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Supplementary Material

Cation effect on the electrochemical reduction of polyoxometalates in room temperature ionic liquids

Juliette I. Phillips[A], *Shinya Azuma*[A,B], *Junqiao Lee*[A], *Tadaharu Ueda*[C,D] and *Debbie S. Silvester*[A,*]

[A]School of Molecular and Life Sciences, Curtin University, GPO Box U1987, Perth, WA 6845, Australia

[B]Graduate School of Integrated Arts and Sciences, Kochi University, Kochi 780-8520, Japan

[C]Department of Marine Resource Science, Faculty of Agriculture and Marine Sciences, Kochi University, Nankoku 783-8520, Japan

[D]Centre for Advanced Marine Core Research, Kochi University, Nankoku 783-8502, Japan

*Correspondence to: Email: d.silvester-dean@curtin.edu.au

Dissolving polyoxometalates in different ionic liquids

To determine if mM concentrations of POMs were soluble in the different RTILs, a small amount (~1 mg) of the POM (*n*-$Bu_4N)_6[P_2W_{18}O_{62}]$ solid was added to a vial and ~30 μL of the RTIL was added, followed by heating to ~60°C under magnetic stirring for several hours to encourage dissolution. The samples were then left overnight to ensure that they were not simply a suspension, but dissolved in the RTIL. It was visually observed that only six out of the twelve RTILs ($[C_4mpyrr][TFSI]$, $[C_4mim][TFSI]$, $[N_{4,1,1,1}][TFSI]$, $[P_{14,6,6,6}][TFSI]$, $[C_4mim][BF_4]$ and $[C_4mim][PF_6]$) had fully dissolved the POM at the 3 mM concentration. The remaining six solutions had visible precipitate present in the bottom of the vial.

It is noted that a blue colour was observed for some POM/RTIL solutions by simply dissolving the POM in the RTIL. This effect has also been reported before, and is ascribed to the presence of reduced or mixed valence POMs.[1] The most intense blue colour was observed when the POM was dissolved in $[C_4mim][PF_6]$ and $[N_{1.8.8.8}][TFSI]$, and less intense, but still obvious blue colour was seen in $[C_2mim][TFSI]$, $[C_4mpyrr][TFSI]$, $[C_4mim][BF_4]$ and $[P_{14,6,6,6}][TFSI]$. After electrochemical experiments of reducing and oxidising the POM in all the RTILs, a vivid blue colour was also observed in some RTILs.

Data from cyclic voltammetry in RTILs where only two reduction processes were clearly visible:

Table S1: Peak-to-peak separation (ΔE_p) of (n-$Bu_4N)_6[S_2W_{18}O_{62}$] (first two reduction peaks) at different scan rates in $[S_{2,2,1}]$[TFSI], $[C_2mim]$[BETI] and $[N_{4,1,1,1}]$[TFSI] on a Pt TFE (d = 1 mm)

Scan Rate (mV/s)	ΔE_p (mV)					
	$[S_{2,2,1}]$[TFSI]		$[C_2mim]$[BETI]		$[N_{4,1,1,1}]$[TFSI]	
	Peak I	Peak II	Peak I	Peak II	Peak I	Peak II
10	68	107	137	134	88	107
20	76	100	139	129	88	107
50	76	95	112	117	90	107
100	78	95	115	127	90	117
200	78	110	112	115	103	122
400	83	120	103	139	110	149
700	83	166	90	137	142	176
1000	100	190	112	149	129	178

Table S2: Peak-to-peak separation (ΔE_p) of (n-$Bu_4N)_6[S_2W_{18}O_{62}$] (first two reduction peaks) at different scan rates in $[N_{8,2,2,2}]$[TFSI], $[C_4mim][BF_4]$ and $[N_{1,8,8,8}]$[TFSI] on a Pt TFE (d = 1 mm)

Scan Rate (mV/s)	ΔE_p (mV)					
	$[N_{8,2,2,2}]$[TFSI]		$[C_4mim][BF_4]$		$[N_{1,8,8,8}]$[TFSI]	
	Peak I	Peak II	Peak I	Peak II	Peak I	Peak II
10	66	127	59	83	105	137
20	68	129	88	103	127	159
50	85	120	125	132	159	205
100	98	120	142	132	190	249
200	110	132	142	137	259	254
400	122	151	132	132	286	303
700	129	166	125	115	386	293
1000	139	176	112	127	364	273

Data from cyclic voltammetry in RTILs where 5 or 6 reduction processes were visible:

Table S3: Peak-to-peak separation (ΔE_p) of (n-$Bu_4N)_6[S_2W_{18}O_{62}$] (for all six reduction peaks) at different scan rates in [C_2mim][FSI] on a Pt TFE (d = 1 mm)

