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## Cryo-solvatochromism in ionic liquids†

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Cryo-solvatochromism (blue to green) in response to cooling from room temperature to well below 0 °C can have many applications, and has been achieved in an ionic liquid, 1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate, containing di-(1-butyl-3-methylimidazolium) tetrachloro-nickelate and excess 1-butyl-3-methylimidazolium chloride.

Many transition metal complexes exhibit thermochromic responses upon interaction with an appropriate donor solvent, due to energy alternation of the d-d transitions and configuration changes.<sup>1,2</sup> Such thermochromic systems and devices have potential for many applications (e.g. smart windows and food packages), but solvent evaporation in prolonged heating-cooling cycles is inevitable and shortens the service life.<sup>3–10</sup> Because of their nonvolatile nature,<sup>11</sup> 1-hydroxyalkyl-3-methylimidazolium cation based ionic liquids have been used as the donor solvents that participate in formation of chloro-nickel complexes. As a result, highly stable thermo-solvatochromic solutions have been prepared,<sup>12</sup> and applied in practical solar-thermochromic films for utilisation of solar heat to drive thermochromism.<sup>8,10</sup>

In fact, there are other forms of thermochromic materials, and some of these undergo colour changes in very wide temperature ranges from well above ambient to cryogenic conditions.<sup>13–24</sup> In technological terms, the colour changing temperature range (CCTR) is a crucial parameter that determines the usefulness and effectiveness of a thermochromic material. Unfortunately, the CCTR is almost an intrinsic property of many thermochromic materials, whilst attempts to modulate the CCTR of a material are rarely reported. On the

other hand, the majority of studies are on colour changing in response to heating (from room temperature to a higher temperature), whilst little is reported on how to cause a reversible colour change by cooling from room temperature to below 0 °C. We propose to name the latter as cryochromism. Of course, cryochromism still falls in the same scientific area of thermochromism, but the emphasis on cooling to below 0 °C may help draw research attention and effort to practical uses. Examples include, but not limited to, freezing indicator of water supply pipes in winter, vision guide of cooled beverages and ice creams, smart packaging for cryo-storage of medicines and living cells, and safety control for energy storage in liquid air or nitrogen.

This communication describes the cryo-solvatochromism in solutions of chloro-nickel complexes in a 1-hydroxyalkyl-3-methylimidazolium cation based ionic liquid containing added Cl<sup>–</sup> ions. A typical example is presented in Fig. 1, showing the colour change of the ionic liquid solution from blue to green upon cooling from 22 °C to –13 °C. In addition, the ionic liquid solution was combined with polyvinylidene fluoride (PVDF) into a thin composite film in a similar way as described elsewhere.<sup>10</sup> As shown in Fig. S1 in the ESI,† this liquid–polymer composite film also changed its colour from light blue at 22 °C to pale green at –13 °C. To better understand this phenomenon, the following discussion will focus on the modulation of the CCTR of the ionic liquid solution in the presence of different concentrations of added Cl<sup>–</sup> ion.

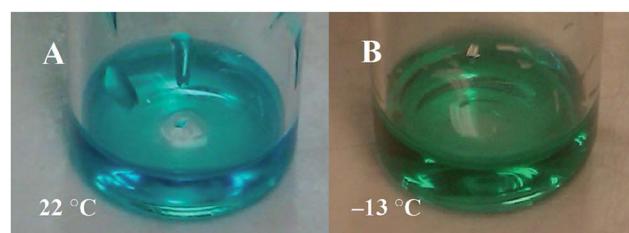


Fig. 1 Photographs of 0.14 mol L<sup>–1</sup> [bmim]<sub>2</sub>NiCl<sub>4</sub> and 1.4 mol L<sup>–1</sup> [bmim]Cl in [C<sub>2</sub>OHmim]BF<sub>4</sub> at (A) 22 °C and (B) –13 °C (in freezer).

