

## Electronic Supplementary Information

### High Seebeck Coefficient Redox Ionic liquid Electrolytes for Thermal Energy Harvesting

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#### *Ionic liquids Synthesis*

##### 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl) amide.

[C<sub>2</sub>mim][NTf<sub>2</sub>]

1-ethyl-3-methylimidazolium bromide (Merck, used without further purification) (50.00 mmol, 9.552 g) was dissolved in ~50mL of water and treated with lithium bis(trifluoromethanesulfonyl)amide (purchased from 3M and used without further purification) (50.00 mmol, 14.35 g) and the solution was stirred at room temperature for one hour. The product was then extracted from water with dichloromethane and washed with deionized water (5 x 50mL). Dichloromethane was then evaporated via rotary evaporation and the product was further dried under high vacuum for 8 hours. Yield: 13.35g, 68%. <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ (ppm) 1.42 (triplet, J= 7.3Hz, 3H), 3.84 (singlet, 3H), 4.19 (quartet, J= 7.3Hz, 2H), 7.67 (singlet, 1H), 7.76 (singlet, 1H), 9.10 (singlet, 1H). <sup>13</sup>C-NMR (DMSO-*d*<sub>6</sub>): δ (ppm) 14.98, 35.63, 44.11, 119.47 (quartet, J<sub>C-F</sub> = 320 Hz), 121.92, 123.53, 136.21. MS (ESI): (+) 111.1, (-)279.9.

1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl) amide, [C<sub>4</sub>mpyr][NTf<sub>2</sub>]

1-butyl-1-methylpyrrolidinium bromide (Merck, used without further purification) (50.00 mol, 11.109 g) was dissolved in ~60mL of water and combined slowly with lithium bis(trifluoromethanesulfonyl)amide (3M, used without further purification) (55.00 mmol, 15.779 g) then stirred at room temperature for one hour. The oil product was extracted from water with dichloromethane (reagent grade, Emsure) and washed with deionized water (5 x 50mL). Dichloromethane was then evaporated via rotary evaporation and the product was further dried under high vac. Yield: 13.507g, 64%. <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>): δ 0.94 (triplet, J= 7.2 Hz, 3H), 1.33 (sextet, J= 7.2 Hz, 2H), 1.70 (quintet, J= 8.0 Hz, 2H), 2.10 (singlet, 4H), 2.99 (singlet, 3H), 3.46 (multiplet, 4H). <sup>13</sup>C-NMR (DMSO-*d*<sub>6</sub>): δ 13.37, 19.25, 21.03, 24.87, 47.48, 62.90, 62.92, 63.39, 63.41, 119.45 (quartet, J<sub>C-F</sub> = 320 Hz). <sup>19</sup>F-NMR (DMSO-*d*<sub>6</sub>): δ -78.93. MS (ESI): (+)142.2, (-)279.9.

**Discussion of the relationship:  $\partial E(T)/\partial T = \Delta S^{\circ}_{rc}/nF$**

The thermal temperature coefficient relationship to the entropy change accompanying the redox reaction relies on two assumptions: the entropy of migration transport (also known as the Soret redistribution) is small and not present over the course of the measurement<sup>[1]</sup>; and the Nernst equation term due to the redox species can be approximated to 1 as discussed below.

(i) Soret term

It is known that the initial thermal temperature coefficient is higher than the long-term steady state value by a small degree, however it can take days for this decrease due to the Soret redistribution to occur and therefore, under the present experimental conditions which determine initial temperature dependences, the Soret term is not an important contribution to the measurement.<sup>[1, 2]</sup> References 1 and 2 discuss the origins of this term in more depth.

(ii) Nernst Equation term:

For a general  $\text{Ox} + n\text{e}^- \rightarrow \text{Red}$  reaction:

$$E = E^\circ - \frac{RT}{nF} \ln \frac{a_{\text{red}}}{a_{\text{ox}}} \quad (1)$$

where “a” is the activity of the redox species. The activity can be described in general by  $a = \gamma c$  where  $\gamma$  is an activity coefficient and  $c$  is the concentration of each redox species. If, as is the case in the present work, the redox species are present in the solution at the same concentration then equation 1 reduces to:

$$E = E^\circ - \frac{RT}{nF} \ln \frac{\gamma_{\text{red}}}{\gamma_{\text{ox}}}$$

