¹, $r_0 = 1.579$ Å) and the periodic cos potential for F – P – F angle ($k = 190$ kcal mol⁻¹, $b = 1$, $n = 4$) to ensure the octahedral configuration.

We used two strands of PIM **13**, eight units long each (712 atoms), per a simulation box, as shown in **Supplementary Fig. 53**. For the oxygens and nitrogen atoms of the cage we used NBO charges listed in **Supplementary Table 6**. We performed simulation of pure DMC (to test the proper choice of the force field capable to reproduce the bulk density of the solvent), and two different concentrations of LiPF₆ (0.2 M and 0.7 M) in the presence of the polymers to see the population of the occupied cages. A typical simulation box is shown in **Supplementary Fig. 54**. Parameters of simulation boxes are summarized in **Supplementary Table 9**.

We performed classical free energy sampling to evaluate the free energy profiles along the collective variables (CV) of interest. For one-dimensional free energy sampling we used r_1 , the distance between the Li⁺-ion and the center of the masses of a cage; for two-dimensional free energy analysis, we used linear combinations $d = r_1 - r_2$ and $s = r_1 + r_2$ of distances r_1 and r_2 between the Li⁺-ion and the centers of the masses of two cages (see further details below). Specifically, we use the metadynamics^{40,41} protocol to evaluate the potential of mean force (PMF) along the collective variables. For a system of N particles in a canonical ensemble at temperature T , the probability density associated with a generalized coordinate λ having a value of λ_0 can be expressed in terms of a generalized partition function:

$$\Omega(\lambda_0) = \int dq^{3N} dp^{3N} \delta(\lambda - \lambda_0) e^{-\beta H(q^N, p^N)},$$

where q and p are conjugated generalized coordinates and momenta of particles and we assume that additional constraints associated with general integrals of motion are already subtracted. Accordingly, the configurational part of the partition function can be written as $Z(\lambda_0) = \int dq^{3N} \delta(\lambda - \lambda_0) e^{-\beta H(q^N; \lambda)}$. The PMF is then defined as $W(\lambda) = -kT \ln \Omega(\lambda) + \text{const}$. The integration constant is chosen so $\min \{W(\lambda)\} = W(\lambda_{\min}) = 0$, where $\lambda_{\min}$ is the value of CV at which $W(\lambda)$ reaches its global minima.

In **Supplementary Figure 55** we show the definitions of collective variables used in our free energy analysis. Since we want to explore the free energy profile along the pathway from one cage to another as close as possible to the backbone of the polymer, just $\mathbf{r}_1$ and $\mathbf{r}_2$ will not be an appropriate choice for collective variables for 2D free energy sampling. To solve this problem we used $\mathbf{d} = \mathbf{r}_1 - \mathbf{r}_2$ and $\mathbf{s} = \mathbf{r}_1 + \mathbf{r}_2$ and apply a constraint that limits the range for $\mathbf{d}$ and $\mathbf{s}$ in such a way that we explore efficiently the phase space available for a system when a Li^+ ion moves along the plausible way that connects adjacent cages. Therefore, we limit the phase space: $|\mathbf{d}| \leq D$ and $s \geq D + \Delta$, with D —the distance between centers of masses of cages and Δ —denoting limits for how far from the straight line connecting the centers of cages the Li^+ ion can deviate. **Supplementary Fig. 56** illustrates the meaning of the constraints.

For a motion with $d = \text{const}$ or $s = \text{const}$ the Li^+ ion will move along hyperbolae and ellipses (in 2D) described by equations:

$$\begin{aligned} \frac{x^2}{d^2} - \frac{y^2}{D^2 - d^2} &= \frac{1}{4}, d = \text{const}, |d| \leq D, \\ \frac{x^2}{s^2} + \frac{y^2}{s^2 - D^2} &= \frac{1}{4}, s = \text{const}, s \geq D. \end{aligned}$$

$d = -D$ and $s = D$ corresponds to the Li^+ ion in the cage A, and $d = D$ and $s = D$ are when Li^+ ion in the cage B (in centers of their masses, as defined). The phase space in coordinates $\mathbf{d}$ and $\mathbf{s}$ is shown in **Supplementary Fig. 57**. The left and right bottom corners of the rectangles correspond to centers of cages A and B. In simulations we do not control the positions and the mutual distance between centers of adjacent cages, so the actual distance D fluctuates, so do the minima of the free energies corresponding to local minima of the Li^+ ion residing inside the cages. These fluctuations explain the tilt of the regions around the minima.

Classical MD Metadynamics Protocol. An equilibrated simulation cell with solvent molecules, two polymer strands and ions (see regular classical MD simulations section) was used as initial configuration for free energy sampling with the metadynamics protocol. We employed dilute limit (one Li^+ and one PF_6^- per box). In **Supplementary Table 6**, we summarize the parameters of the metadynamics free energy sampling: height of the Gaussian hills (H , kcal mol^{-1}), frequency of hill creation ($freq$, steps), and width of hills (W , Å) along with the ranges for the collective variables, and the overall simulation times (T , ns) for each system. The free energy profile as a function of r_1 is shown in **Supplementary Fig. 58**.

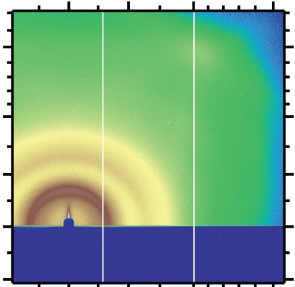
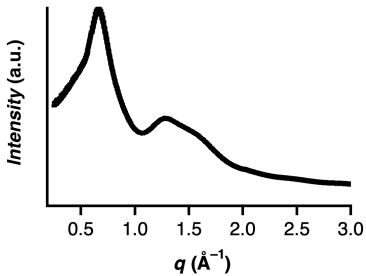
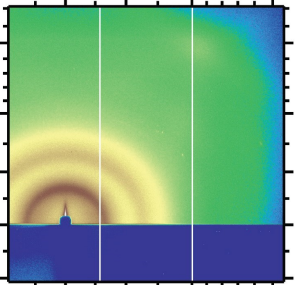
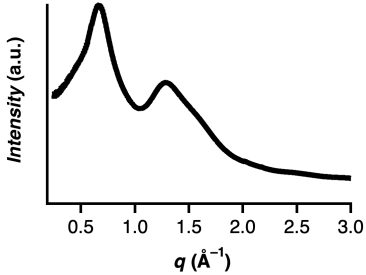
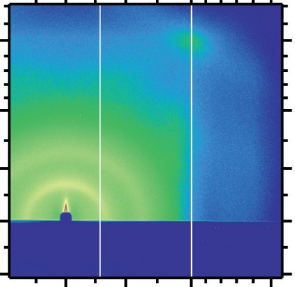
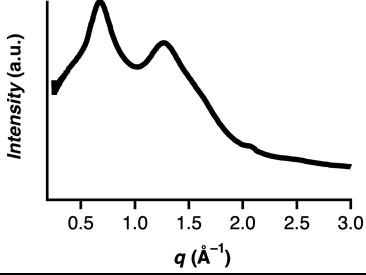
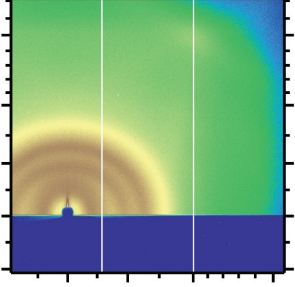
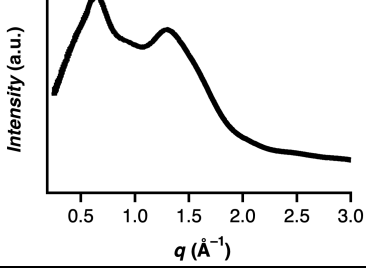
To ensure the convergence of the sampling, we ran metadynamics until the diffusive motion along the CV is reached, as previously suggested.⁴¹ In **Supplementary Fig. 59**, we show the time evolution of the collective variable.

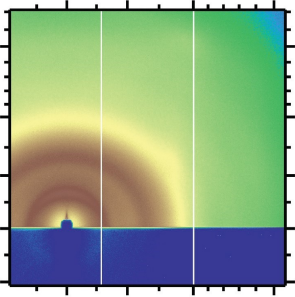
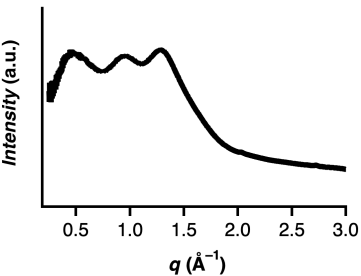
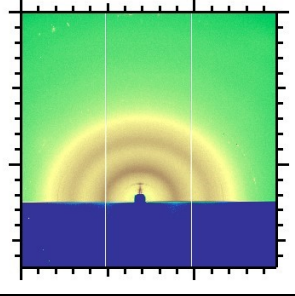
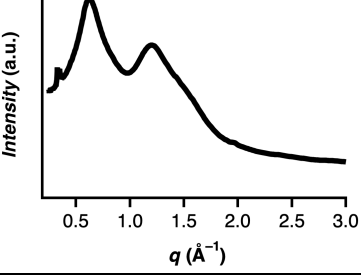
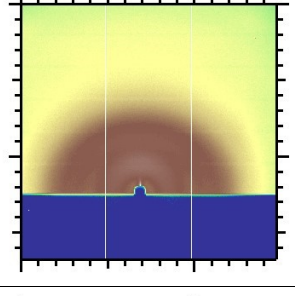
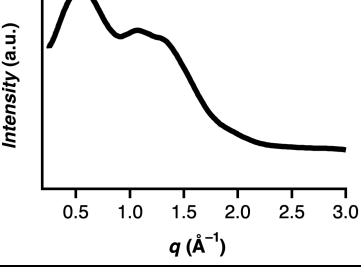
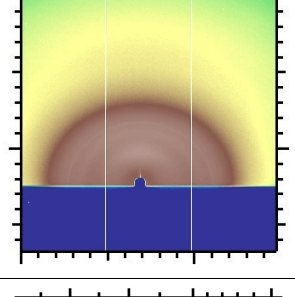
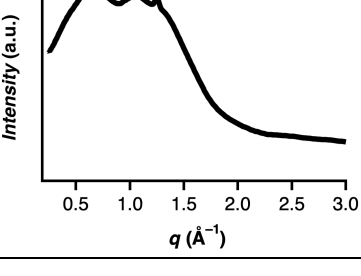
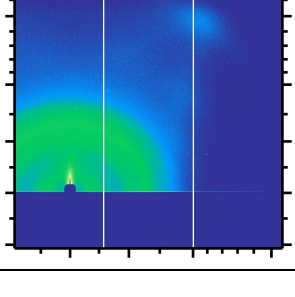
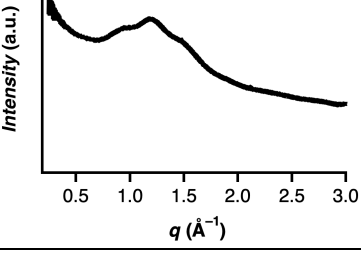
Supplementary Tables

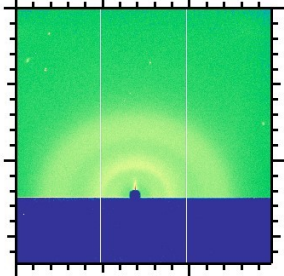
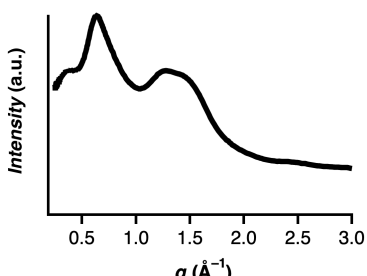
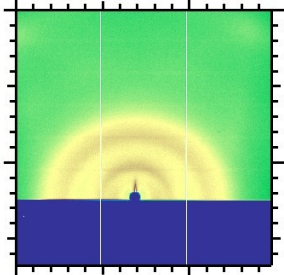
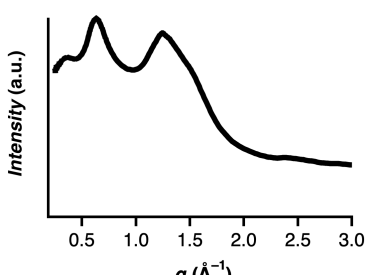
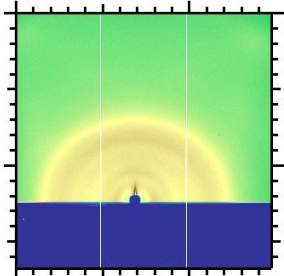
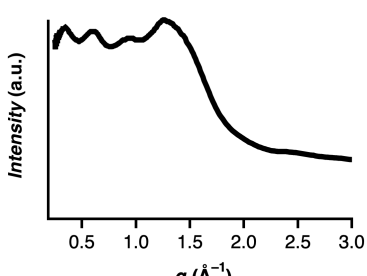
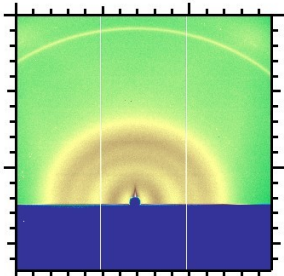
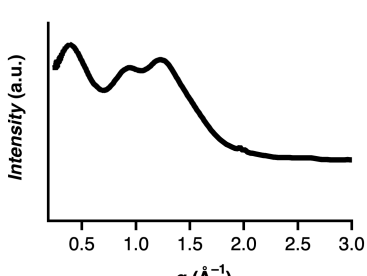
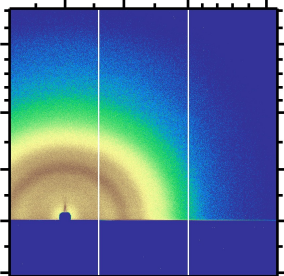
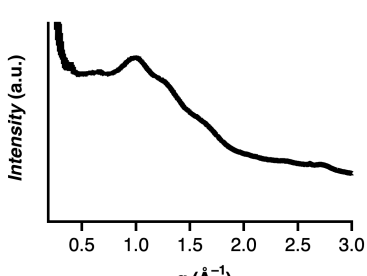
Supplementary Table 1. Polymer solubility in a variety of organic solvents, where +++ indicates highly soluble, + indicates slightly soluble, and – indicates insoluble.

