## **Applications of Voltammetric Ion Selective Electrodes to Complex Matrices**

## **Supporting Information**

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 $C_6H_{13} = C_14H_{29}$ 

Figure S1. Structures of ionic liquids.

Table S1: Statistical data from the AEROSET 2 at the John Radcliffe Hospital.

Ion	Lower calibrant	Coefficient	Upper calibrant	Coefficient
	average activity /mM	of Variation	average activity /mM	of Variation
Na <sup>+</sup>	122	0.9	156	0.5
$K^{+}$	2.7	1.7	6.2	0.9
Ca <sup>2+</sup>	1.86 *	1.5	2.77 *	1.1

<sup>\*</sup>total concentration

- E<sub>m</sub> using EPG vs SCE
- E<sub>m</sub> using screen printed electrode vs Ag/AgCl

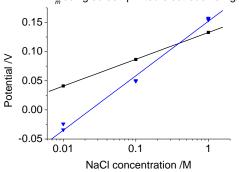


Figure S2.  $E_m$  versus NaCl concentration calibration curve of the TCNQ microcrystal sensor and response using the  $10^{th}$  potential cycle on EPG with an SCE reference electrode (black) and on a planar macrodisc screen printed electrode with a Ag/AgCl reference electrode with no salt bridge (blue).

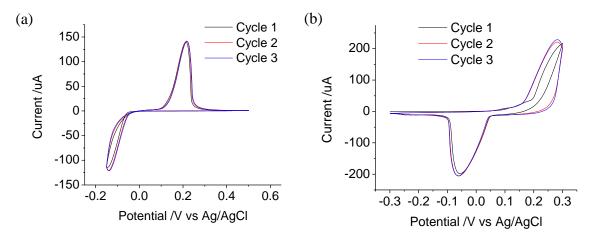


Figure S3: First three potential cycles in 0.1 M NaCl, 50 mM TRIS and HEPES at a scan rate of 100 mV s<sup>-1</sup> of mechanically adhered (a) TCNQ and (b) TTF on screen printed planar electrodes.

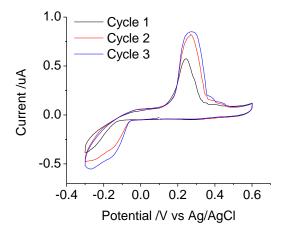


Figure S4: Screen printed planar electrodes with 5 % w/w TCNQ added to the carbon ink working electrode coated with Nafion in 0.1 M NaCl, 50 mM TRIS and HEPES at a scan rate of  $100 \text{ mV s}^{-1}$ .

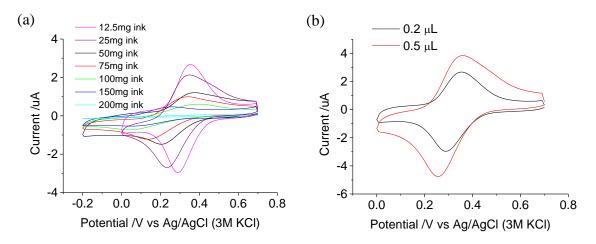


Figure S5. Cyclic voltammetry of a dielectric ink supported thin film VISE with 20 mM Na ionophore VI in 100 mM NaCl at a scan rate of 100 mV s<sup>-1</sup> (a) varying amount of dielectric ink (b) varying volume of thin film.

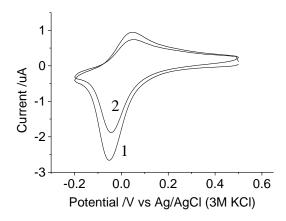


Figure S6. Cyclic voltammetry of a dielectric ink supported thin film in 100 mM NaCl at a scan rate of 100 mV s<sup>-1</sup> without ionophore. The numbers 1 and 2 refer to the first and second cycle of the potential respectively.