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† Electronic supplementary information (ESI) available: Molecular structures, general thermo-solvatochromic reaction, and further visual evidence of cryo-solvatochromism. See DOI: 10.1039/c4ra08116a

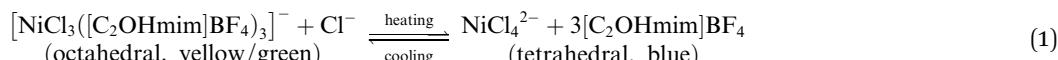


In this work, 1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate ( $[C_2OHmim]BF_4$ , IoLiTec) and 1-butyl-3-methylimidazolium chloride ( $[bmim]Cl$ , Sigma-Aldrich) were used as the donor solvent and  $Cl^-$  ion source, respectively (ESI, Scheme S1†). The synthesis and characterisation of the chloro-nickel complex, di-(1-butyl-3-methylimidazolium) tetrachloronickelate ( $[bmim]_2NiCl_4$ ) were reported elsewhere.<sup>12</sup> The solution of  $[bmim]_2NiCl_4$  in  $[C_2OHmim]BF_4$  was green in colour at room temperature.<sup>12</sup> Upon heating up to 80 °C, the solution changed colour from green to blue, demonstrating thermochromism as explained by the following simplified coordination reaction (1) (ref. 12) in which the tetrahedral  $NiCl_4^{2-}$  complex is converted to one octahedral complex upon cooling. This simplification is based on the observation of only two absorption bands on the Vis-spectra for a given solution within the CCTR<sup>12</sup> as will also be discussed below. In the ESI,† reaction (S1) is presented as a general description of the equilibria, involving one tetrahedral ion and four possible octahedral ions.

recorded in the cooling and heating scans at different scan rates. Similar DSC curves were also reported for other imidazolium based ionic liquids.<sup>25</sup> In this work, the thermal scans of pure  $[C_2OHmim]BF_4$  and the solution of 0.70 mol L<sup>-1</sup>  $[bmim]Cl$  in  $[C_2OHmim]BF_4$  showed also almost parallel straight lines (curves 1 and 2 in Fig. 2C and D). These straight lines are indicative of sensible heat transfer only, and high thermal stability of both liquids over the tested temperature range.

Curves 3–7 in Fig. 2C and D represent thermal scans of 0.14 mol L<sup>-1</sup>  $[bmim]_2NiCl_4$  in  $[C_2OHmim]BF_4$  in the absence and presence of 0.28, 0.70, 1.12 and 1.40 mol L<sup>-1</sup>  $[bmim]Cl$ , respectively. For each of these ionic liquid solutions, there was always an exothermic band (upward) during cooling, while an endothermic band (downward) during heating. Particularly, the DSC signals on curves 3 in both Fig. 2C and D agree well with previous findings that reaction (1) is an endothermic reaction with a positive enthalpy change.<sup>12</sup>

An interesting and unprecedented finding from this work is that the central temperatures of both the exothermic and



The green-to-blue change also occurred at room temperature upon addition of excess  $[bmim]Cl$ , following solvatochromism.<sup>12</sup> As shown in Fig. 1A, the solution of 0.14 mol L<sup>-1</sup>  $[bmim]_2NiCl_4$  in  $[C_2OHmim]BF_4$  containing 1.4 mol L<sup>-1</sup>  $[bmim]Cl$  was blue, instead of green at 22 °C. This observation indicates a forward shift of the equilibrium of reaction (1) caused by increasing the  $Cl^-$  ion activity in the solution. In principle, this solution should change back to green if cooled to a sufficiently low temperature, which was indeed observed when the vial containing the solution was cooled to –13 °C in a freezer. This phenomenon can be predicted from reaction (1), but surprisingly it has not yet been reported in the literature. More importantly, it represents the first example of cryo-solvatochromism in ionic liquids, and deserves further studies.

