Supporting Information

Quantitative Analysis of Redox-Inactive Ions by AC Voltammetry at a Polarised Interface between Two Immiscible Electrolyte Solutions

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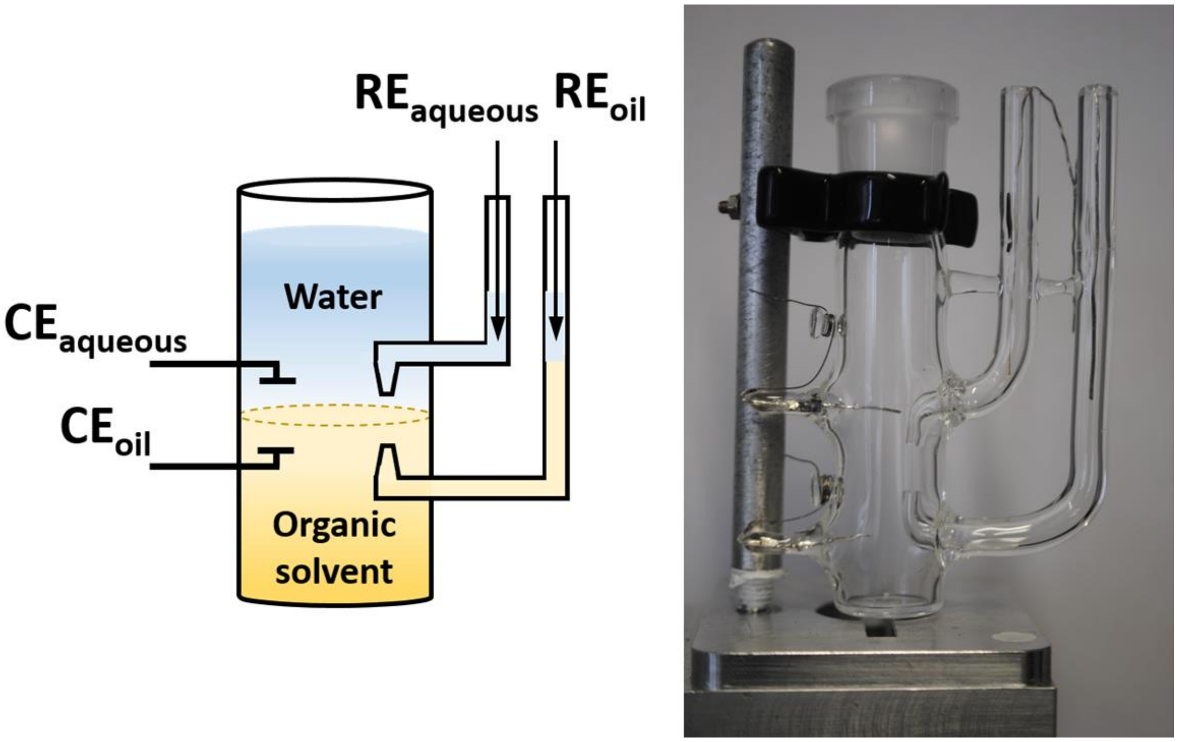

Figure S1. Schematic and image of the glassware of a four-electrode electrochemical cell. The aqueous and organic counter electrodes (CE) are platinum wires and the aqueous and organic reference electrodes (RE) are Ag/AgCl wires. The liquid-liquid interface is always situated mid-way between the two Luggin capillaries. The organic phase is a halogenated solvent (either α,α,α-trifluorotoluene or 1,2-dichloroethane) with a greater density than water and therefore is the bottom layer.

