Supporting information for:
Tunable Anion Selective Transport through
Monolayer Graphene and Hexagonal Boron Nitride

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S1: Illustrated example of data analysis

For a typical example of the data analysis, Figure S1 presents data for a graphene membrane with 10mM HfCl₄ in the cis reservoir and 100mM, 10mM and 1mM of HfCl₄ in the trans reservoir respectively. To assess the degree of selectivity in this case, we extract the current (circles) and voltage (diamonds) intercepts from IV curves in Figure S1b. These current and voltage offset values are shown as a function of trans concentration in Figure S1c. The voltage intercepts are a direct measure of the built-up membrane potential, or reversal potential, and in line with this equation we find a linear behavior of the reversal potential with changing trans concentration on a log-linear scale. Inspection of the Nernst equation, shows that the slope of this line should be directly related to the percentage selectivity, S. As such, gradients from Figure S1b, are used to provide a measure of the selectivity as the change in reversal voltage with concentration (mV/log[M]). The gradient of the current plot (nA/log[M]) confirms the direction of selectivity and provides an idea of the selective ionic flux across the pore(s). Here, a negative gradient in the plot of voltage offset against [trans] corresponds to a positive selective current (from the definition of conventional current), and thus indicates anion selectivity. The opposite behavior would be expected for cation selective membranes. The direction of these gradients can therefore establish toward which ions the membrane is selective with the magnitude of the gradient indicative of the magnitude of selectivity. A greater variety of concentrations are used within full analysis, omitted here for simplicity. For reference, here the GHK fit shows that the selectivity toward anions is ~248 greater than toward cations.
Figure S1: Establishing Anion Selectivity using HfCl₄. (a) Experimental IV curves shown with a GHK fit, circles indicating current offsets and diamonds the reversal potentials. Cis concentration is fixed, trans salt concentration varying according to legend. (b) Extracted voltage and current offset data from (a) is shown against trans concentration. The gradient of the linear fit is a measure of selectivity. (c) GHK modelled fit to the reversal potential data allowing extraction of a selectivity ratio, another measure of selectivity. Dashed line shows the GHK output for a cation selective membrane.
S2: Further examples with Zirconium Tetrachloride (ZrCl₄)

Extending our work beyond HfCl₄, experiments with graphene are repeated using zirconium tetrachloride, ZrCl₄. Figure S2 shows the current and voltage selectivity for this system. For all cis concentrations, the membrane remains anion selective showing 63% selectivity ($S=0.63$) with 10mM in the cis reservoir and $\sim73\%$ for both 100mM and 1M in the cis reservoir. As expected, due to the high conductivity of 1M, the current selectivity is greater in magnitude for 1M than 100mM and 10mM. In all cases, the positive direction once again indicates anion selectivity.

![Graph](image)

**Figure S2:** Anion selectivity in different concentrations of ZrCl₄ with graphene. (a) 10mM in cis reservoir, (b) 100mM in cis reservoir and (c) 1M in the cis reservoir. The voltage offset and current offset are shown as a function of trans concentration, all indicating anion selectivity. Gradients of each line are given in the legend.

Within Figure S3, experimental data presented from Figure S2 is fit to the expanded GHK equation. It can be seen that the data is fit reasonably well to the GHK equation, providing selectivity ratios indicative of anion selection. These ratios range from $\sim57$ for
10mM to \( \sim 1080 \) for 1M. These are broadly similar to those of HfCl\(_4\), which is expected given their similar valency.