The forward and backward shifts of reaction (1) are endothermic and exothermic, respectively. To confirm the heat flow, differential scanning calorimetry (DSC) was applied to obtain quantitative information about the  $Cl^-$  ion effect on the equilibrium of reaction (1) and the induced cryo-solvatochromism under specific conditions. The Q2000 differential scanning calorimeter equipped with RCS-90 refrigerated cooling system (TA Instruments) was used to detect the presumed endothermic and exothermic signals. In each DSC experiment, about 12 mg of the ionic liquid sample was loaded in a hermetic aluminium pan (TA Instruments) covered and sealed by a lid to prevent contamination to the equipment. All samples were pre-dried at 65 °C in a vacuum oven overnight before experiments. Fig. 2A and B compare the DSC curves of pure  $[C_2OHmim]BF_4$  at different scan rates (2 to 10 °C min<sup>-1</sup>) during cooling and heating between –30 to 100 °C. Only straight lines were

endothermic bands (or the colour changing temperature) decreased from above room temperature to well below 0 °C when the concentration of  $[bmim]Cl$  was increased. In other words, the DSC curves in Fig. 2C and D demonstrate the transformation from a thermo-solvatochromic solution to a cryo-solvatochromic solution, resulting simply from increasing the  $Cl^-$  ion activity.

Derivation of the enthalpy change from the DSC curves in Fig. 2C and D was attempted. Integration of the DSC curve gives the total enthalpy change, which can be normalised against the total mass of the solution. The results derived from curves 3 (without added  $Cl^-$  ions), 4 (with 0.28 mol L<sup>-1</sup> added  $Cl^-$ ) and 5 (with 0.79 mol L<sup>-1</sup> added  $Cl^-$ ) are presented in Table S1.† Further, without added  $Cl^-$ , according to previous observations upon the colour change during cooling through the CCTR, about 1/3 of the initially added  $NiCl_4^{2-}$  ion would be converted to the  $NiCl_3([C_2OHmim]BF_4)_3$  ion via reaction (1).<sup>12</sup> Assuming a density of *ca.* 1.37 g cm<sup>-3</sup> for the ionic liquid solutions,<sup>12</sup> the molar enthalpy change was estimated to be *ca.* 59 kJ mol<sup>-1</sup>. In the presence of added  $Cl^-$ , the conversion would increase in proportion to the amount of heat transferred as measured by DSC. Thus, using curve 3 as a reference, the molar enthalpy changes were also derived for curves 4 and 5. The results were very consistent as shown in Table S1.†

Obviously, the change of the  $NiCl_4^{2-}$  ion concentration upon cooling (or heating) should be measured more accurately by an independent analytical method. Therefore, the thermo- and cryo-solvatochromic phenomena of  $[bmim]_2NiCl_4$  in  $[C_2OHmim]BF_4$  in the absence and presence of added  $[bmim]Cl$  were investigated by UV-Vis spectroscopy (Lambda 25, Perkin