Scan Rate (mV/s)	ΔE_p (mV) in [C_2mim][FSI]					
	Peak I	Peak II	Peak III	Peak IV	Peak V	Peak VI
10	78	78	88	93	98	68
20	73	76	90	98	107	73
50	73	85	93	100	125	83
100	78	83	93	102	129	12
200	76	88	93	102	132	132
400	81	88	90	100	132	139
700	78	85	90	95	120	103
1000	83	83	88	100	115	90

Table S4: Peak-to-peak separation (ΔE_p) of (n-$Bu_4N)_6[S_2W_{18}O_{62}$] (for all six reduction peaks) at different scan rates in [C_2mim][TFSI] on a Pt TFE (d = 1 mm)

Scan Rate (mV/s)	ΔE_p (mV) in [C_2mim][TFSI]					
	Peak I	Peak II	Peak III	Peak IV	Peak V	Peak VI
10	122	132	154	195	144	159
20	107	112	125	188	129	103
50	81	85	105	168	122	110
100	81	81	95	161	134	41
200	83	81	95	168	134	24
400	93	83	95	181	110	17
700	90	83	98	203	88	37
1000	90	83	100	229	46	39

Table S5: Peak-to-peak separation (ΔE_p) of (n-$Bu_4N)_6[S_2W_{18}O_{62}$] (for all six reduction peaks) at different scan rates in [C_4mim][TFSI] on a Pt TFE (d = 1 mm)

Scan Rate (mV/s)	ΔE_p (mV) in [C_4mim][TFSI]					
	Peak I	Peak II	Peak III	Peak IV	Peak V	Peak VI
10	71	78	98	93	117	117
20	78	81	95	100	134	142
50	73	88	98	103	142	129
100	83	103	110	110	144	132
200	88	107	120	117	159	100
400	95	132	134	127	142	78
700	110	146	146	144	137	107
1000	129	171	156	149	146	103

Table S6: Peak-to-peak separation (ΔE_p) of (n-$Bu_4N)_6[S_2W_{18}O_{62}$] (for all six reduction peaks) at different scan rates in [C_4mpyrr][TFSI] on a Pt TFE (d = 1 mm)

Scan Rate (mV/s)	ΔE_p (mV) in [C_4mpyrr][TFSI]					
	Peak I	Peak II	Peak III	Peak IV	Peak V	Peak VI
10	85	93	95	100	95	103
20	88	98	103	105	103	100
50	95	112	115	117	120	115
100	112	127	132	125	137	132
200	139	156	146	142	154	156
400	168	181	173	161	169	178
700	198	210	181	178	186	188
1000	225	237	220	183	178	173

Table S7: Peak-to-peak separation (ΔE_p) of (n-$Bu_4N)_6[S_2W_{18}O_{62}$] (for all six reduction peaks) at different scan rates in [C_4mim][PF_6] on a Pt TFE (d = 1 mm)

Scan Rate (mV/s)	ΔE_p (mV) in [C_4mim][PF_6]					
	Peak I	Peak II	Peak III	Peak IV	Peak V	Peak VI*
10	78	78	103	110	81	44
20	73	71	103	122	85	29
50	76	81	115	127	103	24
100	83	88	127	124	107	54
200	90	93	117	122	122	44
400	98	93	132	129	90	44
700	107	93	132	129	71	39
1000	110	88	117	151	95	54

*It is noted that the final peak was very close to the edge of the electrochemical window. Therefore, attempts were made to measure the peak-to-peak separations, but they may not be fully accurate because of the broad shape.

Table S8: Peak-to-peak separation (ΔE_p) of (n-$Bu_4N)_6[S_2W_{18}O_{62}$] (for five reduction peaks) at different scan rates in [$P_{14,6,6,6}$][TFSI] on a Pt TFE (d = 1 mm)

Scan Rate (mV/s)	ΔE_p (mV) in [$P_{14,6,6,6}$][TFSI]				
	Peak I	Peak II	Peak III	Peak IV	Peak V
10	115	125	132	93	85
20	127	142	142	100	110
50	156	168	171	112	127
100	195	208	200	142	161
200	256	256	237	171	171
400	315	320	291	203	188
700	378	403	349	244	237
1000	444	471	386	269	247