Figure S3: Selectivity ratio according to the GHK equation. GHK fit shown with the selectivity ratio as fitting parameter. Experimental error is shown. Legends indicate the salt in cis - (a) 10mM ZrCl\(_4\) is shown to be \( \sim 57 \) more selective to anions over cations. (b) 100mM ZrCl\(_4\) is shown to be \( \sim 1835 \) and (c) 1M ZrCl\(_4\) \( \sim 1080 \) more selective to anions over cations.
S3: Selectivity with hexagonal Boron Nitride (hBN)

In order to demonstrate that the ion selectivity we see is not limited to graphene we have shown transport across hexagonal Boron Nitride (hBN). In Figure S4 we repeat key experiments with hBN in systems with reservoirs containing solution of only KCl, only HfCl₄ and mixed environments. In Figure S4a we show selectivity with KCl, indicating cation selectivity. Figure S4b shows anion selectivity with HfCl₄. Note here that data for voltage and current is shown together. Finally, we see the crossing over from cation to non-selective to anion selectivity in Figure S4c with addition of increasing concentrations of a constant HfCl₄ background.

Figure S4: Ionic selectivity across hexagonal Boron Nitride (hBN). (a) KCl showing cation selectivity, (b) HfCl₄ showing anion selectivity. In (c) behaviour switches from cation selective through to non-selective and anion selective based on the concentration of HfCl₄ background added to a KCl gradient.
S4: Solution pH

As discussed, substrate conditions around a 2D material affect its surface charge. With a floating membrane, the salt solution acts as its substrate. The pH of a solution could thus have an effect on the effective surface charge on the membrane. It has been shown previously\textsuperscript{31} that by altering the pH of 100mM KCl, graphene and hBN can be made non-selective when acidic, with cation selectivity restored from neutral through to a basic regime.

In this paper, we study the transport of ions and the effect of multivalent ionic charge on the surface therefore solutions are unbuffered with unaltered pH levels - these are shown in Table S1.

Table S1: pH values for common salts used in our system. Unbuffered solution pH values as prepared for hafnium tetrachloride and potassium chloride.

|         | KCl | HfCl\textsubscript{4} | ZrCl\textsubscript{4} | KCl + 0.01mM HfCl\textsubscript{4} | KCl + 0.1mM HfCl\textsubscript{4} | KCl + 1mM HfCl\textsubscript{4} |
|---------|-----|-----------------------|------------------------|-----------------------------------|-----------------------------------|----------------------------------|
| 1M      | 7.04| 0                     | 0                      | 4.64                              | 3.96                              | 2.9                              |
| 100mM   | 6.7 | 0.96                  | 0.76                   | 4.78                              | 3.92                              | 2.95                             |
| 10mM    | 6.3 | 1.92                  | 1.68                   | 4.68                              | 3.86                              | 2.87                             |
| 1mM     | 5.8 | 2.82                  | 2.64                   | 4.8                               | 3.85                              | 2.85                             |

In looking at the effect of pH we first repeat measurements using 100mM KCl with adjusted pH levels from 0 to 14. Selectivity measured for both graphene and hBN using these solutions are presented in Figure S5. It is shown here that with a monovalent salt, an acidic pH renders the membrane non-selective and above a neutral pH, cation selectivity is restored, consistent with previous observations.\textsuperscript{31} To further probe the effect of pH, we attempt to detangle the effects of solution concentration, ionic charge and pH.

Adjusting the pH of the two multivalent solutions used in this paper, HfCl\textsubscript{4} and ZrCl\textsubscript{4}, resulted in precipitation. However, trivalent solutions lanthanum chloride (LaCl\textsubscript{3}) and cerium chloride (CeCl\textsubscript{3}) also exhibit tunable ionic selectivity and their pH can be more readily altered. Figure S6 presents a comparison of selectivity percentage for HfCl\textsubscript{4}, un-altered LaCl\textsubscript{3} and LaCl\textsubscript{3} acidified (A-LaCl\textsubscript{3}) to the level of HfCl\textsubscript{4}. In this figure, the labels indicate the solution pH level. In cases of LaCl\textsubscript{3} and A-LaCl\textsubscript{3}, the membrane exhibits cation selectivity up
Figure S5: Ionic selectivity for KCl across graphene and hBN. For pH levels of 6 and above, the membranes exhibit cation selectivity with 100mM KCl. At acidic pH levels below 6, ionic selectivity is negligible, rendering the membrane non-selective.

to a cis concentration of 10mM, after which it switches to anion selectivity. The behaviour correlates with the cis concentration and not with the solution pH level. At like for like concentration and pH levels, 1mM and 10mM HfCl₄ exhibits anion selectivity whilst A-LaCl₃ shows cation selective behavior. This further indicates that the selective behaviour is not simply a pH effect.