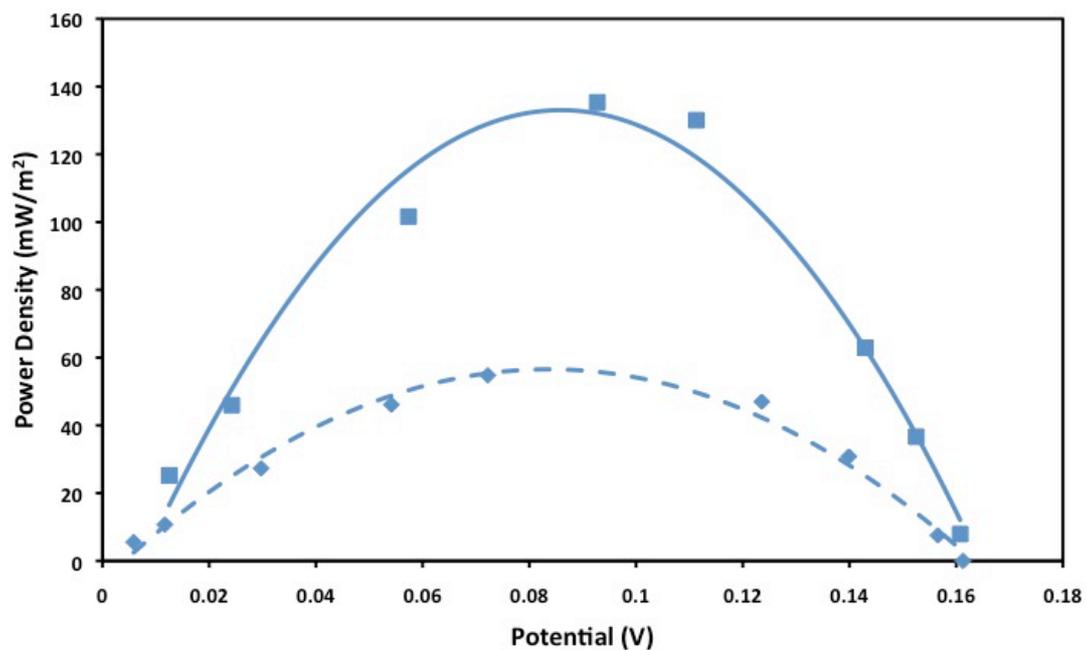
Activity coefficients of redox couple species arising in the ionic liquid media are unknown and therefore only approximations can be made at this stage. Assuming the activity coefficient *ratio* does not deviate far from 1, at a first level of approximation the *ln* term vanishes and hence  $E = E^\circ$ . Therefore, with the 1:1  $\text{Co}(\text{bpy})_3^{2+/3+}$  redox reaction considered here,

$$\frac{\partial E}{\partial T} = \frac{\partial E^\circ}{\partial T}$$

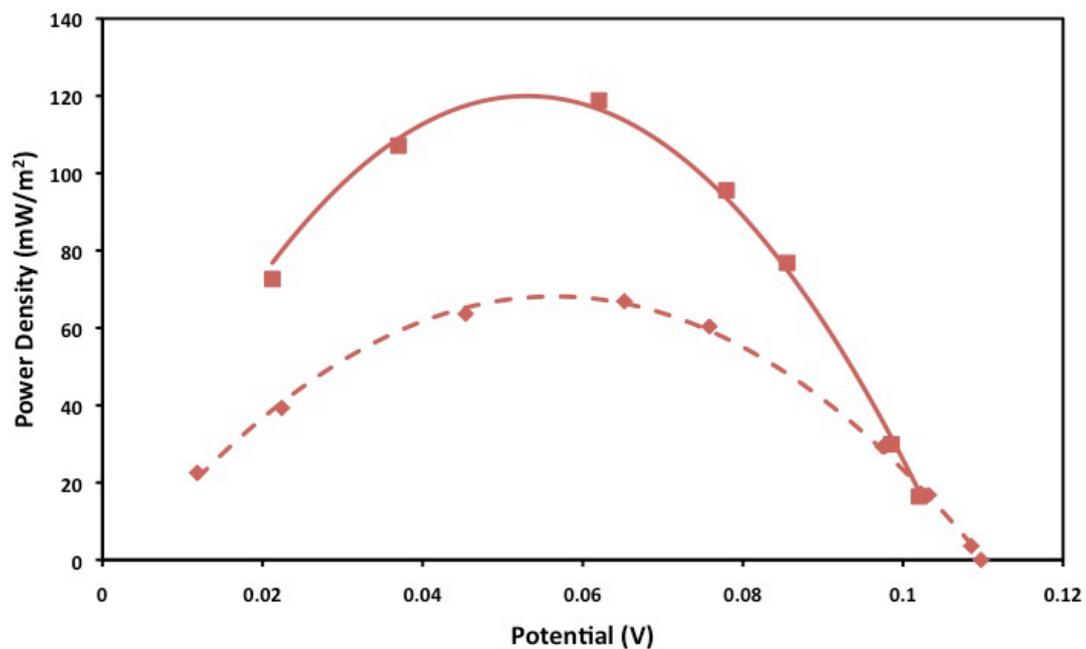
A further issue arises in connection with the reference scale used to determine the potentials. DeBethune *et al.*<sup>2</sup> define a quantity  $\partial E_{\text{isotherm}} / \partial T$  which is determined from measurements at different temperatures in a cell having no temperature gradient, using a standard hydrogen electrode reference electrode. Because of the varying potential of the SHE as a function of temperature on an absolute scale, this quantity differs from the practical quantity  $\partial E_{\text{therm}} / \partial T$  determined in a cell involving a single redox reaction operating in a thermal gradient. The latter is the quantity measured in this work as it embodies the practical situation in an operational thermoelectrochemical cell.

