

Electronic Supporting Information (ESI) for

“Enhancing thermoelectrochemical properties by tethering ferrocene to the anion or cation of ionic liquids: Altered thermodynamics and solubility”

Leigh Aldous^{a,b*} Jeffrey J. Black,^b Maximo C. Elias,^b Bruno Gélinas^c and Dominic Rochefort^c

^a Department of Chemistry, King’s College London, London, SE1 1DB, UK.

^b School of Chemistry, UNSW Australia, Sydney, NSW 2052, Australia.

^c Département de chimie, Université de Montréal, CP6128 Succ. Centre-Ville, Montréal, Québec, H3C 3J7, Canada.

* Corresponding author: leigh.aldous@kcl.ac.uk

Contents:

1. Synthesis and characterisation	ii
1.1 Synthesis of the ionic liquid [Emim][NTf ₂]	ii
1.2 Synthesis of [FcNTf] redox ionic liquid	iii
1.3 Synthesis of [EimFc] redox ionic liquid	iv
2. Scan rate data for the three redox couples, and simulation fitting methodology	v
3. Literature values utilised in the construction of Figure 5	ix
4. Cyclic voltammograms comparing AcFc and NTfFc	x
5. References	xi

1. Synthesis and characterisation

The synthesized compounds were characterized by ^1H , ^{19}F and ^{13}C NMR on a Bruker AMX 300 MHz spectrometer at room temperature using DMSO- d_6 . Accurate mass values were obtained by Agilent LC-MSD TOF using electrospray ionization. Elemental analysis of organic electroactive species was performed on the EAS 1108 apparatus from Fisons Instruments SPA. The water used in the procedures was purified with a Milli-Q system to a resistivity of 18.2 M Ω ·cm (25 °C).

1.1 Synthesis of the ionic liquid [Emim][NTf₂]

The ionic liquid precursor [Emim]Br was prepared by reacting 1-methylimidazole (1 eq.) with bromoethane (2 eq.) in a large excess of HPLC-grade acetonitrile. The reagents were mixed at room temperature and stirred overnight in an oil bath (to act as a heat sink) before being heated at 60°C. Heating was continued until 1-methylimidazole was completely absent by NMR. The acetonitrile and excess bromoethane were then removed under vacuum, and the crude off-white 1-ethyl-3-methylimidazolium bromide was then dissolved in a minimum of dichloromethane and crashed out of solution with a large excess of ethyl acetate. The fine white crystals were washed with ethyl acetate, then stored in the dark under ethyl acetate until required.

The 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide was prepared by metathesis of 1-ethyl-3-methylimidazolium bromide with 1.1 eq. lithium bis(trifluoromethylsulfonyl)imide. Both solids were mixed, a large excess of Milli-Q water introduced, and then stirred for 1 hour after adding the minimum amount of dichloromethane required to achieve clear phase separation. The organic-ionic liquid phase was then isolated, washed with water repeatedly until a silver nitrate test demonstrated the aqueous phase was halide free. The organic-ionic liquid phase was then washed a further three times, and then finally stirred vigorously with an excess of water overnight. The ionic liquid was then isolated and dried *in vacuo* at 70°C for at least 72 h. This yielded 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide that was optically transparent, pure by NMR, and halide-free based upon cyclic voltammetry using a gold macroelectrode.

1.2 Synthesis of [FcNTf] redox ionic liquid

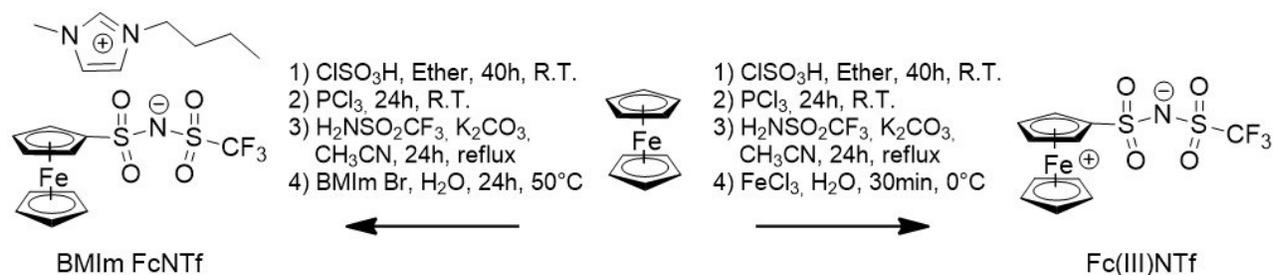


Figure S1. Synthetic pathway of [BMIm] [FcNTf] and [Fc(III)NTf].