Figure S6: Selectivity is shown for hafnium tetrachloride (HfCl₄), lanthanum chloride (LaCl₃) and lanthanum chloride acidified to match HfCl₄ (A-LaCl₃). Data point labels indicate the pH of the solution. Selectivity is shown as a percentage against respective cis reservoir concentrations.

At the other end of the pH scale, potassium phosphate (K₃PO₄) has a basic pH ranging
from 11 to 13 for 10mM to 1M. In Figure S7 the selectivity is shown for K$_3$PO$_4$, KCl and KCl made basic to match K$_3$PO$_4$ (B-KCl). We can see that both K$_3$PO$_4$ and KCl exhibit cation selectivity for all cis concentrations tested. B-KCl shows the expected cation selective behavior. The pH changes here have, once again, not altered the direction of selective behaviour. In both the acidic and basic regimes, the altered magnitude of selectivity could be due to changes in conductivity as a result of altering pH levels.

![Graph](image)

**Figure S7:** Selectivity is shown for a potassium phosphate (K$_3$PO$_4$), potassium chloride (KCl) and KCl acidified to match K$_3$PO$_4$ (B-KCl). Data point labels indicate the pH of the solution. Selectivity is shown as a percentage against respective cis reservoir concentrations.
S5: Selectivity with trivalent and divalent ions

The effect of charge inversion studied in this paper using tetravalent ions can also be achieved with use of trivalent ions. Figure S8 and S9 present data for selectivity experiments on graphene using cerium chloride (CeCl₃) and lanthanum chloride (LaCl₃). In both, the membrane is weakly anion selective at 100mM and higher cis concentrations. At 10mM we see a transitional point from anion to cation selective behaviour, consistent with theoretical observations.⁸² In Figure S8, three distinct regimes are seen with 10mM in the cis reservoir, sometimes the membrane is cation or anion selective and sometimes non-selective. If the critical concentration is close to 10mM, this would provide an explanation for this behavior. In Figure S9, LaCl₃ shows a similar behavior. In both cases, the membrane is cation selective at 1mM cis concentration. The implication here is that trivalent ions require a higher concentration of between 1mM - 10mM to invert the charge on the membrane surface, compared to tetravalent ions which exhibit only anion selective behavior.

As with tetravalent salts, in Figure S10 selectivity is measured for a KCl gradient with a constant addition of LaCl₃. In this system we find that cation selectivity with 100mM KCl remains despite an addition of 10mM LaCl₃. Upon increasing this addition to 100mM, the system becomes less cation selective, ultimately inverting to anion selective behavior at 1M LaCl₃ addition.

Given the ability for multivalent ions to alter the system selectivity it remains to probe the behavior of a divalent ion. Figure S11 presents selectivity data for magnesium chloride (MgCl₂). Given the transition point from cation to anion was around 10mM-100mM for trivalent salts, the expected value would be higher than 100mM for a divalent species. For cis concentrations ranging from 10mM to 1M we see only cation selective behaviour. This observation is consistent with literature.⁸²,⁸³
Figure S8: Selectivity on graphene for cerium chloride (CeCl₃). Anion selective behaviour seen for cis concentrations above 10mM and cation behavior below 10mM. At a cis concentration of 10mM, the membrane exhibits some anion/cation/non-selective behavior.
Figure S9: Selectivity on graphene for lanthanum chloride (LaCl₃). Anion selective behavior seen for cis concentrations above 10mM and cation behavior below 10mM. At a cis concentration of 10mM, the membrane exhibits some anion/cation/non-selective behavior.
Figure S10: Tunable ionic selectivity on graphene using a trivalent salt - lanthanum chloride (LaCl₃). Voltage offsets for 100mM KCl with a background concentration of LaCl₃ showing a change in the selectivity from cation to anion with increasing concentration of LaCl₃.

