

Supporting Information

Electrochemistry of Ferrocene-functionalized Phosphonium Ionic Liquids

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This supplement contains:

- a.** Specific synthetic details for ionic liquids **A, B, C**
- b.** Figures expanding on the experimental details and observations
- c.** Description and details of electronic migration corrections

Reference numbers are those in the manuscript.

Synthetic Procedures

Synthesis of [(*n*-Bu)₃P(CH₂)₅COFc]Br

The reaction of acylated ferrocene (**Fc-CO(CH₂)₅Br**) (0.255 g, 0.702 mmol) with tributyl phosphine (0.164 g, 0.810 mmol) according to the general procedure described in the text afforded the desired product with an isolated yield of 0.327 g (83%). ¹H NMR (CDCl₃, δ/ppm): 0.95 (s, 9H), 1.51 (s, 18H), 1.74 (br s, 2H), 1.97 (br s, 2H), 2.36 (br s, 4H), 2.71 (br s, 2H), 4.15 (s, 5H), 4.47 (s, 2H), 4.75 (s, 2H); ¹³C NMR (CDCl₃, δ/ppm): 13.4, 18.9, 19.4, 21.2, 23.5, 23.8, 24.1, 30.9, 39.1, 69.3, 69.8, 72.3; ³¹P NMR (CDCl₃, δ/ppm): 35.100; ESI MS [M⁺] = 485, [M₂Br⁺] = 1049; TGA: decomposition onset = 144.6 °C.

Synthesis of [(*n*-Bu)₃P(CH₂)₆Fc]Br

The reaction of alkylated ferrocene (**Fc-(CH₂)₆Br**) (0.284 g, 0.813 mmol) and trioctyl phosphine (0.181 g, 0.894 mmol) according to the general procedure afforded 0.219 g of the desired product with an isolated yield of 57%. ¹H NMR (CDCl₃, δ/ppm): 0.96 (m, 9H), 1.51 (m, 20H), 1.85 (br, 8H), 2.31 (t, 2H), 4.02 (s, 4H), 4.07 (s, 5H); ¹³C NMR (CDCl₃, δ/ppm): 13.4, 18.9 (d), 19.2 (d), 21.7 (d), 23.7, 23.9, 28.6, 29.3, 30.5 (d), 30.7, 66.9, 67.9, 68.3; ³¹P NMR (CDCl₃, δ/ppm): 34.819; ESI MS [M⁺] = 471; TGA: decomposition onset = 253.4 °C.

Synthesis of [(*n*-Bu)₃P(CH₂)₆Fc]PF₆ (**A in Figure 1**)

The reaction of [(*n*-Bu)₃P(CH₂)₆Fc]Br (1.60 g, 2.91 mmol) with 1.5 equiv. of NaPF₆ (0.734 g, 4.37 mmol) afforded the desired product with an isolated yield of (1.238 g, 69%). ¹H NMR (CDCl₃, δ/ppm): 0.93 (m, 9H), 1.27 (m, 2H), 1.48 (m, 18H), 2.08 (m, 8H), 2.31 (t, 2H), 4.01 (s, 4H), 4.07 (s, 5H); ¹³C NMR (CDCl₃, δ/ppm): 13.3, 18.1 (d), 18.4 (d), 21.5, 23.5, 23.7 (d), 28.6, 29.4, 30.4 (d), 30.8, 67.1, 68.1, 68.5, 76.7, 77.0, 77.2, 77.3; ³¹P NMR (CDCl₃, δ/ppm): 33.887; ¹⁹F NMR (CDCl₃, δ/ppm): -71.529, -73.426; ESI MS [M⁺] = 471, [(M₂PF₆)⁺] = 1087; TGA: decomposition onset = 191.8 °C.