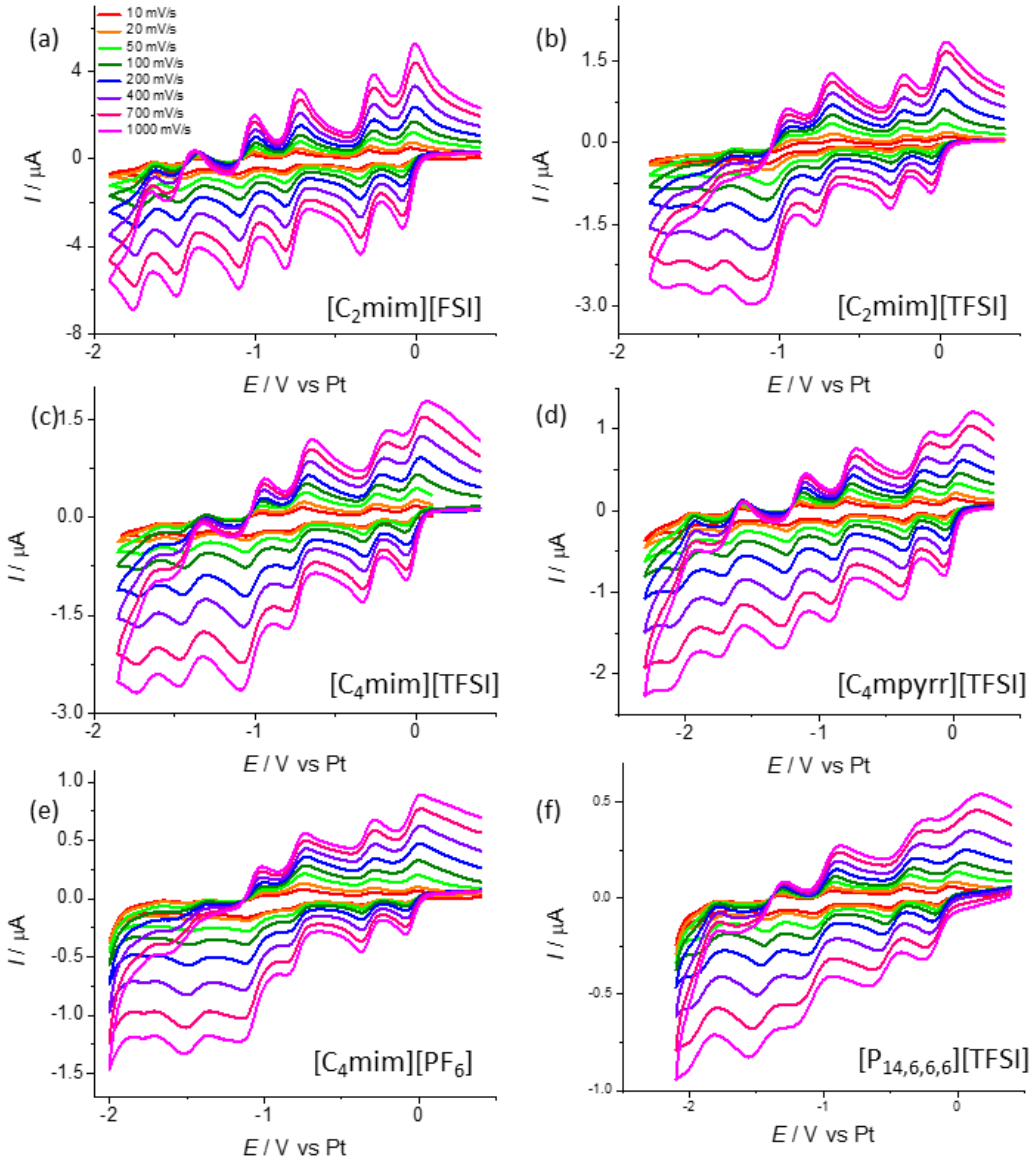

Fig. S1: Cyclic voltammetry for the reduction of the POM (n-$Bu_4N)_6[S_2W_{18}O_{62}$] showing up to 6 peaks in (a) [C_2mim][FSI], (b) [C_2mim][TFSI], (c) [C_4mim][TFSI], (d) [C_4mpyrr][TFSI], (e) [C_4mim][PF_6] and (f) [$P_{14,6,6,6}$][TFSI] at scan rates of 10, 20, 50, 100, 200, 400, 700, and 1000 mV/s on a Pt TFE (d = 1 mm)

