Supplementary Information.

Materials and Sources

Lithium iodide (99.9%), Iodine (99.999%), methoxypropionitrile (98%) and valeronitrile (99.5%) were purchased from Sigma-Aldrich. Valeronitrile was distilled before use. Benzonitrile was purchased from Merck and used without further purification. 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl) $([C_2mim][NTf_2])$ 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl) amide ([C₄mpyr][NTf₂]) and tributylhexyl phosphonium bis(trifluoromethanesulfonyl)amide ([P_{4,4,4,6}][NTf₂]) were synthesised according to literature method and dried before use.1, 2 1-ethyl-3-methylimidazolium tetracyanoborate (high purity. $[C_2mim][B(CN)_4]$ and 1-ethvl-3methylimidazolium tetrafluoroborate (Electronic grade, [C2mim][BF4]) were purchased from Merck and triethylmethoxymethylphosphonium bis(trifluoromethanesulfonyl)amide ([P_{2,2,2,(101)}][NTf₂]) was obtained from Nippon Chemicals.

Electrolyte Preparation

In all aqueous and organic electrolyte solutions, 2 equivalents of lithium iodide and 1 equivalent of iodine were dissolved in solution. Solutions were heated to ensure dissolution of electrolyte and then dilutions were made using volumetric flasks to the desired concentration.

In ionic liquid electrolytes 2 equivalents of 1-ethyl-3-methylimidazolium iodide and 1 equivalent of iodine were dissolved in solution by heating to 100°C for a short period of time to ensure dissolution, then diluted to the desired concentration in volumetric flasks.

Two equivalents of iodide were added to one equivalent of iodine to produce a 1:1 mole ratio of iodide/triiodide via

$$I_2$$
 + $I^ \rightleftharpoons$ I_3^-

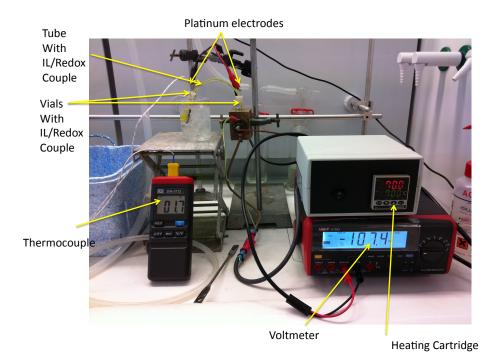


Figure 1. Experimental set up for Seebeck coefficient measurement. Two vials containing ~1mL of solution in each bridged by a tube are kept at different temperatures. A platinum electrode is placed in each and the potential difference created due to the temperature difference is monitored. The "hot" side is a brass block with a slot for the vial to rest attached to a heating cartridge. The "cold" side is either a beaker of ice water or room temperature water, monitored by a RS thermocouple.

- 1. P. Bonhote, A.-P. Dias, N. Papageorgiou, K. Kalyanasundaram and M. Graetzel, *Inorganic Chemistry*, 1996, **35**, 1168-1178.
- 2. C. J. Bradaric, A. Downard, C. Kennedy, A. J. Robertson and Y. Zhou, *Strem Chemiker*, 2003, **20**, 2-11.