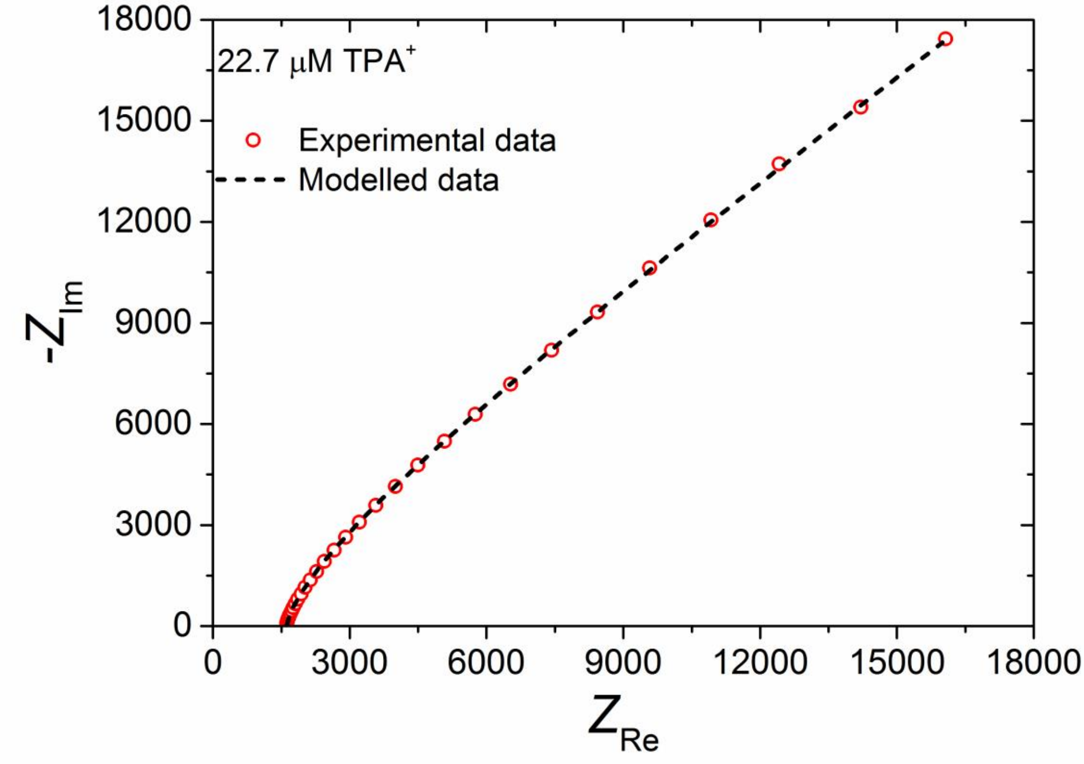

Figure S2. Representative EIS spectrum obtained at the formal ion transfer potential of TPA^+ ($\Delta_o^w \phi_{TPA^+}^{\ominus',w\to o} = 0.013$ V). The dashed black line is the fitting using the equivalent circuit shown in Scheme 2. The red hollow circles show the experimental data. The concentration of TPA^+ in the aqueous phase was 22.7 μM. The configuration of the four-electrode electrochemical cell was as described in Scheme 1 with TFT as the organic solvent. The AC amplitude was 10 mV and the frequency range was between 0.1 and 300 Hz.

Table S1. EIS parameters determined at the formal ion transfer potentials ($\Delta_{\mathbf{o}}^{\mathbf{w}}\boldsymbol{\phi}_{\boldsymbol{i}}^{\ominus',\mathbf{w}\rightarrow\mathbf{o}}$) of either TPA^{+} or TMA^{+}, respectively, using the equivalent circuit shown in Scheme 2. The configuration of the four-electrode electrochemical cell was as described in Scheme 1 with increasing concentrations of either TPA^{+} or TMA^{+} in the aqueous phase and TFT as the organic solvent. The AC amplitude was 10 mV and the frequency range was between 0.1 and 300 Hz.

Circuit		$\Delta_{\mathbf{o}}^{\mathbf{w}}\boldsymbol{\phi}_{\mathbf{TPA^+}}^{\ominus',\mathbf{w}\rightarrow\mathbf{o}} = \mathbf{0.013\ V}$		$\Delta_{\mathbf{o}}^{\mathbf{w}}\boldsymbol{\phi}_{\mathbf{TMA^+}}^{\ominus',\mathbf{w}\rightarrow\mathbf{o}} = \mathbf{0.311\ V}$	
Element	*Parameter*	*Value*	*Estimated error (%)*	*Value*	*Estimated error (%)*
		6.7 μM TPA^{+}		**7.7 μM TMA^{+}**	
R_s	R_s (Ohms)	1000	0.829	1005	0.525
Z_C	C_d (μF)	9.03	1.042	21.6	0.88
Z_W	Y_0 (μS·$s^{1/2}$)	10.9	1.961	23.1	1.591
	χ^2	0.026094		0.013405	
		13.4 μM TPA^{+}		**15.2 μM TMA^{+}**	
R_s	R_s (Ohms)	1015	0.726	1012.4	0.42
Z_C	C_d (μF)	9.11	1.055	22.1	0.813
Z_W	Y_0 (μS·$s^{1/2}$)	16.7	1.413	33.9	1.07
	χ^2	0.020002		0.0085269	
		20.0 μM TPA^{+}		**22.7 μM TMA^{+}**	
R_s	R_s (Ohms)	1019.1	0.43	1017.6	0.232
Z_C	C_d (μF)	9.23	0.772	22.6	0.551
Z_W	Y_0 (μS·$s^{1/2}$)	27.2	0.693	51.8	0.505
	χ^2	0.0068387		0.0025479	
		26.5 μM TPA^{+}		**30.1 μM TMA^{+}**	
R_s	R_s (Ohms)	1023	0.309	1023.4	0.152
Z_C	C_d (μF)	9.50	0.665	23.4	0.437
Z_W	Y_0 (μS·$s^{1/2}$)	37.8	0.456	71.8	0.303
	χ^2	0.0034618		0.0010638	