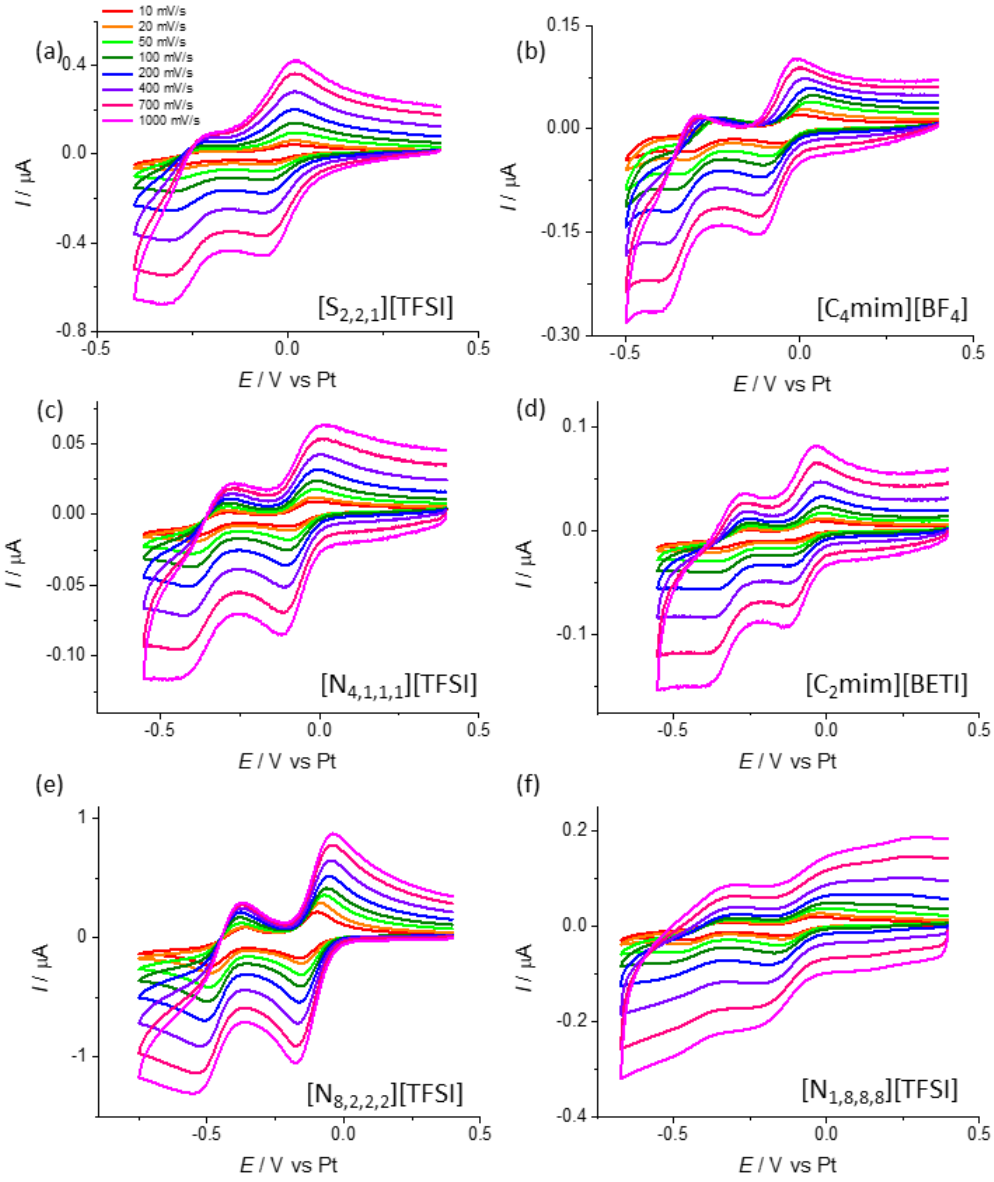

Fig. S2: Cyclic voltammetry for the reduction of the POM (n-$Bu_4N)_6[S_2W_{18}O_{62}$] showing only the first two peaks in (a) $[S_{2,2,1}][TFSI]$, (b) $[C_4mim][BF_4]$, (c) $[N_{4,1,1,1}][TFSI]$, (d) $[C_2mim][BETI]$ (e) $[N_{8,2,2,2}][TFSI]$ and (f) $[N_{1,8,8,8}][TFSI]$ at scan rates of 10, 20, 50, 100, 200, 400, 700, and 1000 mVs^{-1} on a Pt TFE (d = 1 mm)