Figure S11: Ionic selectivity on graphene with a divalent salt - magnesium chloride (MgCl₂). The gradient of the linear fit is shown and is a measure of selectivity. Positive gradients indicate cation selective behavior which is observed for all cis concentrations.
S6: Goldman-Hodgkin-Katz

For an ion species, $x$, the current flux through a pore according to Goldman-Hodgkin-Katz (GHK) is as follows: \(^4\)

$$I_x = \frac{F^2 z_x^2 P_x V_{Nernst} (c_{cis} - c_{trans} \exp(z_x F V_{Nernst}/RT))}{RT} \left(1 - \exp(z_x F V_{Nernst}/RT)\right)$$ \hspace{1cm} (1)

where $P_x$ is the permeability of $x$, $c_{trans}$, $c_{cis}$ ion concentrations and $z_x$ the ionic valency.

Taking the simple monovalent case of KCl:

$$I_{K^+} = \frac{F^2 z_{K^+}^2 P_{K^+} V_{Nernst} (c_{cis} - c_{trans} \exp(z_{K^+} F V_{Nernst}/RT))}{RT} \left(1 - \exp(z_{K^+} F V_{Nernst}/RT)\right)$$

$$I_{Cl^-} = \frac{F^2 z_{Cl^-}^2 P_{Cl^-} V_{Nernst} (c_{cis} - c_{trans} \exp(z_{Cl^-} F V_{Nernst}/RT))}{RT} \left(1 - \exp(z_{Cl^-} F V_{Nernst}/RT)\right)$$

$$I_{total} = I_{K^+} + I_{Cl^-} = 0$$

Giving:

$$\frac{P_{K^+}}{P_{Cl^-}} \frac{(c_{cis} - c_{trans} \exp(F V_{Nernst}/RT))}{1 - \exp(F V_{Nernst}/RT)} + \frac{(c_{cis} - c_{trans} \exp(-F V_{Nernst}/RT))}{1 - \exp(-F V_{Nernst}/RT)} = 0$$

Which simplifies further to:

$$\ln \left( \frac{\frac{P_{K^+}}{P_{Cl^-}} c_{cis} + c_{trans}}{\left(\frac{P_{K^+}}{P_{Cl^-}} c_{trans} + c_{cis}\right)} \right) = \frac{F V_{Nernst}}{RT}$$

Finally rearranging to give:

$$V_{rev} = \frac{RT}{F} \ln \left( \frac{P_{K^+}/Cl^- + c_{trans}}{c_{cis} \left(\frac{P_{K^+}/Cl^-}{c_{cis}} + 1\right)} \right)$$ \hspace{1cm} (2)
The form of GHK presented in equation 2 means the experimentally measured reversal (or Nernst) potential and known concentrations can be used to determine ionic permeability. Experimental data is fit to this equation using the R nonlinear package nlsLM. This uses a Levenberg-Marquardt algorithm with standard experimental error on the value of $V_{rev}$ used as weighting parameters. Standard error is extracted from the fitting and used as bounds on the fitting parameter, $P$.

A similar derivation is followed for divalent ions, giving the following relation:

$$V_{rev} = \frac{RT}{F} \ln \left( \frac{\sqrt{8C'^2 P' + C'^2 + 16C'^2 P'^2 + 2C' + 8P' + 1} + C' - 1}{2(2C'^2 P' + 1)} \right)$$

$$P' = P_{Mg^{2+}/Cl^-}$$

$$C' = \left( \frac{c_{trans}}{c_{cis}} \right)$$

And for tri-valent ions,

$$V_{Nernst} = \frac{RT}{F} \ln \left( \frac{\left( m + \sqrt{4w^3 + (m + s)^2 + s} \right)^{\frac{1}{3}} - \frac{\sqrt[3]{2u}}{t(m + \sqrt{4w^3 + (m + s)^2 + s})^{\frac{1}{3}}} - \frac{1 - C'}{t}}{2} \right)$$