Synthesis of [(*n*-Bu)₃P(CH₂)₅COFc]PF₆ (**B in Figure 1**)

The reaction of compound [(*n*-Bu)₃P(CH₂)₅COFc]Br (0.79 g, 1.40 mmol) and 1.5 equiv. of NaPF₆ (0.353 g, 2.10 mmol) afforded 0.530 g of the desired product with an isolated yield of 60%. ¹H NMR (CDCl₃, δ/ppm): 0.952 (m, 9H), 1.489 (m, 18H), 1.722 (m, 2H), 2.104 (m, 6H), 2.744 (t, 2H), 4.178 (s, 5H), 4.489 (s, 2H), 4.773 (s, 2H); ¹³C NMR (CDCl₃, δ/ppm): 13.3, 18.2, 18.4, 18.7, 18.9, 21.4, 23.3, 23.5, 23.8, 23.9, 30.2, 30.3, 38.9; ³¹P NMR (CDCl₃, δ/ppm): 33.961; ¹⁹F NMR (CDCl₃, δ/ppm): -71.554, -73.449; ESI MS [M⁺] = 485; TGA: decomposition onset = 165.3 °C.

Synthesis of [(*n*-Bu)₃P(CH₂)₆Fc]OTs (C in Figure 1)

The reaction of compound [(*n*-Bu)₃P(CH₂)₆Fc]Br (0.69 g, 1.08 mmol) and ~2 equiv. of toluene sulphonic acid (0.328 g, 1.92 mmol) according to the general procedure afforded the desired product with an isolated yield of (0.492 g, 77%). ¹H NMR (CDCl₃, δ/ppm): 0.89 (t, 9H), 1.42 (d, 18H), 2.24 (m, 12 H), 2.278 (s, 2H), 4.01 (s, 4H), 4.05 (d, 5H), 7.07 (d, 2H), 7.73 (d, 2H); ¹³C NMR (CDCl₃, δ/ppm): 13.3, 18.5 (d), 18.8 (d), 21.1, 21.6 (d), 23.6, 23.7 (t), 28.7, 29.3, 30.5 (d), 30.7, 67.3, 68.4, 68.8, 125.9, 128.2, 138.5, 144.3; ³¹P NMR (CDCl₃, δ/ppm): 33.83; ESI MS [M⁺] = 471, [(M₂OTs)⁺] = 1113; TGA: decomposition onset = 308.5 °C.

Synthesis of [(*n*-Bu)₃P(CH₂)₅COFc]OTs (D in Figure 1)

The reaction of compound [(*n*-Bu)₃P(CH₂)₅COFc]Br (0.588 g, 1.04 mmol) and ~2 equiv. of toluene sulphonic acid (0.356 g, 2.08 mmol) according to the general procedure afforded the desired product with an isolated yield of (0.367 g, 56%). ¹H NMR (CDCl₃, δ/ppm): 0.915 (m, 9H), 1.452 (m, 18H), 1.539 (s, 2H), 1.686 (s, 2H), 2.287 (m, 7H), 2.700 (s, 2H), 4.154 (s, 5H), 4.470 (s, 2H), 4.748 (s, 2H), 7.094 (br s, 2H), 7.759 (br s, 2H); ¹³C NMR (CDCl₃, δ/ppm): 13.302, 18.462, 18.935 (t), 21.244, 21.785 (d), 23.432, 23.775 (t), 24.003, 30.368 (d), 38.981, 35.402, 69.271, 69.767, 72.282, 78.852, 126.048, 128.381, 138.716, 204.358; ³¹P NMR (CDCl₃, δ/ppm): 33.874; ESI-MS [M⁺] = 485, [(M₂OTs)⁺] = 1141; TGA: decomposition onset = 277.4 °C.