Preparation of Potassium Ferrocenylsulfonyl(trifluoromethylsulfonyl)imide.

Trifluoromethanesulfonamide (1 eq., from Synquest Laboratories; all other reagents from Sigma Aldrich and solvents from Fisher) was firstly dissolved in a flask in acetonitrile and anhydrous potassium carbonate (1.5 eq.) was added to the solution. The mixture was stirred for 10 minutes at room temperature. Then, ferrocenylsulfonyl chloride (1 eq.; Synthetic procedure is given in Ref. [1]) was slowly added. The resulting solution was stirred and heated at reflux temperature for 24 hours. The brown solution was filtered and the precipitate was washed with acetone to achieve a white precipitate. Removal of the solvent under reduced pressure yielded a yellow-brown product. Dichloromethane was used to wash the salt which was then dried overnight under reduced pressure at room temperature. Yield: 76 %. ¹H NMR (DMSO-d₆, 300 MHz): δ (ppm) = 4.53 (t, 2H), 4.28 (s, 7H). ¹⁹F NMR (DMSO-d₆, 282 MHz): δ (ppm) = -77.62. ¹³C NMR (DMSO-d₆, 125 MHz): δ (ppm) = 121.90; 119.32; 94.61; 70.44; 69.19; 68.61. (ESI) m/z: [M⁻](calcd for C₁₁H₉F₃FeNO₄S₂⁻): 395.928 Found: 395.926.

Procedure for the preparation of 1-Butyl-3-methylimidazolium ferrocenylsulfonyl(trifluoromethylsulfonyl)imide ([BMIm] [FcNTf]).

Potassium ferrocenylsulfonyl(trifluoromethylsulfonyl)imide and 1-butyl-3-methylimidazolium bromide were dissolved in acetone. The mixture was stirred at room temperature for 24 hours. The solution was then filtered and the solvent removed under reduced pressure produced to yield a dark-brown viscous liquid. The compound was firstly purified by alumina (Al₂O₃) to absorb most impurities and then, by column chromatography using silica (SiO₂) gel as the stationary phase and acetone as eluent. After removing the solvent, the orange product obtained was dried at 65 °C overnight under vacuum and cooled down at room temperature to crystallize. Yield: 90%. ¹H

NMR (DMSO- d_6 , 300 MHz): δ (ppm) = 9.10 (s,1H), 7.76 (t,1H), 7.69 (t,1H), 4.53 (t,2H), 4.28 (s,7H), 4.15 (t,2H), 3.84 (s,3H), 1.76 (q,2H) 1.31-1.19 (m,2H), 0.90 (t,3H). ^{19}F NMR (DMSO- d_6 , 282 MHz): δ (ppm) = -79.08. ^{13}C NMR (DMSO- d_6 , 125 MHz): δ (ppm) = 136.96; 124.08; 122.75; 118.44; 94.57; 70.41; 60.17; 68.60; 48.96; 36.20; 31.80; 19.19; 13.72. (ESI) m/z : $[\text{M}^{*+}]$ (calcd for $\text{C}_8\text{H}_{15}\text{N}_2^+$): 139.12352 found: 139.12341. $[\text{M}^{*-}]$ (calcd for $\text{C}_{11}\text{H}_9\text{F}_3\text{FeNO}_4\text{S}_2^-$): 395.92745 Found: 395.92917. Calcd for $\text{C}_{19}\text{H}_{24}\text{F}_3\text{FeN}_3\text{O}_4\text{S}_2$: N 7.85; C 42.62; H 4.52; S 11.98. Found: N 7.90; C 42.69; H 4.52; S 11.96.

