Supporting Information

Solution-Processable All-Solid-State Chloride-Selective Electrode: Enhanced Sensitivity from Anion Dopant Exchange

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1. Experimental

Materials. PEDOT-PEG, 0.8 wt% dispersion in propylene carbonate (contains ClO_4^- as dopant), high molecular weight poly(vinyl chloride) (PVC), chloride ionophore IV, tridodecylmethylammonium chloride (TDMA*Cl*), 1-(2-nitrophenoxy)octane (NPOE) and tetrahydrofuran (THF) were purchased from Sigma-Aldrich. 2-[4-(2-hydroxyethyl)piperazin-1-yl]ethanesulfonic acid (HEPES buffer) and L-histidine were purchased from TCI Chemicals. All other reagents were of the highest commercially available purity and were used as received. Aqueous solutions of salt and buffer were prepared with ultrapure water (18.2 MΩ) obtained from a PURELAB Option-Q water system. All solutions were prepared as 1M stock and used for serial dilution to prepare working standards; 1M HEPES buffer was prepared and used as-is without further pH adjustments. Carbon (C110) screen-printed electrodes (SPEs) were purchased from Metrohm Dropsens and were used as received.

Preparation of Cl^- SC-ISE. Commercially sourced PEDOT-PEG dispersion was subjected to 30 min of agitation prior to use. 3 µL of PEDOT-PEG was drop-casted onto the working electrode of C110 SPEs and dried at 60 °C for 30 min. The PEDOT-PEG-coated SPEs were immersed in 0.1 M solutions of potassium chloride (K*Cl*) for 3 days for ion exchange, thereafter the SPEs were removed, rinsed with DI water and dried under vacuum overnight. ISM cocktail was prepared by dissolving chloride ionophore IV (1.0 mg), TDMA*Cl* (0.5 mg), PVC (32.9 mg), and NPOE (65.9 mg) in THF (1 mL) for the optimal composition. For fabrication of **C1**, 10 µL of ISM was drop-casted onto the chloride-doped PEDOT-PEG SPEs and dried overnight at ambient temperature, followed by drying under vacuum for 4 h. The SC-ISEs were then conditioned in 1 mM K*Cl* solution overnight prior to use. In the case of non-conditioned use (**C5**), SC-ISEs were used as-is after drying with the omission of the ion exchange step in 0.1 M K*Cl*.

X-ray Photoelectron Spectroscopy (XPS). XPS analysis of the solid-contacts was performed using a Thermo Scientific Theta Probe XPS system with monochromatic Al Kα X-ray source (*hv* = 1486.7 eV) at 400 µm spot size. Photoelectrons were collected at a take-off angle of 50° with respect to surface normal. Wide scan spectra were acquired with pass energy of 200 eV and step size of 1 eV. Fine scans of C 1s, N 1s, S 2p and *Cl* 2p were acquired with pass energy of 40 eV at 0.1 eV step size. Combined electron/ion flooding was used for charge compensation and further charge shift correction was done based on the C-C peak of C 1s at 284.8 eV.

XPS analysis of the SC-ISEs was performed using Kratos AXIS Supra+spectrometer with monochromatic Al Kα excitation source (hv=1486.7 eV). Wide scans were acquired at pass energy of 160 eV and step size of 1 eV. Fine scans of C 1s, N 1s, S 2p and *Cl* 2p were acquired with pass energy of 20 eV and step size of 0.1 eV. Low energy neutralisation electrons were used for charge compensation and further charge shift correction was done based on peak position of adventitious C 1s at 284.8 eV.

Raman spectroscopy. Raman spectroscopy was performed using Renishaw inVia confocal Raman microscope with laser wavelength 532 nm at 50x magnification and 2400 g/mm grating. The spectra were acquired at 10 s acquisition time for 1 accumulation.

Cyclic voltammetry. Measurements were performed at room temperature using a Dropsens Potentiostat (DRP-STAT8000, Metrohm Dropsens) in a 3-electrode setup having Ag|Ag*Cl*|3M K*Cl*|1M LiOAc as the reference electrode, and platinum sheet as the counter electrode. All potentiometric measurements were performed in triplicate. The cyclic voltammagrams of PEDOT-PEG solid contacts were measured between −1.0V and +1.0 V, scan rate v = 0.05 V s^{-1}, in 0.1 M K*Cl* solution.

Open circuit potentiometry. Measurements were performed at room temperature using a Dropsens Potentiostat (DRP-STAT8000, Metrohm Dropsens) in a 2-electrode setup having Ag|Ag*Cl*|3M K*Cl*|1M LiOAc as the reference electrode. All potentiometric measurements were performed in triplicate. Sensitivity. The sensitivity and limit of detection of the SC-ISEs were evaluated by measuring the open

circuit potential in unbuffered K*Cl* solutions with concentration ranging from 0.1M to 1 nM. The measured potentials (EMF) obtained are plotted against the logarithm in base 10 of primary ion activity. The sensitivity corresponds to the change in potential per decade change in concentration and the limit of detection corresponds to the lowest concentration at which there is observable change in potential, which is defined as the point of the intersection between a linear extrapolation of the Nernstian slope, and the horizontal part of the upper curve where the EMF is a constant value.[1] Selectivity. Based on IUPAC recommendations, selectivity coefficients were similarly evaluated with unbuffered solutions using the fixed interference method (FIM).[1–3] The open circuit potential of a cell comprising an ion-selective electrode and a reference electrode is measured with potassium salt solutions of fixed interfering ion, a_B, and varying activity of the primary ion, a_{Cl}. The concentration of Cl^- ion was varied from 0.1 M to 1 nM. The concentrations of interfering species were as follow: dihydrogen phosphate ($H_2PO_4^-$) ion was 0.1 M, bicarbonate (HCO_3^-) and acetate (CH_3COO^-) ions were 10 mM, and nitrate (NO_3^-) and bromide (Br^-) ions were 0.1 mM; less interfering ions could be measured at higher fixed concentration, while more interfering ions were measured at lower fixed concentration. The EMF obtained are plotted against the logarithm in base 10 of primary ion activity. The intersection of the extrapolation of the linear regions of the plot will indicate the value of a_{Cl} which gives the same EMF value as a_B, which is used to calculate selectivity coefficient, $K_{Cl,B}^{pot}$ from the following equation:

$$\log_{10} K_{Cl,B}^{pot} = \log_{10} a_{Cl} - \frac{z_{Cl}}{z_B} \log_{10} a_B$$

pH effect. Measurements were performed in 0.1 M unbuffered K*Cl* (25 mL) spiked with increasing aliquots of concentrated H_2SO_4 or KOH added to achieve a pH range of 1 to 13, as determined by a Metrohm 913 pH meter with Solitrode (with Pt1000) pH probe.