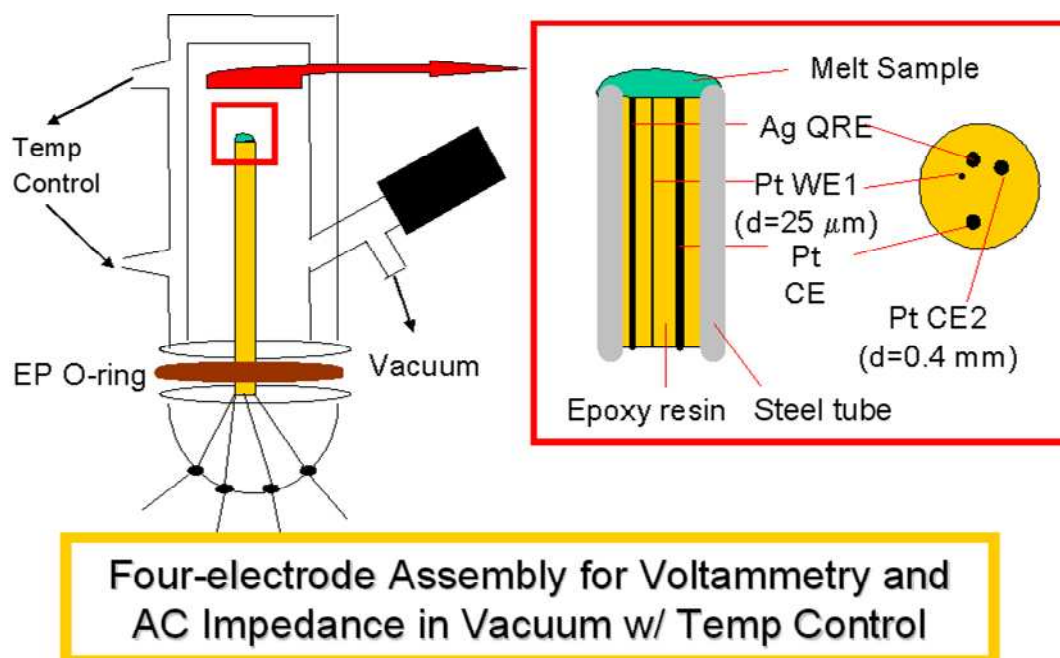


Figure S-1. Cartoon of setup for melt voltammetry.

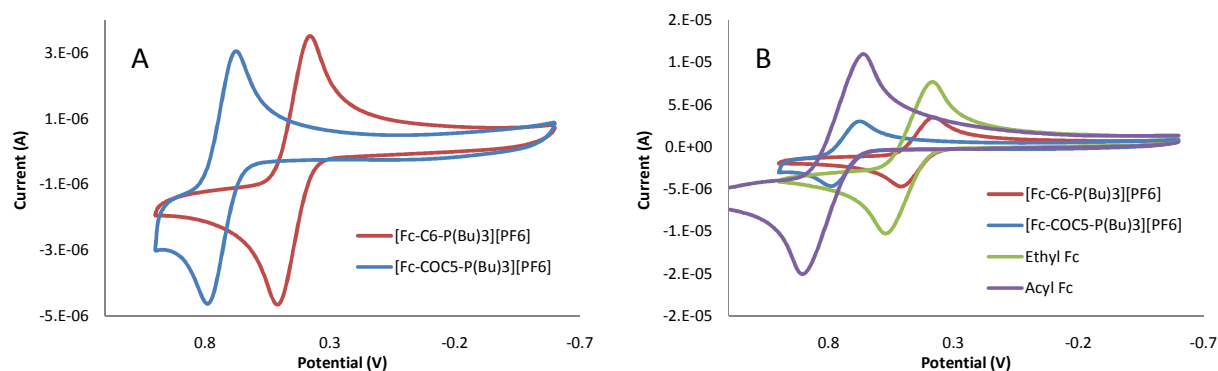


Figure S-2. Panel A. Example $\text{CH}_3\text{CN}/0.1 \text{ M Bu}_4\text{NClO}_4$ dilute solution voltammetry of Samples $[\text{Fc-C6-P(Bu)}_3][\text{PF}_6]$ and $[\text{Fc-COC5-P(Bu)}_3][\text{PF}_6]$ showing the large difference in E^0 (444mV for $[\text{Fc-C6-P(Bu)}_3][\text{PF}_6]$ and 732mV for $[\text{Fc-COC5-P(Bu)}_3][\text{PF}_6]$) between the two types of linker (alkyl and acyl). Panel B. Comparison of $[\text{Fc-C6-P(Bu)}_3][\text{PF}_6]$ to its non-IL counterpart ethylferrocene and $[\text{Fc-COC5-P(Bu)}_3][\text{PF}_6]$ to its counterpart acetylferrocene. The E^0 values of the related linker species differ little.