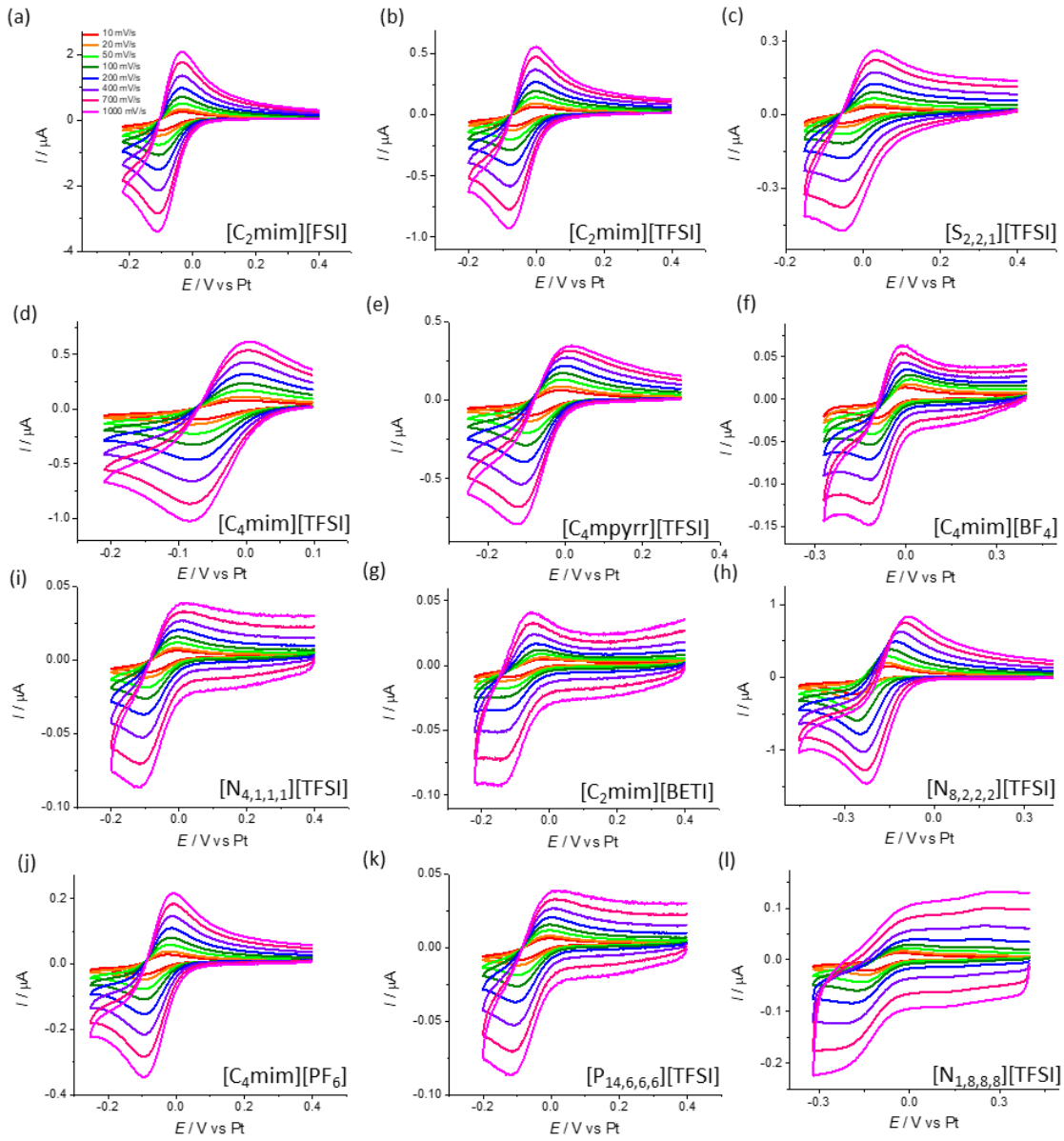

Fig. S3: Cyclic voltammetry for the first reduction peak of the POM (n-$Bu_4N)_6[S_2W_{18}O_{62}$] in (a) [C_2mim][FSI], (b) [C_2mim][TFSI], (c) [$S_{2,2,1}$][TFSI], (d) [C_4mim][TFSI], (e) [C_4mpyrr][TFSI], (f) [C_4mim][BF_4], (g) [$N_{4,1,1,1}$][TFSI], (h) [C_2mim][BETI], (i) [$N_{8,2,2,2}$][TFSI], (j) [C_4mim][PF_6], (k) [$P_{14,6,6,6}$][TFSI], and (l) [$N_{1,8,8,8}$][TFSI] at scan rates of 10, 20, 50, 100, 200, 400, 700, and 1000 mVs^{-1} on a Pt TFE (d = 1 mm)

