Electronic Supplementary Material (ESI) for Soft Matter.

Bio-Inspired Incorporation of Phenylalanine Enhances Ionic Selectivity in Layer-by-Layer Deposited Polyelectrolyte Films

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Supporting Information:

Presented in Figure S1 are the normalized peak heights from the ToF-SIMS analysis used in the semi-quantitative calibration. The peak was identified at m/z = 166.1 and is attributed to Phe with an additional hydrogen (Phe+H). The peak heights have been normalized to a reference peak located at m/z = 117, which is attributed to a sodium adduct of the PAA monomer ($C_3H_3O_2Na_2^+$) in the films. The calibration controls were made by making the PEI and PAA solutions with increasing concentrations of Phe in 0.5 mM increments up to 1.5 mM concentrations in solution. The PEI+Phe and PAA+Phe solutions were then mixed together and then immediately drop cast onto small silicon substrates and allowed to dry. The plot shows an increase in the m/z = 166 peak height as the Phe concentration is increased in the calibration controls. Also shown on the plot is the result from a dip coated silicon substrate that has 5 BL of PE+Phe coated onto it from solutions used to coat the PC membranes used for the selectivity and resistance experiment (PEI and PAA both had 1 mM Phe included in the solutions). The ToF-SIMS analysis of the dip coated sample does reveal there was Phe present in the film and confirms that it is being incorporated into the film during the dip coating procedure. However, the signal from the normalized peak is lower than the drop cast 1 mM calibration control which means the Phe in the solution may not be entirely incorporated into the film or the normalization of the peaks is artificially lowering the resulting peak height of the dip coated sample.

Figure S2 shows structures clusters of Na^+ ion complexes treated in exchange reaction free energy calculations which were not included in the main text. These Na+ ion complexes are shown to be interacting with one or two water ligands with IB^- (A) and (C) and Phe^- (B) and (D). Average distances between Na^+ and ligating oxygens are (A) 2.35 Å, (B) 2.36 Å, (C) 2.43 Å, and (D) 2.45 Å. Ligands at distances greater than 2.4 Å lie outside the nearest neighbor region defined by ab initio molecular dynamics simulations of Na^+ in liquid water.

Table S1 lists the calculated ASR values for the different membranes corresponding to the values plotted in Figure 4B in the main text. The ASR is listed for Bare PC, 5 BL PE, 10 BL PE and 5 BL PE+Phe in 0.1, 1 and 3 M NaCl solutions.

Tables S2 and S3 list the calculated change in Gibbs free energy for a solvated Na^+ ion exchanging coordinating waters for Phe^- and IB^-, respectively. These include the values in both a gaseous state and with an implicit solvent used to represent aqueous solution. The change in energy is calculated for a Na^+ ion exchanging from 1 to 4 of the coordinating waters.

To determine whether our experimentally determined area specific membrane resistance was reasonable, we decided to calculate the membrane resistance for the bare PC membranes. The resistance for a single cylindrical nanochannel was calculated using the following equation: $R = \rho*(4L/\pi d^2)$ where R = resistance of channel, ρ = resistivity of ionic solution, L=length of channel and d=diameter of pore. The resistance for a single pore was then divided by the number of pores in a given area (similar to the calculation equivalent resistors in parallel) to find the area specific resistance. This was used to calculate the area specific resistance of the bare polycarbonate membranes and was found to be 0.673 Ohm/cm^2 which is not far from the experimentally determined 0.48 Ohm/cm^2.

Figure S1: Plot showing the normalized peak heights from ToF-SIMS analysis of the PE+Phe controls and the dip coated PE+Phe coated normally from sequential dip coats.