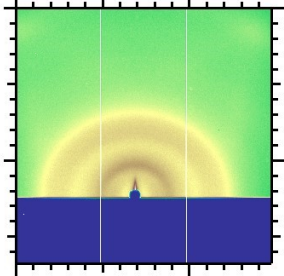
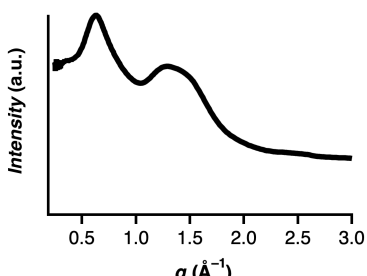
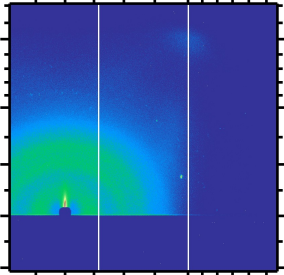
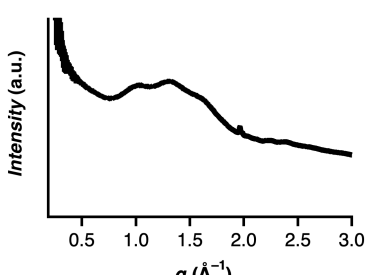
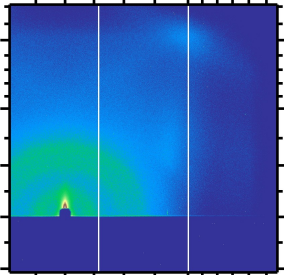
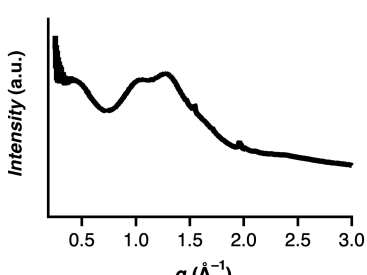
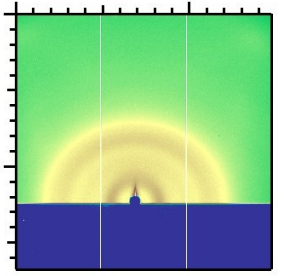
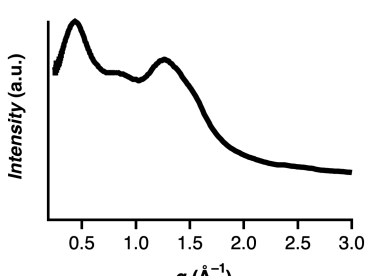
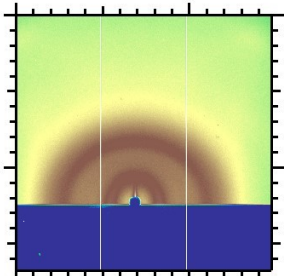
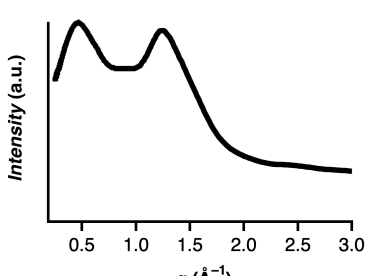
Polymer	Solubility		
	THF	CHCl ₃	DMSO
11	+++	+++	+
12	+++	+++	+
13	+++	+++	+++
14	+++	+++	–
15	+++	+++	+++
16	+++	+	+++
17	+	+	–
18	+	+	+++
19	–	+	+++
20	+++	+	+++
21	+++	+	+++
22	+	+	+++
23	+	+	+++
24	+	–	+++
25	+++	+++	+++
26	+++	–	+
27	–	–	+++
28	+++	+++	+++
29	+	–	+
30	+++	+++	+
31	+++	+++	+

Supplementary Table 2. GIWAXS 2D and 1D plots.

Compound Number	GIWAXS 2-D Plot	GIWAXS 1-D Plot	Peak q value ($\text{\AA}^{-1}$)	Peak d -space value ($\text{\AA}$)
11			0.66 1.28	9.6 4.9
12			0.66 1.28	9.5 4.9
13			0.67 1.27	9.3 5.0
14			0.64 1.29	9.8 4.9

15			0.47 0.95 1.28	13.3 6.6 4.9
16			0.63 1.20	10.0 5.2
17			0.53 1.07 1.32	11.9 5.9 4.8
18			0.65 1.05	9.6 6.0
19			0.93 1.19 1.51	6.8 5.3 4.2

20			0.63 1.40	9.9 4.5
21			0.63 1.25	10.0 5.0
22			0.34 0.60 0.94 1.26	18.4 10.5 6.7 5.0
23			0.39 0.94 1.23	16.0 6.7 5.1
24	N.D.	N.D.	N.D.	N.D.
25			0.99 1.31 1.64	6.3 4.8 3.8

26			0.63 1.37	10.0 4.6
27			1.01 1.31 1.64	6.2 4.8 3.8
28	N.D.	N.D.	N.D.	N.D.
29			1.04 1.27	6.1 4.9
30			0.43 0.86 1.26	14.5 7.3 5.0
31			0.46 1.25	13.5 5.0

Supplementary Table 3. Raw data for the principle component analysis of polymers presented in this paper, used to generate **Fig. 1b**; where M_s is the molecular weight of the side chains per repeat, A_{BET} is the BET surface area, N_{O} , N_{N} , and N_s are the numbers of oxygen atoms, nitrogen atoms, and side groups per unit respectively, M_b is the molecular weight of the main chain repeat unit, and N_c is the number of sites of contortion along the polymer main chain repeat unit.

Polymer	M_s (g mol ⁻¹)	A_{BET} (m ² g ⁻¹)	N_{O}	N_{N}	N_s	M_b (g mol ⁻¹)	N_c
11	284	446	4	4	3	346	1
12	280	434	4	4	3	346	1
13	312	505	6	4	3	346	1
14	427	63	6	6	3	346	1
15	511	234	8	6	3	346	1
16	340	11	6	4	3	346	1
17	278	444	4	4	4	306	1
18	310	19	6	4	4	306	1
20	351	79	6	6	3	346	1
21	379	152	8	6	3	346	1
22	493	10	8	8	3	346	1
23	577	12	10	8	3	346	1
24	376	10	8	6	4	306	1
25	234	7	6	4	2	348	1
26	407	8	6	6	3	346	1
27	234	10	6	4	2	348	1
28	433	24	8	6	4	306	1
29	290	11	6	4	2	348	1
30	463	48	6	6	3	346	1
31	491	31	8	6	3	346	1
Thioamide- PIM-1	180	263	4	2	2	348	1
Amidoxime- PIM-1	178	490	6	4	2	348	1
Amine-PIM-1	120	0	4	2	2	348	1
Carboxylated -PIM-1-5H	150	378	8	0	2	348	1
TZPIM-3	198	30	4	8	2	348	1
PIM-1	112	800	4	2	2	348	1
PIM-EA-TB	72	1030	0	2	3	228	2

PIM-SBI-TB	74	745	0	2	2	268	2
PIM-EA	110	630	4	2	3	308	1
PIM-Trip-TB	90	900	0	2	2	257	2
PIM-TMN-SBI	376	1015	4	2	2	344	1
TPIM-1	162	860	2	2	2	306	1
Tp-Ad-Me	166	615	0	2	3	214	2
PIM-TMN-Trip	318	1050	4	2	3	308	1
PIM-SBF-1	156	803	4	2	2	344	1
PIM-HPB-2	360	537	4	2	2	358	1
PIM-5	218	540	4	0	2	354	2
Cardo-PIM-1	224	621	4	4	2	580	2
Pf5	84	501	6	2	2	348	1
Pf6	206	560	4	2	2	350	1
Pf7	356	895	4	2	2	348	1
PIM-4bIII	381	660	6	3	3	308	1
PIM-c1	156	818	5	2	3	346	1
PIM-PI-1	184	682	8	2	2	572	1
PIM-PI-3	262	471	8	2	3	664	2
PIM-PI-10	258	699	4	2	3	434	1
PIM-PI-11	184	220	4	2	2	502	2
PIM-PI-EA	256	620	4	2	4	458	1
PIM-6FDA-OH	296	225	6	2	4	450	2
PIM-PMDA-OH	158	190	6	2	3	362	1
SPFDA-DMN	302	686	4	2	3	430	1
6FDA-SBF	306	240	4	2	3	448	2
PI-TB-2	140	580	5	4	3	454	2
4MTBDA-6FDA	262	584	4	4	4	454	2
4MTBDA-SBFDA	228	739	4	4	4	500	2
TBDA1-SBI-PI	154	560	8	4	3	718	2

KAUST-PI-4	226	420	9	2	3	628	2
spiroTR-PBO-6F	198	368	2	2	2	460	2
PIM-PBO-3	60	360	6	2	1	584	1
SPDA-SBF-PBO	164	480	6	2	2	718	2

Supplementary Table 4. Raw data for the principle component analysis of polymers presented in this paper, used to generate **Supplementary Fig. 11**; where M_s is the molecular weight of the side chains per repeat, A_{BET} is the BET surface area, N_{O} , N_{N} , and N_s are the numbers of oxygen atoms, nitrogen atoms, and side groups per unit respectively, M_b is the molecular weight of the main chain repeat unit, N_{G} is the number of GIWAXS reflections, and L_{G} , L_{N_2} , and L_{CO_2} are the pore diameters based to the real value of the major GIWAXS reflection, the pore size distributions from the N_2 and CO_2 adsorption isotherms respectively.

Polymer	M_s (g mol ⁻¹)	A_{BET} (m ² g ⁻¹)	N_{O}	N_{N}	N_s	M_b (g mol ⁻¹)	N_{G}	L_{G} (Å)	L_{N_2} (Å)	L_{CO_2} (Å)
11	284	446	4	4	3	346	2	9.6	10.2	
12	280	434	4	4	3	346	2	9.5	5.9	
13	312	505	6	4	3	346	2	9.3	9.5	
14	427	63	6	6	3	346	2	9.8	14.1	
15	511	234	8	6	3	346	3	13.3	14.4	
16	340	11	6	4	3	346	2	10	22.5	6.1
17	278	444	4	4	4	306	3	11.9	10.5	
18	310	19	6	4	4	306	2	9.6	25.5	5.6
20	351	79	6	6	3	346	2	9.9	12.1	
21	379	152	8	6	3	346	2	10	15.2	
22	493	10	8	8	3	346	4	5	24.3	
23	577	12	10	8	3	346	3	16	19.9	8.4
24	376	10	8	6	4	306	N.D.	N.D.	24.3	5.2
25	234	7	6	4	2	348	3	6.3	25.5	5.4
26	407	8	6	6	3	346	2	10	19.9	5.4
27	234	10	6	4	2	348	3	4.8	20.4	5.8
28	433	24	8	6	4	306	N.D.	N.D.	18.5	
29	290	11	6	4	2	348	2	4.9	26.8	5.2
30	463	48	6	6	3	346	3	14.5	14.8	
31	491	31	8	6	3	346	2	13.5	17.6	

Supplementary Table 5. Summary of properties presented in **Fig. 2**

Polymer	BET Surface Area (m ² g ⁻¹)	Conductivity at 25 °C (mS cm ⁻¹)	Activation Energy (eV)	Transference Number
Celgard		0.413	0.092	0.302
PIM-1	800	0.0377	0.109	0.672
11	446	0.0296	0.156	0.664
12	434	0.0280	0.161	0.446
13	505	0.206	0.168	0.696
14	63	0.195	0.165	0.842
15	234	0.0418	0.189	0.760
17	444	0.0279	0.224	0.241
18	19	0.0602	0.222	0.250
21	152	0.0243	0.236	0.390
23	12	0.0634	0.252	0.317
24	10	0.147	0.288	0.718
25	7	0.107	0.310	0.638
26	8	0.100	0.106	0.224
28	24	0.0882	0.225	0.582
30	48	0.122	0.270	0.515
31	31	0.192	0.262	0.612

Supplementary Table 6. NBO charges of the cage atoms

Atom	NBO charges (b3lyp, 6-311++G**)
O1	-0.61560
N1	-0.81660
O2	-0.59112
N2	-0.55780

Supplementary Table 7. Energies of ions, molecules and clusters in a.u. obtained with B3LYP5-D3/6-311++G** and COSMO model.

	Li ⁺ in cage of the polymer unit	Polymer unit	[Li(DMC) ₄] ⁺	Li ⁺	DMC
Vacuum	-2345.6303715028	-2338.1387910	-1381.7020501288	-7.2774402290	-343.5552004527
PCM DMC ε = 3.087	-2345.6851565112	–	-1381.7566919966	-7.3597988781	-343.5621266985

Supplementary Table 8. Binding and solvation energies of molecules and clusters in kcal mol⁻¹ obtained with B3LYP5-D3/6-311++G** and COSMO model.

ΔG_1	ΔG_2	$\Delta G_{g,bind}^o Li(DMC)_4$	$\Delta G_{solv}^*([Li(DMC)_4]^+)$	$\Delta G_{solv}^*(DMC)$	$\Delta G_{sol}^*(Li^+)$	ΔG_{diss}^*
34.377	134.371	-127.889	-34.287	-4.346	-158.214	+10.535

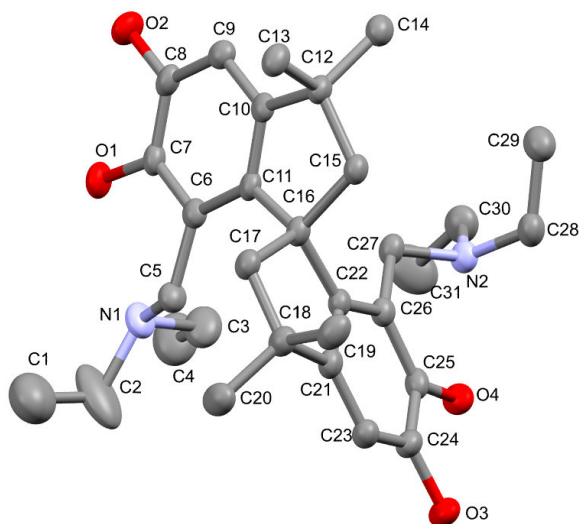
Supplementary Table 9. Parameters of classical MD simulations.

System	# of atoms in the box	Equilibrated box size dimension (Å)
DMC	21600	62.2525 (density 1.09 vs. 1.07 exp)
PIM 13 /LiPF ₆ /DMC (0.7M)	19832	60.2553
PIM 13 /LiPF ₆ /DMC (0.2M)	19360	60.0254
PIM 13 /single LiPF ₆ /DMC	19167	59.4678

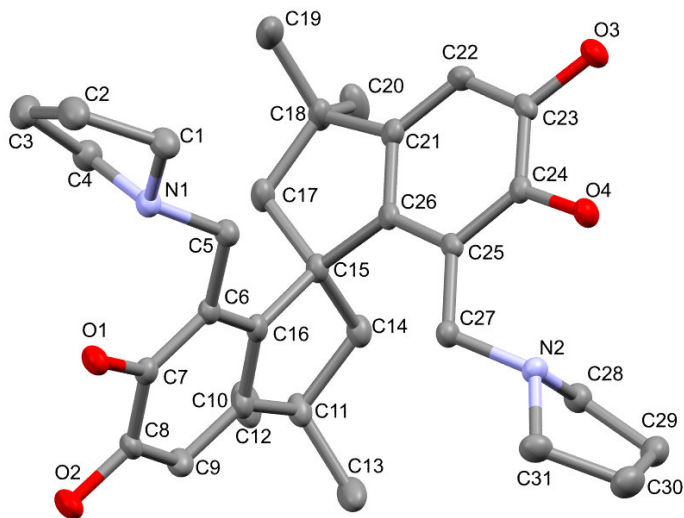
Supplementary Table 10. Parameters of classical MD metadynamics free energy sampling.