## Results

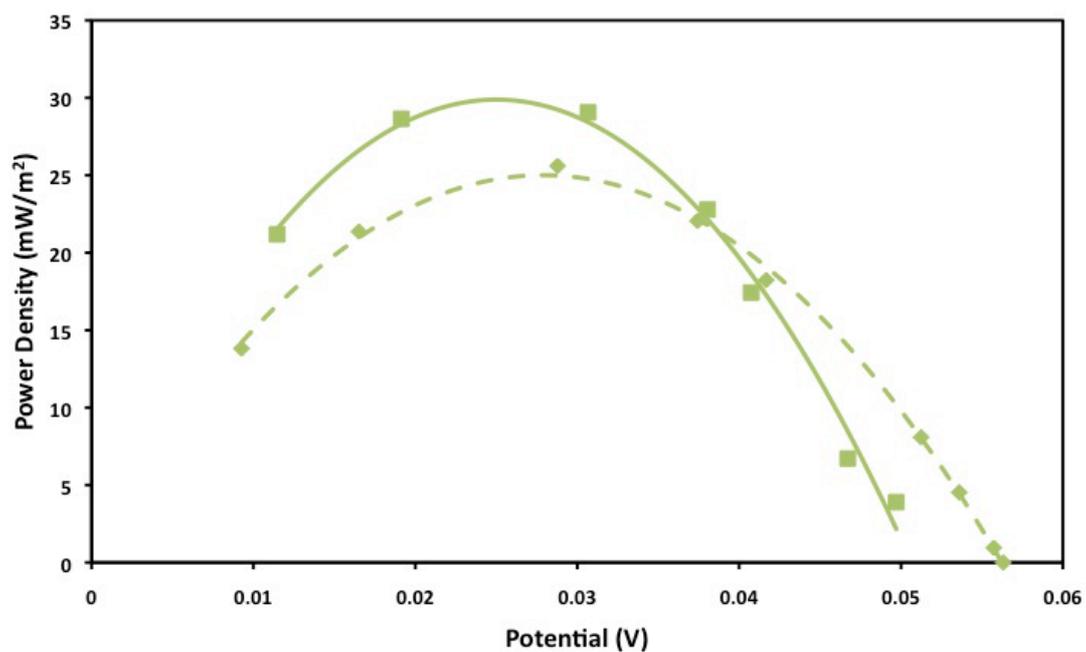
A)



B)

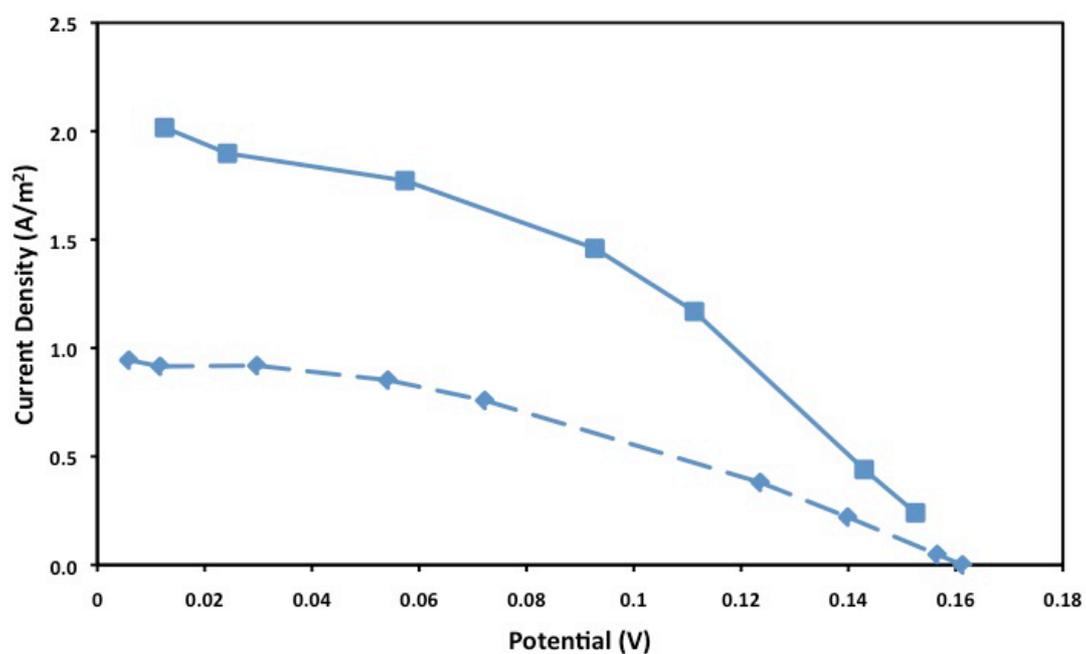


C)