Table S2. Experimental data obtained in the absence of TPA^+ and TMA^+ in the aqueous phase (see Figure 2a, main text). The frequency used to obtain the AC voltammograms was 1 Hz. The configuration of the four-electrode electrochemical cell was as described in Scheme 1 with TFT as the organic solvent. The interfacial area (A) was 1.60 cm^2.

Raw experimental data from AC voltammetry experiment							
ω (rad s^{-1})	Freq. (Hz)	Z_{Re} (Ω)	$-Z_{Im}$ (Ω)	Z (Ω)	E (DC) (V)	$\Delta_o^w\phi$ (V)	C_d (μF·cm^{-2})
6.28318531	1	2350.1162	3156.87734	3935.59662	0.150989517	-0.280010483	31.5095674
6.28318531	1	2458.29089	3516.65622	4290.69518	0.161228157	-0.269771843	28.2859151
6.28318531	1	2206.82913	4016.55496	4582.88213	0.170536019	-0.260463981	24.765462
6.28318531	1	2180.14273	4535.31936	5032.11129	0.180711032	-0.250288968	21.9327089
6.28318531	1	2105.1681	4930.3498	5360.9777	0.190596212	-0.240403788	20.1754122
6.28318531	1	2030.42686	5308.83541	5683.86898	0.20073441	-0.23026559	18.7370359
6.28318531	1	1986.01582	6023.91643	6342.85645	0.210596237	-0.220403763	16.5128186
6.28318531	1	1832.1074	6248.40263	6511.4632	0.220672258	-0.210327742	15.919563
6.28318531	1	1834.8688	6784.945	7028.67144	0.230513628	-0.200486372	14.66067
6.28318531	1	1828.90879	7316.24764	7541.37832	0.240604261	-0.190395739	13.5960187
6.28318531	1	1796.29964	7854.69336	8057.4748	0.250782499	-0.180217501	12.6640004
6.28318531	1	1810.14326	8485.74513	8676.66347	0.260837909	-0.170162091	11.722228
6.28318531	1	1887.17278	9060.40694	9254.85792	0.27064116	-0.16035884	10.9787386
6.28318531	1	1775.85687	9827.65761	9986.81739	0.280696321	-0.150303679	10.1216224
6.28318531	1	1799.25116	10681.8341	10832.3074	0.290598224	-0.140401776	9.31224346
6.28318531	1	1885.21486	11514.6583	11667.9643	0.300596683	-0.130403317	8.63871393
6.28318531	1	1750.49273	12599.6668	12720.685	0.310481694	-0.120518306	7.89479923
6.28318531	1	1825.54294	13611.5513	13733.4241	0.320457874	-0.110542126	7.30789878
6.28318531	1	1841.31194	14932.1788	15045.2781	0.330707655	-0.100292345	6.66157571
6.28318531	1	1892.58736	16275.3993	16385.0697	0.340382603	-0.090617397	6.11179103
6.28318531	1	2035.11833	17445.1707	17563.476	0.350592697	-0.080407303	5.70196996
6.28318531	1	1918.47857	18795.1651	18892.8238	0.360559783	-0.070440217	5.29241638
6.28318531	1	1985.47371	19759.8051	19859.3052	0.370404986	-0.060595014	5.03404961
6.28318531	1	1964.24043	20305.6184	20400.4014	0.380341302	-0.050658698	4.8987348
6.28318531	1	1803.61851	20448.5563	20527.9443	0.390463578	-0.040536422	4.86449203
6.28318531	1	1751.43322	20325.7628	20401.0821	0.400372911	-0.030627089	4.89387977
6.28318531	1	1707.07832	19756.0181	19829.6335	0.410509962	-0.020490038	5.0350146
6.28318531	1	1732.49226	19033.8751	19112.5595	0.420537879	-0.010462121	5.22604245
6.28318531	1	1693.9109	18157.463	18236.3044	0.43033969	-0.00066031	5.47828953
6.28318531	1	1657.23106	17255.1673	17334.567	0.440695225	0.009695225	5.7647566
6.28318531	1	1662.88649	16407.211	16491.2633	0.450448926	0.019448926	6.06269032
6.28318531	1	1654.99145	15584.8717	15672.4989	0.460461631	0.029461631	6.38258957
6.28318531	1	1655.1854	14884.4281	14976.1757	0.470509459	0.039509459	6.68294668
6.28318531	1	1620.87916	14197.0759	14289.3041	0.480486415	0.049486415	7.00650192
6.28318531	1	1604.32314	13560.7321	13655.3033	0.49048443	0.05948443	7.33528535