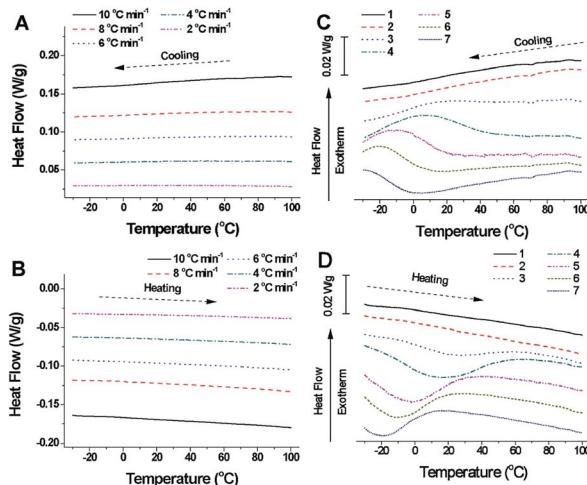


Fig. 2 DSC curves recorded in the temperature range from  $-30$  to  $100$   $^{\circ}\text{C}$ . (A) Cooling and (B) heating of  $[\text{C}_2\text{OHmim}]\text{BF}_4$  at the indicated thermal scan rates. (C) Cooling and (D) heating of different solutions (1–7) at  $10$   $\text{C min}^{-1}$ : (1) pure  $[\text{C}_2\text{OHmim}]\text{BF}_4$  (solid line); (2)  $0.70$   $\text{mol L}^{-1}$   $[\text{bmim}]\text{Cl}$  in  $[\text{C}_2\text{OHmim}]\text{BF}_4$  (dash line); (3)  $0.14$   $\text{mol L}^{-1}$   $[\text{bmim}]_2\text{NiCl}_4$  in  $[\text{C}_2\text{OHmim}]\text{BF}_4$  (dot line); (4)  $0.14$   $\text{mol L}^{-1}$   $[\text{bmim}]\text{Cl}$  in  $[\text{C}_2\text{OHmim}]\text{BF}_4$  (dash dot line); (5)  $0.14$   $\text{mol L}^{-1}$   $[\text{bmim}]_2\text{NiCl}_4$  +  $0.70$   $\text{mol L}^{-1}$   $[\text{bmim}]\text{Cl}$  in  $[\text{C}_2\text{OHmim}]\text{BF}_4$  (dash dot dot line); (6)  $0.14$   $\text{mol L}^{-1}$   $[\text{bmim}]_2\text{NiCl}_4$  +  $1.12$   $\text{mol L}^{-1}$   $[\text{bmim}]\text{Cl}$  in  $[\text{C}_2\text{OHmim}]\text{BF}_4$  (short dash line); and (7)  $0.14$   $\text{mol L}^{-1}$   $[\text{bmim}]_2\text{NiCl}_4$  +  $1.40$   $\text{mol L}^{-1}$   $[\text{bmim}]\text{Cl}$  in  $[\text{C}_2\text{OHmim}]\text{BF}_4$  (short dot line).

Elmer). A Peltier system (PTP-6, Perkin Elmer) was utilised to maintain the ionic liquid sample at a constant temperature in an absorption quartz cell with  $1.0$  cm light path. The absorption cell was sealed with a lid to prevent exchange of the atmospheres inside and outside the cell during the measurement. Samples were pre-dried in the same way as for DSC analyses. The working temperature range of the Peltier system was  $5.0$ – $75.0$   $^{\circ}\text{C}$ , higher than that for DSC analyses. However, from the Vis-spectra of these ionic liquids samples, it is easy to detect the transformation trend of the ionic liquids from thermo-solvatochromism to cryo-solvatochromism affected by varying the  $\text{Cl}^-$  concentration.

The Vis-spectra of two  $[\text{C}_2\text{OHmim}]\text{BF}_4$  solutions of  $[\text{bmim}]\text{NiCl}_4$  in the presence of different amounts of  $[\text{bmim}]\text{Cl}$  are presented in Fig. 3A and B, respectively. At  $25$   $^{\circ}\text{C}$ , two absorption bands (I and II) were observed (purple curves in Fig. 3) in both solutions, which can be attributed to the octahedral and

tetrahedral nickel complexes as indicated in reaction (1), respectively.<sup>12</sup> The insets in both Fig. 3A and B show that only one absorption band I appears at the same wavelength at temperatures below  $35$   $^{\circ}\text{C}$  (Fig. 3A) or  $25$   $^{\circ}\text{C}$  (Fig. 3B). Thus, Fig. 3 suggests one dominant octahedral complex to be responsible for the observed colour change, and justifies the use of reaction (1) as a good approximate of the colour change reaction in the ionic liquid solution. Above  $25$ – $35$   $^{\circ}\text{C}$ , the green-to-blue colour change has completed, and the Vis-spectra were dominated by band II of the tetrahedral  $\text{NiCl}_4^{2-}$  complex, although two insignificantly small bands I' and I'' appeared. It should be mentioned that the general thermo-solvatochromic reaction (ESI,† reaction S(1)) is more complicated than reaction (1) and the octahedral configuration<sup>12</sup> may exist with different chloride-to-solvent ratios.<sup>26–29</sup> However, disregarding if bands I' and I'' were due to other octahedral complexes or some components in the ionic liquids solution, their presence should exert negligible influences on the colour change reaction. Therefore, to obtain an initial insight, it is reasonable to assume the  $[\text{NiCl}_3([\text{C}_2\text{OHmim}]\text{BF}_4)_3]^-$  ion as the representative.<sup>12</sup> Thus, the following discussion is based on reaction (1).