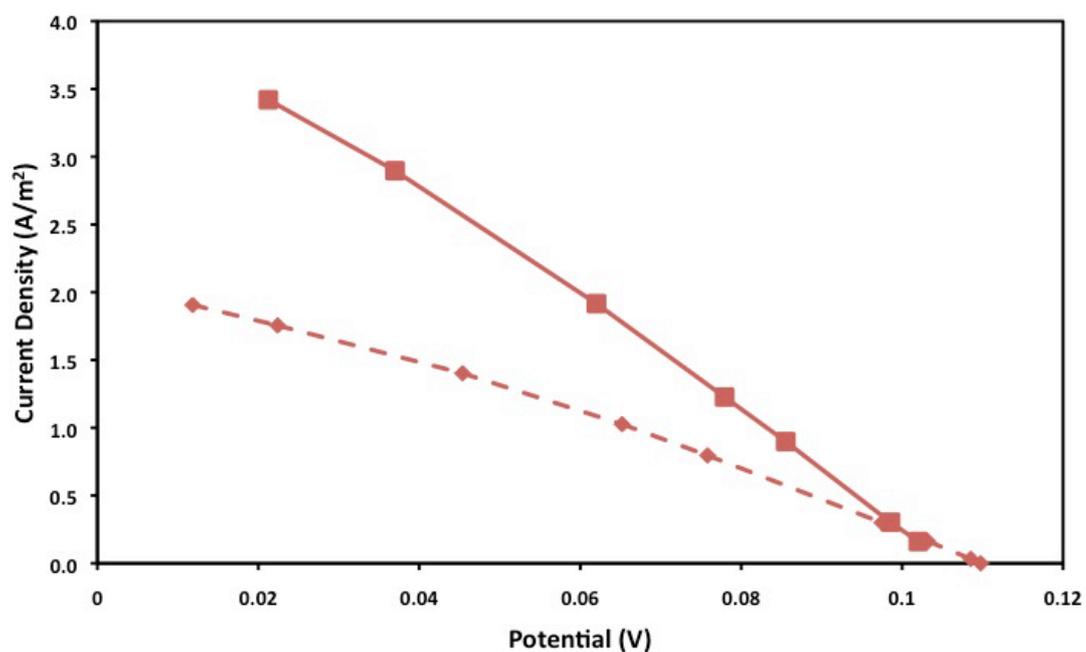


**Figure S1.** Thermochemical cell power-potential plots using ■ ◆ ◆ 0.1M and ◆ ◆ ◆ 0.05M  $\text{Co}^{\text{II/III}}(\text{bpy})_3(\text{NTf}_2)_{2/3}$  in  $[\text{C}_2\text{mim}][\text{NTf}_2]$ :  $T_{\text{hot}} (\text{°C})/T_{\text{cold}} (\text{°C})$ : (A) blue - 130/30, (B) red - 130/60, (C) green 130/90.

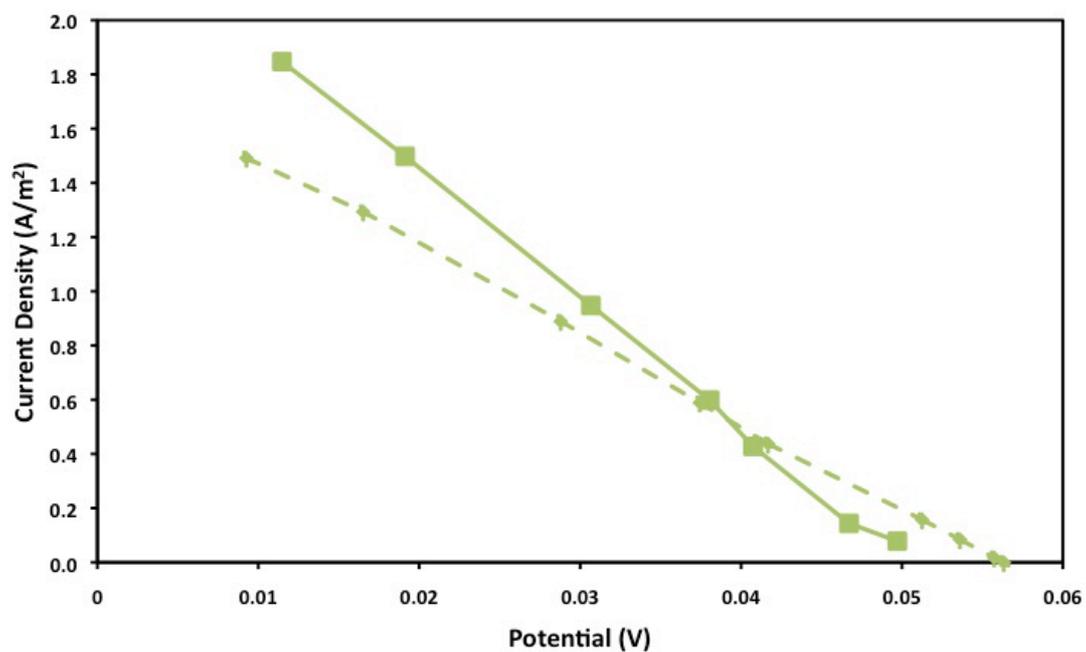
A)