Current reversal chronopotentiometry. Chronopotentiometry was performed using a 3-electrode setup in 1 mM aqueous K*Cl*. A current (± 10 nA) was applied to the working electrode, first positive current for 60 s, followed by negative current for 60 s, while the electrode potential was continuously recorded. The frequency independent total resistance (R_{tot}) was estimated using the equation R_{tot} = E/2i, where i was the applied current (10 nA), by measuring the potential drop (E) at current polarity change; and the low-frequency capacitance (C_{LF}) was estimated from the potential drift after current polarity change via the equation E/ t = *i*/C_{LF}.

Electrochemical Impedance Spectroscopy (EIS). EIS measurements were performed at room temperature using an Autolab Potentiostat (PGSTAT30, Metrohm Autolab). Nyquist plots were collected in the frequency range of 100 kHz to 0.1 Hz with a sinusoidal voltage signal of 100 mV. A 3-electrode setup in 1 mM aqueous K*Cl* was used. All impedance spectra were fitted to equivalent circuits using the Nova 2.1.6 software. To enhance quality of fit, some data points were removed from the high frequency region of each sample.

Preparation of Cl^- and NO_3^- SC-ISE for XPS and Raman analyses of SC-ISEs. To better observe the ion partitioning between the PEDOT-PEG solid-contact and ISM, SC-ISEs with thinner ISM and PEDOT-PEG layers were prepared for XPS surface analysis of the ISM and Raman analysis of the PEDOT_PEG layers. The preparation conditions were the same except that (a) 1 µL of PEDOT-PEG was drop-casted on in-house flexible electrodes and (b) 5 µL of the respective ISM cocktail, diluted by 4 times with THF, was drop-casted on the PEDOT-PEG layer after ion-exchange (if required) and drying. The formulation of the undiluted NO_3^- ISM was: $TDDANO_3$ (10 mg), PVC (47.6 mg), and NPOE (42.4 mg) in THF (1 mL).[4]

Synthetic sample testing. All commercial chemicals used for preparation of synthetic human samples were of the highest purity available. Three different types of synthetic human samples were

prepared: artificial human sweat and blood serum were prepared according to the International Standard Organization (ISO-3160-2-2015 and ISO-10993-15-2000 respectively) while artificial human urine was prepared base on earlier literature.[5] All synthetic human samples prepared are representative of healthy individuals and were used as stock for preparation of actual buffered samples to mimic real sample testing. All artificial human samples were diluted 10 or 100 times with 0.1 M HEPES buffer (pH 6.8). In the case of quantitative analysis of buffered samples, the SC-ISEs were calibrated using buffered K*Cl* solution between the range of 0.1 M to 1 mM and anionic concentrations were used instead of activities because it is difficult to estimate activity coefficients in zwitterionic buffers.

Real sweat sample testing. Real human sweat (forearm samples) was collected from healthy volunteers using 3M Tegaderm +Pad and extracted from the dressing film through a syringe. Four pieces of Tegaderm +Pad were attached onto the forearm of volunteers who then exercised for 1-hour. The forearm was selected for sweat collection such that only sweat which was collected in the dressing film were sampled to avoid any potential contamination (e.g. from clothing etc.). Subsequently, sweat samples collected were diluted 10 or 100 times with 0.1 M HEPES buffer (pH 6.8). In the case of quantitative analysis of buffered samples, the SC-ISEs were calibrated using buffered K*Cl* solution between the range of 0.1 M to 1 mM and anionic concentrations were used instead of activities because it is difficult to estimate activity coefficients in zwitterionic buffers.

2. Characterisation of Solid-Contact

2.1 Open circuit potentiometry of anion exchange

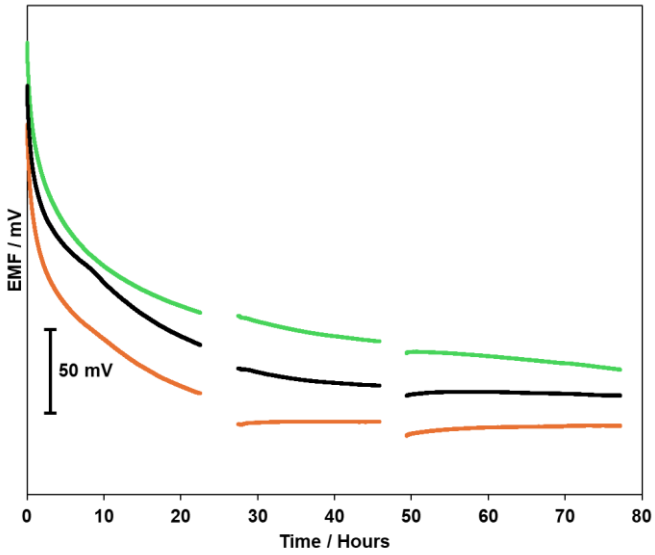

Figure S1. Open circuit potentiometry of anion exchange of **C1** replicates over 77 hours (n = 3). The curves were shifted for clarity of presentation. The experiment was stopped for 3 hours each day as the potentiostat was used for other experiments. Stabilisation of the open circuit potential between 60 to 80 hours indicate that ~ 3 days is sufficient for anion exchange.

2.2 Water Contact Angle (WCA)

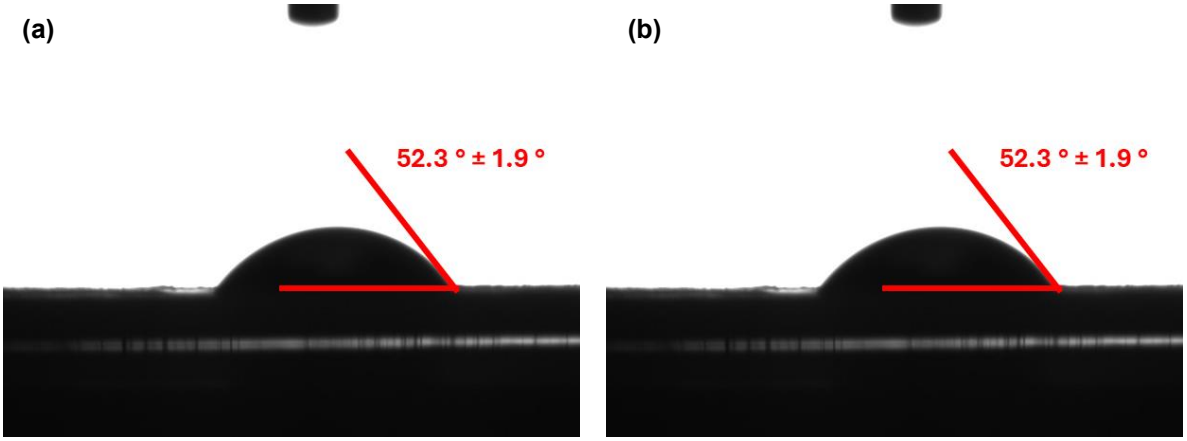

Figure S2. Representative WCA images of (a) PEDOT-PEG:*Cl* and (b) PEDOT-PEG:*Cl*O_4 solid-contacts.

