Supplementary Material

The effect of solvent on the Seebeck coefficient and thermocell performance of cobalt bipyridyl and iron ferri/ferrocyanide redox couples

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Experimental technique

Materials

Potassium ferricyanide ($K_3[Fe(CN)_6].3H_2O$), potassium ferrocyanide ($K_4[Fe(CN)_6]$), ammonium ferrocyanide ($(NH_4)_4Fe(CN)_6$) and tetraethylammonium tetrafluoroborate $[Et_4N]BF_4$ were purchased from Sigma Aldrich and used as received. 1-ethyl-3-methylimidazolium diethylphosphate ($[C_2mim][DEP]$) was purchased from Merck (purity ≥98%), and used as received.

Cobalt-based redox couples ($[Co(bpy)_3][NTf_2]_{2/3}$ and $[Co(bpy)_3][BF_4]_{2/3}$) and $(Et_4N)_3[Fe(CN)_6]$ were prepared following the previously reported procedures.[1]

Electrolyte preparation:

Equimolar of redox complexes ($K_4Fe(CN)_6$/ $K_3Fe(CN)_6$, $[Co(bpy)_3][BF_4]_2$/ $[Co(bpy)_3][BF_4]_3$ or $[Co(bpy)_3][NTf_2]_2$/$[Co(bpy)_3][NTf_2]_3$) were dissolved in solvent (water or MPN) to prepare a liquid electrolytes. For example, to prepare 0.01 M $[Co(bpy)_3][BF_4]_{2/3}$ in water, 24 mg (0.03 mmol) of $[Co(bpy)_3][BF_4]_3$ and 21 mg (0.03 mmol) of $[Co(bpy)_3][BF_4]_3$ were mixed and dissolved in minimum of water, then the volume of solution was reached to 3 ml by addition of water.

Electrochemical behaviour, Seebeck and Diffusion coefficient

A non-isothermal cell setup with two platinum wires (electrodes) was used to measure the Seebeck coefficient of redox couple. The temperature of one side was increased by 5 °C, while the temperature

of other side was at room temperate, and the potential difference between two electrodes was measured using a *UNI-T UT803 TRMS* voltameter.

A three-electrode set-up, equipped with a platinum working electrode (1.6 mm diameter, ASL, Japan) and two platinum wires as reference and counter electrodes, was used to study the electrochemical behaviour. Diffusion coefficient or redox ions was measured using chronoamperometry technique to scan between -0.5 V and +0.5 V and calculated using the Cottrell equation.

The thermo-electrochemical cell

A Teflon cell with a 9 mm internal diameter (representing the active electrode area) and electrode spacing (thickness of Teflon cell) of 1cm sandwiched between two platinum disks (18 mm diameter) was used to measure the performance of cell containing liquid electrolytes. During the operation, the cell setup was kept in horizontal configuration (two vertical electrodes).

A heating system containing a cartridge heater inside a copper block - connected to a *Manson NP-9613 DC* regulated power supply- and a *TE Technology cold plate cooler CP- 031* were used to control the temperature of electrodes. The temperatures of the hot electrode was set on 60 $^\circ$C, while the cold electrode was set on 20 $^\circ$C. The temperatures of electrodes were measured using a sensor connected to *Novous NI020* temperature controllers with an accuracy of ± 0.1 °C. To study the performance of cell, the power and current output of the cell were measured through applying different resistance using a *Bio-Logic SP-200* and *EC-Lab* software and Constant Load Discharge (CLD) technique. To get a constant and steady power and current output, the performance of cell at each applied resistance was measured after 10 minutes.

Fourier Transform Infrared (FTIR) and UV-Vis Spectroscopy Measurement

An ATR-FTIR spectrometer (Perkin Elmer) was used to study the IR absorbance. Each sample was measured over 64 scans with resolution of 4 cm^{-1} in the range of 600 to 4000 cm^{-1}. The absorbance spectra of liquid electrolytes was obtained between 200 nm and 800 nm using a Shimadzu UV-Vis spectrophotometer (UV-2600), and a quartz cuvettes (Starna), with path length of 5 mm and internal width of 2 mm.

For FT-IR study, 0.1 M solutions of $[Co(bpy)_3][BF_4]_2$ or $[Co(bpy)_3][BF_4]_3$ in DMSO and in mixed solvents were prepared. Due to the low solubility of $[Co(bpy)_3][BF_4]_2$ and $[Co(bpy)_3][BF_4]_3$ in water, 0.05 M solutions of cobalt ions in pure water were prepared. 0.1 M solutions of $K_3Fe(CN)_6^{3-}$ in water or mixed solvents were prepared and to study using FTIR. $K_4Fe(CN)_6^{4-}$, has lower solubility compared with $K_3Fe(CN)_6^{3-}$, and it was not possible to prepare 0.1 M solution of $K_4Fe(CN)_6^{4-}$ in water mixed with DMSO or Isopropanol. So, only 0.1 M solutions of $K_4Fe(CN)_6^{4-}$ in pure water, mixed water/ MPN and mixed water/ ethylene glycol were studied in FT-IR.

