

Cryo-solvatochromism in Ionic Liquids

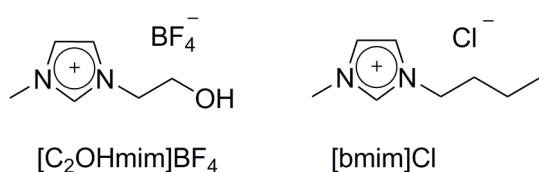
Linpo Yu and George Z. Chen*

Department of Chemical and Environmental Engineering, and Energy and Sustainability Research Division, Faculty of Engineering, University of Nottingham, Nottingham, NG7 2RD UK.

Fax: +44-115-9514115; Tel: +44-115-9514171; E-mail: george.chen@nottingham.ac.uk

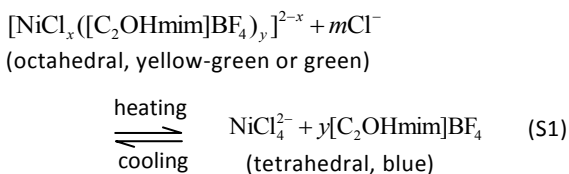
Electronic Support Information

1. Molecular structures



Scheme S1 Molecular structures of (left) the ionic liquid, $[\text{C}_2\text{OHmim}]\text{BF}_4$, as the donor solvent, and (right) the Cl^- source compound, $[\text{bmim}]\text{Cl}$.

2. General thermo-solvatochromic reaction



where $0 \leq x \leq 4$, $2 \leq y \leq 6$, $x + y = 6$, and $m + x = 4$. These restrictions lead to a maximum of four octahedral complex ions. Charge balancing ions (CBIs: BF_4^- , $[\text{bmin}]^+$ and/or $[\text{C}_2\text{OHmim}]^+$) are not shown in Reaction (S1). The type and number of CBIs in (S1) depend on the value of x , y and m . In Reaction (1), $x = y = 3$, $m = 1$, and the CBI is $[\text{bmin}]^+$.

3. Enthalpy changes derived from DSC curves 3 to 5 in Fig. 2C and 2D (Table S1)

Solutions (in $[\text{C}_2\text{OHmim}]\text{BF}_4$)	ΔH (J g^{-1}) Cooling	ΔH (J g^{-1}) Heating	ΔH^* (kJ mol^{-1}) Cooling	ΔH^* (kJ mol^{-1}) Heating
$0.14 \text{ mol L}^{-1} [\text{bmim}]_2\text{NiCl}_4$	2.01	2.02	59.1	59.4
$0.14 \text{ mol L}^{-1} [\text{bmim}]_2\text{NiCl}_4$ + $0.28 \text{ mol L}^{-1} [\text{bmim}]\text{Cl}$	3.98	4.06	59.1	59.3
$0.14 \text{ mol L}^{-1} [\text{bmim}]_2\text{NiCl}_4$ + $0.70 \text{ mol L}^{-1} [\text{bmim}]\text{Cl}$	3.42	3.81	59.0	59.3

* Estimated using density of $[\text{C}_2\text{OHmim}]\text{BF}_4$ (1.37 g mL^{-1}).

4. Cryochromic film and ionic liquid

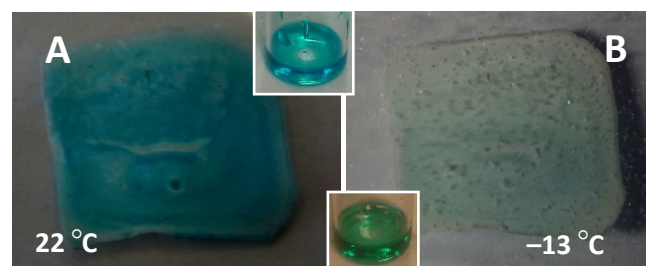


Fig. S1 Photographs of a composite film ($2 \text{ cm} \times 2 \text{ cm}$) of $[\text{C}_2\text{OHmim}]\text{BF}_4$ - $[\text{C}_2\text{OHmim}]\text{Cl}$ - $[\text{bmim}]_2\text{NiCl}_4$ -PVDF (mass ratio: 5:7:1:10) at (A) $22 \text{ }^\circ\text{C}$, (B) $-13 \text{ }^\circ\text{C}$ (in freezer). The insets show the ionic liquid solution at the respective temperatures. Note that the tiny spots in (B) were ice dusts.

5. Colours at different temperatures

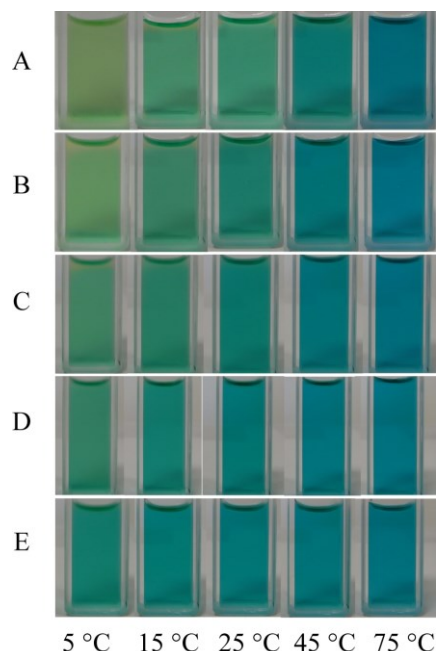


Fig. S2 Photographs of $0.0207 \text{ mol L}^{-1} [\text{bmim}]_2\text{NiCl}_4$ in $[\text{C}_2\text{OHmim}]\text{BF}_4$ in the absence (row A) and presence (rows B to E) of $[\text{bmim}]\text{Cl}$ at indicated temperatures and the following concentrations: (A) without $[\text{bmim}]\text{Cl}$; (B) 0.04, (C) 0.10, (D) 0.20, and (E) $0.40 \text{ mol L}^{-1} [\text{bmim}]\text{Cl}$.