	PIM 13 /single LiPF ₆ /DMC 1D, r ₁ , [0; 12] Å	PIM 13 /single LiPF ₆ /DMC 2D, d , [-8; 8] Å	PIM 13 /single LiPF ₆ /DMC 2D, s , [7; 10] Å
<i>H</i>	0.02	0.02	0.02
<i>W</i>	0.05	0.1	0.05
<i>freq</i>	500	200	200
<i>T</i>	300	700	

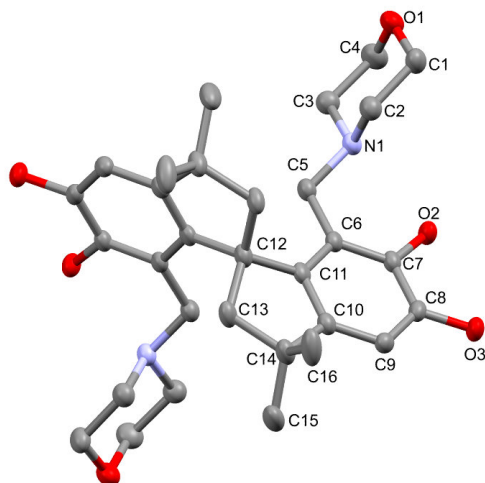
Supplementary Figures



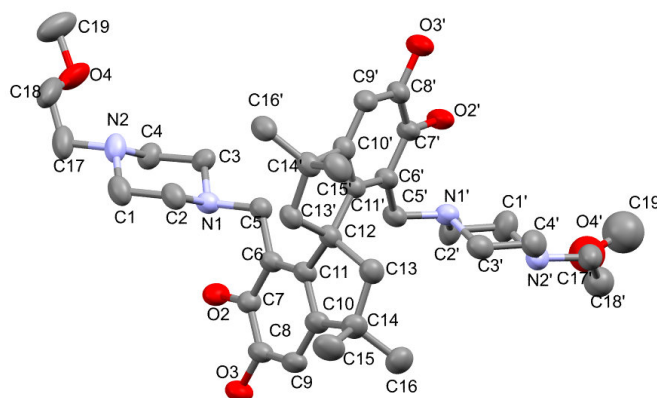
Supplementary Figure 1: Structure of compound 3 determined by single crystal X-ray diffraction. Hydrogen atoms have been omitted for clarity, 50% probability ellipsoids, red oxygen, blue nitrogen and grey carbon. Crystallographic data for compound 3 is available free of charge from the Cambridge Crystallographic Date Centre (www.ccdc.cam.ac.uk) under reference number 2061993.



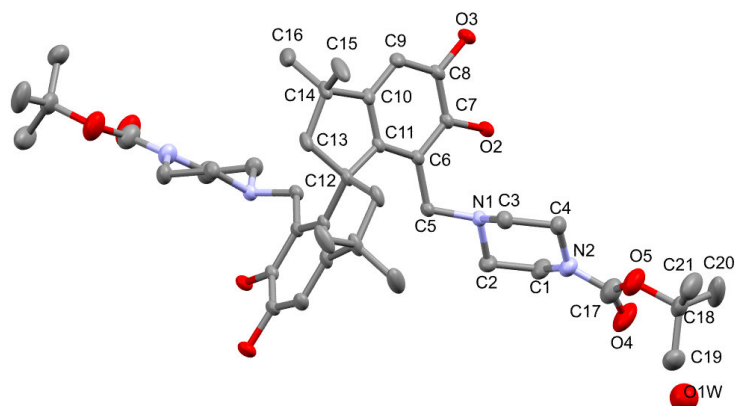
Supplementary Figure 2: Structure of compound 4 determined by single crystal X-ray diffraction. Hydrogen atoms have been omitted for clarity, 50% probability ellipsoids, red oxygen, blue nitrogen and grey carbon. Crystallographic data for compound 4 is available free of charge from the Cambridge Crystallographic Date Centre (www.ccdc.cam.ac.uk) under reference number 2061994.



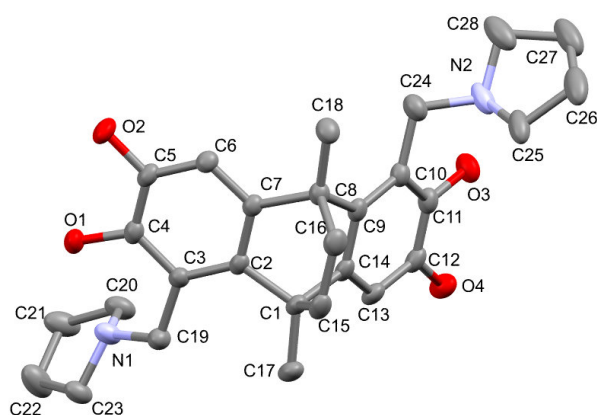
Supplementary Figure 3: Structure of compound 5 determined by single crystal X-ray diffraction. Hydrogen atoms have been omitted for clarity, 50% probability ellipsoids, red oxygen, blue nitrogen and grey carbon. As half the molecule is generated by symmetry only the asymmetry unit has been labelled. Crystallographic data for compound **5** is available free of charge from the Cambridge Crystallographic Date Centre (www.ccdc.cam.ac.uk) under reference number 2061995.



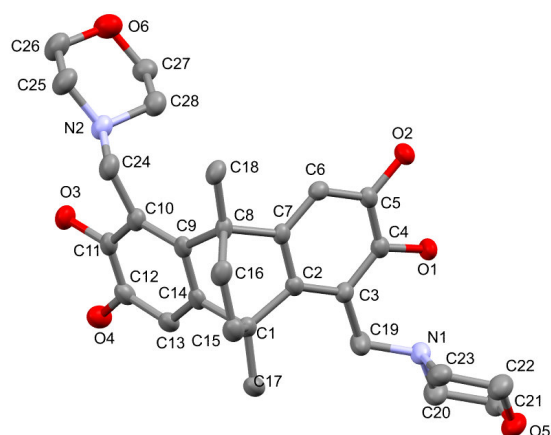
Supplementary Figure 4: Structure of compound 6 determined by single crystal X-ray diffraction. Hydrogen atoms and minor component of the methoxy group disorder have been omitted for clarity, 50% probability ellipsoids, red oxygen, blue nitrogen and grey carbon. Crystallographic data for compound **6** is available free of charge from the Cambridge Crystallographic Date Centre (www.ccdc.cam.ac.uk) under reference number 2061996.



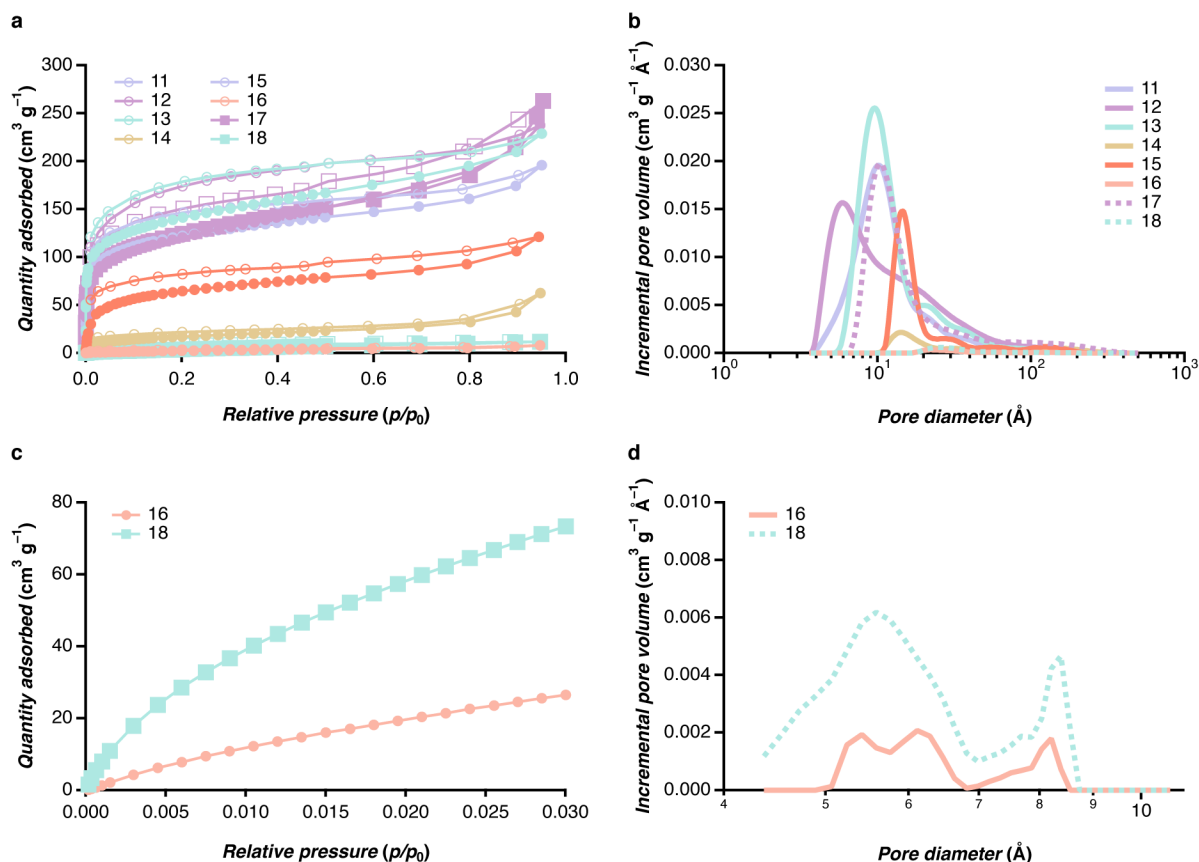
Supplementary Figure 5: Structure of compound 7 determined by single crystal X-ray diffraction. Hydrogen atoms and minor component of the *tert*-butoxy group disorder have been omitted for clarity, 50% probability ellipsoids, red oxygen, blue nitrogen and grey carbon. As half the molecule is generated by symmetry only the asymmetry unit has been labelled. Crystallographic data for compound 7 is available free of charge from the Cambridge Crystallographic Date Centre (www.ccdc.cam.ac.uk) under reference number 2061997.



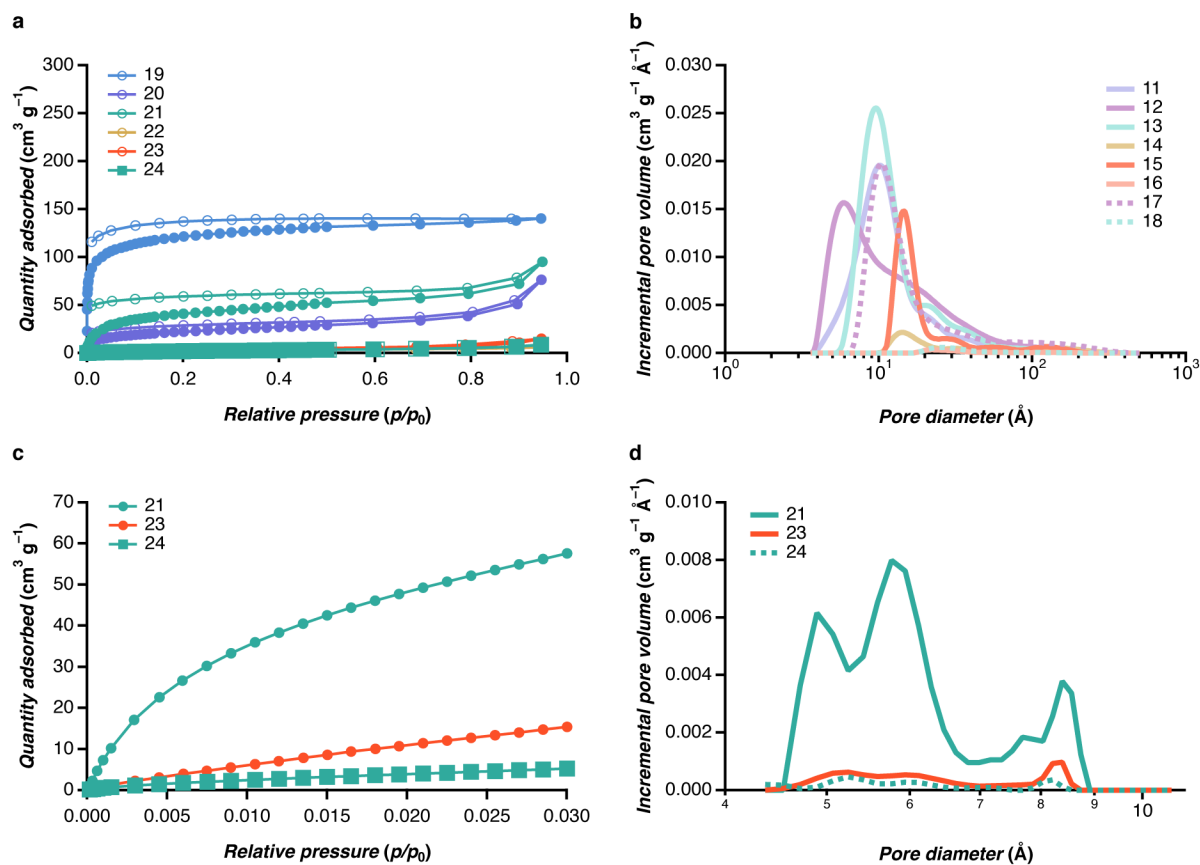
Supplementary Figure 6: Structure of compound 9 determined by single crystal X-ray diffraction. Hydrogen atoms and minor component of the pyrrolidine disorder have been omitted for clarity, 50% probability ellipsoids, red oxygen, blue nitrogen and grey carbon. Crystallographic data for compound 9 is available free of charge from the Cambridge Crystallographic Date Centre (www.ccdc.cam.ac.uk) under reference number 2061999.



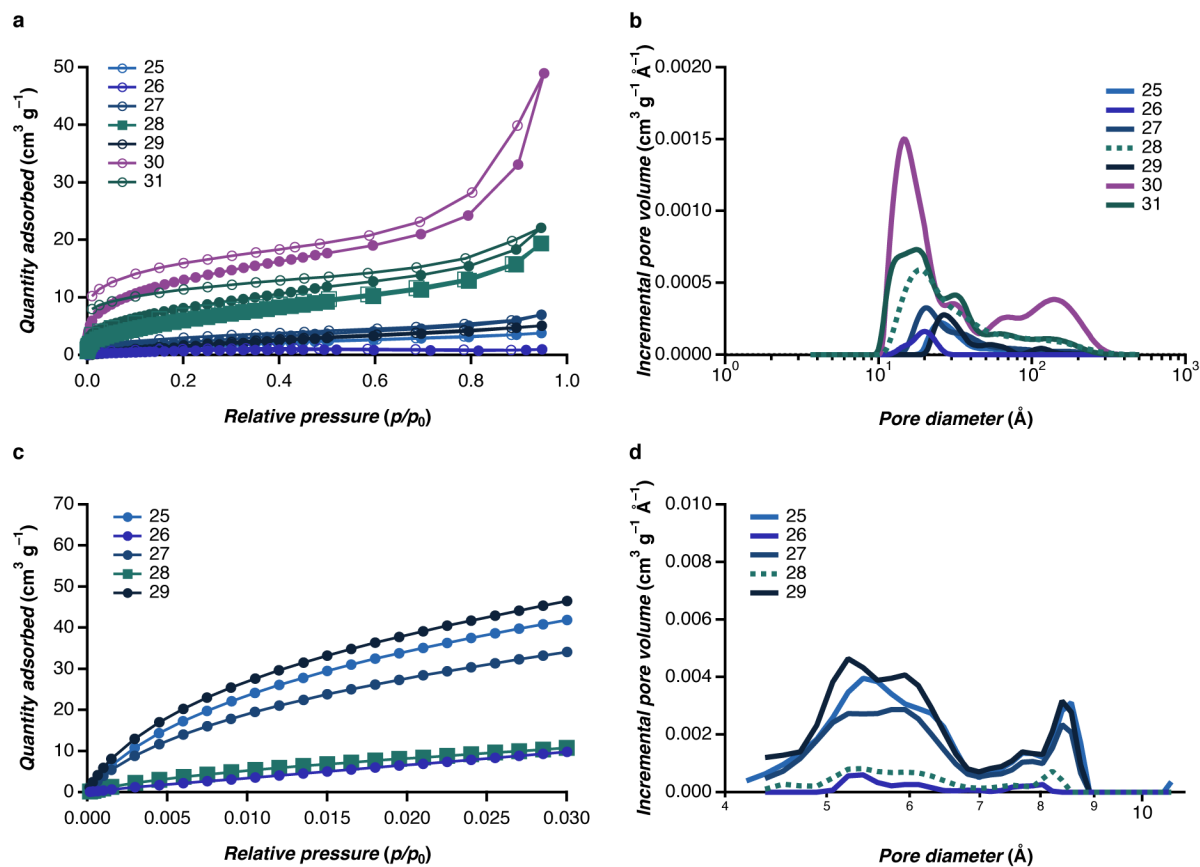
Supplementary Figure 7: Structure of compound 10 determined by single crystal X-ray diffraction. Hydrogen atoms have been omitted for clarity, 50% probability ellipsoids, red oxygen, blue nitrogen and grey carbon. Crystallographic data for compound **10** is available free of charge from the Cambridge Crystallographic Date Centre (www.ccdc.cam.ac.uk) under reference number 2061998.