where,

$$P' = P_{La^{3+}/Cl^-}$$

$$C' = \left( \frac{c_{trans}}{c_{cis}} \right)$$

$$u = (-9C'^2 P' - C'^2 + 9C'^2 P' + C' + 2)$$

$$s = 486C'^2 P'^2 + 27C'^2 P' + 15C' + 81P' + 7$$

$$t = 3(3C'^2 P' + 1)$$

$$m = 243C'^3 P'^2 + 27C'^3 P' + 2C'^3 + 729C'^2 P'^3 + 108C'^2 + P' + 3C'^2$$

For tetravalent ions, the analytical derivation into a form useful for direct fitting is difficult. Using the following form,
\[ 4P_{H^+}^{4+/\text{Cl}^-} \frac{(1 - c_{\text{trans}}/c_{\text{cis}} \exp(4FV_{\text{Nernst}}/RT))}{1 - \exp(4FV_{\text{Nernst}}/RT)} + \frac{(1 - C_{\text{trans}}/c_{\text{cis}} \exp(-FV_{\text{Nernst}}/RT))}{1 - \exp(-FV_{\text{Nernst}}/RT)} = 0 \] 

(5)

implicit curve fitting can be used. The applicability of the GHK model is limited by assumptions\textsuperscript{54} but is otherwise broad. Although adjustment to the GHK equation with a weighting for the Dukhin number\textsuperscript{55} would make the model more robust it would introduce assumptions about the surface charge of the membrane. Furthermore, despite not making such adjustments, there is excellent conformity between experimental data and the GHK model.
S7: Further Characterization of Graphene and hBN

Figure S12: a) A map of 2D/G ratio (I) and corresponding histogram showing mean value of around 2.9 and b) the 2D FWHM map (I) and histogram showing an average 2D width of 27.5 cm\(^{-1}\) (ii).

The graphene was transferred by using a PMMA scaffold to support the graphene whilst the Cu foil beneath is etched with ammonium persulphate. It was transferred onto 280 nm SiO\(_2\) on Si. Graphene characterization is carried out using Raman spectroscopy maps over 150 x 150 \(\mu\)m\(^2\) area. The well understood response of graphene from Raman spectra\(^{66}\) allows for extraction of a breadth of information. Figure S12 presents Raman maps for graphene transferred onto SiO\(_2\). Figure S12a.i is a Raman map of the 2D/G peak ratios, with values shown in the legend. A histogram of the 2D/G peak ratio is shown in Figure S12a.ii, with a nominal ratio of \(~2.7\) indicative of mono-layer graphene. In Figure S12b.i a map of the
full width at half maximum (FWHM) of the 2D width is presented with the histogram in b.ii - the narrow width indicates a sharp 2D peak, characteristic of high quality mono-layer graphene.

![Image](image_url)

Figure S13: hBN growth and characterisation. (a) A SEM image of monolayer hBN domains (dark) with small patches of multilayer (white) grown on Fe, showing large domains size. (b) A SEM image of monolayer hBN film after the domains coalesce (some patches of multilayer may be present). (c) Raman spectrum of monolayer hBN transferred to 285 nm SiO$_2$/Si substrates, where the intensity of the signal is sufficient to observe the E$_{2g}$ peak of 1369 cm$^{-1}$ with a FWHM of 17 cm$^{-1}$. Scale bars in (a-b) are 100 µm.

In characterising hBN growth quality, SEM and Raman spectroscopy techniques are used. Figure S13a shows a scanning electron microscope (SEM) image of as-grown monolayer hBN domains (dark triangles) on Fe, exhibiting large lateral dimensions of around 100 µm. When the monolayer hBN domains coalesce, they form a continuous full-coverage film as shown in Figure S13b (uniform dark contrast) which were used for the experiments discussed in the main text. Some patches of multilayers may be present (white triangles or speckles).