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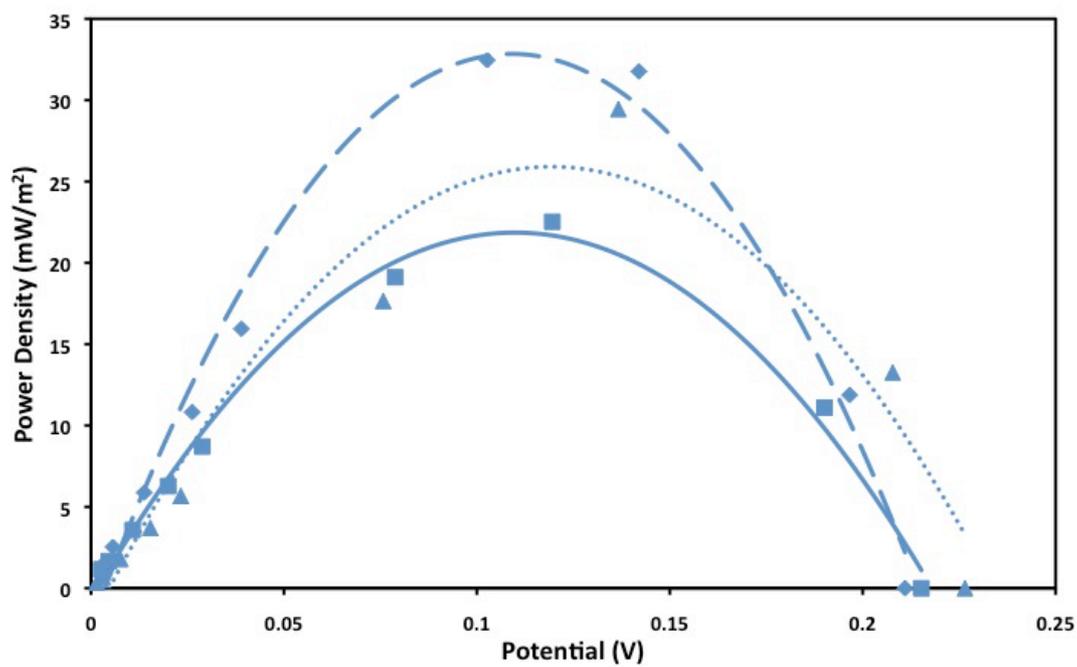


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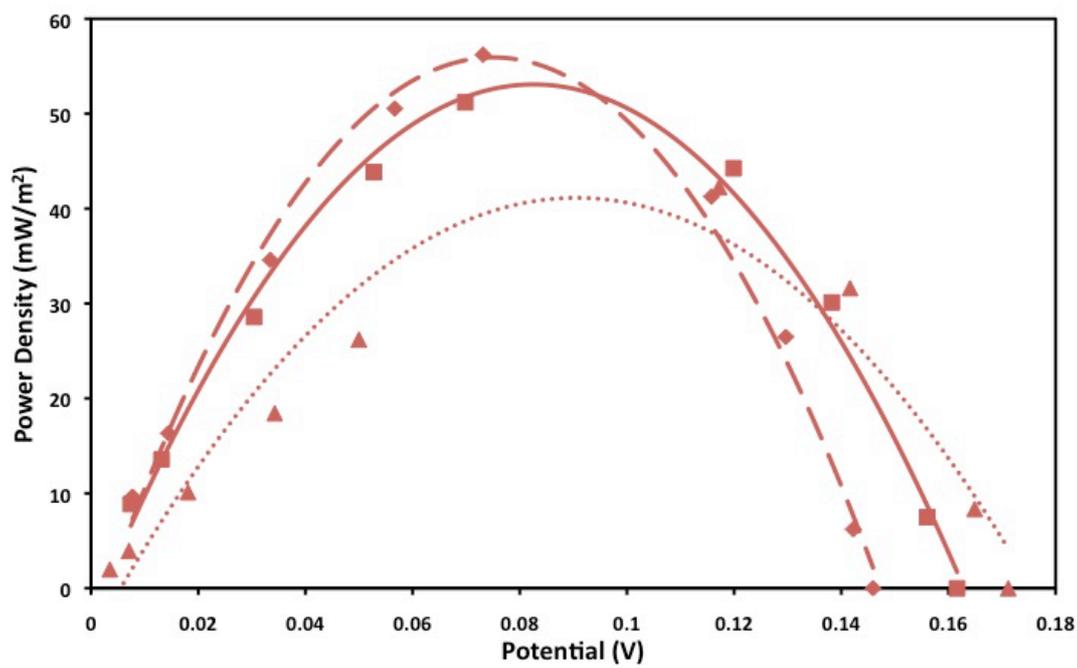


**Figure S2.** Thermoelectrochemical cell current-potential plots using ■ ■ ■ 0.1M and ◆ ◆ ◆ 0.05M  $\text{Co}^{\text{II/III}}(\text{bpy})_3(\text{NTf}_2)_{2/3}$  in  $[\text{C}_2\text{mim}][\text{NTf}_2]$ :  $T_{\text{hot}} (\text{°C})/T_{\text{cold}} (\text{°C})$ : (A) blue - 130/30, (B) red - 130/60, (C) green 130/90