2.3 Scanning Electron Microscopy (SEM)

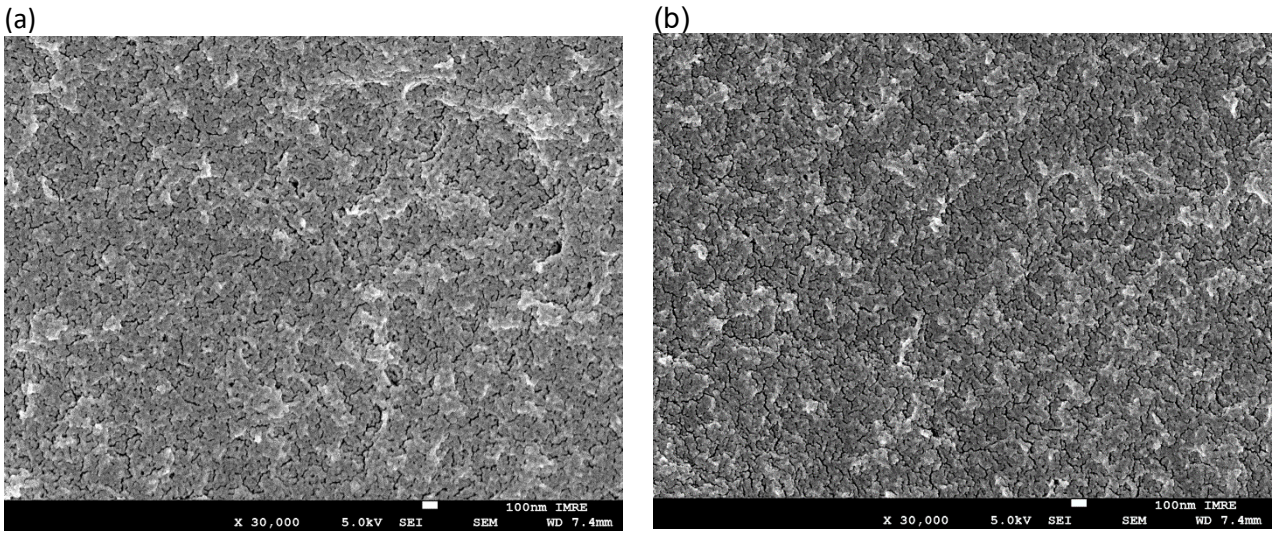

Figure S3. SEM images showing the morphology of (a) PEDOT-PEG:*Cl* and (b) PEDOT-PEG:*Cl*O_4 solid-contacts. SEM was performed using JEOL JSM6700F Field Emission Scanning Electron Microscope at 30,000x magnification.

2.4 X-ray Photoelectron Spectroscopy (XPS)

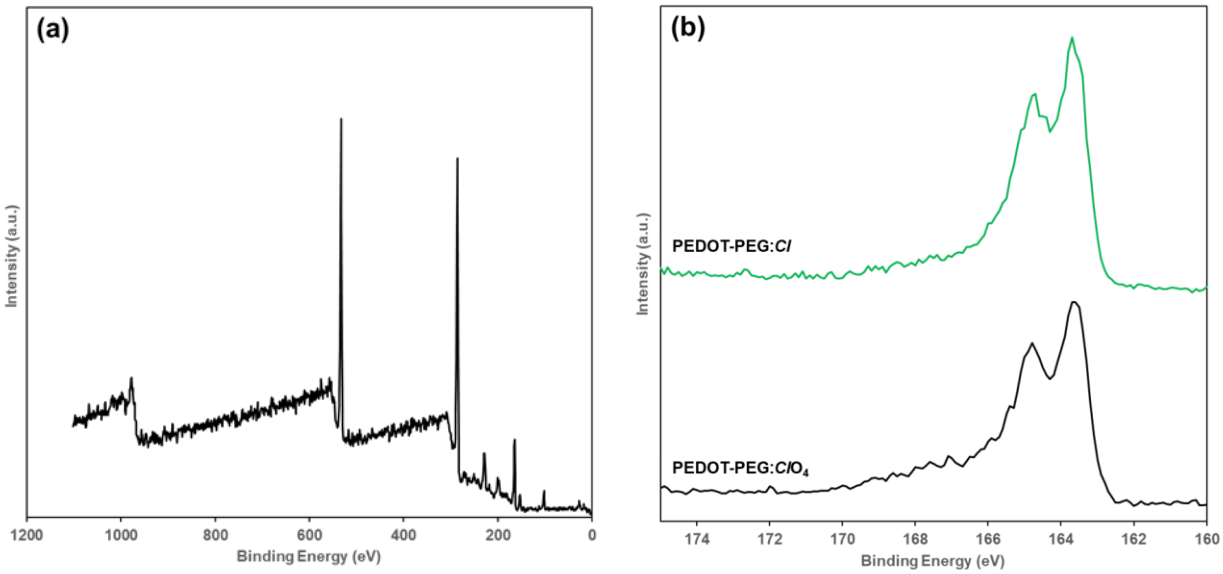

Figure S4. (a) XPS wide scan of Cl^--doped PEDOT-PEG; (b) S 2p fine scans of PEDOT-PEG solid-contacts with different dopants.

Table S1. Estimated dopant concentration of PEDOT-PEG solid-contact through XPS analysis.

SC-ISE	PEDOT-PEG dopant	Dopant at% [c]	S at% [c]	Dopant:S ratio
C1	Cl^- [a]	0.8	10.3	0.078
C4	ClO_4^- [b]	2.1	10.0	0.211

[a] Ion exchange was performed for 3 days in 0.1 M KCl solution. [b] No ion-exchange was performed. [c] Atomic percentage (at%) of dopant and sulfur element from thiophene moiety are estimated using Thermo Scientific Avantage software with Scofield sensitivity factors applied.