Raman characterisation was performed on an inVia Renishaw system with a 532 nm laser, 100x objective and ~10 mW power. The E$_{2g}$ vibrational mode can be used for hBN characterisation. The position of the E$_{2g}$ peak was between 1369-1371 cm$^{-1}$ with the FWHM value of around 17 cm$^{-1}$, consistent with high quality monolayer hBN material.$^{87}$

In transferring hBN, an electrochemical bubbling transfer method$^{88}$ is used. A solution of poly(bisphenol A carbonate) (PC, 5% in chloroform) was spin-coated (1000 rpm) onto the hBN/Fe substrates and the PC/hBN stack was detached from Fe by passing a current through a 1M NaOH solution (the Fe foil was connected to the negative electrode). The
Figure S14: hBN characterisation after transfer to KCl salt substrates. (a) An optical image of hBN showing visible multilayer regions, while the surrounding monolayer film is transparent. (b) A high magnification environmental SEM image of the monolayer hBN region directly on salt substrates showing presence of steps and wrinkles that were imprinted from the iron catalyst by the monolayer hBN film. Scale bars in (a), (b) are 50 µm and 2 µm respectively.

samples were then washed in deionised water to remove the NaOH solution. For the SiO$_2$ substrate, the PC/hBN stack was picked up from water. For the KCl substrates, the PC/hBN stack was transferred to a 4 M saturated KCl solution and picked up with KCl crystal. Finally, the samples were dried and PC was dissolved in chloroform. Following this transfer, Figure S14 shows optical and SEM images of the material. Visibly, there are regions of multi-layer growth alongside surrounding regions of monolayer hBN. The SEM image in Figure S14b shows some wrinkles and steps in the hBN film from the iron catalyst used in growth.
S8: Processing of TEM images

In an effort to image beyond the diffraction limit and closer to the information limit, a technique referred to as ‘exit wave reconstruction’ can be used. Due to lens aberrations and aperture limitations, recorded images from a transmission electron microscope (TEM) will be a degraded version of the true image. These factors can be described by the contrast transfer function (CTF),\textsuperscript{8} formulation of which requires microscope aberrations to be well-known. With knowledge of the phase and amplitude of the electron wave, the wave function can be obtained iteratively.\textsuperscript{10}

In order to obtain the phase information, a through focal series is used. The CTF is focal plane sensitive and thus an image series taken through the focal plane will contain both amplitude and phase data. In the images presented in Figure 4, a focal series of 51 images, taken at 1nm steps is used. Using the QSTEM system,\textsuperscript{11} the python library PyQSTEM is used to provide the transfer function generation using the microscope parameters in Table S2. Following this, the inverse of the assumed CTF is used to decouple the aberration degradation and obtain the ‘true’ electron exit wave. With this, the final ‘true’ phase image is generated. The source code developed can be found here: https://github.com/muscaglar/HRTEM_Recon

Table S2: Aberration factors for the TEAM 0.5 (Lawrence Berkeley Laboratory) used in exit wave reconstruction.

| Parameter                      | Value |
|--------------------------------|-------|
| Voltage (kV)                   | 80    |
| Divergence (mrad)              | 0.1   |
| Cs (mm)                        | -0.012|
| Cs5 (mm)                       | 5     |
| Focus Spread (Å)               | 10    |
| Lens Aperture (1/Å)            | 1.0   |
| Phase Correlation Cut-off (1/Å)| 0.6   |
S9: Membrane Conductance

Quartz nanocapillaries are an integral part of our system and so careful characterisation is important. Capillaries are ‘pulled’ using calibrated recipes the resultant capillary sizes of which are confirmed using both conductance measurements and SEM images. Figure S15a shows a typical micrograph of a pulled capillary indicating a diameter of around 150nm (accounting for gold coating), which is around the expected value. From conductance measurements, statistics can be gathered on the distribution of nanocapillary sizes, Figure S15b. Variability here could indicate larger/smaller than expected pore or one with a distorted shape amongst other possibilities such as blockages, therefore this check allows for discarding unsuitable capillaries.