Results

Table S1 Seebeck coefficient, $P_{max}/(\Delta T)^2$ and diffusion coefficient of $[Co(bpy)_3]^{2+/3+}$ ions in DMSO, water, mixed solvent (water/ DMSO) in different ratios.

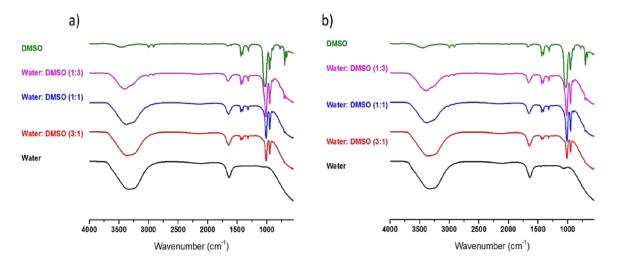| Solvent	Seebeck coefficient (mV/K)	$P_{max}/(\Delta T)^2$ (mW K^{-2} m^{-2})	Diffusion coefficient D$\times 10^6$ cm^2 s^{-1}	
			$[Co(bpy)_3]^{2+}$	$[Co(bpy)_3]^{3+}$
Water	1.22 ± 0.04	0.0036	6.58 ± 0.22	10.62 ± 1.12
Water : DMSO (3:1)	1.42 ± 0.02	0.0032	3.16 ± 0.16	4.02 ± 0.55
Water : DMSO (1:1)	1.58 ± 0.03	0.0023	2.19 ± 0.11	2.55 ± 0.21
Water : DMSO (1:3)	1.81 ± 0.09	0.0028	1.43 ± 0.07	1.72 ± 0.20
DMSO	2.65 ± 0.02	0.0063	0.67 ± 0.13	1.62 ± 0.26

Figure S1 FT-IR spectra of solutions of a) $[Co(bpy)_3][BF_4]_2$ and b) $[Co(bpy)_3][BF_4]_3$ in DMSO or mixed solvent (0.1 M) and in water (0.05 M).

The FT-IR spectra of [Co(bpy)$_3$][BF$_4$]$_2$ and [Co(bpy)$_3$][BF$_4$]$_3$ overlap with solvent's peak. Stretching and bending modes of water are observed as broad peaks at 3500 and 1600 cm^{-1}, respectively.[2] In DMSO solution, peaks related to DMSO are observed at 2900 cm^{-1} (Asymmetric C-H stretch), 2800 cm^{-1} (symmetric C-H stretch), 1400 cm^{-1} (CH$_3$), 1300 cm^{-1} (CH$_3$), 1200 cm^{-1} (S-O stretch), 1000 cm^{-1} (CH$_3$) and 750 cm^{-1} (S-C stretch).[3]

To study the UV-Vis absorbance spectra, 0.1 mM solutions of [Co(bpy)$_3$][BF$_4$]$_2$ or [Co(bpy)$_3$][BF$_4$]$_3$ were prepared in pure organic solvent (DMSO), water or mixed water/organic solvents. 1 mM solutions of K$_3$Fe(CN)$_6$$^{3-}$or K$_4$Fe(CN)$_6$$^{4-}$ were prepared in pure water or mixed with organic solvents.
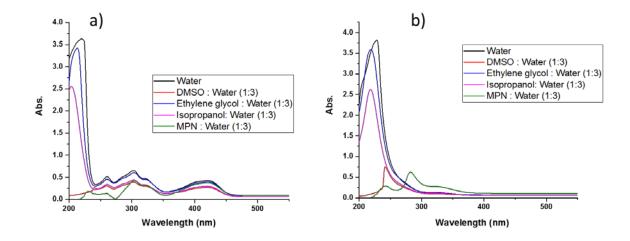

Figure S2 UV-vis spectra of 1 mM a) K$_3$Fe(CN)$_6$$^{3-}$ and b) K$_4$Fe(CN)$_6$$^{4-}$ in different solvents.
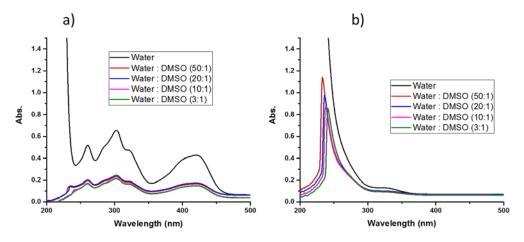

Figure S3 UV-vis spectra of: a) 1 mM K$_4$Fe(CN)$_6$ and b) 1 mM K$_3$Fe(CN)$_6$, using mixed water/DMSO as solvent in different ratios.

[1]   a) T. J. Abraham, D. R. MacFarlane, J. M. Pringle, *Energy Environ. Sci.* **2013**, *6*, 2639; b) A. Cabrera-García, A. Vidal-Moya, Á. Bernabeu, J. Sánchez-González, E. Fernández, P. Botella, *Dalton Trans.* **2015**, *44*, 14034; c) Y. Katayama, S. Nakayama, N. Tachikawa, K. Yoshii, *J. Electrochem. Soc.* **2017**, *164*, H5286.

[2]   W. Thompson, *Trans. Faraday Soc.* **1966**, *62*, 2667.

[3]   F. Cotton, R. t. Francis, W. Horrocks Jr, *J. Phys. Chem.* **1960**, *64*, 1534.