2.5 Cyclic Voltammetry (CV)

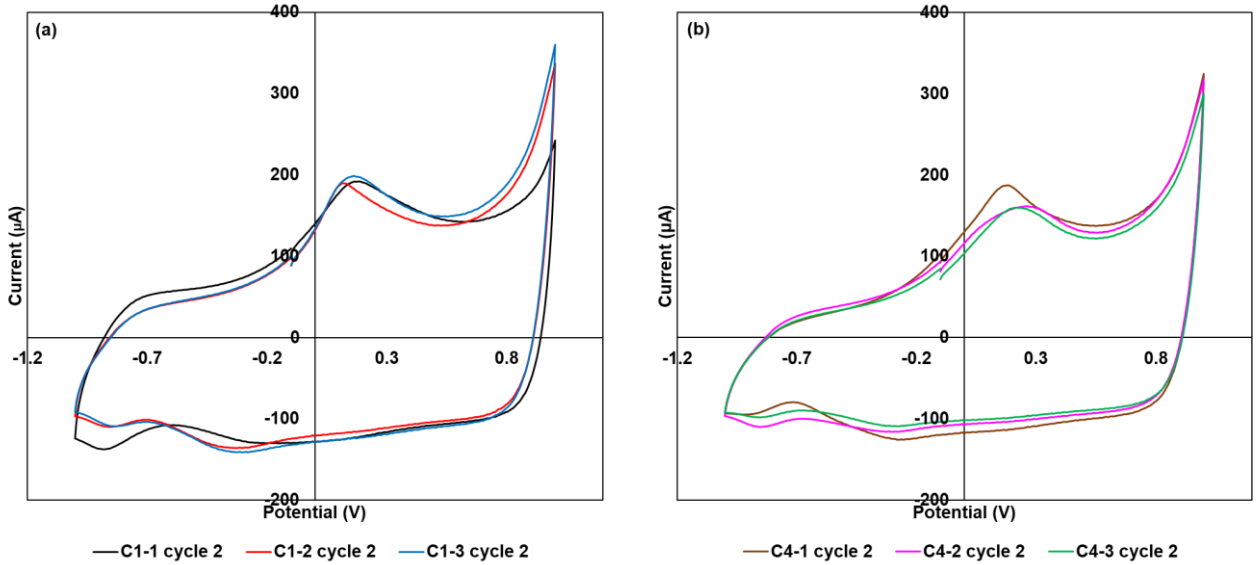

Figure S5. CV curves of (a) PEDOT-PEG:*Cl* PEDOT-PEG and (b) PEDOT-PEG:ClO_4 solid-contacts in 0.1 M K*Cl* at cycle 2 (n = 3). PEDOT-PEG:*Cl* exhibits higher capacitance than its ClO_4^--doped counterpart.

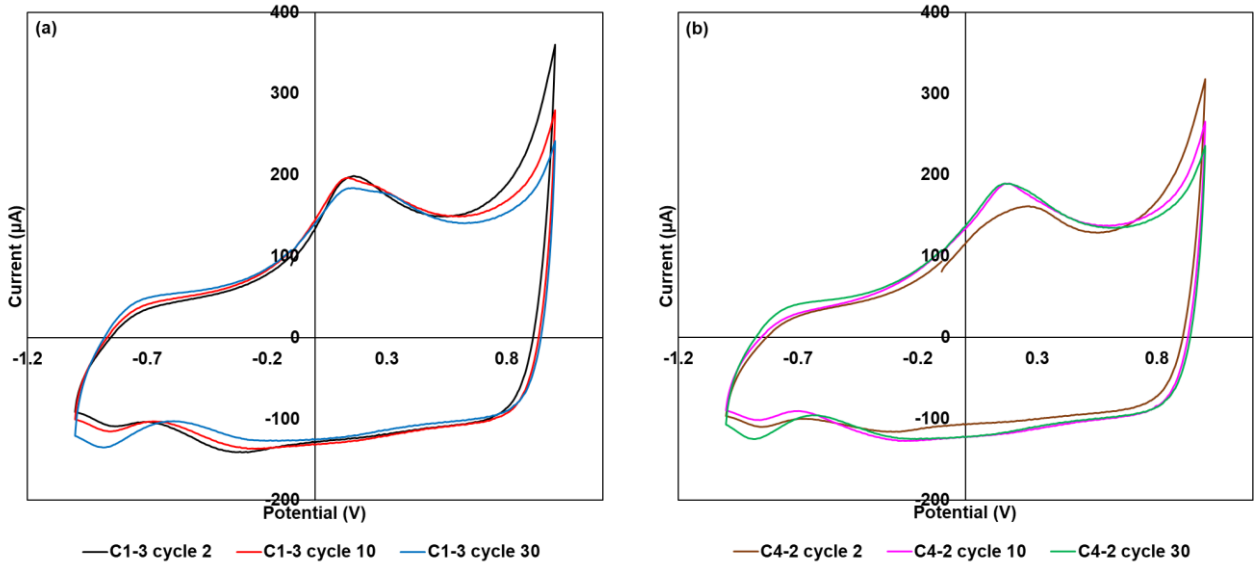

Figure S6. Representative CV curves of (a) PEDOT-PEG:*Cl* and (b) PEDOT-PEG:ClO_4 solid-contacts in 0.1 M K*Cl* at cycle 2, 10 and 30 (n = 3). The ClO_4^--doped PEDOT-PEG solid-contacts exhibited a leftwards shift in oxidation potential and an increase in current which stabilized after 10 cycles, indicating that anion exchange likely occurred.