6.28318531	1	1594.56406	12979.0866	13076.671	0.500375822	0.069375822	7.6640092
6.28318531	1	1614.64544	12465.6387	12569.7744	0.510333527	0.079333527	7.97968252
6.28318531	1	1640.17868	11964.1838	12076.0872	0.520514541	0.089514541	8.31413499
6.28318531	1	1604.53441	11567.6024	11678.3541	0.530097237	0.099097237	8.59917519
6.28318531	1	1584.44526	11153.5646	11265.5434	0.540258219	0.109258219	8.91839008
6.28318531	1	1663.07145	10823.9316	10950.9498	0.550142257	0.119142257	9.18999149
6.28318531	1	1624.1299	10502.3824	10627.2214	0.560265438	0.129265438	9.47135952
6.28318531	1	1606.94586	10178.7851	10304.8504	0.570297429	0.139297429	9.7724668
6.28318531	1	1618.69585	9909.08357	10040.424	0.580400501	0.149400501	10.0384499
6.28318531	1	1618.93673	9630.34034	9765.47035	0.590401822	0.159401822	10.3290056
6.28318531	1	1607.14674	9396.66054	9533.10809	0.600183631	0.169183631	10.5858713
6.28318531	1	1632.3807	9195.8256	9339.58646	0.610165225	0.179165225	10.8170646
6.28318531	1	1648.64093	8946.14789	9096.78949	0.620201035	0.189201035	11.1189576
6.28318531	1	1646.12444	8797.7747	8950.45057	0.63017113	0.19917113	11.3064772
6.28318531	1	1677.55031	8617.30138	8779.06931	0.640204574	0.209204574	11.5432703
6.28318531	1	1659.28983	8421.53179	8583.43989	0.650186927	0.219186927	11.8116089
6.28318531	1	1674.93307	8303.77642	8471.0155	0.660242463	0.229242463	11.9791086
6.28318531	1	1669.29493	8108.1824	8278.23456	0.670193843	0.239193843	12.2680811
6.28318531	1	1682.59758	7959.08291	8134.9945	0.680217934	0.249217934	12.4979021
6.28318531	1	1694.55327	7786.86822	7969.11711	0.690115026	0.259115026	12.7743063
6.28318531	1	1693.54948	7710.77886	7894.56905	0.700261861	0.269261861	12.9003621
6.28318531	1	1689.33663	7509.81512	7697.4789	0.710127162	0.279127162	13.2455777
6.28318531	1	1713.78829	7370.26473	7566.89318	0.72040682	0.28940682	13.4963727
6.28318531	1	1720.9325	7378.76514	7576.79244	0.73053839	0.29953839	13.4808247
6.28318531	1	1680.95555	7048.38373	7246.05581	0.740307447	0.309307447	14.1127162
6.28318531	1	1763.22084	6939.14023	7159.65186	0.75016545	0.31916545	14.334894
6.28318531	1	1747.64642	6761.35282	6983.56355	0.760231174	0.329231174	14.711825
6.28318531	1	1757.22801	6580.21447	6810.80558	0.770031084	0.339031084	15.1168081
6.28318531	1	1673.0038	6314.55576	6532.42345	0.780068915	0.349068915	15.752785
6.28318531	1	1808.00097	6239.73594	6496.39686	0.790124043	0.359124043	15.9416745
6.28318531	1	1848.02608	6013.23106	6290.79869	0.800082264	0.369082264	16.5421615
6.28318531	1	1862.87109	6117.61443	6394.95856	0.810073706	0.379073706	16.2599066
6.28318531	1	1915.40376	5726.46333	6038.3072	0.819971321	0.388971321	17.3705538
6.28318531	1	1967.72616	5598.32954	5934.07447	0.829949748	0.398949748	17.7681286
6.28318531	1	1806.29951	5417.38485	5710.58461	0.840138938	0.409138938	18.3615974
6.28318531	1	1917.91359	5083.18401	5432.96901	0.849911846	0.418911846	19.5688055
6.28318531	1	1912.28673	5397.65817	5726.39103	0.86005932	0.42905932	18.428703
6.28318531	1	1906.27354	4736.17784	5105.4147	0.87012302	0.43912302	21.0025558
6.28318531	1	1959.68377	4521.75409	4928.14575	0.879934866	0.448934866	21.9985071
6.28318531	1	1953.35654	4464.27429	4872.91973	0.889986601	0.458986601	22.281749
6.28318531	1	1926.15592	4096.55514	4526.79143	0.899752857	0.468752857	24.2818261