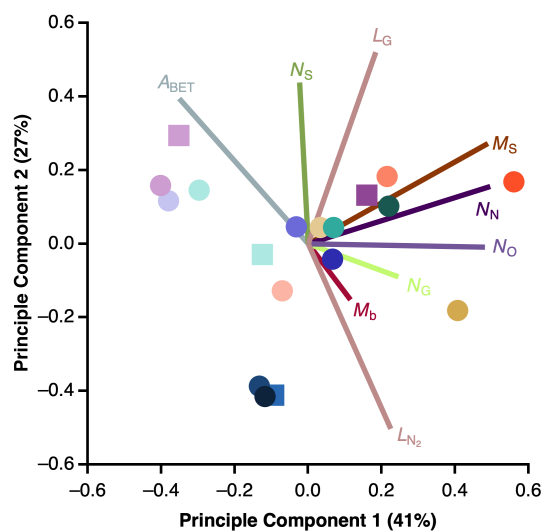
Supplementary Figure 8: PIM 11–18 gas adsorption. **a**, N₂ adsorption isotherm and **b**, pore size distribution for PIMs 11–18, and **c**, CO₂ adsorption and **d**, pore size distributions for those with low surface area (<30 m² g⁻¹) by N₂.



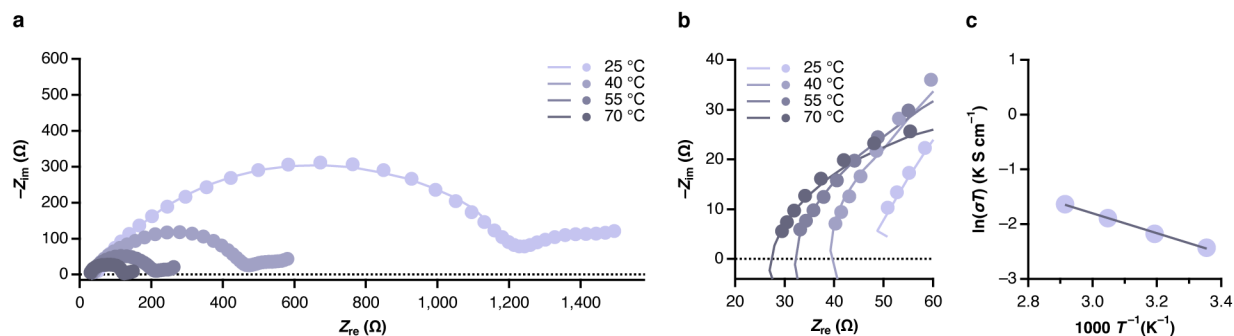
Supplementary Figure 9: PIM 19–24 gas adsorption. **a**, N₂ adsorption isotherm and **b**, pore size distribution for PIMs 19–24, and **c**, CO₂ adsorption and **d**, pore size distributions for those with low surface area (<30 m² g⁻¹) by N₂.



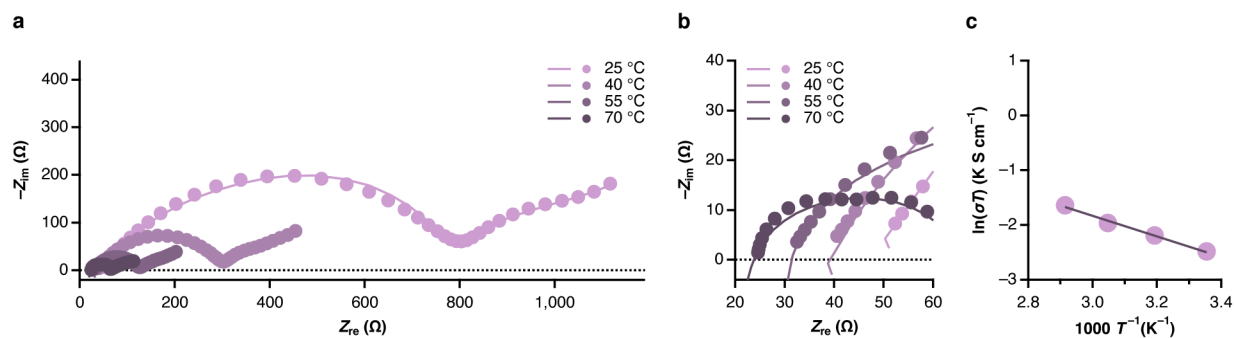
Supplementary Figure 10: PIM 25–31 gas adsorption. **a**, N_2 adsorption isotherm and **b**, pore size distribution for PIMs 25–31, and **c**, CO_2 adsorption and **d**, pore size distributions for those with low surface area ($<30 \text{ m}^2 \text{g}^{-1}$) by N_2 .



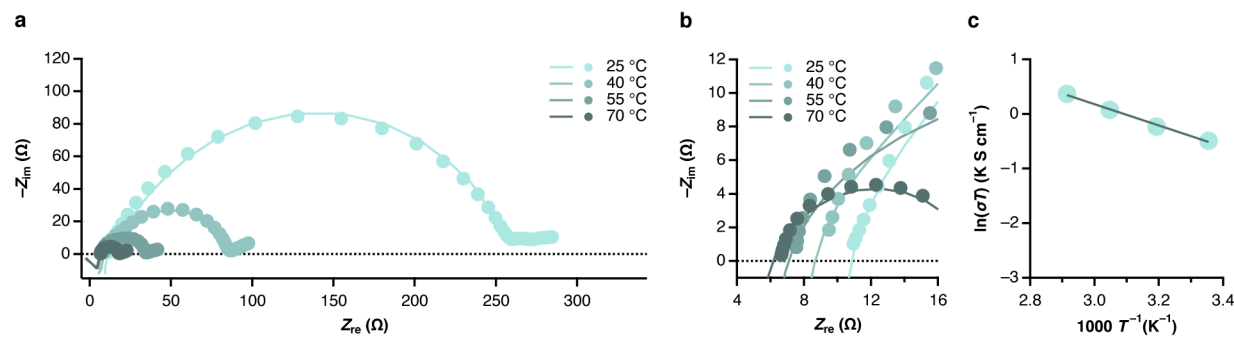
Supplementary Figure 11: Expanded PCA 2 for the DOS PIMs Library.



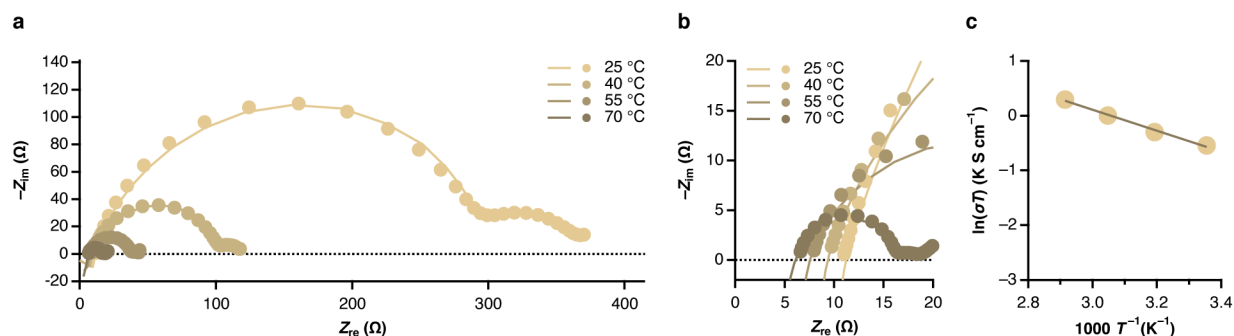
Supplementary Figure 12: PIM 11 variable temperature EIS. **a**, Full Nyquist plot and **b**, zoom in on high frequency, and **c**, Arrhenius plot at 25 °C, 40 °C, 55 °C, and 70 °C.



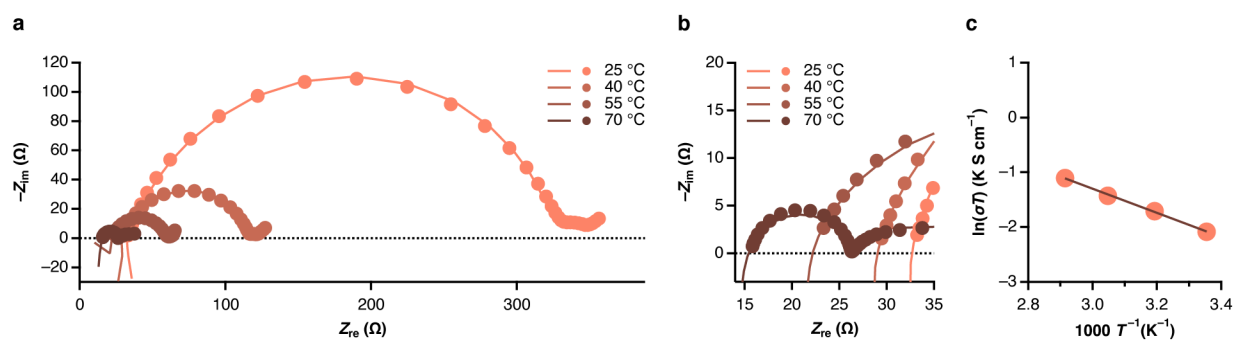
Supplementary Figure 13: PIM 12 variable temperature EIS. **A**, Full Nyquist plot and **b**, zoom in on high frequency, and **c**, Arrhenius plot at 25 °C, 40 °C, 55 °C, and 70 °C.



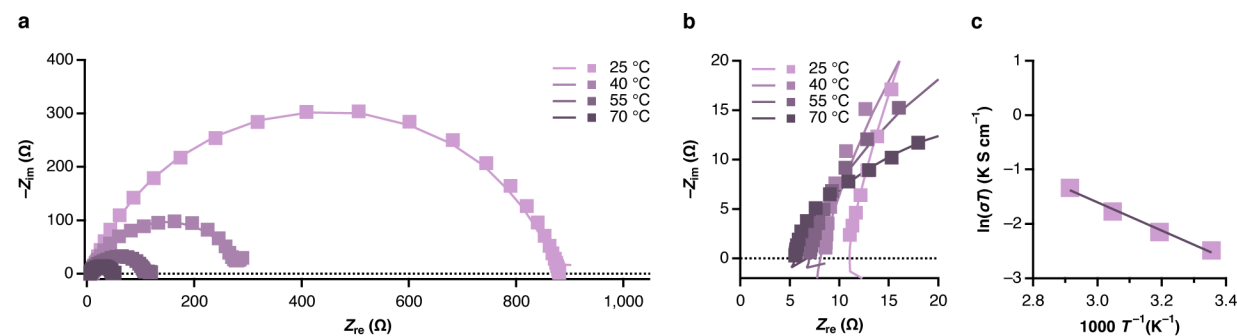
Supplementary Figure 14: PIM 13 variable temperature EIS. **a**, Full Nyquist plot and **b**, zoom in on high frequency, and **c**, Arrhenius plot at 25 °C, 40 °C, 55 °C, and 70 °C.



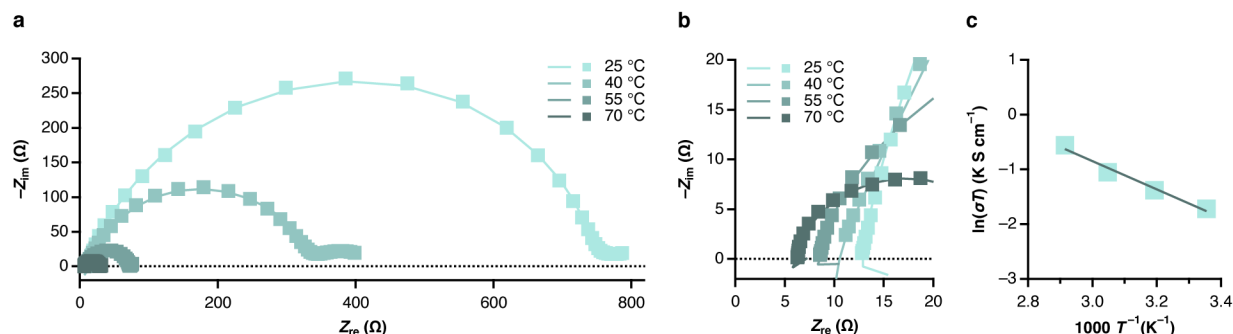
Supplementary Figure 15: PIM 14 variable temperature EIS. **A**, Full Nyquist plot and **b**, zoom in on high frequency, and **c**, Arrhenius plot at 25 °C, 40 °C, 55 °C, and 70 °C.



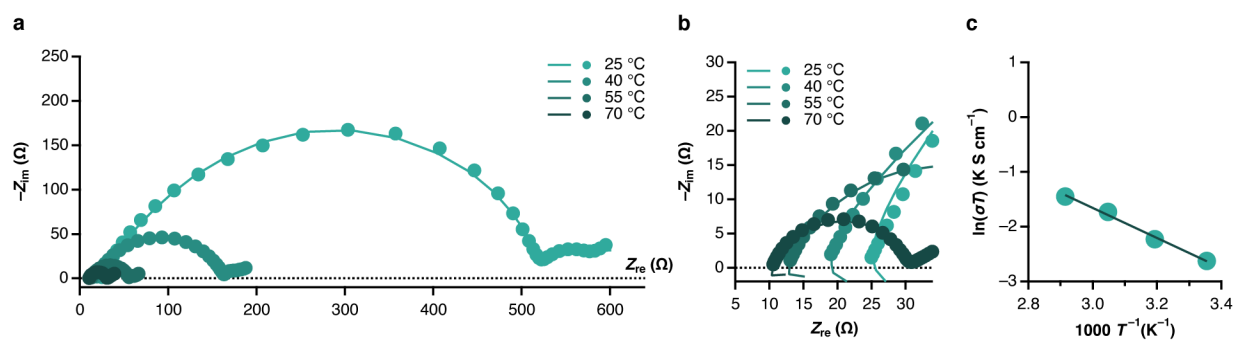
Supplementary Figure 16: PIM 15 variable temperature EIS. **a**, Full Nyquist plot and **b**, zoom in on high frequency, and **c**, Arrhenius plot at 25 °C, 40 °C, 55 °C, and 70 °C.



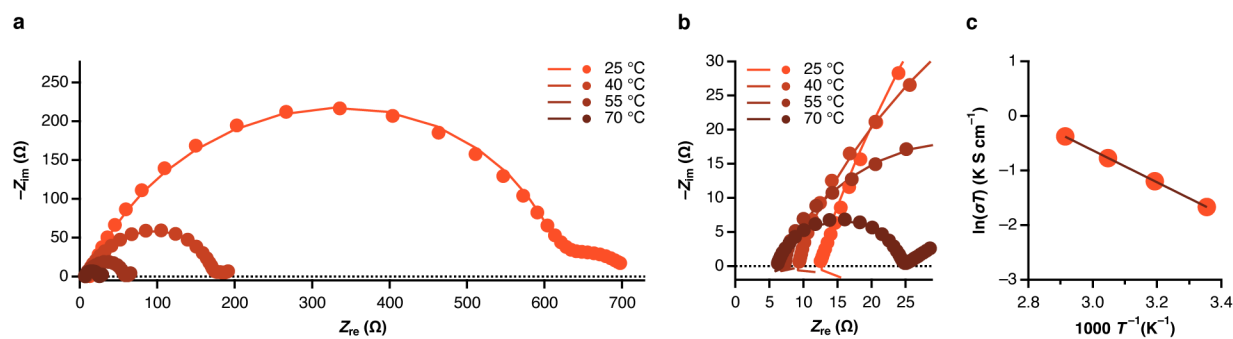
Supplementary Figure 17: PIM 17 variable temperature EIS. **A**, Full Nyquist plot and **b**, zoom in on high frequency, and **c**, Arrhenius plot at 25 °C, 40 °C, 55 °C, and 70 °C.