Preparation of ferrocenium sulfonyl(trifluoromethylsulfonyl)imide (Fc(III)NTf). Potassium ferrocenylsulfonyl (trifluoromethylsulfonyl) imide (1 eq.) and iron(III) chloride hexahydrate (3 eq) were dissolved in Milli-Q water at 0 °C. A blue precipitate was formed instantly and the mixture was stirred for 30 minutes at 0 °C. The mixture was filtered and the blue precipitate was washed with cold Milli-Q water and diethyl ether. The salt was dried overnight under reduced pressure at room temperature. Yield: 75 %. Elementary analysis: Calcd for $\text{C}_{11}\text{H}_9\text{F}_3\text{FeNO}_4\text{S}_2$: N 3.54, C 33.35, H 2.29, S 16.19. Found: N 3.45 C 33.42, H 2.24, S 16.20.

1.3 Synthesis of [EimFc] redox ionic liquid

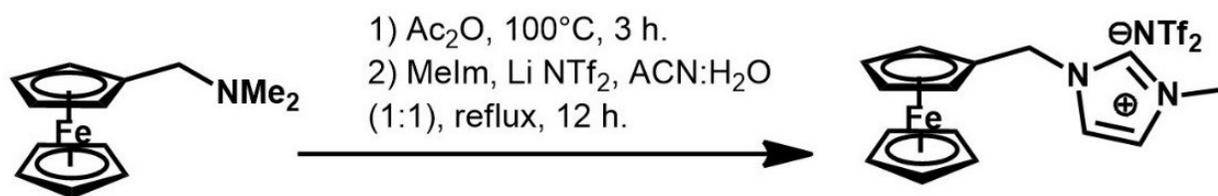


Figure S2. Synthetic pathway of [EimFc][NTf₂].

Preparation of ferrocenylmethylacetate. In acetic anhydride, N,N-dimethylaminomethyl ferrocene (reactant: reagent 1:9 w/v) was dissolved and the reaction flask was transferred in an oil bath kept at 100°C. The mixture was stirred for 3 hours, then the reaction was quenched with an aqueous solution with high concentration of Na_2CO_3 and the mixture was stirred in an ice bath

until complete deactivation. The product was extracted using diethyl ether (3x50 mL) and the organic phase was washed with Milli-Q water (3x60 mL) and with a saturated solution of NaHCO₃. The organic phase was dried with magnesium sulfate, then filtered and dried. The solvent was then removed under vacuum, and the residue was purified by flash column chromatography using silica gel as the stationary phase and diethyl ether:hexane (1:1) as the eluent. A mixture of chloroform/hexane was used for recrystallization to obtain an orange crystal. Yield: 82 %. ¹H RMN (CDCl₃, 300 MHz): δ (ppm) = 4.90 (s,2H), 4.29 (t,2H), 4.20 (t,2H), 4.18 (s,5H), 2.05 (s,3H). ¹³C RMN (CDCl₃, 125 MHz): δ (ppm) = 170.94; 81.21; 69.67; 68.89; 68.89; 68.58; 62.89; 21.03. (ESI) m/z: [M⁺](calcd for C₁₃H₁₄FeO₂ : 258.03377 Found: 258.03415. Elementary analysis: Calcd for C₁₃H₁₄FeO₂: C 60.50; H 5.47. Found: C 60.58; H 5.56.

Preparation of 1-(methylferrocenyl)-3-methylimidazolium ([EimFc][NTf₂]).