Conversion of "E (DC) (V)", *i.e.*, the applied potential *versus* Ag/AgCl in the four-electrode electrochemical cell, to the Galvani scale ($\Delta_{o}^{w}\phi$ (V)). The standard ion transfer potential of TMA^{+} from water to TFT ($\Delta_{o}^{w}\phi_{tr.}^{\ominus,w\rightarrow TFT}(TMA^{+})$) is 0.311 V (see reference 26 in main text). Herein, TMA^{+} was added to the aqueous phase and acted as a "secondary" reference ion for the calibration of the polarisable potential window to the Galvani potential scale using the following relationship between the applied potential (E), the Galvani potential difference ($\Delta_{o}^{w}\phi$), the experimentally measured half-wave potential of TMA^{+} ($E_{1/2}^{w\rightarrow TFT}(TMA^{+})$) and the standard ion transfer potential of TMA^{+} ($\Delta_{o}^{w}\phi_{tr.}^{\ominus,w\rightarrow TFT}(TMA^{+})$):

$$\Delta_{o}^{w}\phi - \Delta_{o}^{w}\phi_{tr.}^{\ominus,w\rightarrow TFT}(TMA^{+}) = E - E_{1/2}^{w\rightarrow TFT}(TMA^{+}) \qquad (S1)$$

Re-arranging Equation (S1) we get:

$$\Delta_{o}^{w}\phi = E - [E_{1/2}^{w\rightarrow TFT}(TMA^{+}) - \Delta_{o}^{w}\phi_{tr.}^{\ominus,w\rightarrow TFT}(TMA^{+})] \qquad (S2)$$

This can be further simplified to:

$$\Delta_{o}^{w}\phi = E - \Delta E_{ref.} \qquad (S3)$$

Herein, $E_{1/2}^{w\rightarrow TFT}(TMA^{+})$ was measured as 0.742 V using our experimental setup at the and, thus, $\Delta E_{ref.}$ was determined as 0.431 V.

Determining the double-layer capacitance, C_{d}. The latter, in units of $\mu F\cdot cm^{-2}$, is determined by the following relationship:, where $A = 1.60\ cm^{2}$.

$$C_{d} = -\frac{10^{6}}{\omega Z_{Im} A} \qquad (S4)$$

Table S3. Experimental data obtained in the presence of 22.7 μM TPA^+ and 25.9 μM TMA^+ in the aqueous phase (see Figures 2b & 3a, main text). The frequency used to obtain the AC voltammograms was 1 Hz. The configuration of the four-electrode electrochemical cell was as described in Scheme 1 with TFT as the organic solvent. The interfacial area (*A*) was 1.60 cm^2.