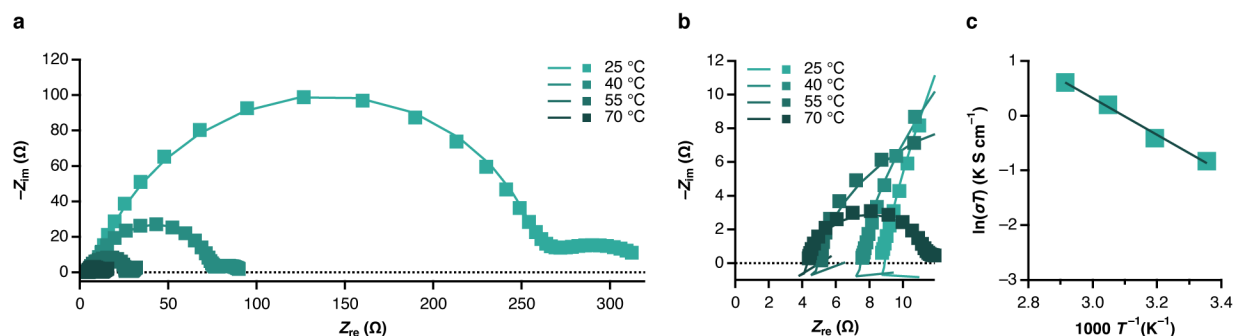
Supplementary Figure 18: PIM 18 variable temperature EIS. **a**, Full Nyquist plot and **b**, zoom in on high frequency, and **c**, Arrhenius plot at 25 °C, 40 °C, 55 °C, and 70 °C.



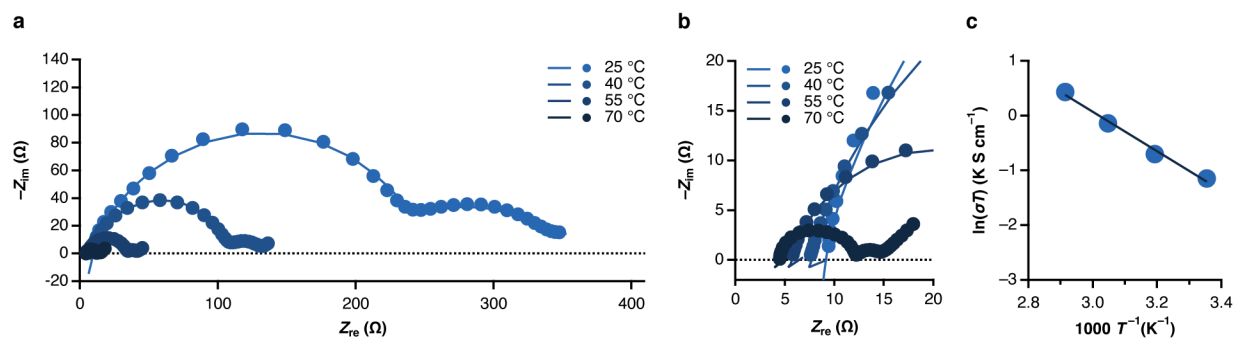
Supplementary Figure 19: PIM 21 variable temperature EIS. **a**, Full Nyquist plot and **b**, zoom in on high frequency, and **c**, Arrhenius plot at 25 °C, 40 °C, 55 °C, and 70 °C.



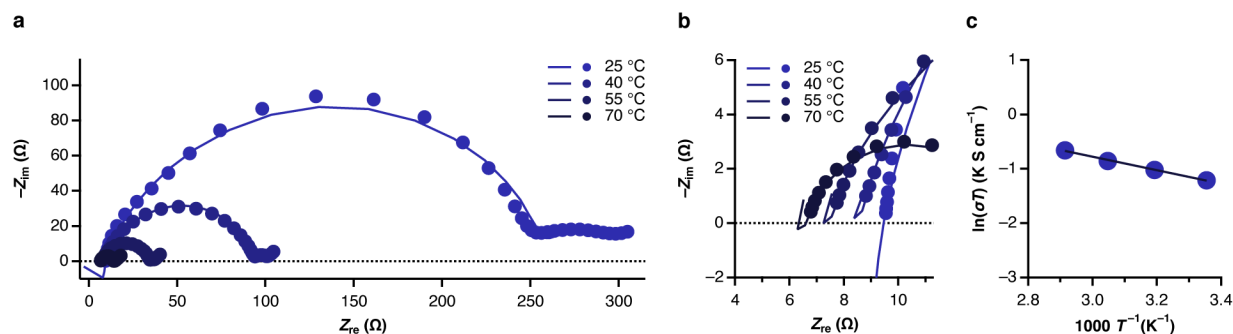
Supplementary Figure 20: PIM 23 variable temperature EIS. **a**, Full Nyquist plot and **b**, zoom in on high frequency, and **c**, Arrhenius plot at 25 °C, 40 °C, 55 °C, and 70 °C.



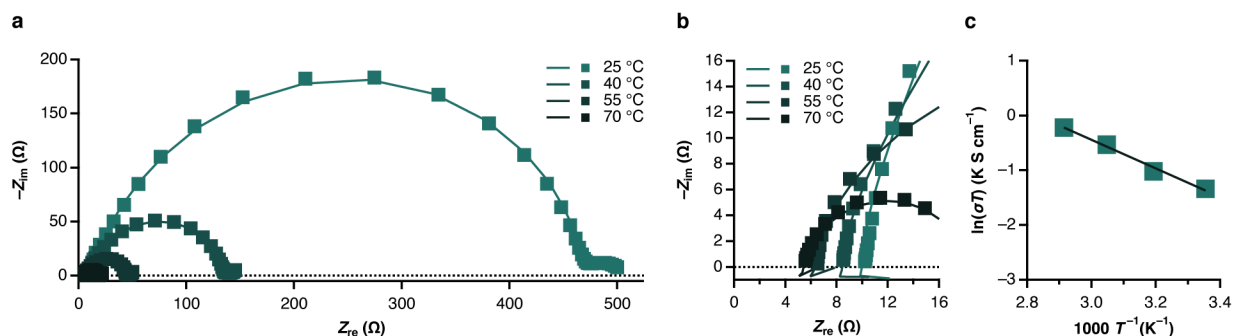
Supplementary Figure 21: PIM 24 variable temperature EIS. A, Full Nyquist plot and b, zoom in on high frequency, and c, Arrhenius plot at 25 °C, 40 °C, 55 °C, and 70 °C.



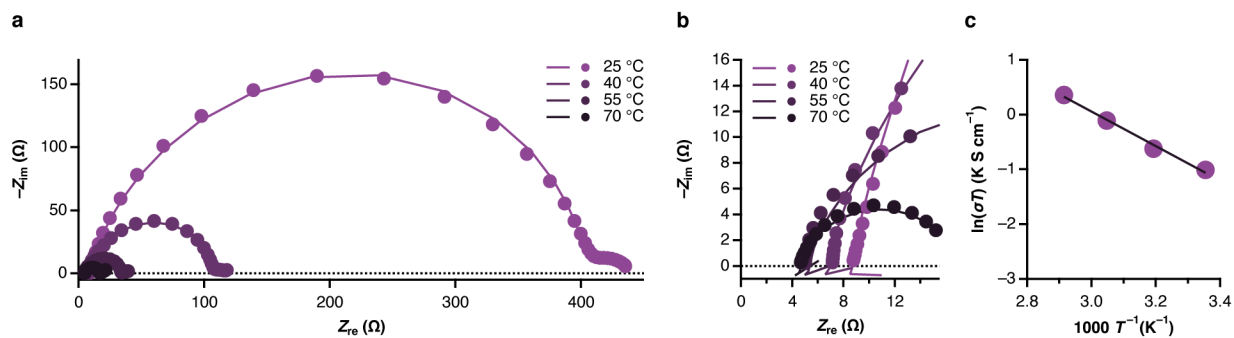
Supplementary Figure 22: PIM 25 variable temperature EIS. a, Full Nyquist plot and b, zoom in on high frequency, and c, Arrhenius plot at 25 °C, 40 °C, 55 °C, and 70 °C.



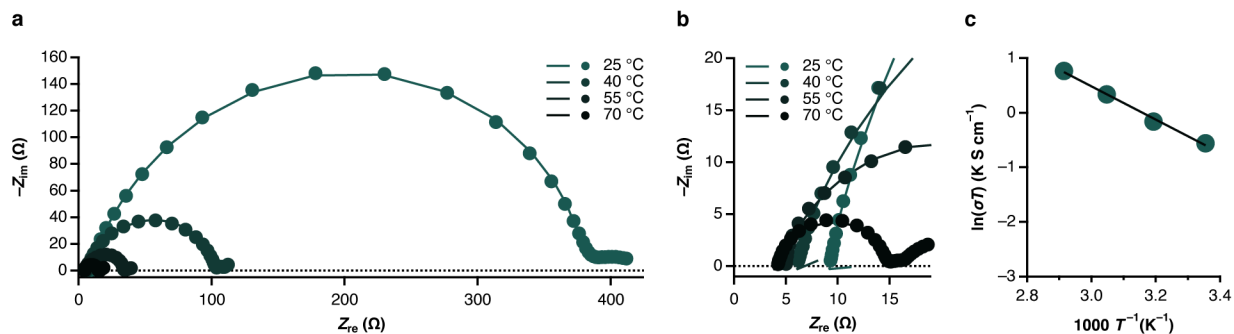
Supplementary Figure 23: PIM 26 variable temperature EIS. A, Full Nyquist plot and b, zoom in on high frequency, and c, Arrhenius plot for at 25 °C, 40 °C, 55 °C, and 70 °C.



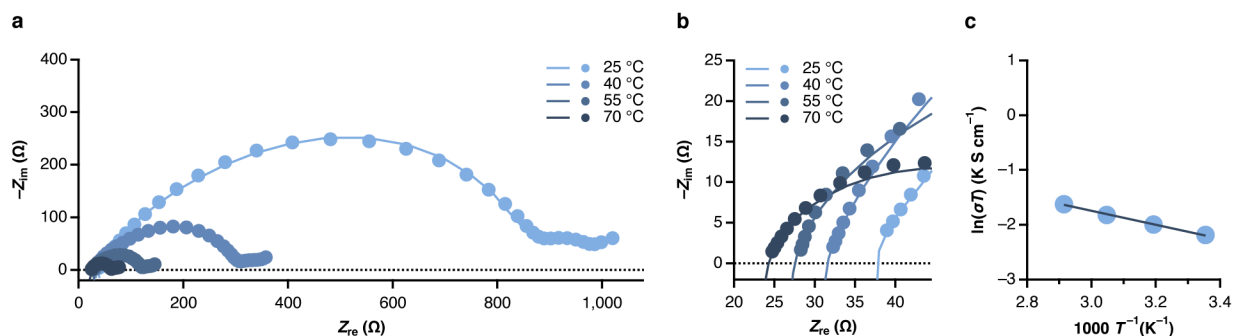
Supplementary Figure 24: PIM 28 variable temperature EIS. a, Full Nyquist plot and **b,** zoom in on high frequency, and **c,** Arrhenius plot at 25 °C, 40 °C, 55 °C, and 70 °C.



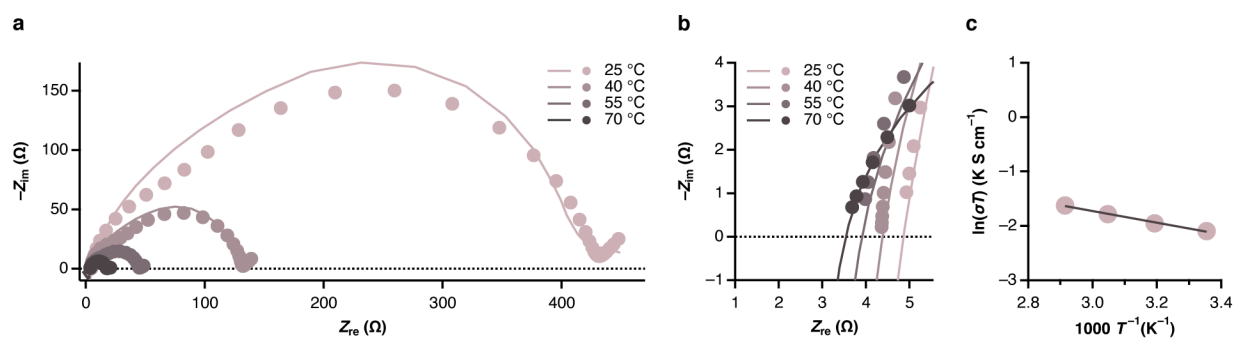
Supplementary Figure 25: PIM 30 variable temperature EIS. A, Full Nyquist plot and **b,** zoom in on high frequency, and **c,** Arrhenius plot at 25 °C, 40 °C, 55 °C, and 70 °C.



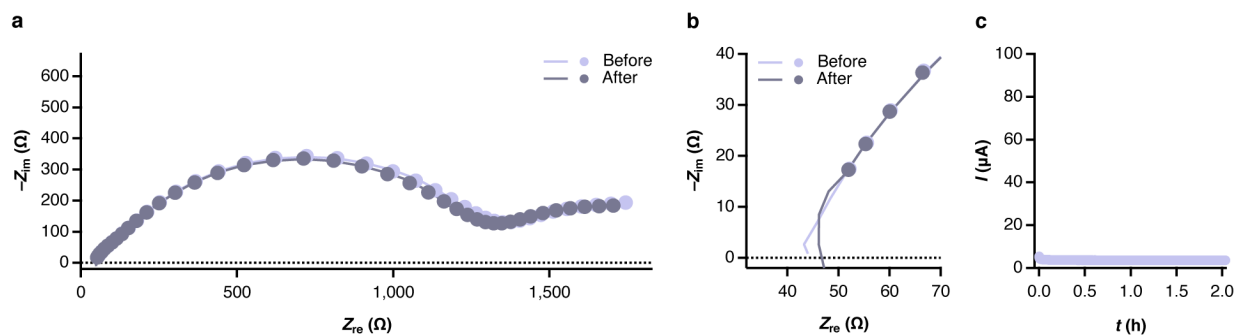
Supplementary Figure 26: PIM 31 variable temperature EIS. a, Full Nyquist plot and **b,** zoom in on high frequency, and **c,** Arrhenius plot at 25 °C, 40 °C, 55 °C, and 70 °C.