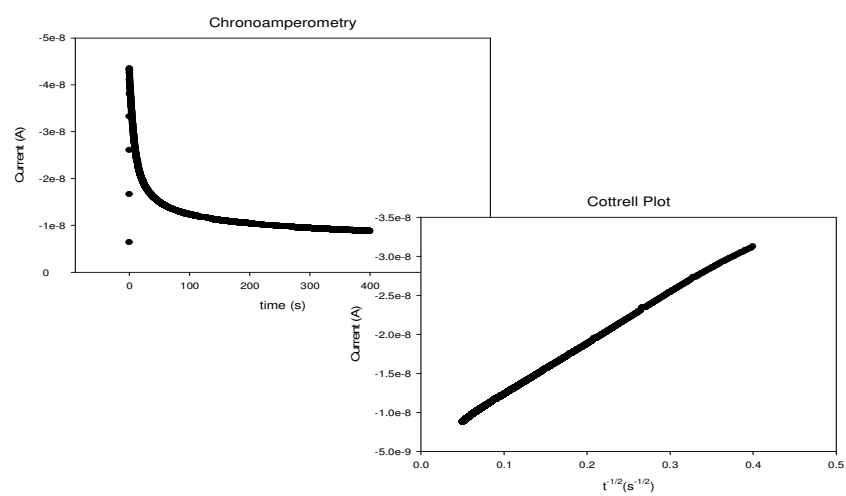


Fig. S-3. Example of current-time chronoamperometric response and associated Cottrell plot.