Raw experimental data from AC voltammetry experiment								
ω (rad s^{-1})	Freq. (Hz)	Z_{Re} (Ω)	$-Z_{Im}$ (Ω)	Z (Ω)	E (DC) (V)	$\Delta_o^w\phi$ **(V)**	γ **(μF·cm^{-2})**	**Analytical Signal (μF·cm^{-2})**
6.28319	1	2317.32	3306.73	4037.87	0.1513	-0.2797	30.08161088	-1.427956516
6.28319	1	2230.14	3756.61	4368.71	0.161071	-0.269929	26.47913016	-1.806784965
6.28319	1	2144.91	4175.7	4694.37	0.170949	-0.260051	23.82157845	-0.943883578
6.28319	1	2062.19	4591.94	5033.74	0.181165	-0.249835	21.6622528	-0.270456114
6.28319	1	1989.64	4998.49	5379.92	0.190902	-0.240098	19.90036294	-0.275049246
6.28319	1	1927.04	5410.16	5743.11	0.201086	-0.229914	18.38610413	-0.350931738
6.28319	1	1875.13	5825.93	6120.26	0.210763	-0.220237	17.0739719	0.561153269
6.28319	1	1835.65	6263.57	6527.01	0.220867	-0.210133	15.88100159	-0.038561425
6.28319	1	1808.56	6713.38	6952.72	0.230788	-0.200212	14.81694245	0.156272486
6.28319	1	1787.09	7193.17	7411.84	0.240897	-0.190103	13.82864094	0.232622287
6.28319	1	1779.82	7692.32	7895.54	0.250827	-0.180173	12.93130878	0.267308425
6.28319	1	1787.45	8226.23	8418.18	0.260828	-0.170172	12.09202334	0.369795304
6.28319	1	1809.18	8779.83	8964.29	0.270988	-0.160012	11.32957758	0.350838982
6.28319	1	1862.47	9365.91	9549.3	0.280945	-0.150055	10.62061937	0.498996961
6.28319	1	1954.94	9974.85	10164.6	0.291091	-0.139909	9.97225674	0.660013278
6.28319	1	2108.16	10576.1	10784.2	0.301013	-0.129987	9.405335156	0.766621224
6.28319	1	2358.63	11166.2	11412.5	0.311023	-0.119977	8.908291553	1.013492324
6.28319	1	2718.38	11647.8	11960.8	0.320991	-0.110009	8.539961636	1.232062853
6.28319	1	3251.94	11930.6	12365.8	0.331051	-0.099949	8.337532491	1.675956779
6.28319	1	3919.4	11837.2	12469.2	0.340977	-0.090023	8.403318786	2.291527758
6.28319	1	4653.5	11223.4	12149.9	0.350986	-0.080014	8.862890491	3.160920536
6.28319	1	5225.62	10071.2	11346.2	0.3608	-0.0702	9.876853318	4.584436939
6.28319	1	5473.91	8535.03	10139.5	0.370765	-0.060235	11.65453023	6.620480615
6.28319	1	5378.78	6959.34	8795.67	0.380912	-0.050088	14.29327568	9.394540876
6.28319	1	5043.09	5549.22	7498.44	0.390856	-0.040144	17.92535981	13.06086777
6.28319	1	4639.3	4482.24	6450.86	0.40062	-0.03038	22.19242279	17.29854302
6.28319	1	4269.08	3705.71	5653.08	0.410834	-0.020166	26.84283582	21.80782122
6.28319	1	3990.78	3209.22	5121.08	0.420863	-0.010137	30.99562047	25.76957803
6.28319	1	3826.11	2954.08	4833.8	0.430744	-0.000256	33.6726714	28.19438187
6.28319	1	3775.1	2900.38	4760.63	0.440688	0.009688	34.29611469	28.53135809
6.28319	1	3821.16	3038.05	4881.71	0.450783	0.019783	32.74197763	26.67928731
6.28319	1	3956.84	3392.44	5212.03	0.460682	0.029682	29.32159895	22.93900938
6.28319	1	4152.18	3968.22	5743.47	0.470753	0.039753	25.06709939	18.38415271
6.28319	1	4356.82	4795.17	6478.85	0.480869	0.049869	20.74415821	13.73765629