Ferrocenylmethylacetate (1.0 eq) was firstly dissolved in a acetonitrile:Milli-Q water (1:1) mixture. Methylimidazole (1.5 eq) and Li [NTf₂] (1.2 eq) were then added to the solution and the resulting mixture was stirred and heated at reflux temperature for 12 hours. The solvent was removed under reduced pressure and the product was dissolved in dichloromethane. The organic phase was washed with Milli-Q water (3x100 mL). The organic phase was dried with magnesium sulfate. [EimFc][NTf₂] was triturated with diethyl ether and was purified by flash column chromatography using silica gel as the stationary phase and acetone as the eluent. The salts were dried overnight under reduce pressure at 65 °C to give red-brown oil or red-yellow solid. Yield: 69 %. ¹H NMR (300 MHz, DMSO-d₆) δ (ppm): 9.06 (s, 1H); 7.71 (t, 1H); 7.63 (t, 1H); 5.15 (s, 2H); 4.43 (t, 2H); 4.23 (m, 7H); 3.81 (s, 3H). ¹⁹F NMR (DMSO-d₆, 282 MHz): δ (ppm) = -80.13. ¹³C NMR (125 MHz, DMSO-d₆) δ (ppm): 136.34; 124.04; 122.45; 122.10; 117.82; 113.58; 81.34; 69.19; 48.78; 36.21. (ESI) m/z: [M⁺](calcd for C₁₅H₁₇FeN₂ : 281.07412 Found: 281.07577; m/z: [M^{*}](calcd for C₂F₆NO₄S₂ : 279.91784 Found: 279.91857. Elementary analysis: Calcd for C₁₇H₁₇F₆FeN₃O₄S₂: N 7.49; C 36.38; H 3.05; S 11.43. Found: N 7.41; C 36.53; H 2.87; S 11.44.

2. Scan rate data for the three redox couples, and simulation fitting methodology

Figure 2 displays cyclic voltammograms (CVs) of the three different redox couples, and Figure 3 displays a comparison of the experimental and simulated data. Fitting between experimental and simulated data was achieved over 5 scan rates (25, 50, 100, 200 and 400 mV s^{-1} , covering 16-fold time ranges). Table S1 displays the peak potentials and peak-to-peak separation for all three systems over the 5 scan rates, while Table S2 displays the peak current values and ratio of peak heights, for the first scan. The first scan is shown visually at 50 mV s^{-1} in Figure 2, and the second scan for all scan rates are displayed visually in Figure S3.

Simulation was initially performed at 50 mV s^{-1} using the auto-fitting tool in DigiElch 7. These parameters were then used to compare simulation *vs* experimental at the other scan rates (*i.e.* 1 slower scan and 3 faster scans). The parameters were then manually altered in the 50 mV s^{-1} simulation and applied to the other scan rates, until a reasonable fit could be observed over all scan rates. Fitting was therefore biased towards the scan rate of 50 mV s^{-1} , while ensuring that a good match with the peak-to-peak separation, ratio of peak currents and other features were also achieved at faster and slower scan rates.

Table S1: Peak potential values and peak-to-peak separation values recorded by scan rate studies of 10 mM Fc, [EimFc][NTf₂] or [Bmim][FcNTf], dissolved in [Emim][NTf₂].

	Scan rate / mV s ⁻¹				
	25	50	100	200	400
Redox couple	Fc → Fc⁺ + e⁻				
E _{p,ox} / V	0.390	0.390	0.395	0.400	0.410
E _{p,red} / V	0.310	0.305	0.305	0.305	0.300
ΔE _p / mV	80 ± 5	85 ± 5	90 ± 5	95 ± 5	110 ± 5
Redox couple	EimFc⁺ → EimFc²⁺ + e⁻				
E _{p,ox} / V	0.645	0.645	0.650	0.660	0.670
E _{p,red} / V	0.555	0.555	0.550	0.545	0.530
ΔE _p / mV	90 ± 5	90 ± 5	100 ± 5	115 ± 5	140 ± 5
Redox couple	FcNTf⁻ → FcNTf^{+·-} + e⁻				
E _{p,ox} / V	0.570	0.575	0.585	0.585	0.590
E _{p,red} / V	0.495	0.495	0.500	0.500	0.500
ΔE _p / mV	75 ± 5	80 ± 5	85 ± 5	85 ± 5	90 ± 5

Table S2: Peak current values and the ratio of peak current values recorded by scan rate studies of 10 mM Fc, [EimFc][NTf₂] or [Bmim][FcNTf], dissolved in [Emim][NTf₂].