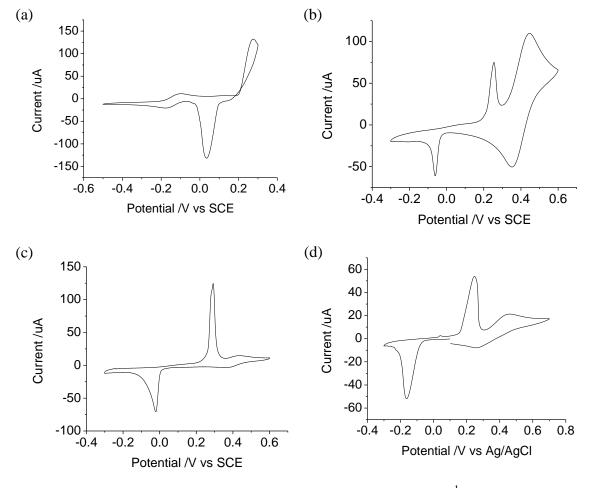


Figure S7: Voltammetry in 0.1 M NaCl at a scan rate of 100 mV s<sup>-1</sup> on an EPG electrode of mechanically adhered (a) TTF (0.5 mM 1,4-benzoquinone, 3<sup>rd</sup> potential cycle) and (b) TCNQ (0.1 M TRIS pH9 and 5 mM 1,1'-ferrocenedicarboxylic acid, 3<sup>rd</sup> potential cycle). Mechanically adhered TCNQ coated with Nafion with (c) 1 mM 1,1'-ferrocenedicarboxylic acid, 1 M NaCl, 50mM TRIS and HEPES, 12<sup>th</sup> potential cycle on an EPG electrode at a scan rate of 200 mV s<sup>-1</sup> and (d) mechanically adhered 1,1'-ferrocenedicarboxylic acid in 0.1 M NaCl, 50mM TRIS and HEPES, 1<sup>st</sup> potential cycle on a screen printed electrode at a scan rate of 100 mV s<sup>-1</sup>.

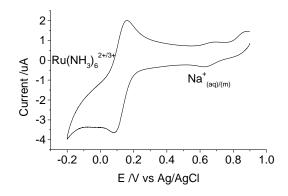


Figure S8. Calibration of a thin film VISE with 10 mM Na ionophore VI in 1 M NaCl at a scan rate of 100 mV s<sup>-1</sup> versus Ru(NH<sub>3</sub>)<sub>6</sub>Cl<sub>3</sub>.

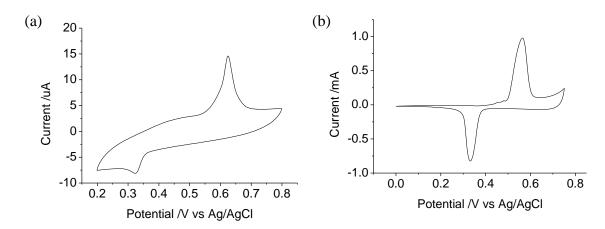


Figure S9: (a) Cyclic voltammetry at an EPG electrode of mechanically adhered TCNQ coated with Nafion at a scan rate of  $100 \text{ mV s}^{-1}$ ,  $10^{th}$  potential cycle in seawater. (b)  $6^{th}$  potential cycle of mechanically adhered TTF on an EPG electrode in seawater at a scan rate of  $100 \text{ mV s}^{-1}$ .

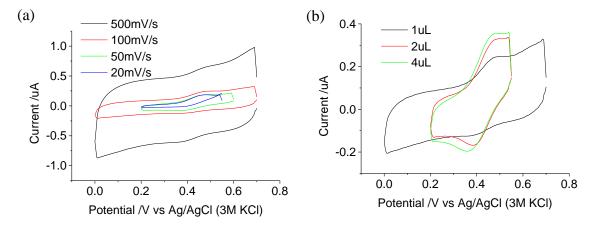


Figure S10. Cyclic voltammetry of a thin film VISE with 20mM Ca ionophore II in plasma varying (a) scan rate of 100 mV s<sup>-1</sup> with a 1  $\mu$ L thin film (b) thin film thickness at a scan rate of 100 mV s<sup>-1</sup>.

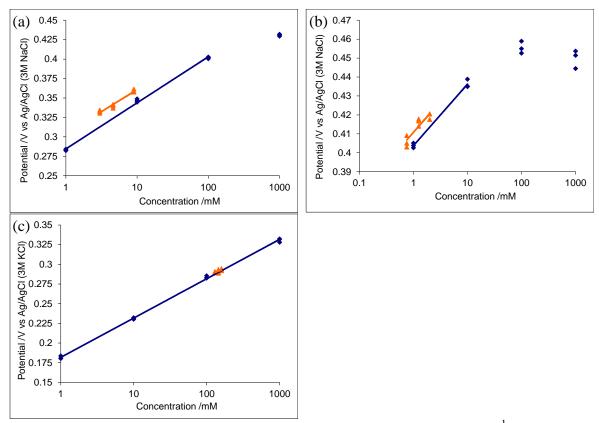


Figure S11. Sensitivity of a 0.2 μL thin film VISE at a scan rate of 100 mV s<sup>-1</sup> varying NaCl concentration in pure electrolyte (blue) or high ionic strength calibrant solutions (orange) with (a) 20 mM K ionophore III, (b) 20 mM Ca ionophore II or (c) 20 mM Na ionophore VI.