6.28319	1	4476.53	5816.89	7339.99	0.490772	0.059772	17.10050648	9.765221126
6.28319	1	4440.54	6988.42	8279.88	0.500743	0.069743	14.23379893	6.569789731
6.28319	1	4205.14	8115.84	9140.57	0.510579	0.079579	12.25649657	4.276814049
6.28319	1	3806.77	9048.52	9816.68	0.520516	0.089516	10.99315304	2.679018051
6.28319	1	3338.75	9705.03	10263.3	0.53064	0.09964	10.2495062	1.650331008
6.28319	1	2908.19	10088.5	10499.3	0.540545	0.109545	9.859916255	0.941526176
6.28319	1	2567.29	10213.2	10530.9	0.550603	0.119603	9.73952974	0.549538249
6.28319	1	2319.63	10188.8	10449.5	0.560731	0.129731	9.762853833	0.291494317
6.28319	1	2167.04	10026.4	10257.9	0.570715	0.139715	9.920985113	0.148518312
6.28319	1	2106.38	9803.69	10027.4	0.580572	0.149572	10.1463597	0.107909757
6.28319	1	2106.7	9507.68	9738.28	0.590521	0.159521	10.46225421	0.133248599
6.28319	1	2161.66	9163.8	9415.31	0.600578	0.169578	10.8548599	0.268988563
6.28319	1	2280.1	8760.86	9052.71	0.610467	0.179467	11.35410966	0.537045068
6.28319	1	2439.22	8290.5	8641.89	0.620492	0.189492	11.99828299	0.879325353
6.28319	1	2639.14	7739.14	8176.75	0.630682	0.199682	12.85307736	1.546600124
6.28319	1	2859.82	7102.39	7656.53	0.6404	0.2094	14.00539327	2.462122928
6.28319	1	3061.81	6358.95	7057.68	0.650533	0.219533	15.64279718	3.831188326
6.28319	1	3215.58	5554.1	6417.78	0.660531	0.229531	17.90961004	5.930501457
6.28319	1	3292.86	4722.43	5757.11	0.670664	0.239664	21.06368229	8.795601161
6.28319	1	3283.88	3942.57	5131.05	0.680606	0.249606	25.23018365	12.7322815
6.28319	1	3206.1	3255.71	4569.32	0.690632	0.259632	30.55301766	17.7787114
6.28319	1	3089.55	2706.05	4107.06	0.700493	0.269493	36.75902705	23.85866494
6.28319	1	2973.97	2303.95	3762.01	0.710519	0.279519	43.17444612	29.92886846
6.28319	1	2880.82	2040.55	3530.29	0.720637	0.289637	48.74752647	35.2511538
6.28319	1	2826.35	1909	3410.65	0.73062	0.29962	52.1067392	38.62591449
6.28319	1	2814.08	1895.99	3393.2	0.740413	0.309413	52.46428786	38.35157164
6.28319	1	2841.96	2000.73	3475.58	0.750289	0.319289	49.7177356	35.38284162
6.28319	1	2895.41	2222.98	3650.35	0.760383	0.329383	44.74703557	30.03521057
6.28319	1	2955.58	2563	3912.09	0.770503	0.339503	38.810677	23.69386889
6.28319	1	2991.85	3012.73	4245.91	0.780493	0.349493	33.01715226	17.26436724
6.28319	1	2966.78	3515.65	4600.17	0.790283	0.359283	28.29398977	12.35231525
6.28319	1	2868.82	4042.18	4956.75	0.800439	0.369439	24.60844523	8.066283702
6.28319	1	2703.27	4490.19	5241.14	0.810386	0.379386	22.15313052	5.893223899
6.28319	1	2503.77	4827.89	5438.51	0.820411	0.389411	20.60356908	3.23301526
6.28319	1	2310.96	5027.1	5532.83	0.83025	0.39925	19.78710691	2.018978265
6.28319	1	2145.71	5112.33	5544.37	0.840225	0.409225	19.45722697	1.095629594
6.28319	1	2020.7	5085.65	5472.39	0.850343	0.419343	19.55930218	-0.009503351
6.28319	1	1938.41	4982.89	5346.64	0.860299	0.429299	19.96266527	1.53396225
6.28319	1	1886.05	4825.09	5180.6	0.87034	0.43934	20.61552533	-0.387030501
6.28319	1	1859.42	4632.55	4991.79	0.880275	0.449275	21.47235651	-0.526150581
6.28319	1	1851.69	4412.21	4785.02	0.890271	0.459271	22.54465792	0.262908875
6.28319	1	1854.65	4190.27	4582.37	0.900166	0.469166	23.73874837	-0.543077692

Determining the *gamma* term, γ. The latter, in units of μF·cm^{-2}, is determined by the following relationship, where $A = 1.60$ cm^2:

$$\gamma = -\frac{10^6}{\omega Z_{\mathrm{Im}} A} \qquad \text{(S5)}$$

Determining the Analytical Signal ($\frac{Y_0\sqrt{2}}{\omega^{1/2}}$). Re-arranging Equation (9) from the main text, the analytical signal, in units of μF·cm^{-2}, is determined by subtracting the double-layer capacitance, C_{d} (from Table S2), of a "blank" in the absence of transferring ionic analyte from the *gamma* term, γ (from Table S3), in the presence of transferring ionic analyte at each potential applied on the Galvani potential scale ($\Delta_{\mathrm{o}}^{\mathrm{w}}\phi$ / V):

$$\frac{Y_0\sqrt{2}}{\omega^{1/2}} = (\gamma - C_{\mathrm{d}}) \qquad \text{(S6)}$$