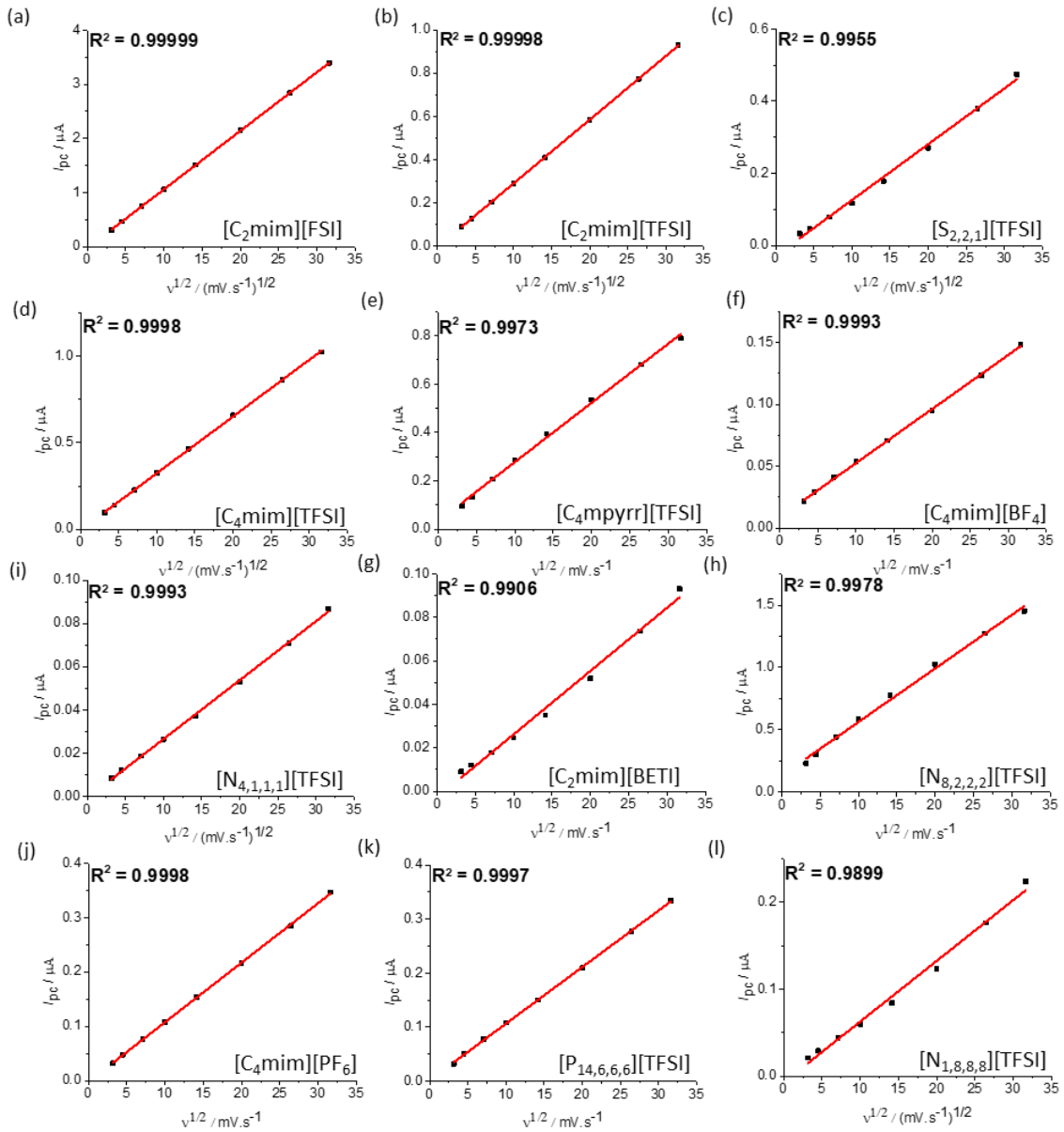

Fig. S4: Plot of peak cathodic current (I_{pc}) vs the square root of the scan rate ($\nu^{1/2}$) for the first reduction peak of the POM (n-$Bu_4N)_6[S_2W_{18}O_{62}$] in (a) [C_2mim][FSI], (b) [C_2mim][TFSI], (c) [$S_{2,2,1}$][TFSI], (d) [C_4mim][TFSI], (e) [C_4mpyrr][TFSI], (f) [C_4mim][BF_4], (g) [$N_{4,1,1,1}$][TFSI], (h) [C_2mim][BETI], (i) [$N_{8,2,2,2}$][TFSI], (j) [C_4mim][PF_6], (k) [$P_{14,6,6,6}$][TFSI], and (l) [$N_{1,8,8,8}$][TFSI] at scan rates of 10, 20, 50, 100, 200, 400, 700, and 1000 mVs^{-1} on a Pt TFE (d = 1 mm)