	Scan rate / mV s ⁻¹				
	25	50	100	200	400
Redox couple	Fc → Fc⁺ + e⁻				
I _{p,ox} / μA	5.9	8.2	11.7	16.3	22.5
I _{p,red} / μA	-4.1	-6.0	-8.4	-11.3	-15.3
Ratio: I _{p,red} / I _{p,ox}	0.7	0.7	0.7	0.7	0.7
Redox couple	EimFc⁺ → EimFc²⁺ + e⁻				
I _{p,ox} / μA	3.9	5.5	7.4	10.2	13.6
I _{p,red} / μA	-2.4	-3.7	-5.1	-6.5	-8.1
Ratio: I _{p,ox} / I _{p,red}	0.6	0.7	0.7	0.6	0.6
Redox couple	FcNTf⁻ → FcNTf^{+,-} + e⁻				
I _{p,ox} / μA	5.4	7.1	9.8	14.0	20.2
I _{p,red} / μA	-2.8	-3.8	-6.4	-9.5	-13.4
Ratio: I _{p,ox} / I _{p,red}	0.5	0.5	0.7	0.7	0.7

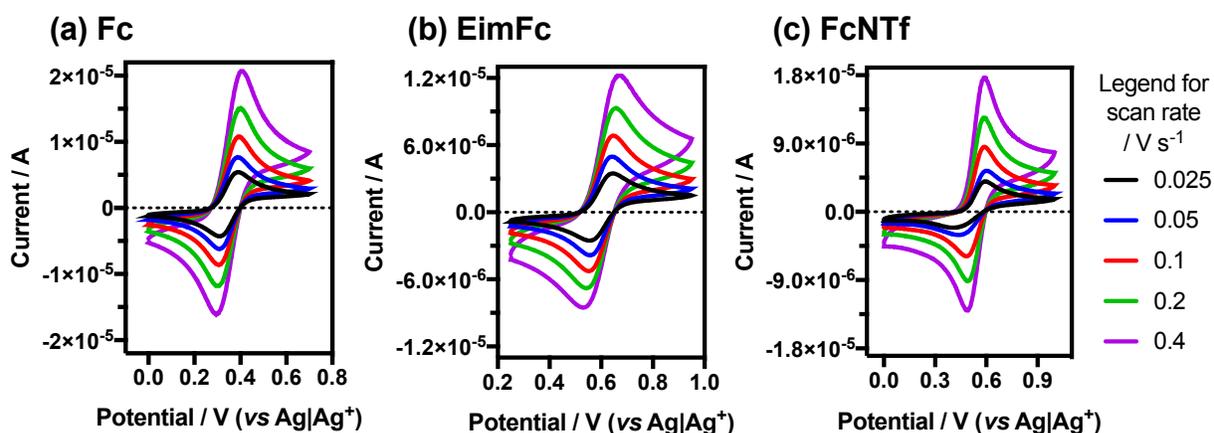


Figure S3: Overlaid cyclic voltammograms showing scan rate studies of (a) Fc, (b) [EimFc][NTf₂] and (c) [Bmim][FcNTf]. All show the second scan, for 10 mM of the compound dissolved in [Emim][NTf₂], recorded at a Pt electrode (full details of cell found in Experimental section in the manuscript)

3. Literature values utilised in the construction of Figure 5

Table S3: The five Fe- and Cr-based redox couples redox couples previously investigated by Migita *et al.* and their reported physicochemical parameters.[2] These values were used to generate the five data points (●) shown in Figure 5.

Redox couple	r / nm	dE/dT / mV K ⁻¹	ΔS / J mol ⁻¹ K ⁻¹
[FeCl ₄] ⁻²⁻ □	0.40	-0.48 ± 0.02	-46 ± 2
[FeBr ₄] ⁻²⁻	0.43	-0.42 ± 0.01	-40 ± 1
Fc ⁺⁰	0.38	0.10 ± 0.01	10 ± 1
[Cr(bpy) ₃] ^{3+/2+}	0.68	0.43 ± 0.03	41 ± 3
[Fe(bpy) ₃] ^{3+/2+}	0.68	0.48 ± 0.02	46 ± 2