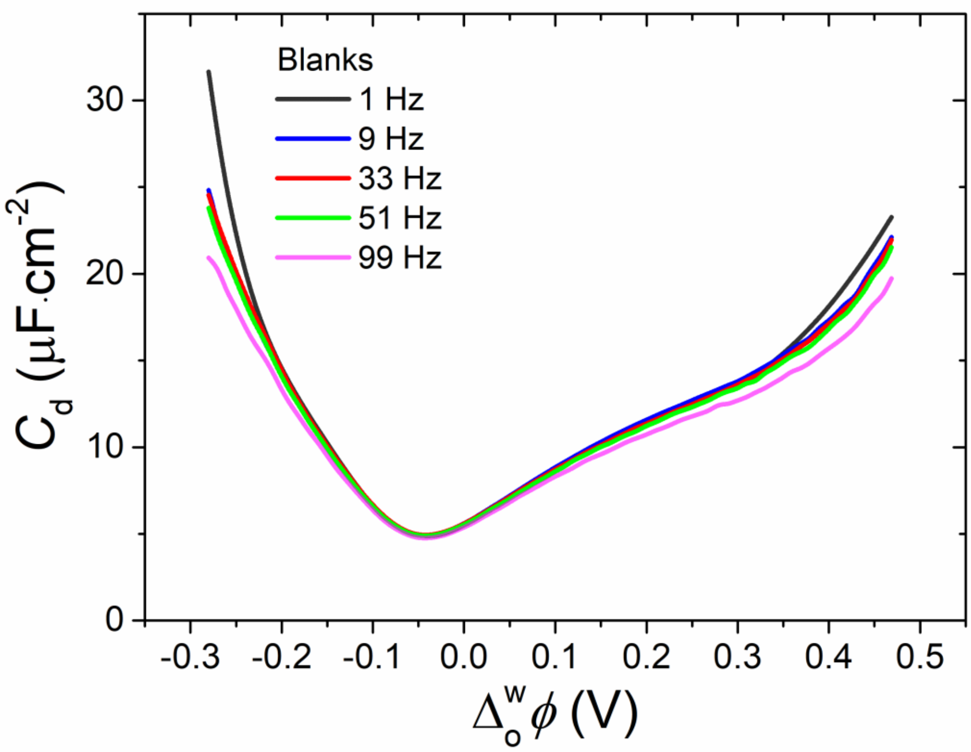

Figure S3. The effect of the applied frequency on the AC voltammetry on the "blank" electrochemical cell response. All C_{d} *vs.* $\Delta_{\mathrm{o}}^{\mathrm{w}}\phi$ curves were obtained in the presence of background electrolytes only. The configuration of the four-electrode electrochemical cell was as described in Scheme 1 with TFT as the organic solvent and no tetraalkylammonium cations present in the aqueous phase.

Table S4. Statistical data of the linear trend estimations in Figure 3b, main text.

Statistical data	**TMA^+**	**TPA^+**
Slope ($\mu F\ cm^{-2}\ \mu M^{-1}$)	1.510	1.311
Standard deviation of the slope ($\mu F\ cm^{-2}\ \mu M^{-1}$)	0.012	0.032
Intercept ($\mu F\ cm^{-2}$)	–1.992	–2.207
Standard deviation of the intercept ($\mu F\ cm^{-2}$)	0.209	0.484
Standard deviation of the data (y axis) ($\mu F\ cm^{-2}$)	0.247	0.573
r^2	0.999	0.997

Table S5. Statistical data of linear trend estimations in Figure 5d, main text.

Statistical data	**TMA^+**	**TEA^+**
Slope ($\mu F\ cm^{-2}\ \mu M^{-1}$)	1.800	1.802
Standard deviation of the slope ($\mu F\ cm^{-2}\ \mu M^{-1}$)	0.041	0.061
Intercept ($\mu F\ cm^{-2}$)	–2.102	–2.772
Standard deviation of the intercept ($\mu F\ cm^{-2}$)	0.460	0.595
Standard deviation of the data (y axis) ($\mu F\ cm^{-2}$)	0.536	0.693
r^2	0.997	0.994