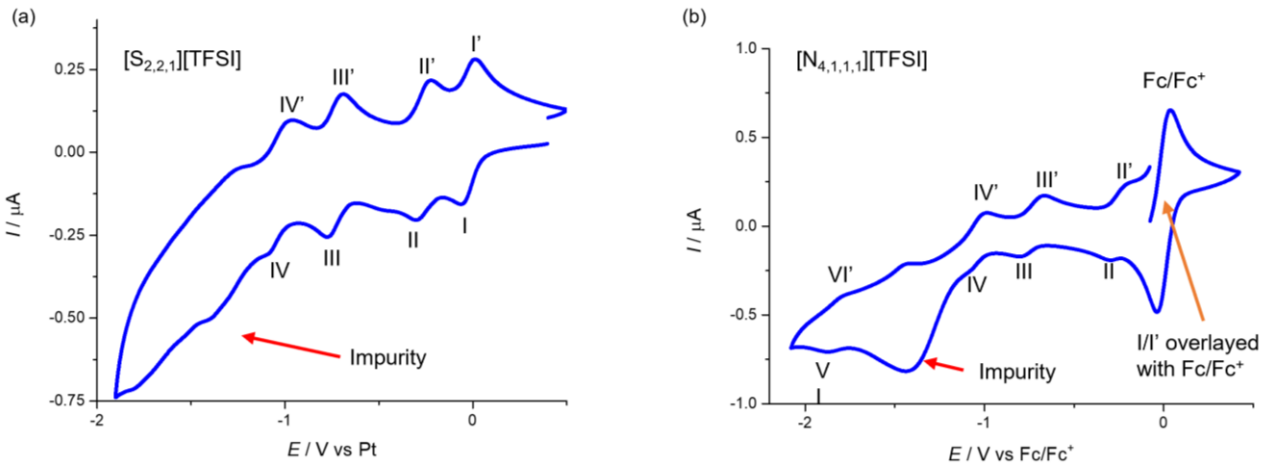

Fig. S5: Cyclic voltammetry for the multiple reduction processes of (n-$Bu_4N)_4[S_2W_{18}O_{62}]$ in (a) $[S_{2,2,1}][TFSI]$,and (b) $[N_{4,1,1,1}][TFSI]$ on a Pt TFE (d = 1 mm) at a scan rate of 100 mVs^{-1}.

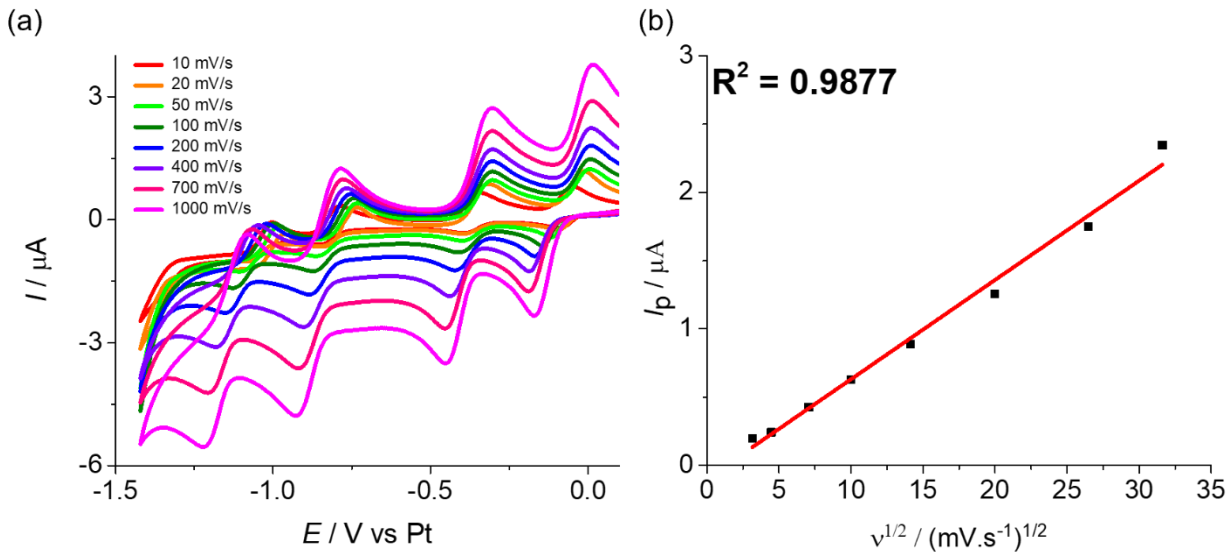

Fig. S6: (a) Cyclic voltammetry for the reduction of the POM (n-$Bu_4N)_3[PW_{12}O_{40}]$ in $[C_2mim][FSI]$ at scan rates of 10, 20, 50, 100, 200, 400, 700, and 1000 mVs^{-1} on a Pt TFE (d = 1 mm) and (b) plots of the peak cathodic current (I_{pc}) vs the square root of the scan rate ($v^{1/2}$) for the first reduction peak of the POM (n-$Bu_4N)_3[PW_{12}O_{40}]$ in $[C_2mim][FSI]$