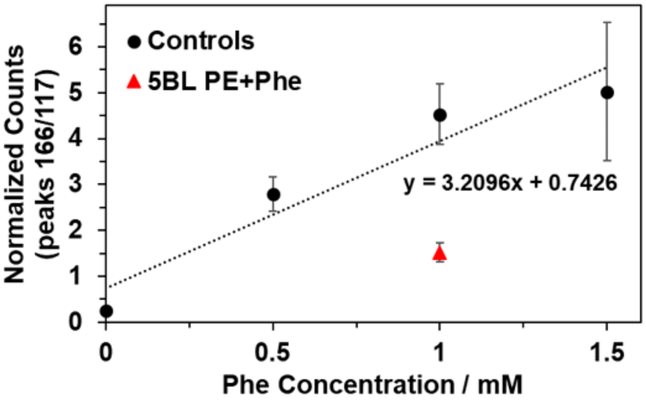

Figure S2: Additional clusters treated in exchange reaction free energy calculations. These Na^+ ion complexes are shown with one or two coordinated water ligands interacting with IB^- (A) and (C) respectively as well as with Phe^- (B) and (D) respectively. Average distances between Na^+ and ligating oxygens are (A) 2.35 Å, (B) 2.36 Å, (C) 2.43 Å, and (D) 2.45 Å. Spheres are color coded with carbon shown as gray, hydrogen as white, oxygen as red, nitrogen as blue and sodium as purple.

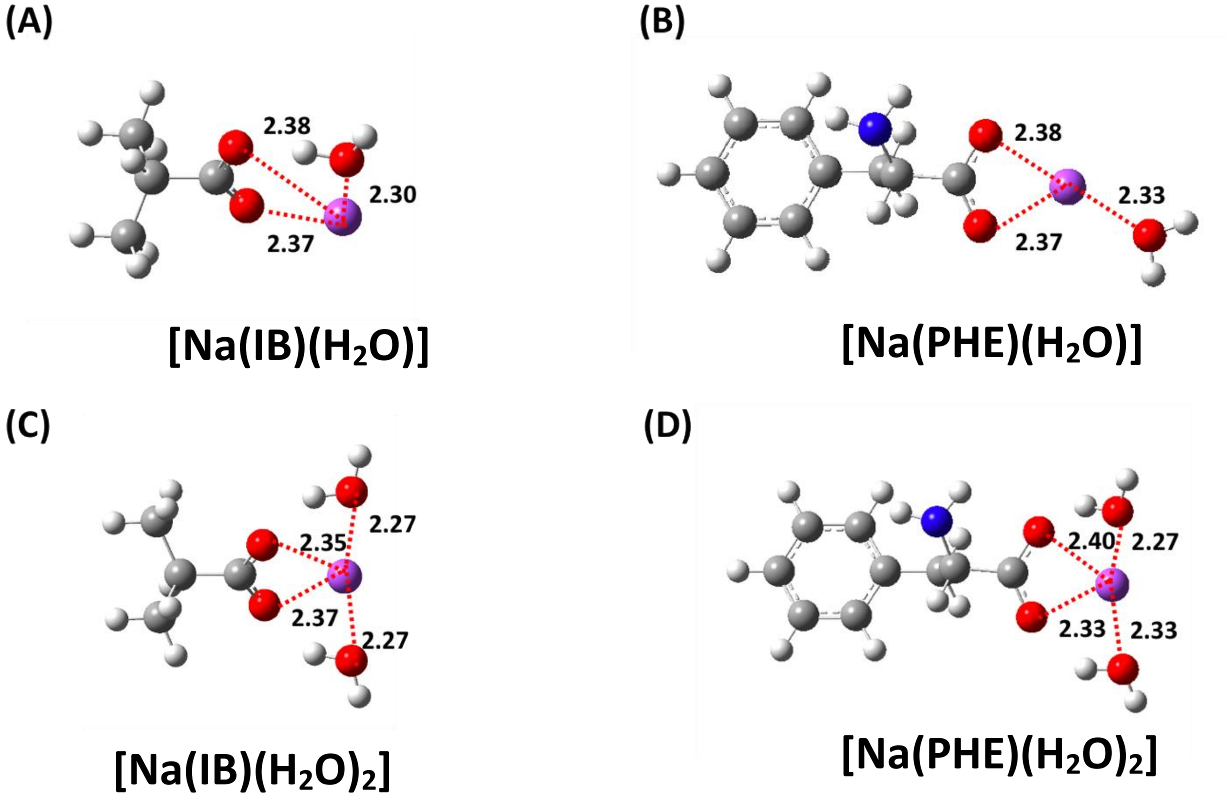

Table S1: Calculated ASR values for various membranes in different salt concentrations.