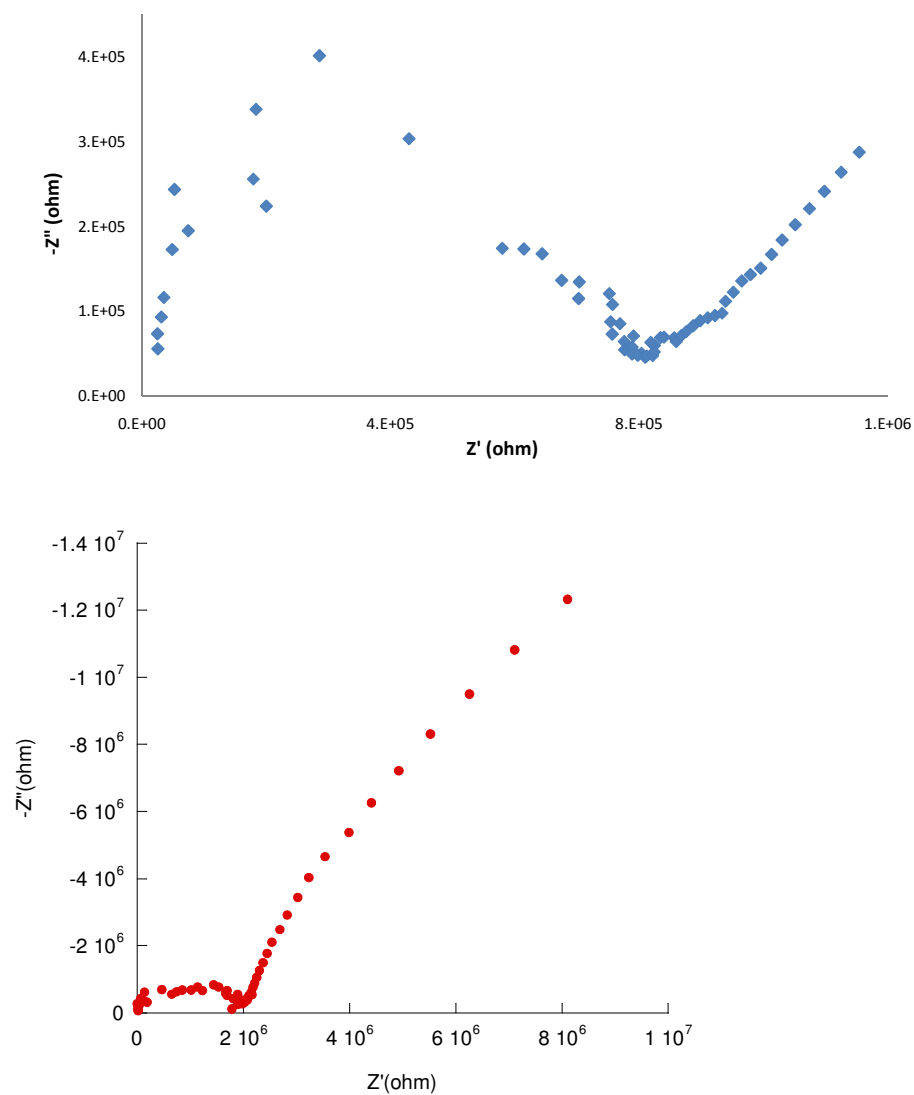


Figure S- 4 Upper: Sample AC impedance plot for ferrocenated phosphonium **A** ([Fc-C6-P(nBu)₃][PF₆]). **Lower:** ferrocenated phosphonium **B** ([Fc-C6-P(nBu)₃][Tos]). Measurements taken on neat, (solvent free) samples under vacuum with temperature controlled at 76°C.

$k_{EX,APP}$ Migration Correction

The corrections described here follow previous analyses^{8-13,15,16} of charge transport in (polyether-based) ionic liquid melts. They correct for electronic migration effects, which occur when (real) values of electron diffusion coefficients are comparable to larger than the counterion diffusion coefficient D_{CION} . This mis-match can produce an electrical field gradient which accelerates the rate of electron hopping, producing erroneously inflated D_{APP} values. A relatively straightforward correction can be applied¹² based on theory by Saveant et al. that described the effects of electronic migration.²⁷ Table S-1 shows the initial D_{APP} and D_{CION} values obtained in the present work, factors ($\log(i/i^0)$) required to perform corrections for electronic migration effects, and finally the $D_{APP,CORR}$ values. The latter are converted to $k_{EX,CORR}$ values for presentation in the main text, Table 1.

Comparison of corrected and uncorrected values reveals that there was an obvious electronic migration effect in the experimental data; each sample shows smaller D_{APP} values after correction. This effect has been previously seen in almost every electroactive IL sample studied to date.

Table S-1

Sample	Temp	D_{app}	D_{cion}	D_{cion}/D_{app}	$\log(D_{cion}/D_{app})$	$\log(i/i^{\circ})$	$D_{app(Corr)}$	$D_{cion}/D_{app(Corr)}$
[Fc-C6-P(nBu)3][PF6]	353	1.5E-08	2.2E-09	0.14	-0.84	0.10	1.2E-08	0.18
	340	8.3E-09	1.1E-09	0.13	-0.88	0.11	6.4E-09	0.17
	329	5.1E-09	6.7E-10	0.13	-0.88	0.11	3.9E-09	0.17
	319	2.8E-09	3.9E-10	0.14	-0.85	0.10	2.2E-09	0.18
	309	1.5E-09	2.1E-10	0.14	-0.85	0.10	1.2E-09	0.18
[Fc-C6-P(nBu)3][Tos]	350	3.5E-09	8.3E-10	0.24	-0.63	0.08	3.0E-09	0.28
	339	2.4E-09	5.3E-10	0.22	-0.66	0.08	2.0E-09	0.26
	329	1.2E-09	3.4E-10	0.29	-0.54	0.07	1.0E-09	0.33
	319	7.4E-10	2.2E-10	0.30	-0.53	0.06	6.4E-10	0.34
	309	3.7E-10	1.4E-10	0.38	-0.42	0.05	3.3E-10	0.43
[Fc-COC5-P(nBu)3][PF6]	350	6.4E-09	4.1E-10	0.06	-1.19	0.21	3.9E-09	0.10
	339	4.0E-09	2.1E-10	0.05	-1.28	0.24	2.3E-09	0.09
	329	2.7E-09	9.5E-11	0.04	-1.45	0.27	1.4E-09	0.07
	319	1.3E-09	4.7E-11	0.04	-1.44	0.27	6.9E-10	0.07
	309	5.0E-10	2.1E-11	0.04	-1.38	0.25	2.8E-10	0.07