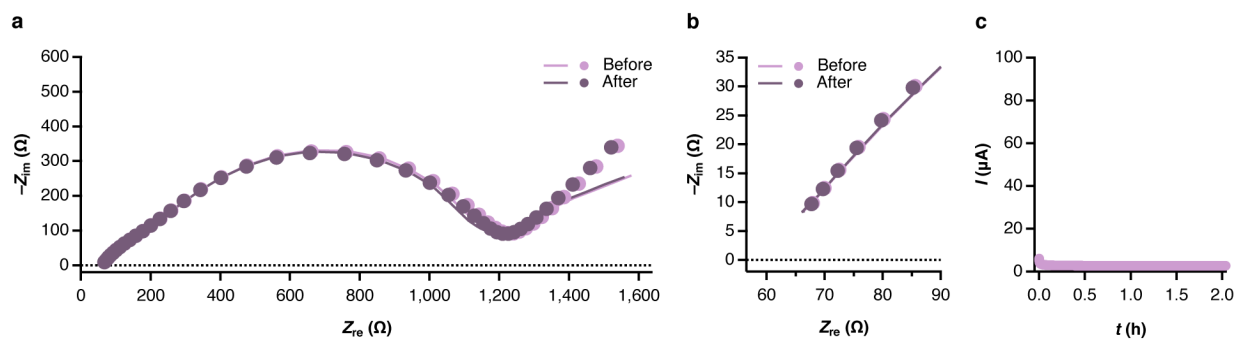
Supplementary Figure 27: PIM-1 variable temperature EIS. **a**, Full Nyquist plot and **b**, zoom in on high frequency, and **c**, Arrhenius plot at 25 °C, 40 °C, 55 °C, and 70 °C.



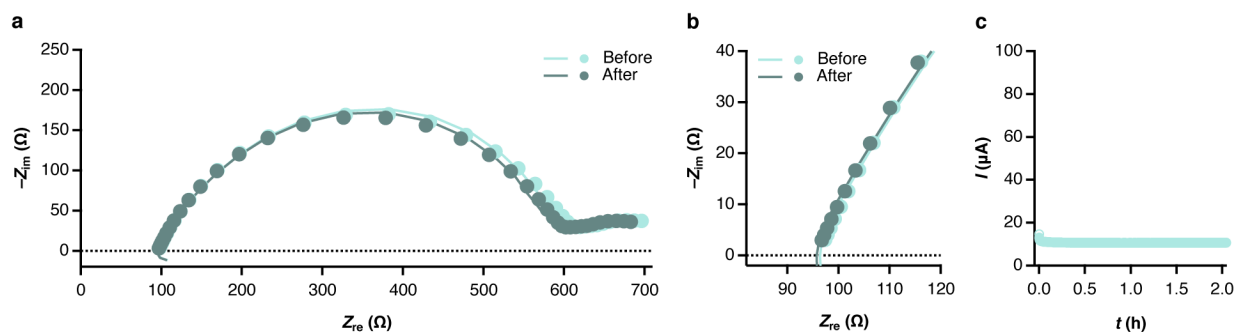
Supplementary Figure 28: Celgard variable temperature EIS. **a**, Full Nyquist plot and **b**, zoom in on high frequency, and **c**, Arrhenius plot for 25 °C, 40 °C, 55 °C, and 70 °C.



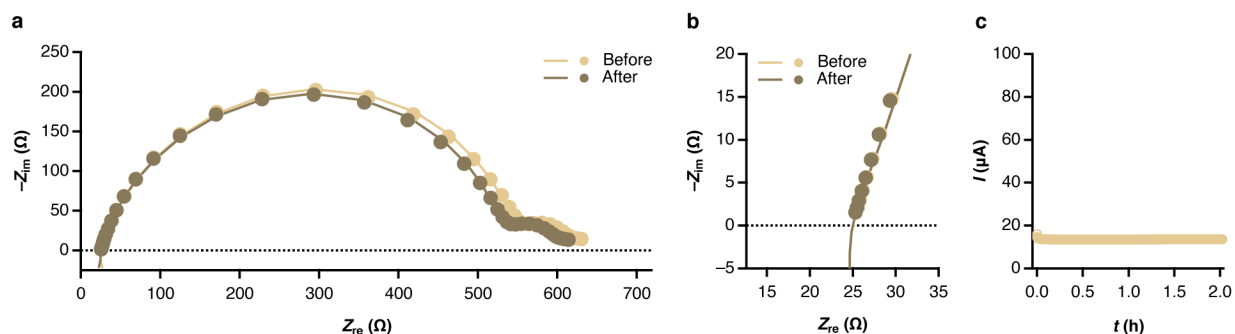
Supplementary Figure 29: Transference number determination for PIM 11. **a**, Full Nyquist plot and **b**, zoom in on high frequency region before and after polarization, and **c**, current over time during potentiostatic polarization at 10 mV.



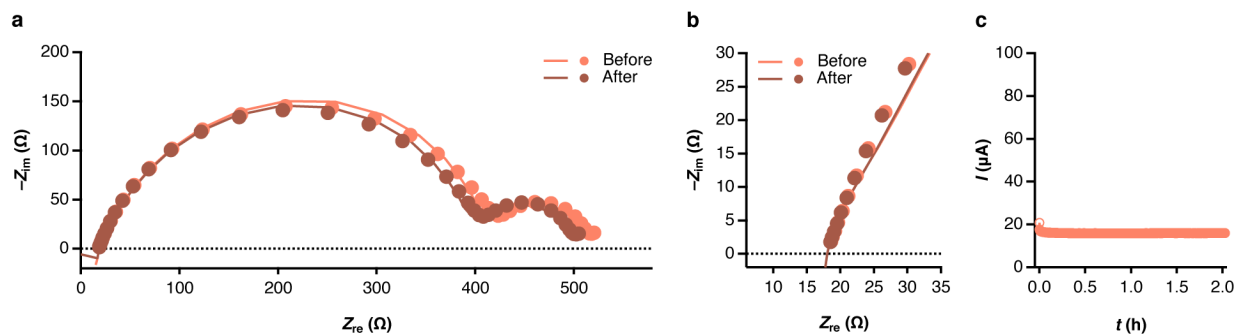
Supplementary Figure 30: Transference number determination for PIM 12. **a**, Full Nyquist plot and **b**, zoom in on high frequency region before and after polarization, and **c**, current over time during potentiostatic polarization at 10 mV.



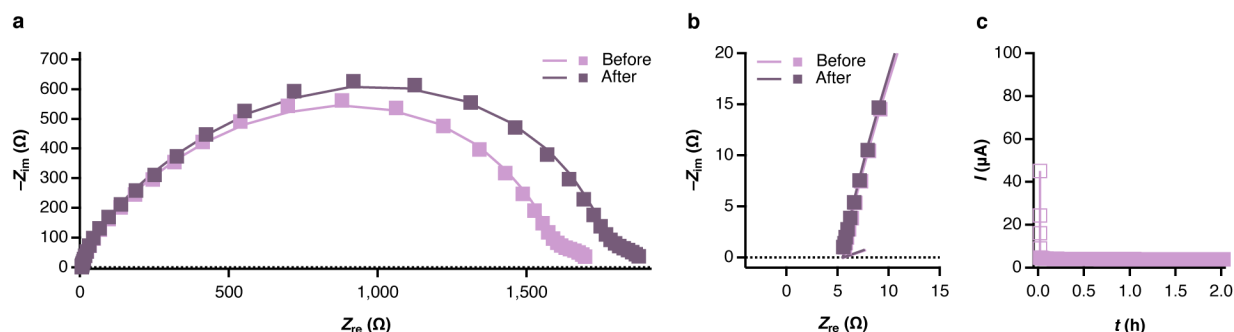
Supplementary Figure 31: Transference number determination for PIM 13. **a**, Full Nyquist plot and **b**, zoom in on high frequency region before and after polarization, and **c**, current over time during potentiostatic polarization at 10 mV.



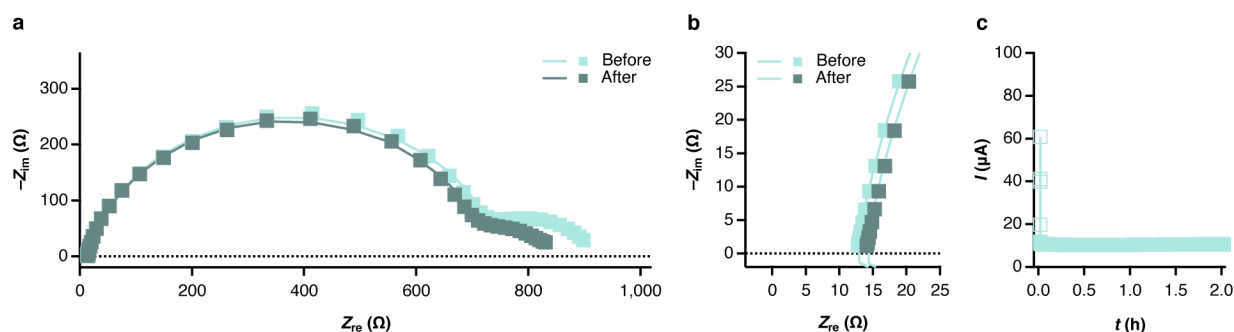
Supplementary Figure 32: Transference number determination for PIM 14. **a**, Full Nyquist plot and **b**, zoom in on high frequency region before and after polarization, and **c**, current over time during potentiostatic polarization at 10 mV.



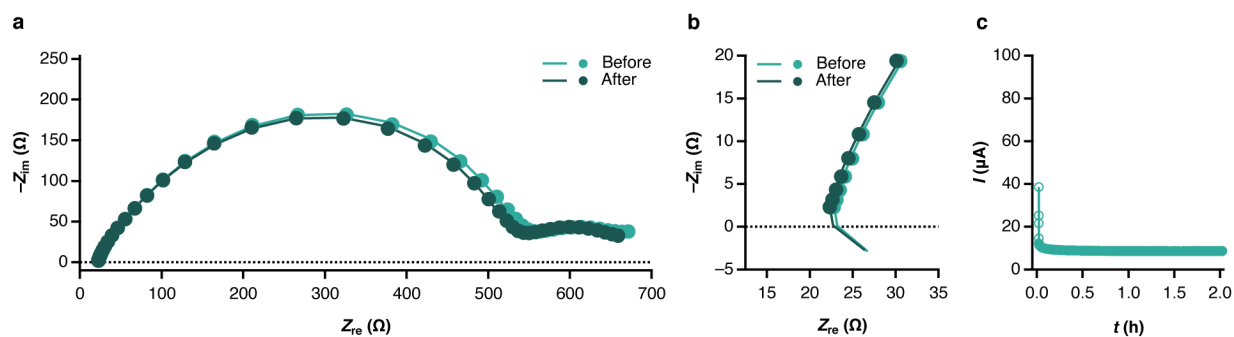
Supplementary Figure 33: Transference number determination for PIM 15. **a**, Full Nyquist plot and **b**, zoom in on high frequency region before and after polarization, and **c**, current over time during potentiostatic polarization at 10 mV.



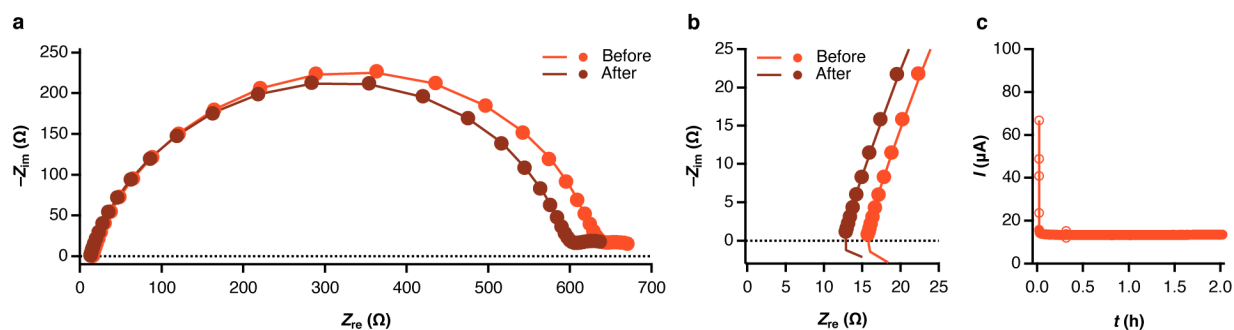
Supplementary Figure 34: Transference number determination for PIM 17. **a**, Full Nyquist plot and **b**, zoom in on high frequency region before and after polarization, and **c**, current over time during potentiostatic polarization at 10 mV.



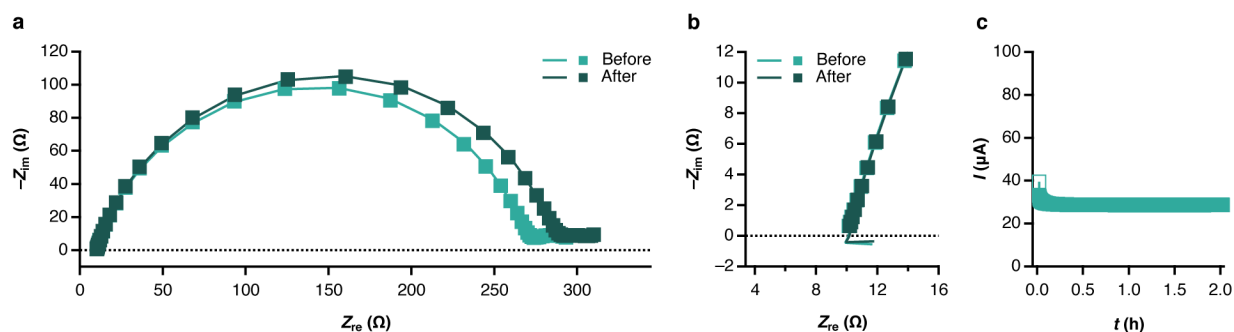
Supplementary Figure 35: Transference number determination for PIM 18. **a**, Full Nyquist plot and **b**, zoom in on high frequency region before and after polarization, and **c**, current over time during potentiostatic polarization at 10 mV.



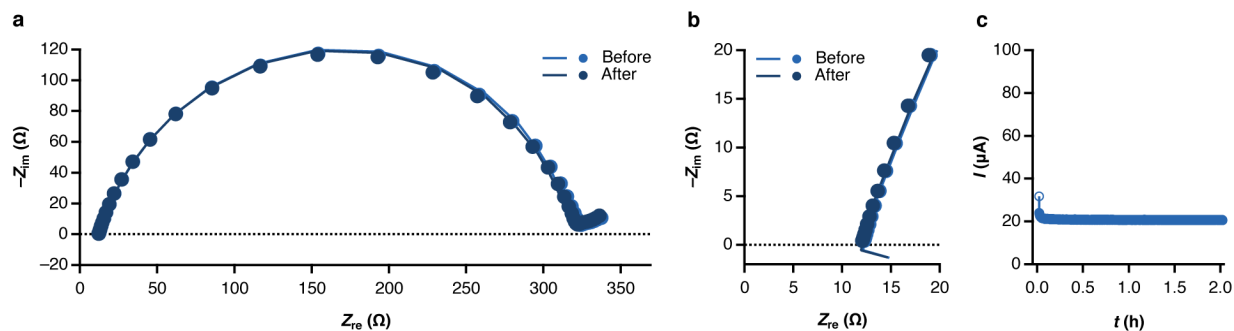
Supplementary Figure 36: Transference number determination for PIM 21. a, Full Nyquist plot and b, zoom in on high frequency region before and after polarization, and c, current over time during potentiostatic polarization at 10 mV.