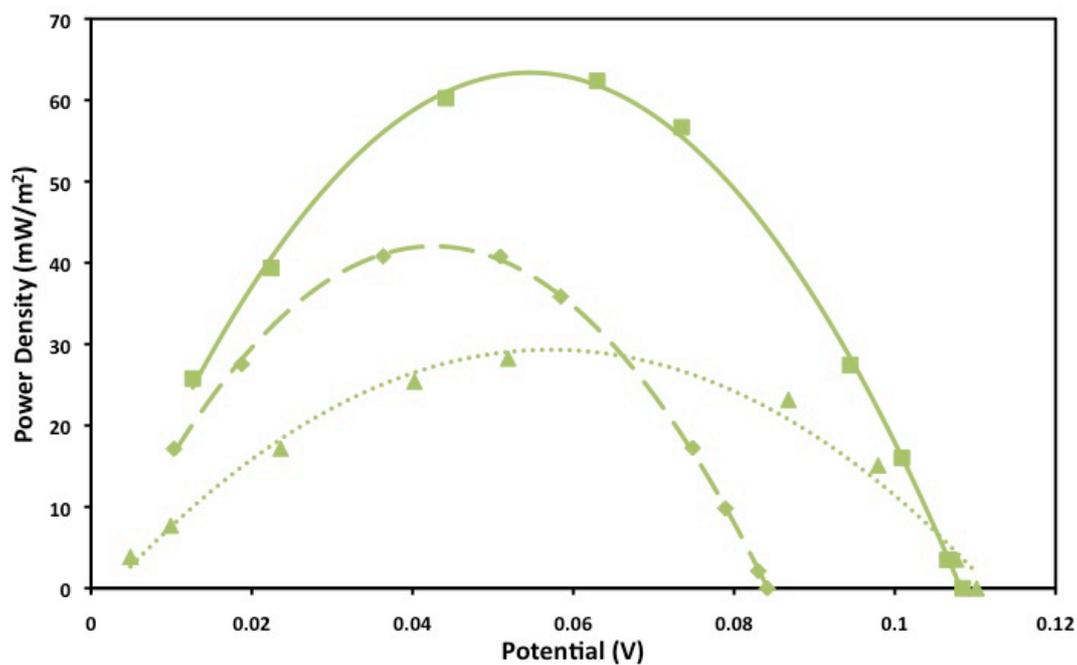
A)



B)

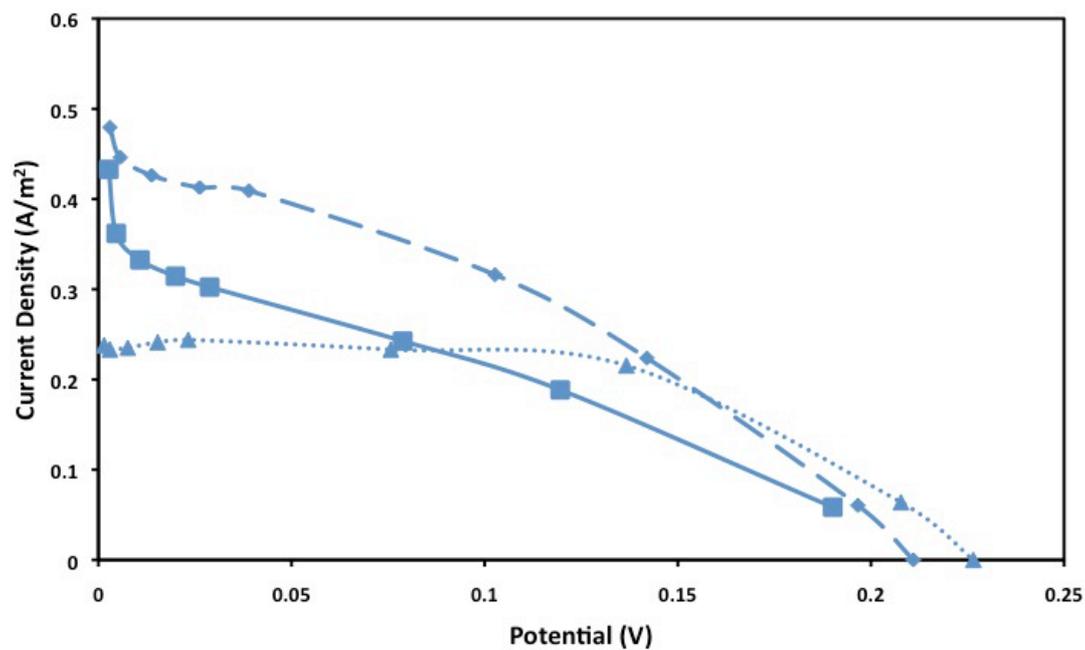


C)