Where Fc = ferrocene and bpy = bipyridine

4. Cyclic voltammograms comparing AcFc and NTfFc

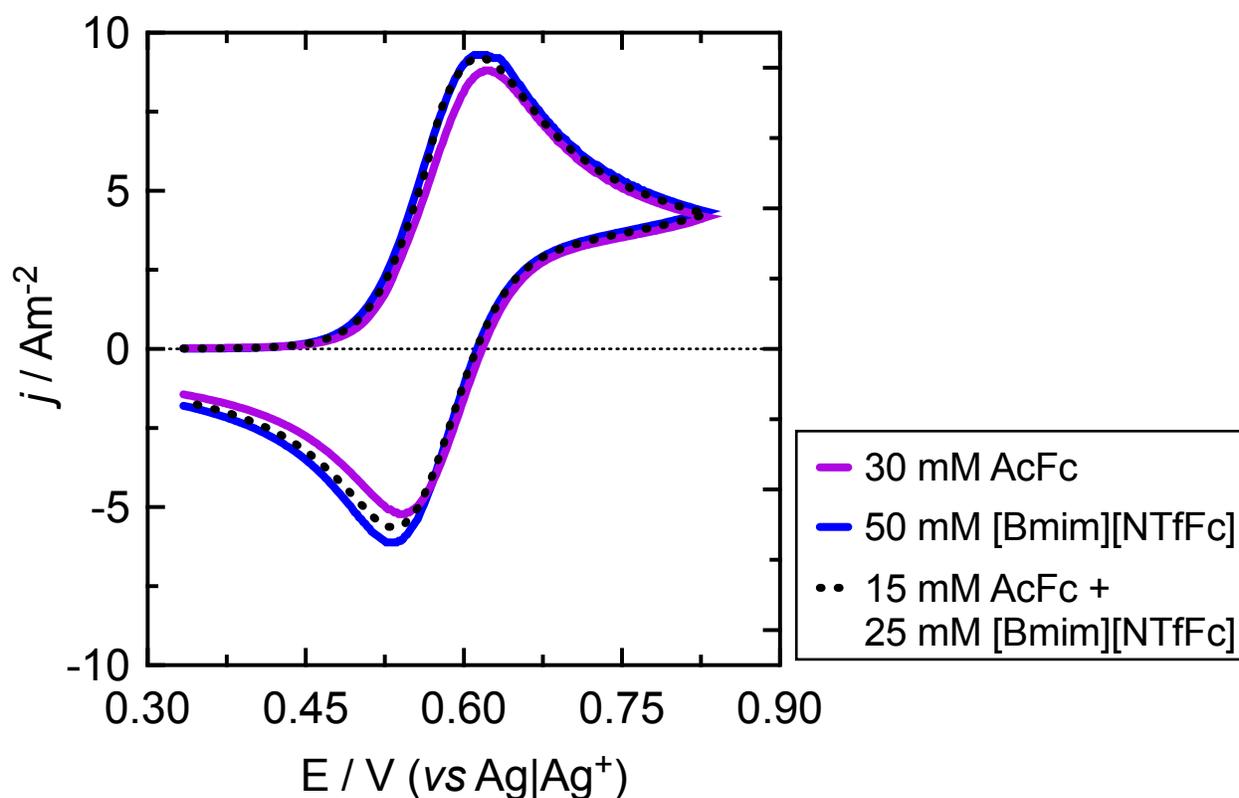


Figure S4: Overlaid cyclic voltammograms in [Emim][NTf₂] for (purple line) 30 mM AcFc, or (dark blue line) 50 mM [Bmim][FcNTf], or (dashed black line) a mixture of 15 mM AcFc and 25 mM [Bmim][FcNTf]. All recorded at a Pt electrode at 25 mV s⁻¹.

5. References

- [1] J. Zhang, B. Yang, Y. Yang, B. Zhang, *Frontiers of Chemistry in China*, 2009, **4**, 52-57.
- [2] T. Migita, N. Tachikawa, Y. Katayama and T. Miura, *Electrochemistry*, 2009, **77**, 639-641.