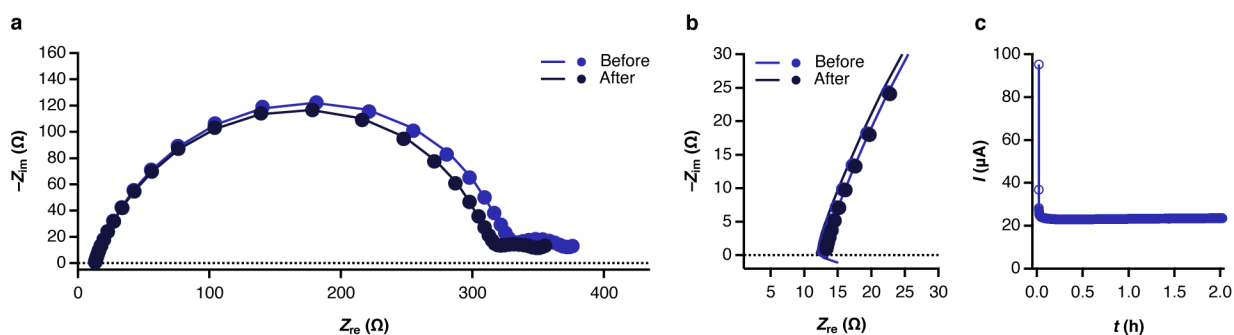
Supplementary Figure 37: Transference number determination for PIM 23. a, Full Nyquist plot and b, zoom in on high frequency region before and after polarization, and c, current over time during potentiostatic polarization at 10 mV.



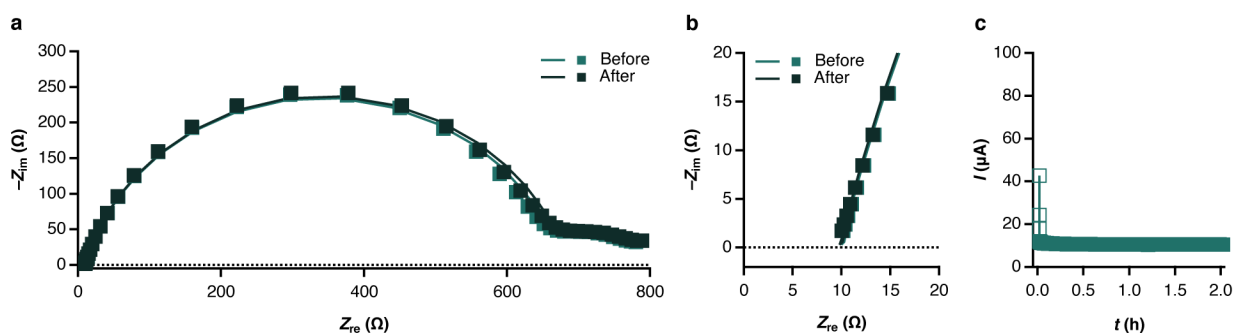
Supplementary Figure 38: Transference number determination for PIM 24. a, Full Nyquist plot and b, zoom in on high frequency region before and after polarization, and c, current over time during potentiostatic polarization at 10 mV.



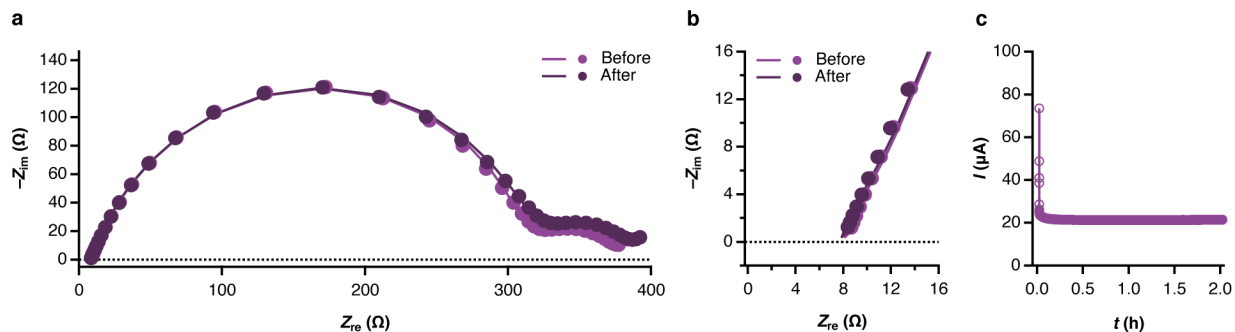
Supplementary Figure 39: Transference number determination for PIM 25. a, Full Nyquist plot and b, zoom in on high frequency region before and after polarization, and c, current over time during potentiostatic polarization at 10 mV.



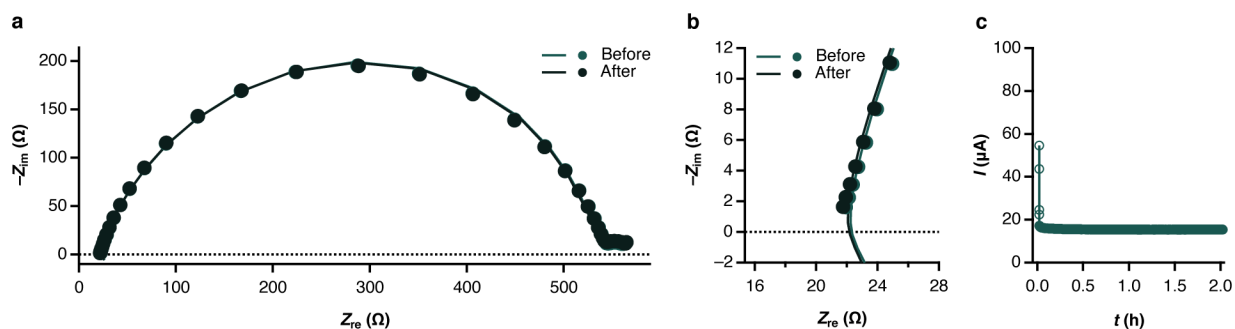
Supplementary Figure 40: Transference number determination for PIM 26. a, Full Nyquist plot and b, zoom in on high frequency region before and after polarization, and c, current over time during potentiostatic polarization at 10 mV.



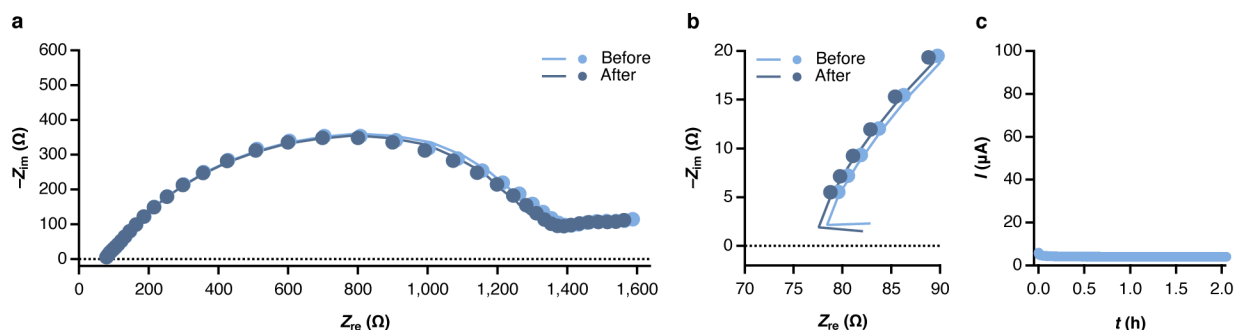
Supplementary Figure 41: Transference number determination for PIM 28. a, Full Nyquist plot and b, zoom in on high frequency region before and after polarization, and c, current over time during potentiostatic polarization at 10 mV.



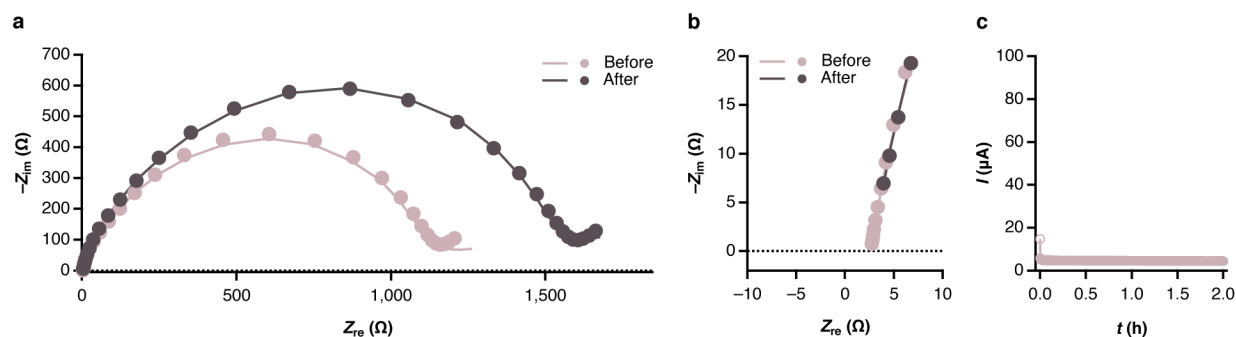
Supplementary Figure 42: Transference number determination for PIM 30. **a**, Full Nyquist plot and **b**, zoom in on high frequency region before and after polarization, and **c**, current over time during potentiostatic polarization at 10 mV.



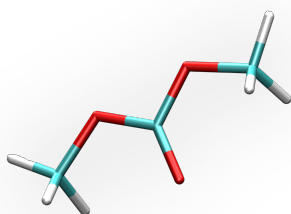
Supplementary Figure 43: Transference number determination for PIM 31. **a**, Full Nyquist plot and **b**, zoom in on high frequency region before and after polarization, and **c**, current over time during potentiostatic polarization at 10 mV



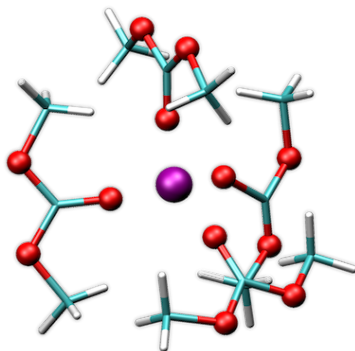
Supplementary Figure 44: Transference number determination for PIM-1. **a**, Full Nyquist plot and **b**, zoom in on high frequency region before and after polarization, and **c**, current over time during potentiostatic polarization at 10 mV.



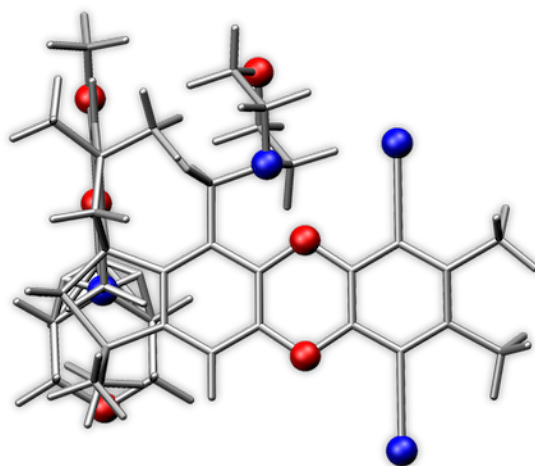
Supplementary Figure 45: Transference number determination for Celgard. a, Full Nyquist plot and b, zoom in on high frequency region before and after polarization, and c, current over time during potentiostatic polarization at 10 mV.



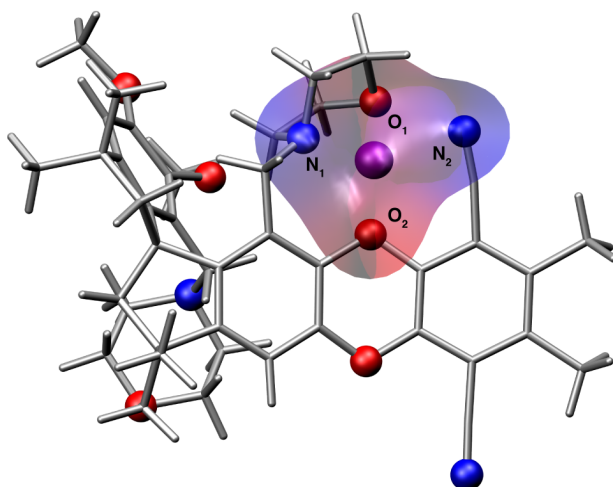
Supplementary Figure 46: Equilibrium geometry of DMC.



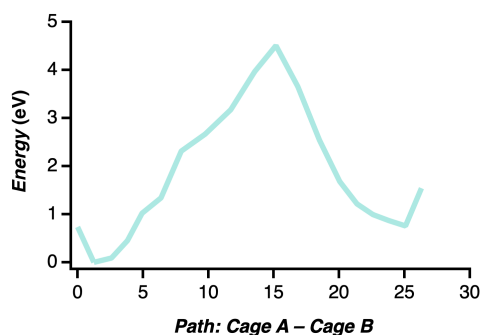
Supplementary Figure 47: Equilibrium geometry of a Li⁺/4DMC molecular cluster.



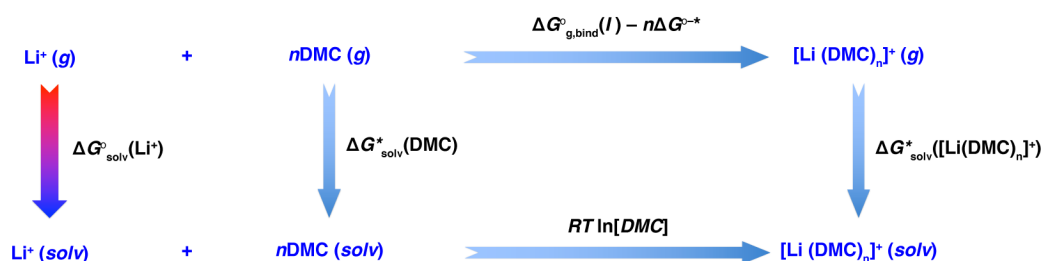
Supplementary Figure 48: Equilibrium geometry of the PIM 13 fragment.



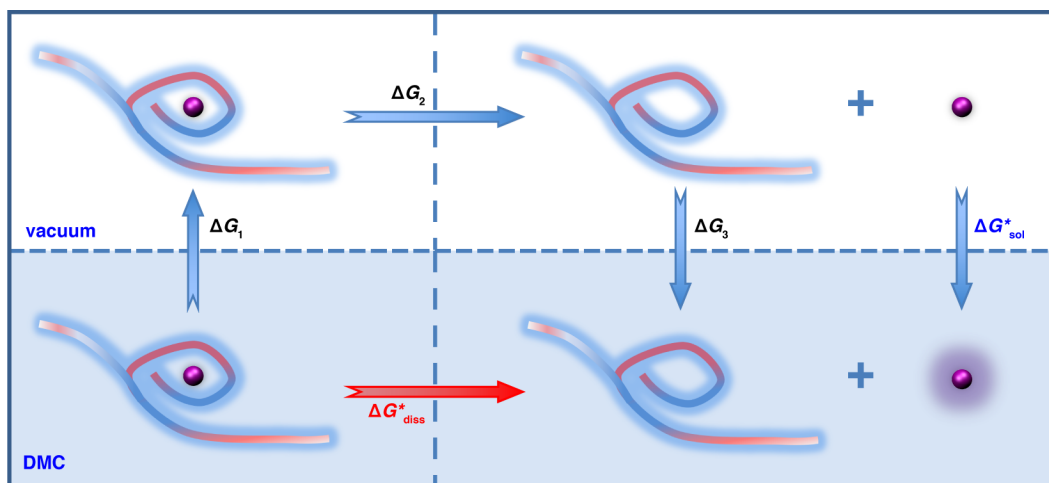
Supplementary Figure 49: Equilibrium geometry of the PIM 13 fragment and the Li^+ ion in the cage.