	Area Specific Resistance / Ω*cm^2		
	0.1 M NaCl	**1 M NaCl**	**3 M NaCl**
Bare PC	**1.21 ± 0.11**	**0.48 ± 0.13**	**0.26 ± 0.09**
5 BL PE	**1.87 ± 0.33**	**0.89 ± 0.05**	**0.45 ± 0.08**
10 BL PE	**2.75 ± 0.28**	**2.01 ± 0.33**	**1.32 ± 0.13**
5 BL PE+Phe	**1.81 ± 0.33**	**1.19 ± 0.11**	**0.61 ± 0.04**

Table S2: Sodium (Na^+) binding to IB^- with exchange of 0-4 waters that ligate Na^+ and calculated changes in Gibbs free energy, obtained from DFT calculations with implicit solvent used to represent aqueous (aq.) solution as well as in the gaseous state for comparison.

Reactions	$\Delta G_{aq.}$ / kcal mol^{-1}	ΔG_{gas} / kcal mol^{-1}
Na^+ (aq.) + IB^- (aq). ⇋[Na(IB)] (aq.)	-36.07	-126.94
$[Na(H_2O)_4]^+$ (aq.) + IB^- (aq.) ⇋ [Na(IB)] (aq.) + $4H_2O$ (aq.)	-47.46	-75.29
$[Na(H_2O)_4]^+$ (aq.) + IB^- (aq.) ⇋ $[Na(IB)(H_2O)]$ (aq.) + $3H_2O$ (aq.)	-44.45	-81.85
$[Na(H_2O)_4]^+$ (aq.) + IB^- (aq.) ⇋ $[Na(IB)(H_2O)_2]$ (aq.) + $2H_2O$ (aq.)	-39.55	-85.15
$[Na(H_2O)_4]^+$ (aq.) + IB^- (aq.) ⇋ $[Na(IB)(H_2O)_3]$ (aq.) + $1H_2O$ (aq.)	-31.55	-87.16

Table S3: Sodium (Na^+) binding to Phe^- with exchange of 0-4 waters that ligate Na^+ and calculated changes in Gibbs free energy, obtained from DFT calculations with implicit solvent used to represent aqueous (aq.) solution as well as in the gaseous state for comparison.

Reactions	**$\Delta G_{aq.}$ / kcal mol^{-1}**	**ΔG_{gas} / kcal mol^{-1}**
Na^+ (aq.) + Phe^- (aq.) $\leftrightharpoons$ [Na(Phe)] (aq.)	-66.55	-131.11
$[Na(H_2O)_4]^+$ (aq.) + Phe^- (aq.) $\leftrightharpoons$ [Na(Phe)] (aq.) + $4H_2O$ (aq.)	-77.94	-78.81
$[Na(H_2O)_4]^+$ (aq.) + Phe^- (aq.) $\leftrightharpoons$ $[Na(Phe)(H_2O)]$ (aq.) + $3H_2O$ (aq.)	-73.23	-82.98
$[Na(H_2O)_4]^+$ (aq.) + Phe^- (aq.) $\leftrightharpoons$ $[Na(Phe)(H_2O)_2]$ (aq.) + $2H_2O$ (aq.)	-68.52	-90.70
$[Na(H_2O)_4]^+$ (aq.) + Phe^- (aq.) $\leftrightharpoons$ $[Na(Phe)(H_2O)_3]$ (aq.) + $1H_2O$ (aq.)	-61.25	-90.64