Figure S15: a. Micrograph of a quartz nanocapillary coated in gold. Diameter of the pore opening is around 150nm after accounting for the gold coating. b. Distribution of nanocapillary diameter based on conductance measurements. c. Micrograph of nanocapillary images on the side, contrast enhanced image shows inner wall with the taper angle denoted.

In addition to measuring the conductance of the nanocapillary with no adhered material (bare), conductance with material sealed onto the tip (sealed) is recorded as an indication of the quality of seal achieved. This sealed conductance contains information about the membrane as well as the bare capillary and therefore to use the conductance as characterisation
of the membrane it is necessary to subtract the effect of the capillary. Figure S16 shows this analysis process. With known parameters of the capillary such as taper angle and solution conductance, the bare conductance is used to calculate the capillary diameter and extract the cone resistance.\textsuperscript{S12,S13} This cone resistance is subtracted from the sealed conductance leaving the membrane resistance. Using an empirical formula from Garaj \textit{et al.},\textsuperscript{S14} we are able to use this membrane resistance to estimate the combined equivalent pore size that would account for this resistance.

![Flow chart showing the steps taken in collecting current-voltage/conductance data from quartz nanocapillaries with no adhered material (bare) and with material (sealed). Input and output are indicated with a red arrow and the formulas used for any calculations are shown.](image)

Figure S16: Flow chart showing the steps taken in collecting current-voltage/conductance data from quartz nanocapillaries with no adhered material (bare) and with material (sealed). Input and output are indicated with a red arrow and the formulas used for any calculations are shown.
Table S3 provides a selection of capillary details for a variety of solutions. The worked example shows a range of pore sizes and capillary diameters across a wide cross section of solution conductances and capillary resistances. The taper angle is calculated from a variety of SEM images as demonstrated in Figure S15c and is thus a known value for a batch of capillaries following the same pulling protocol.

Table S3: Selection of examples of capillary conductance within a variety of solutions with subsequent sealed characteristics and calculated parameters.

| Bare Capillary Resistance (MΩhm) | Sealed Capillary Resistance (MΩhm) | Taper Angle (degrees) | Solution | Solution Conductance (mS/cm) | Estimated Capillary Diameter (nm) | Estimated Total Pore Diameter (nm) |
|---------------------------------|-----------------------------------|-----------------------|----------|-----------------------------|----------------------------------|----------------------------------|
| 95.7                            | 570.8                             | 5.5                   | HfCl₄ 10mM | 0.56                        | 132                              | 4.2                              |
| 67.9                            | 1815.9                            |                       | CeCl₃ 100mM | 2.36                        | 154                              | 3.5                              |
| 19.6                            | 340.6                             |                       | KCl 1M    | 10.05                       | 186                              | 14.2                             |
| 17.3                            | 518.6                             |                       |          |                             | 182                              | 6.9                              |
| 3.8                             | 19.8                              |                       |          |                             |                                   |                                  |
| 3.9                             | 60.5                              |                       |          |                             |                                   |                                  |
S10: Effective Screening Lengths in our System

Debye screening lengths are readily calculated from the Debye-Hückel approximation for a symmetric monovalent electrolyte,

$$\kappa^{-1} = \sqrt{\frac{\epsilon_r \epsilon_0 RT}{2 \cdot 10^3 F^2 C_0}}$$

where $\epsilon_r$ and $\epsilon_0$ are dielectric constant and permittivity of free space respectively, $C_0$ is the concentration of electrolyte (M), $T$ is temperature (K) and $R$ and $F$ are gas and Faraday constants respectively. However, at increasing concentrations and for asymmetric ions, the linear approximation is not valid and analytical solutions to the relationship are needed. Using empirical and modelled curves from McBridge et al.,$^{15}$ we can estimate Debye screening lengths for concentrations and ionic valences relevant to our system.