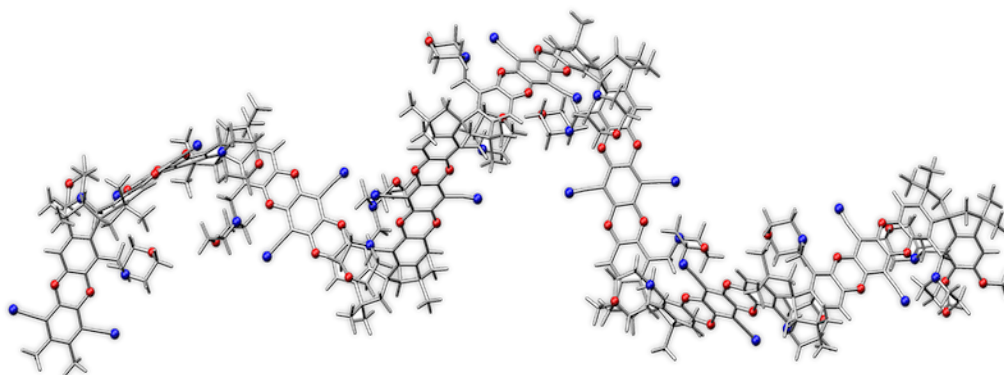
Supplementary Figure 50: NEB energies along the optimal pathway of the Li^+ ion from one cage to another in the PIM 13 unit used in quantum chemistry calculations (Supplementary Figures 48–49).



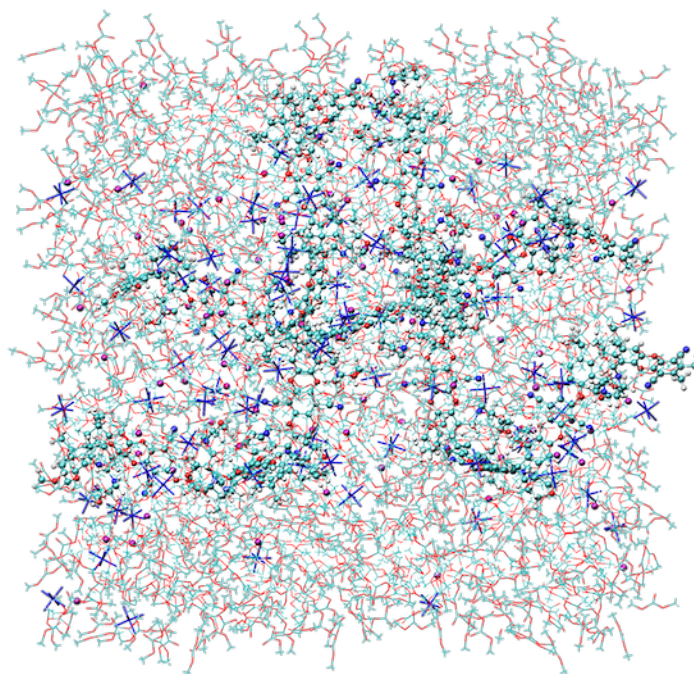
Supplementary Figure 51: Monomer thermodynamic cycle for calculation of the solvation free energy of the Li^+ ion in DMC.



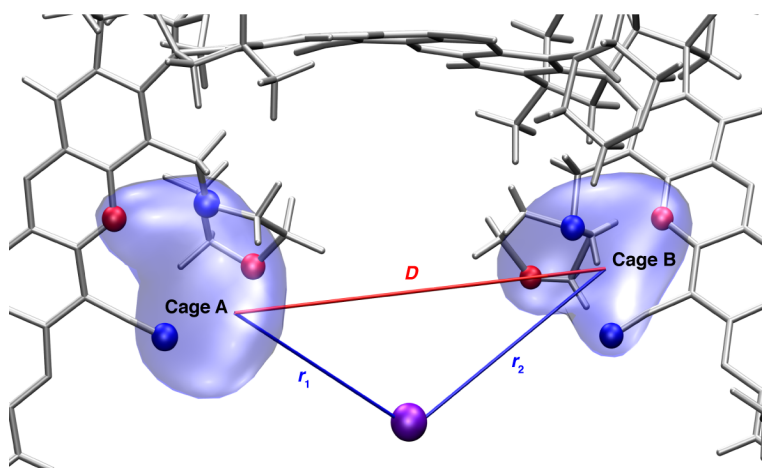
Supplementary Figure 52: Thermodynamic cycle for calculations of free energy of dissociation of the Li^+ ion in the bulk DMC solvent.



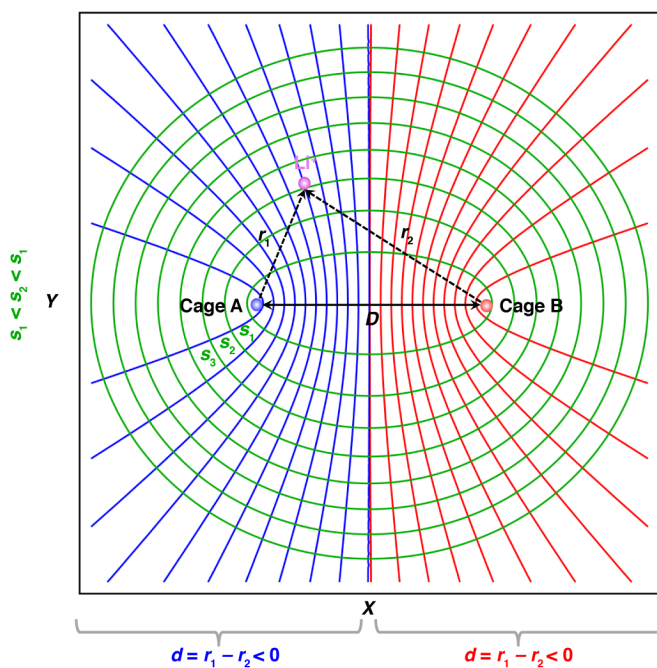
Supplementary Figure 53: A strand of PIM 13 (8 units) used in MD simulations.



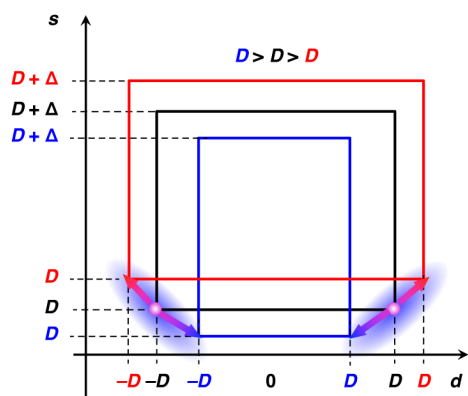
Supplementary Figure 54: A typical simulation box containing two strands of PIM 13 (8 units each) and 84 pairs of $\text{Li}^+/\text{PF}_6^-$ in DMC (0.7 M) used in MD simulations.



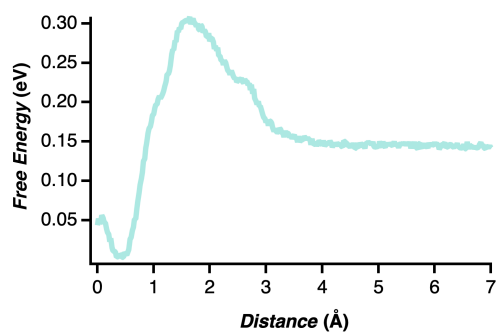
Supplementary Figure 55: Definitions of collective variables. r_1 , $d = r_1 - r_2$ and $s = r_1 + r_2$. D is the distance between centers of masses of two cages.



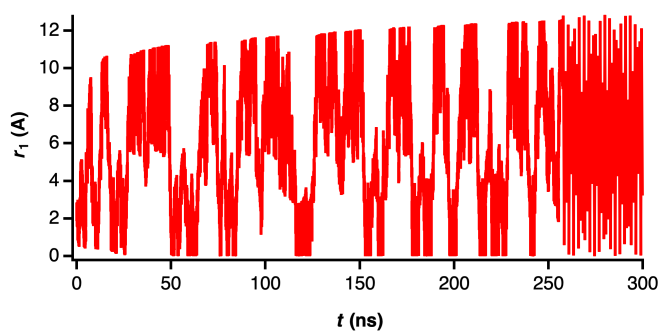
Supplementary Figure 56: Meaning of constraints on collective variables. r_1 , $d = r_1 - r_2$ and $s = r_1 + r_2$. D is the distance between centers of masses of two cages.



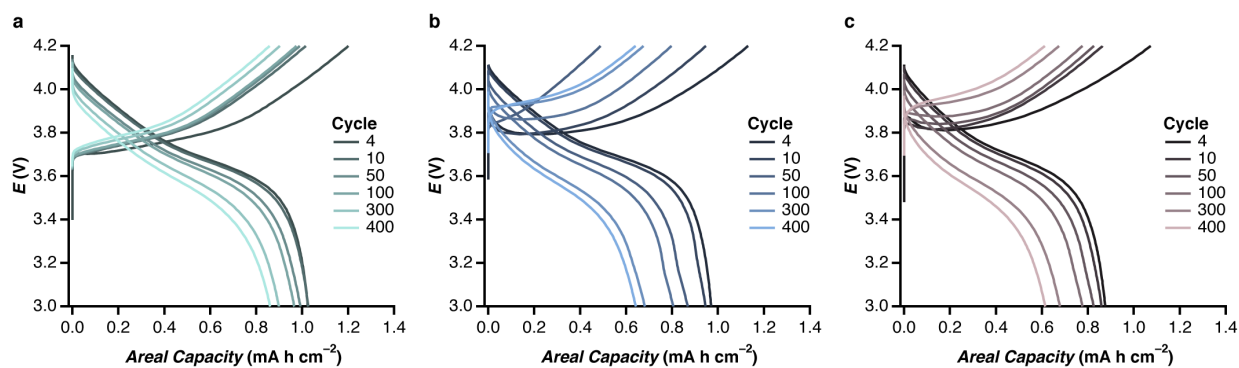
Supplementary Figure 57: Meaning of the phase space in $d = r_1 - r_2$ and $s = r_1 + r_2$ coordinates and the constraint Δ .



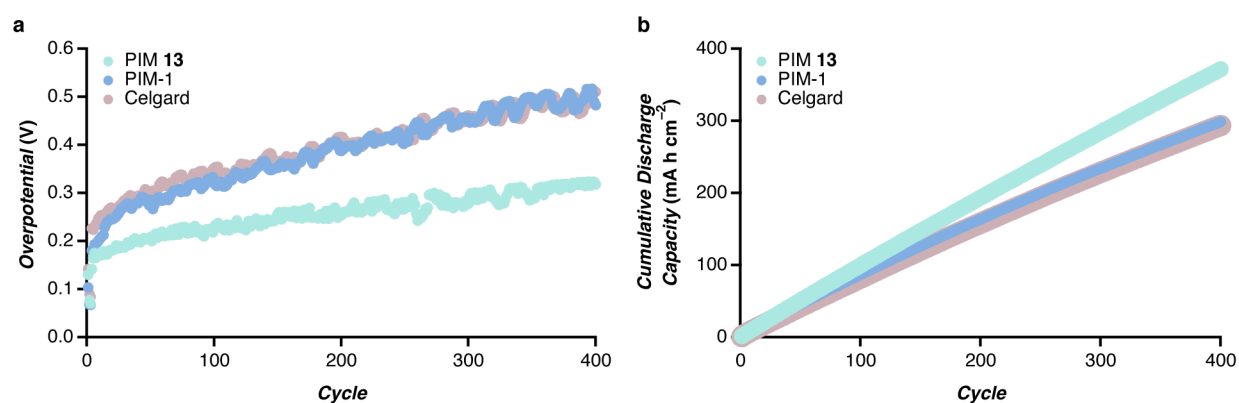
Supplementary Figure 58: Free energy profile as a function of r_1 – distance between the Li^+ and the center of mass of a cage.



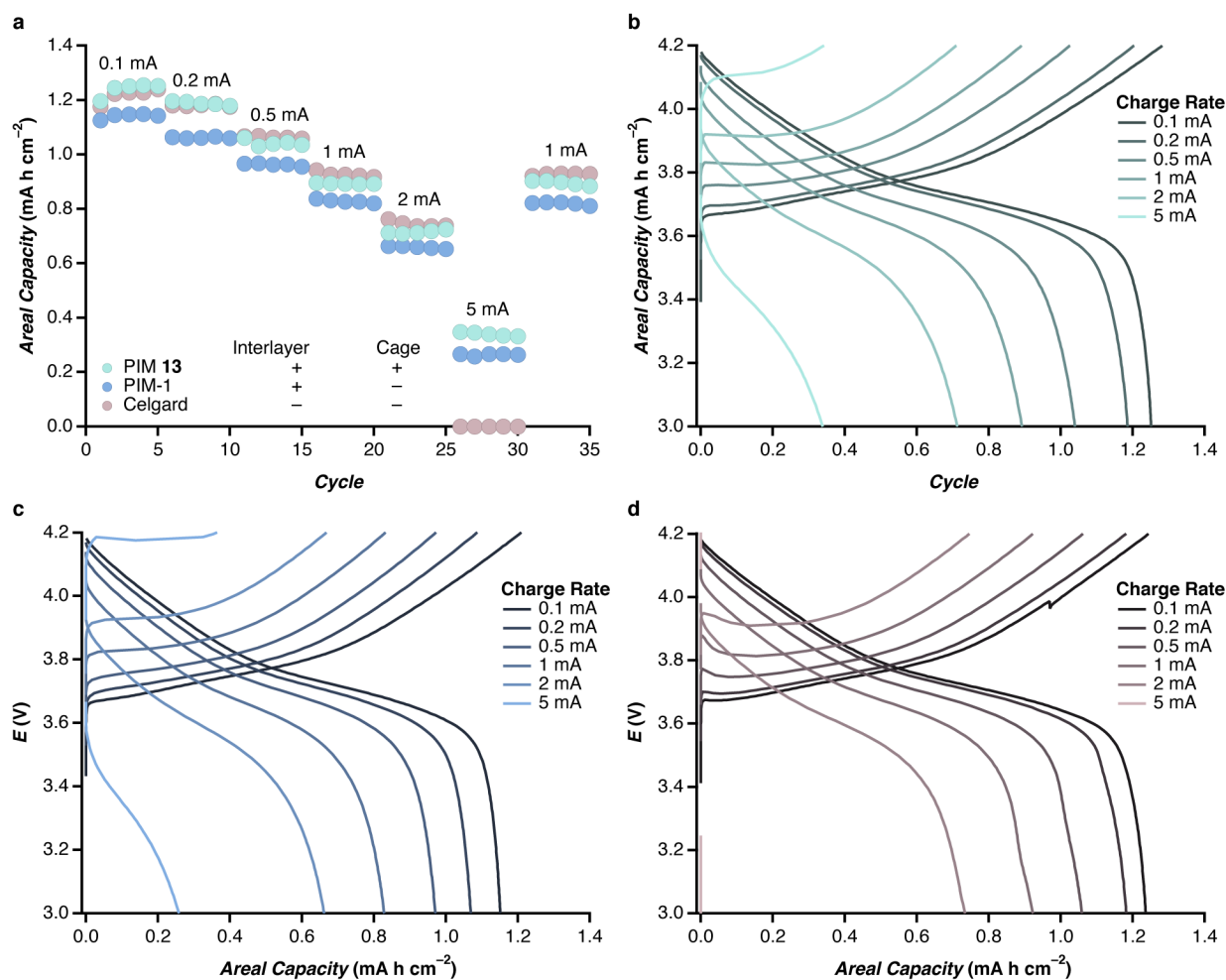
Supplementary Figure 59: Time evolution of r_1 in the metadynamics protocol.



Supplementary Figure 60: Full cell charge-discharge curves. a–c, Charge-Discharge curves for PIM 13, PIM-1, and Celgard Li-NMC622 cells, respectively.



Supplementary Figure 61: Full cell performance metrics. a, Overpotential, and b, Cumulative discharge capacity for the cycling of Li-NMC622 cells.



Supplementary Figure 62: Full cell rate performance. **a**, Discharge capacity and **b–c**, Charge–Discharge curves for the cycling of PIM 13, PIM-1, and Celgard, respectively, at different charge rates.

Supplementary References

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