3. Potentiometric Data

3.1 Open-Circuit Potentiometry of Anion Exchange by Soaking in KCl

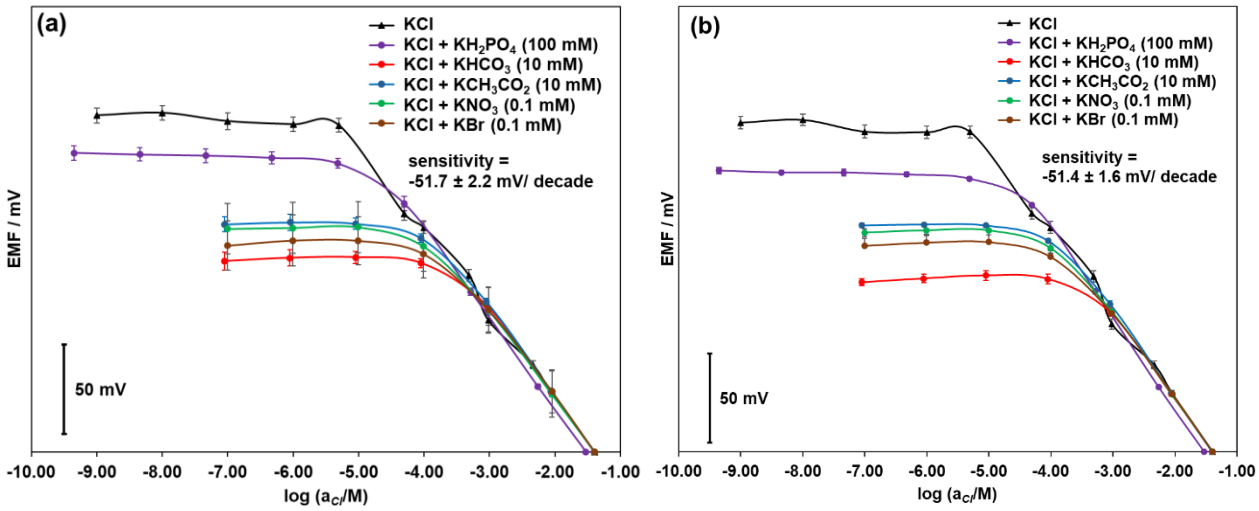

Figure S7. Potentiometric response of (a) **C2** and (b) **C3** towards Cl^- anion in pure (black) and mixed solutions containing fixed amounts of interfering ions.

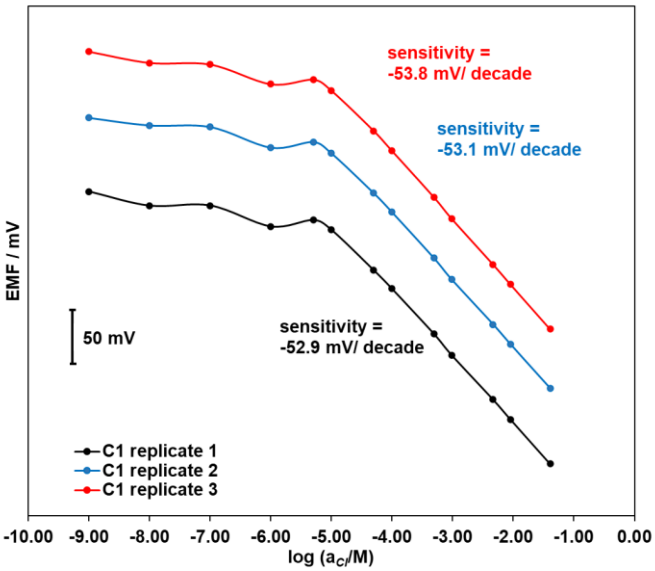

Figure S8. Reproducibility of SC-ISE **C1** replicates (n = 3). The replicates are shifted up and down for clarity of presentation.

Table S2. Potentiometric Performance and Selectivity Coefficients of chloride SC-ISE

SC-ISE	Ionophore wt%	PEDOT-PEG dopant	sensitivity/ mV dec^{-1}	LOD[d] / $\log_{10}(a_{Cl}$/ M)	$\log_{10} K_{Cl,H2PO4}$	$\log_{10} K_{Cl,HCO3}$	$\log_{10} K_{Cl,CH3CO2}$	$\log_{10} K_{Cl,NO3}$	$\log_{10} K_{Cl,Br}$
C1 [a]	1	Cl^-	-53.3 ± 0.5	-5.22 ± 0.05	-3.78 ± 0.14	-1.55 ± 0.08	-1.98 ± 0.15	0.50 ± 0.11	0.59 ± 0.10
C2 [a]	3	Cl^-	-51.7 ± 2.2	-5.01 ± 0.08	-3.63 ± 0.07	-1.49 ± 0.10	-1.88 ± 0.08	0.17 ± 0.27	0.33 ± 0.27
C3 [a]	5	Cl^-	-51.4 ± 1.6	-4.95 ± 0.07	-3.45 ± 0.03	-1.29 ± 0.04	-1.87 ± 0.02	0.19 ± 0.04	0.22 ± 0.08
C4 [a]	1	ClO_4^-	-33.4 ± 1.8	-4.46 ± 0.28	N.D. [c]	-1.43 ± 0.12	-2.07 ± 0.09	0.44 ± 0.09	0.46 ± 0.08
CV1 [b]	1	Cl^-	-48.8 ± 2.4	-5.11 ± 0.26	-3.48 ± 0.27	-1.41 ± 0.31	-2.00 ± 0.19	0.66 ± 0.01	0.60 ± 0.08
C5 [c]	1	Cl^-	-51.4 ± 0.9	-5.06 ± 0.11	-3.70 ± 0.23	-1.71 ± 0.12	-2.42 ± 0.37	0.42 ± 0.03	0.57 ± 0.04
C6 [d]	1	ClO_4^-	-22.0 ± 1.0	-3.32 ± 0.15	N.D. [c]	-0.85 ± 0.17	N.D. [c]	N.D. [c]	N.D. [c]

[a] SC-ISE was conditioned for overnight in 1 mM K*Cl* prior to use; [b] Anion exchange was performed by cyclic voltammetry; [c] SC-ISE was not conditioned prior to use; [d] N.D. = not determined; selectivity coefficient for these anions could not be determined via fixed interference method due to poor sub-Nernstian slope; [d] LOD = limit of detection.

3.2 Open-Circuit Potentiometry of Anion Exchange by Cyclic Voltammetry (**CV1**)

To investigate the effect of anion exchange by cyclic voltammetry, the PEDOT-PEG:ClO_4 solid-contacts were first subjected to 30 CV cycles (see SI Section 2.5), then rinsed and dried under vacuum. The solid-contacts were then coated with the same *Cl*-ISM formulation as in **C1**. These ISEs are denoted as **CV1**. Their potentiometric response demonstrated improved sensitivity over the unexchanged **C4**, but still could not match the optimized **C1**.

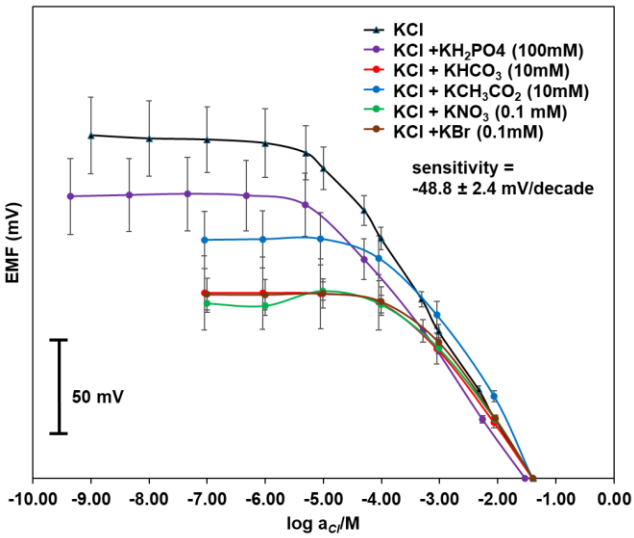

Figure S9. Potentiometric response of **CV1** towards Cl^- anion in pure (black) and mixed solutions containing fixed amounts of interfering ions (n = 3).