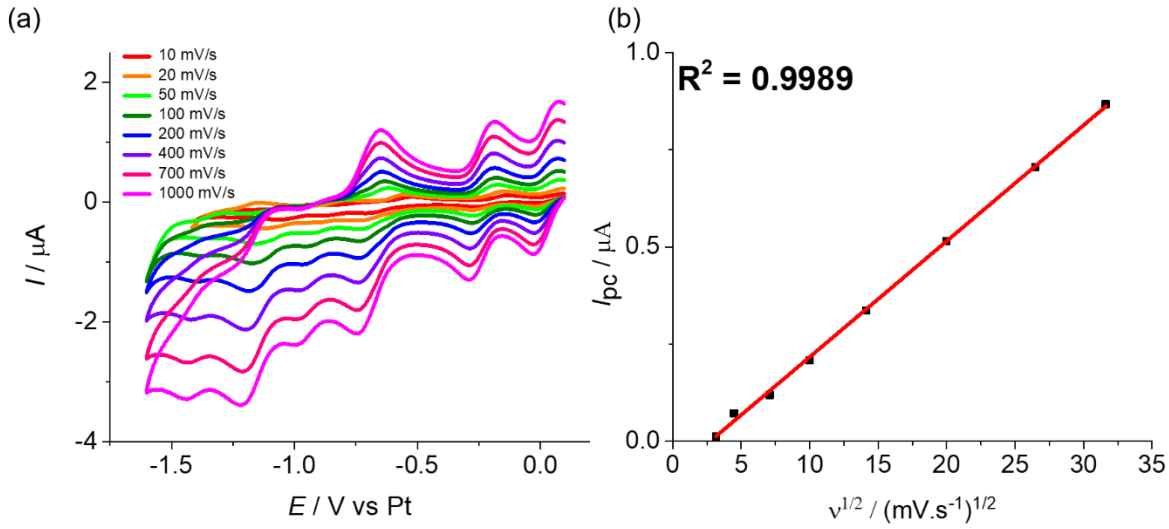

Fig. S7: (a) Cyclic voltammetry for the reduction of the POM (n-$Bu_4N)_6[P_2W_{18}O_{62}]$ in $[C_2mim][FSI]$ at scan rates of 10, 20, 50, 100, 200, 400, 700, and 1000 mVs^{-1} on a Pt TFE (d = 1 mm) and (b) plot of the peak cathodic current (I_{pc}) vs the square root of the scan rate ($v^{1/2}$) for the first reduction peak of the POM (n-$Bu_4N)_6[P_2W_{18}O_{62}]$ in $[C_2mim][FSI]$

Digital Simulation studies

The digital simulation program DigiSim 3.03b (BAS Technicol)[2] was used in an attempt to model cyclic voltammetry obtained for the four asymmetric reduction peaks of the $[PW_{12}O_{40}]^{3-}$ POM using a planar electrode geometry with a finite diffusion model. The working electrode area used in the simulation was its geometric area (0.00785 cm^2) with a diffusion thickness of 0.001 cm. The analyte bulk concentration was set at 0.001 $molL^{-1}$ (or 1 mM) based on its approximate solubility, and the scan rate was set at 100 mVs^{-1}. The mechanism was set as four individual charge transfers. All species parameters were set to 'open right boundary' (ORB), meaning all species can freely 'communicate' with the bulk solution.

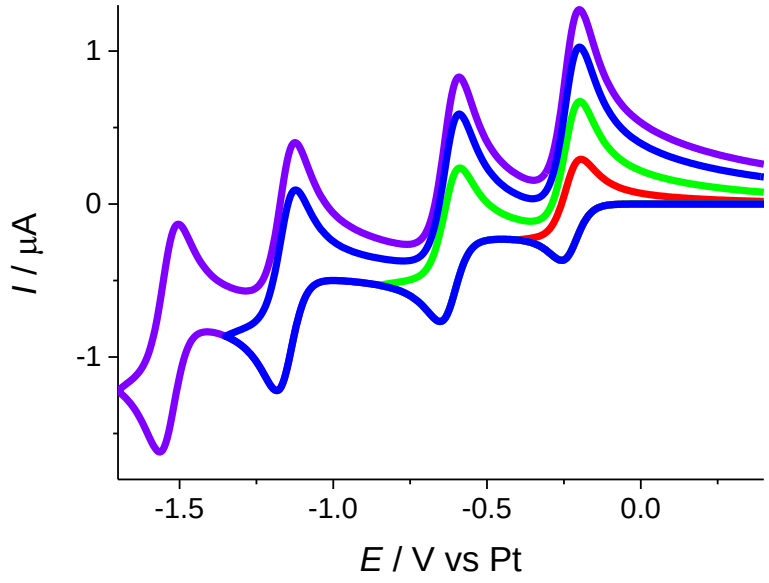

Fig. S8: Cyclic voltammetry simulation results (obtained from the simulation program DigiSim®) for the 4-electron reduction of $[PW_{12}O_{40}]^{3-}$ at chosen reduction formal potentials of -0.198, -0.576, -1.138 and -1.462 V, with the scans being reversed at -0.5, -0.85, -1.35 and -1.7 V. Asymmetric behaviour was obtained by changing some of the boundary conditions from ORB (open to the bulk solution) to BRB (blocked from interacting with the bulk solution).

References

[1] T. Ueda. *ChemElectroChem*. **2018**, *5*, 823–838.

[2] M. Rudolph, D. P. Reddy, S. W. Feldberg. *Anal. Chem.* **1994**, *66*, 589–600.