At  $25$   $^{\circ}\text{C}$  and lower temperatures, it is obvious that the intensity of band II in Fig. 3B is much higher than that in Fig. 3A. In contrast, the intensities of band I in Fig. 3A and B differ only slightly under the same condition. These differences are directly responsible for the colour changes of the ionic liquid solutions (ESI, Fig. S2,† rows B vs. E at  $25$   $^{\circ}\text{C}$ ). Similar effects were also found in the  $[\text{C}_3\text{OHmim}]\text{ClO}_4$  solution containing  $\text{Ni}(\text{ClO}_4)_2$ , in which the solvatochromism was realised by addition of different amounts of  $\text{Cl}^-$  ion source species.<sup>12</sup> However, over the whole temperature range shown in Fig. 3, a lower temperature is required to achieve the same intensity of band II for the  $[\text{C}_2\text{OHmim}]\text{BF}_4$  solution of  $[\text{bmim}]\text{NiCl}_4$  in the presence of  $\text{Cl}^-$  ions with a higher concentration, e.g.  $0.40$   $\text{mol L}^{-1}$ . It can be concluded that varying the  $\text{Cl}^-$  activity can modulate the colour-changing temperature of the original thermo-solvatochromic solution.

Further visible evidence of modulation of the colour-changing temperature by addition of  $[\text{bmim}]\text{Cl}$  into the thermo-solvatochromic solution is presented in the ESI, Fig. S2,† A series of photographs were taken from the solutions of  $0.02$   $\text{mol L}^{-1}$   $[\text{bmim}]_2\text{NiCl}_4$  in  $[\text{C}_2\text{OHmim}]\text{BF}_4$  without and with added  $[\text{bmim}]\text{Cl}$  when the temperature was varied between  $5$  and  $75$   $^{\circ}\text{C}$ . In the absence of  $[\text{bmim}]\text{Cl}$ , the solution was yellow green at  $5$   $^{\circ}\text{C}$ , and blue at  $75$   $^{\circ}\text{C}$ . With increasing the  $[\text{bmim}]\text{Cl}$  concentration, the solution became blue green (more blue) at  $5$   $^{\circ}\text{C}$ , but already very blue at  $25$   $^{\circ}\text{C}$  (ESI, Fig. S2,† rows B to E), indicating formation of tetrahedral  $\text{NiCl}_4^{2-}$  ions in this lower temperature range. The trends of colour change in both the vertical and horizontal directions in Fig. S2,† project clearly the green or yellow green colour at a temperature well below  $0$   $^{\circ}\text{C}$ , which is in agreement with the observation shown in Fig. 1.

Based on the Vis-spectra collected at  $5$  to  $75$   $^{\circ}\text{C}$ , the equilibrium constant,  $K$ , of reaction (1) was estimated from eqn (2) below,<sup>12</sup> assuming the concentration of  $[\text{C}_2\text{OHmim}]\text{BF}_4$  to be constant due to its excess presence.