3.3 Open-Circuit Potentiometry of Coated Wire Electrode (*CWE Cl*)

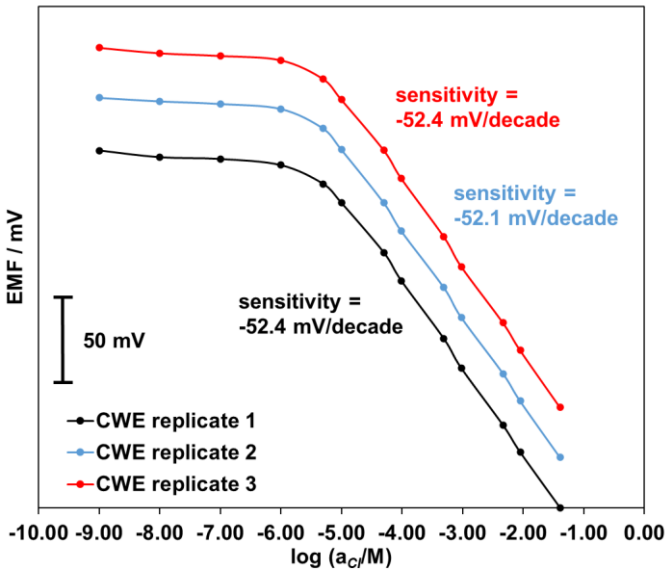

Figure S10. Sensitivity response of *CWE Cl* replicates towards Cl^- anion (n = 3). The replicates are shifted up and down for clarity of presentation.

3.4 pH Test

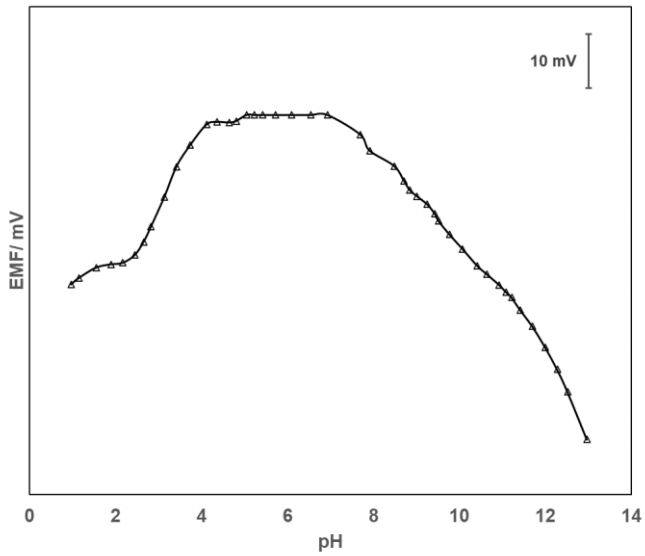

Figure S11. Effect of pH on the response of **C1**.

3.5 Aqueous Layer Test

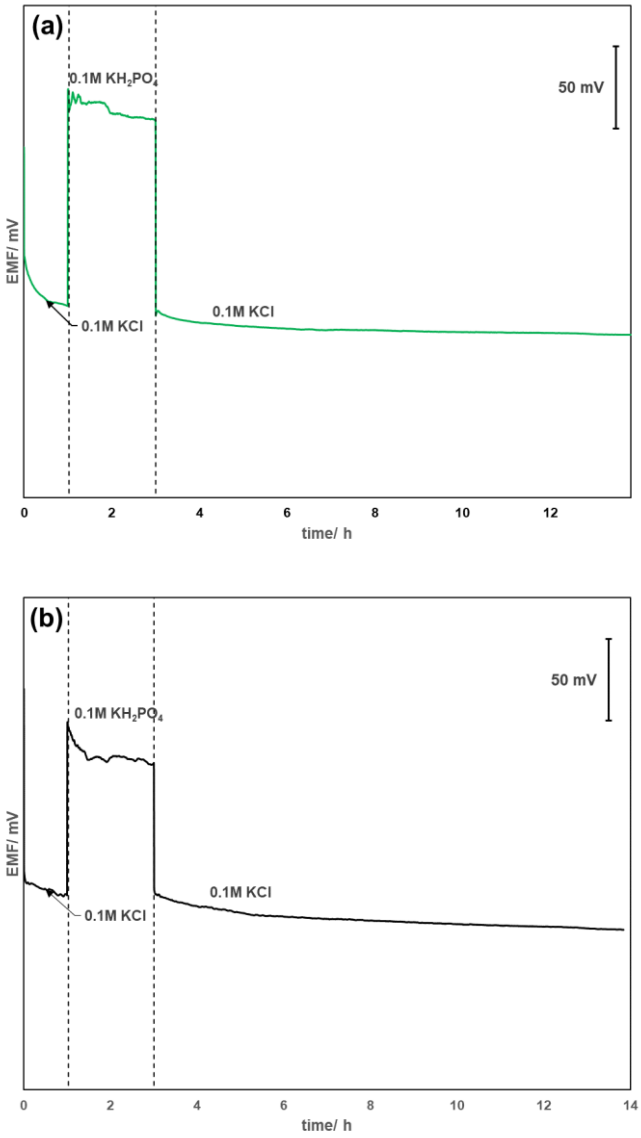

Figure S12. Aqueous layer test of (a) **C1** and (b) **C4**.