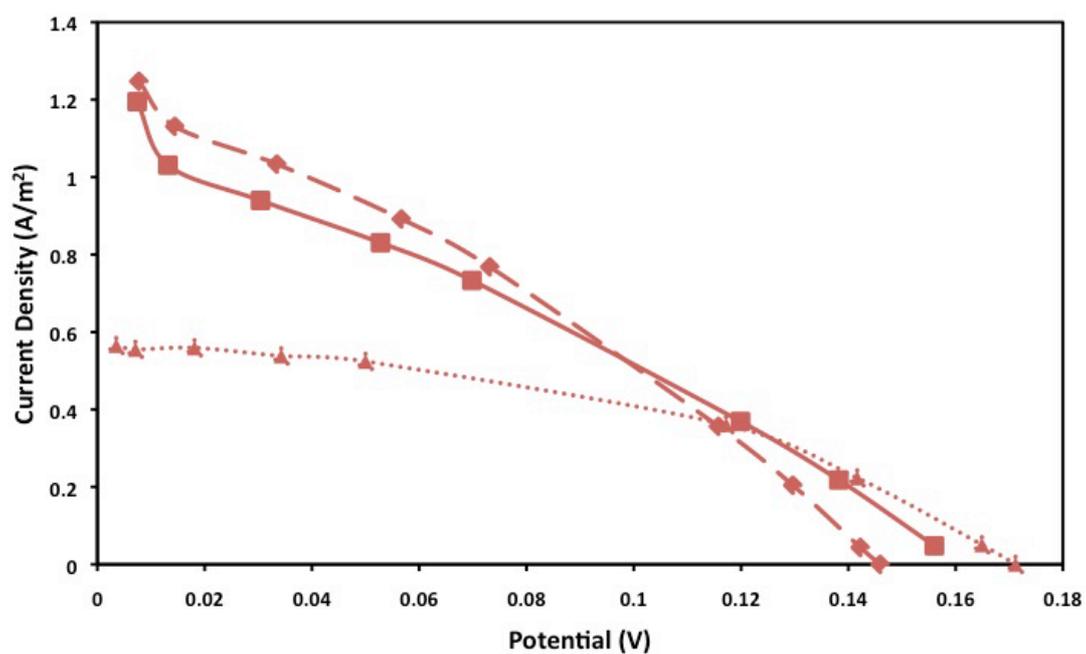


**Figure S3.** Thermoelectrochemical cell power - potential plots using ■■■ 0.1M, ◆◆◆ 0.05M, ▲▲▲ 0.01M Co<sup>II/III</sup>(bpy)<sub>3</sub>(NTf<sub>2</sub>)<sub>2/3</sub> in [C<sub>2</sub>mim][eFAP]: T<sub>hot</sub> (°C)/T<sub>cold</sub> (°C): (A) blue - 130/30, (B) red - 130/60, (C) green 130/90.

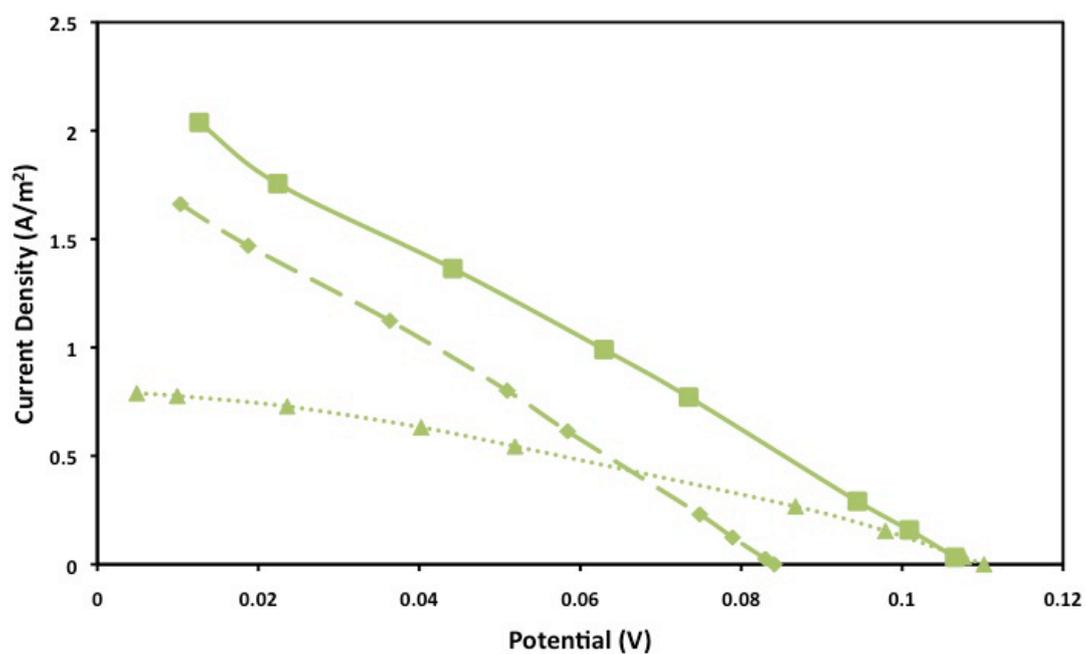
A)