Table S4: Debye screening lengths for multivalent electrolytes. For symmetric monovalent salts (1:1), screening lengths are calculated from Debye-Hückel relations. Debye lengths for asymmetric salts are estimated and modelled.$^{15}$

| Ion charge ratio | 4:1 | 3:1 | 2:1 | 1:1 |
|------------------|-----|-----|-----|-----|
| 1M               | 0.11 nm | 0.15 nm | 0.21 nm | 0.33 nm |
| 100mM            | 0.36 nm | 0.46 nm | 0.66 nm | 1.04 nm |
| 10mM             | 1.13 nm | 1.5 nm  | 2.1 nm  | 3.3 nm  |
| 1mM              | 3.56 nm | 4.65 nm | 6.65 nm | 10.4 nm |
| 0.1mM            | 11.27 nm | 14.7 nm | 21 nm  | 32.3 nm |

Table S4 presents the Debye lengths for electrolytes ranging from asymmetric tetravalent (4:1) to monovalent (1:1). Of primary importance for our system and findings is the case for tetravalent electrolytes, such as HfCl₄ and ZrCl₄. In these cases, for cis concentrations where we see selectivity, the Debye screening length is at most ~3nm. Moreover, in Figure S17, a comparison of selectivity across a range of ions are presented. The hydrated radii for the ions participating in selective transport is estimated$^{16}$ and shown against their selectivity. There is no clear trend with selectivity and ionic radii, further implying that steric effects are not chiefly responsible for selectivity but instead electrostatics is playing a large role.
Figure S17: Selectivity is shown against estimated hydrated ionic radii for the respective ion participating in selective transport. Anion/cation transport is denoted by symbol color. No clear trend is seen between ionic radii and selectivity.
Finally, in Figure S18 the magnitude of selectivity is shown as the estimate combined pore size - a measure of the membrane conductance. Here we see that though there exists variability, a clear trend relating the selectivity achieved with the membrane conductance is absent. This holds for a monovalent, divalent, trivalent and tetravalent salts across cis concentrations ranging from 10mM to 1M.

Figure S18: Magnitude of selectivity is shown against estimated combined pore size which is a measure of membrane conductance. No clear trend is seen between membrane conductance and selectivity.
**S11: Raman Shifts**

Graphene and indeed most materials, possess a surface charge in solution. This has been previously estimated that as -0.6 C/m² for graphene\textsuperscript{17} and -0.16 C/m² for hBN.\textsuperscript{18} Moreover, given the nature of Raman spectroscopy, the peak positions of the Raman signature of graphene will be affected by such parameters as surface charge.\textsuperscript{19} In Figure S19 we show the peak positions from *in situ* Raman for graphene on various salt solutions. The data here is from several accumulations and repeats with a Lorentzian curve fit used to extract peak positions. In all cases of graphene on KCl we see an increase in peak position relative to the position measured with MilliQ water (MQ). Conversely, in all cases of HfCl\textsubscript{4} we see a decrease in peak position. The inset provides full example spectra of three different cases.

![Graph showing Raman Shifts](image)

Figure S19: *In situ* Raman spectra of graphene on salt solution as labelled in the legend. Several accumulations are averaged and a Lorentzian curve is fit to extract peak positions.

Our *in situ* Raman spectra method means we do not have a sufficiently high SNR to delve into the specific details of the spectral properties. Therefore, we cannot, with confidence, use this data to extract specific surface charging values. More important here is to see that there is clearly an affect on the surface charge due to the extrinsic salt solution environment.
S12: GHK Fits

For data presented in Figure 5 within the Main text, Figure S20 presents the respective GHK fits, showing good agreement.

Figure S20: Fit to GHK equation. (a),(b) KCl, with [cis] reservoirs containing 10mM and 100mM. Both are cation selectivity with ~12 and ~30 selectivity ratios. (c),(d) is for 10mM and 100mM [cis] HfCl₄ showing anion selective behaviour with ~100 and ~500 ratios respectively. (e),(f) KCl transport ([cis] 100mM) in presence of constant HfCl₄ background, 0.1mM and 1mM respectively. Response is cation (~18) and anion (~500) selective respectively.
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