3.6 Lifespan Testing

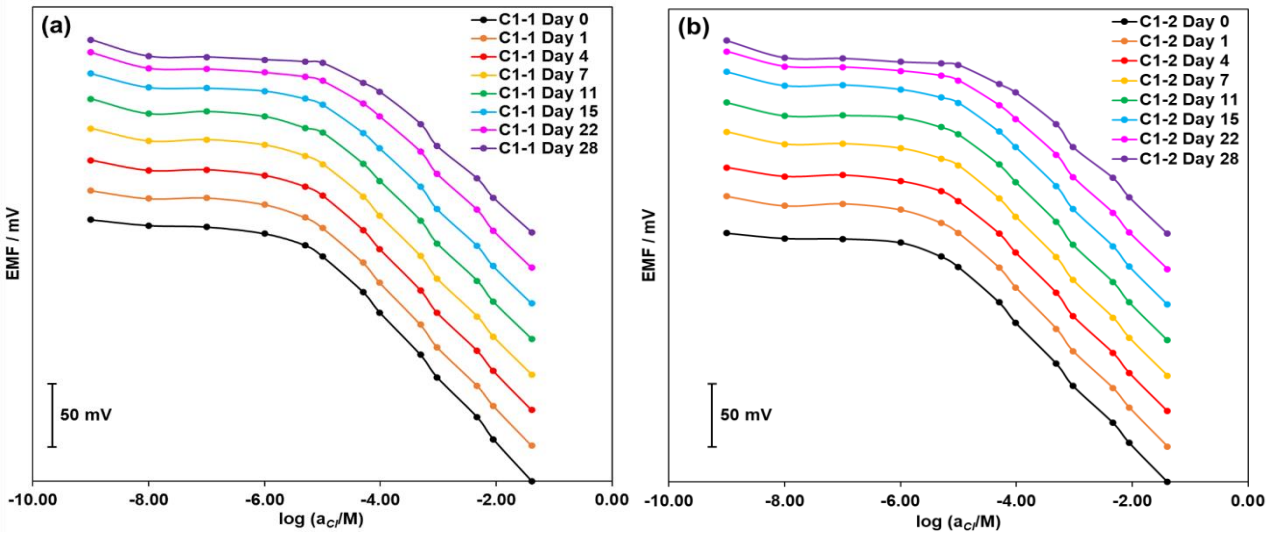

Figure S13. Lifespan testing of **C1** over a period of 28 days. Curves show sensitivity response towards Cl^- anion for replicates (a) **C1**-1 and (b) **C1**-2. The curves are shifted up and down for clarity of presentation.

4. Electrochemical Characterization

4.1 Current Reversal Chronopotentiometry

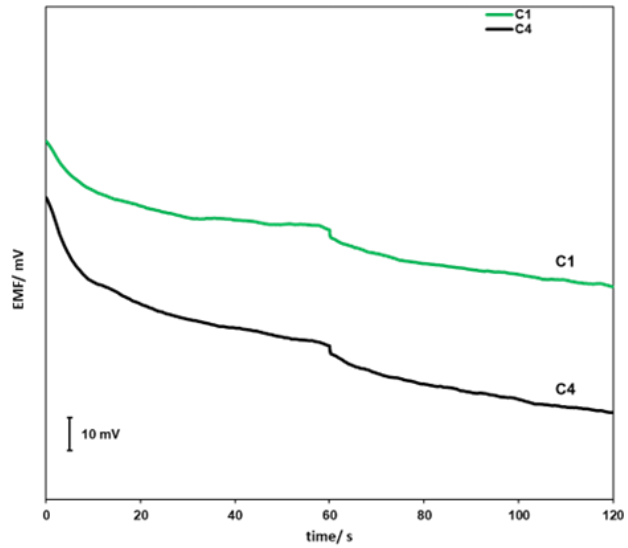

Figure S14. Current reversal chronopotentiograms of **C1** and **C4**.

Table S3. Electrical parameters of SC-ISEs **C1** and **C4** as determined by current reversal chronopotentiometry.

SC-ISE	R_{total} (kΩ)	ΔE / Δt (mV/s)	C_{LF} (μF)
C1	54.76	0.1961	50.99
C4	38.10	0.2482	40.29

4.2 Electrochemical Impedance Spectroscopy (EIS) of Cl-ISE

Table S4. Equivalent circuit values for the impedance data of CWE *Cl* and **C1** and **C4** doped with Cl^- and ClO_4^-, respectively.

SC-ISE	R1	CPE1 [a]		R2	CPE2 [a]		CPE3 [b]	
	R (Ω)	Y (Ω^{-1} s^n)	n	R (Ω)	Y (Ω^{-1} s^n)	n	Y (Ω^{-1} s^n)	n
CWE *Cl*	51206	1.30×10^{-8}	0.81	109750	4.70×10^{-6}	0.73	4.21×10^{-6}	0.46
C1	62008	2.52×10^{-8}	0.68	-	8.83×10^{-6}	0.46	-	-
C4	80791	4.47×10^{-10}	0.92	1268400	1.18×10^{-5}	0.51	-	-

[a] Y and n refer to constant phase element (CPE) magnitude and exponent components respectively. [b] The Warburg element (Z_w) is fitted as CPE for CWE *Cl*.

5. Investigating the Effect of Anion Dopant Exchange

5.1 Improvement in selectivity for NO_3^- SC-ISE[4]

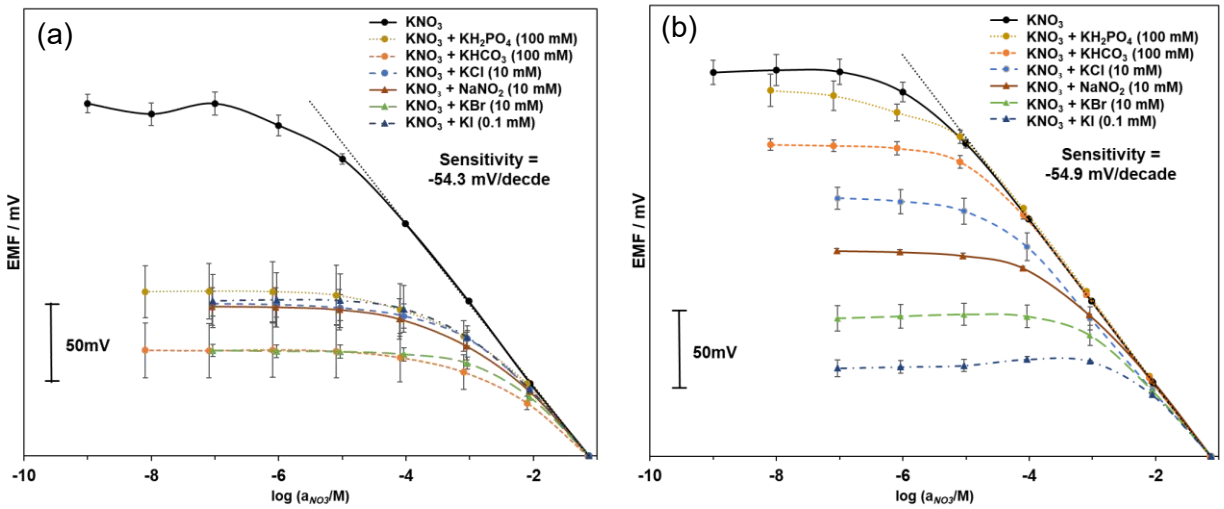

Figure S15. Potentiometric response of NO_3^- SC-ISE with PEDOT-PEG transduction layer towards NO_3^- anion in pure (black) and mixed solutions containing fixed amounts of interfering ions: (a) with ClO_4^- as dopant (without anion exchange) and (b) NO_3^- as dopant (after anion exchange). This demonstrates that anion exchange improved selectivity in this system where no ionophore was used in the ISM.[4]