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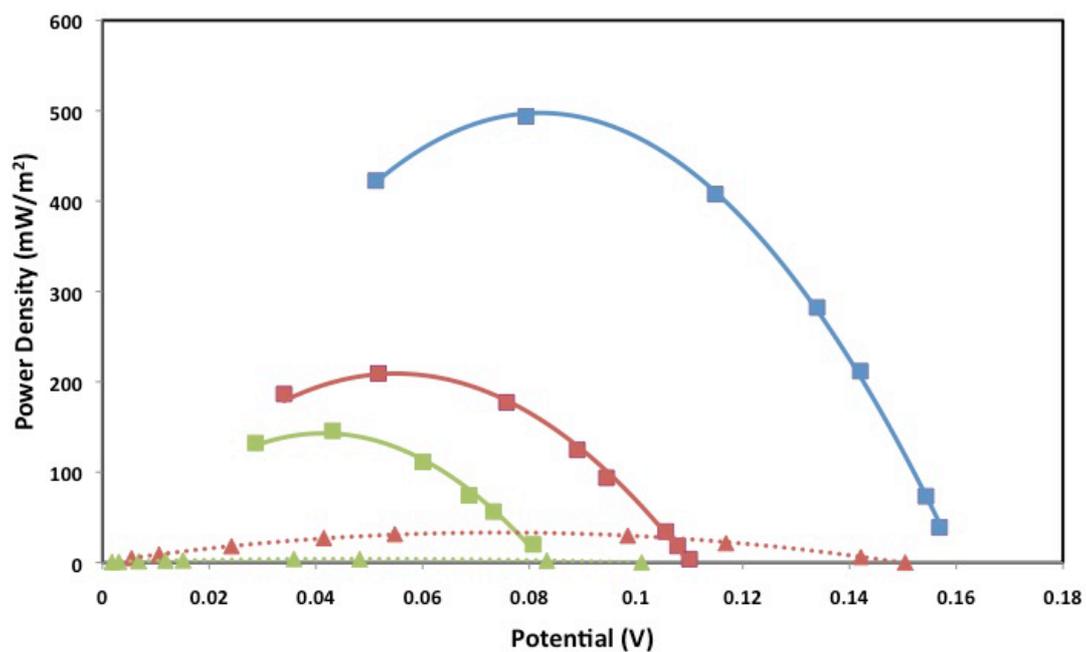


C)

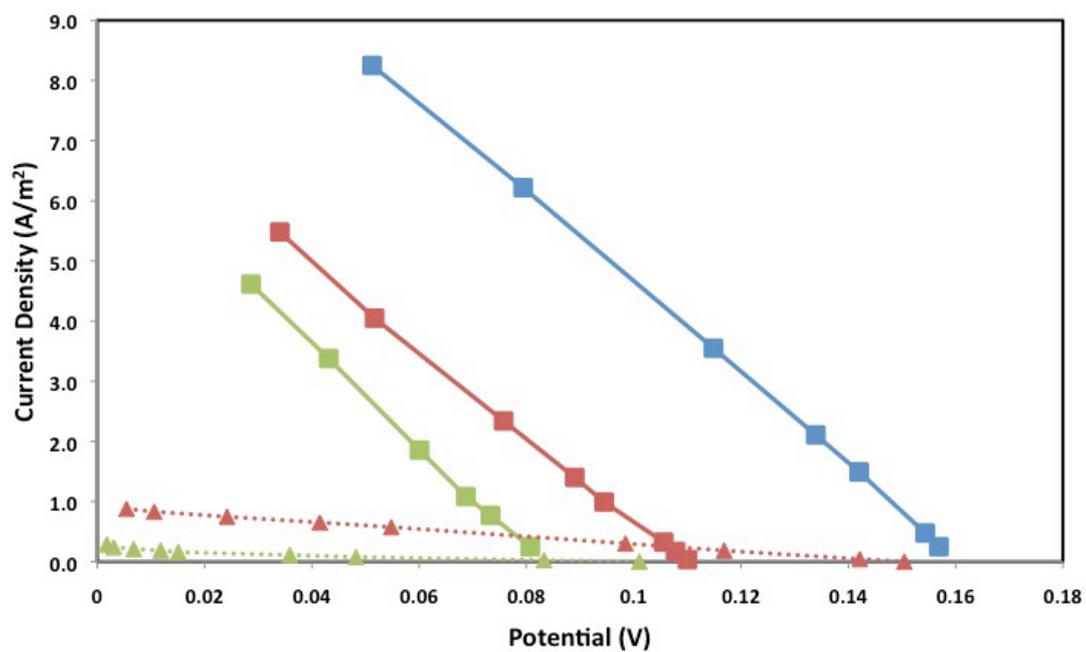


**Figure S4.** Thermochemical cell current - potential plots using  $\blacksquare$   $\blacklozenge$   $\blacktriangle$  0.1M,  $\blacklozenge$   $\blacktriangle$  0.05M,  $\blacktriangle$  0.01M  $\text{Co}^{\text{II/III}}(\text{bpy})_3(\text{NTf}_2)_{2/3}$  in  $[\text{C}_2\text{mim}][\text{eFAP}]$ :  $T_{\text{hot}}$  ( $^{\circ}\text{C}$ )/ $T_{\text{cold}}$  ( $^{\circ}\text{C}$ ): (A) blue - 130/30, (B) red - 130/60, (C) green 130/90.

A)



B)



**Figure S5.** Thermochemical cell power (A) and current (B) potential plots using  $\blacksquare$   $\blacksquare$   $\blacksquare$  0.1M,  $\blacklozenge$   $\blacklozenge$   $\blacklozenge$  0.05M,  $\blacktriangle$   $\blacktriangle$   $\blacktriangle$  0.01M  $\text{Co}^{\text{II/III}}(\text{bpy})_3(\text{NTf}_2)_{2/3}$  in MPN:  $T_{\text{hot}} (\text{°C})/T_{\text{cold}} (\text{°C})$ : blue - 130/60, red - 130/70, green 130/90.

## References:

1. T. I. Quickenden and Y. Mua, *Journal of the Electrochemical Society* **142** (11), 3985-3994 (1995).
2. A. J. DeBethune, T. S. Licht and N. Swendeman, *Journal of the Electrochemical Society* **106**, 616-625 (1959).