5.2 Electrochemical Impedance Spectroscopy (EIS) of NO_3^- SC-ISE[4]

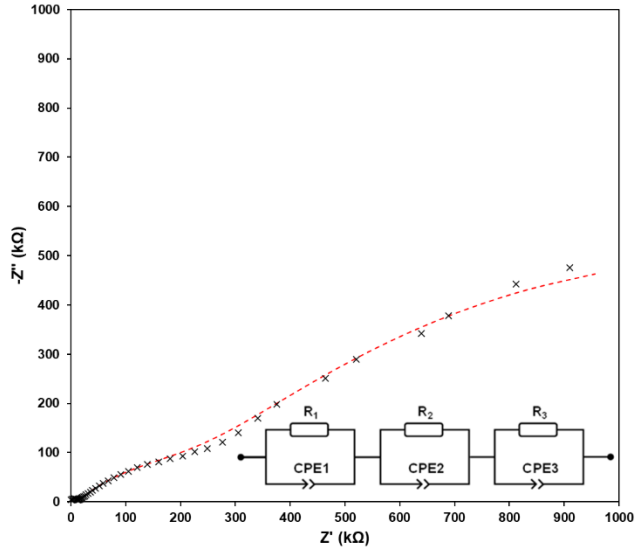

Figure S16. Nyquist plots and fitted impedance spectrum of NO_3^- SC-ISE with PEDOT-PEG transduction layer with ClO_4^- as dopant (without anion exchange). The equivalent circuits used for fitting impedance data are shown in the spectrum. Frequency range: 100 kHz to 1 mHz; amplitude potential: 100 mV; solution: 1 mM KNO_3.[4]

5.3 XPS Measurements on ISM surface in SC-ISEs

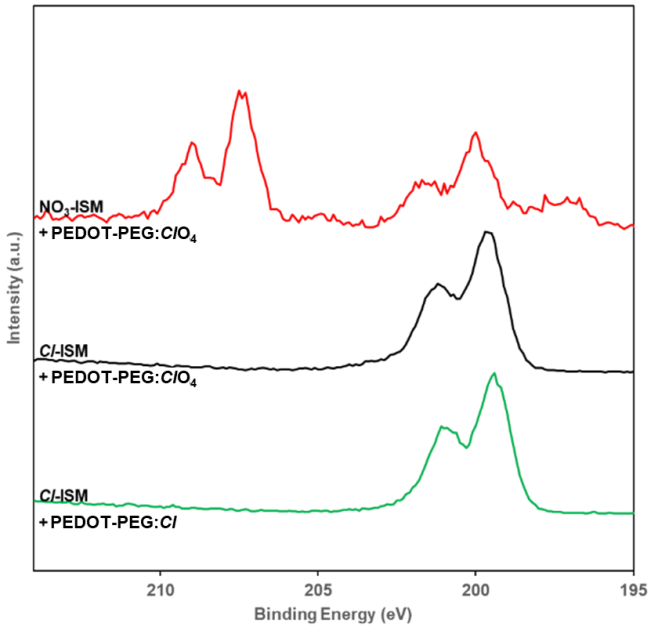

Figure S17. *Cl* 2p fine scans of surface of NO_3^- and Cl^- ISM on PEDOT-PEG solid-contacts with different dopants.

5.4 Raman measurements of PEDOT-PEG layer in SC-ISEs

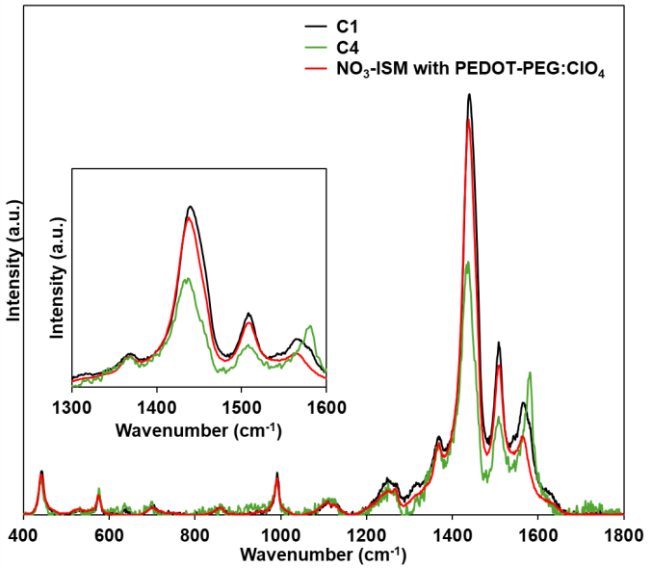

Figure S18. Normalized Raman spectra (532 nm) of PEDOT-PEG layers in SC-ISEs.

6. Real Sample Quantification

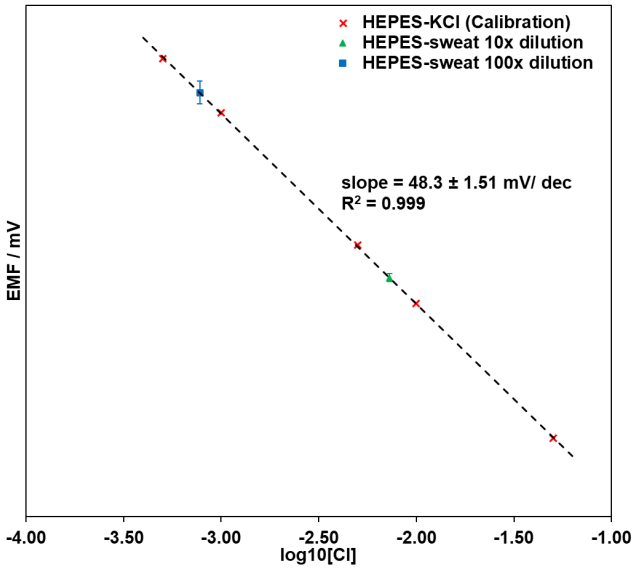

Figure S19. Calibration (×) and quantification of real human sweat at 10-times dilution (▲) and 100-times dilution (■) using **C1**. All samples and standards were buffered with 100 mM HEPES, pH 6.8.

7. References

[1] R.P. Buck, E. Lindner, Recomendations for nomenclature of ion-selective electrodes (IUPAC recommendations 1994), Pure Appl. Chem. 66 (1994) 2527–2536. https://doi.org/10.1351/pac199466122527.

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