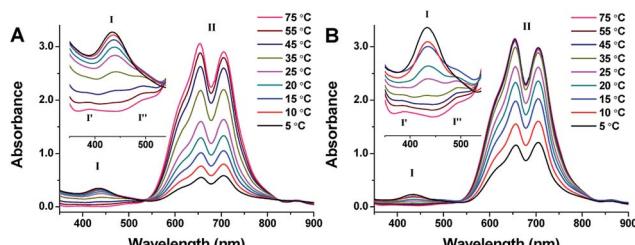


Fig. 3 Vis-spectra of  $0.0207$   $\text{mol L}^{-1}$   $[\text{bmim}]_2\text{NiCl}_4$  in  $[\text{C}_2\text{OHmim}]\text{BF}_4$  with (A)  $0.04$  and (B)  $0.40$   $\text{mol L}^{-1}$   $[\text{bmim}]\text{Cl}$  at indicated temperatures.



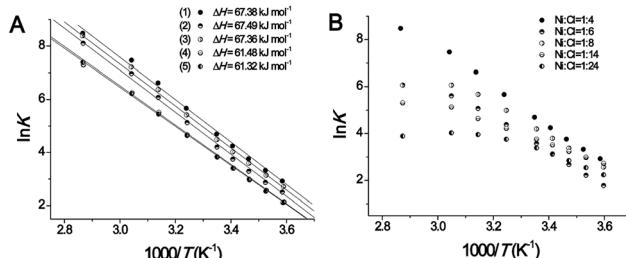


Fig. 4 Correlations between the equilibrium constant ( $K$ ) of reaction (1) and the temperature ( $T$ ) in  $[\text{C}_2\text{OHmim}]\text{BF}_4$  containing (A)  $[\text{bmim}]_2\text{NiCl}_4$  at different concentrations: (1) 0.0052, (2) 0.0081, (3) 0.0104, (4) 0.0161, and (5) 0.0207 mol  $\text{L}^{-1}$ , and (B) 0.0052 mol  $\text{L}^{-1}$   $[\text{bmim}]_2\text{NiCl}_4$  and different amounts of  $[\text{bmim}]\text{Cl}$  to reach the indicated Ni to Cl molar ratios.

$$K = \frac{C_{\text{NiCl}_4^{2-}}}{C_{[\text{NiCl}_3([\text{C}_2\text{OHmim}]\text{BF}_4)_3]^{-}} C_{\text{Cl}^-}} \quad (2)$$

The enthalpy changes,  $\Delta H$ , of reaction (1) can be derived from the calculated  $K$  values, using the van't Hoff Equation (which is well recognised for reactions whose enthalpy and entropy changes remain constant with changing the temperature in a suitable and small range):

$$\frac{d\ln K}{d(1/T)} = -\frac{\Delta H}{R} \quad (3)$$

Fig. 4 plots  $\ln K$  against  $1/T$  with data points collected from the Vis-spectra. The data points in Fig. 4A were collected from solutions without added  $\text{Cl}^-$  ions, and fit into a set of straight lines over a wider temperature range. These linear relations agree well with the Vis-spectra finding of only one absorption band due to the octahedral complex, and verify again reaction (1) to be indeed a valid representative of the real thermochromic changes at relatively low  $[\text{bmim}]_2\text{NiCl}_4$  concentration (0.0052 to 0.0207 mol  $\text{L}^{-1}$ ). The calculated  $\Delta H$  values (61–68 kJ mol $^{-1}$ ) are fairly constant, as indicated in Fig. 4A, and are in good agreement with the results from DSC measurements as presented in Table S1.† The slightly lower DSC derived values of  $\Delta H$  ( $ca.$  59 kJ mol $^{-1}$ ) are likely due to the assumed 1/3 conversion *via* reaction (1) without added  $\text{Cl}^-$  ions being possibly underestimated. Note that (i) the calculations for Fig. 4A were based on equal concentrations of the  $[\text{NiCl}_3([\text{C}_2\text{OHmim}]\text{BF}_4)_3]^-$  and  $\text{Cl}^-$  ions according to reaction (1), and (ii) the data points at the very high temperature (75 °C) show slight downward deviation from the fitted straight lines. Similar deviations were in fact observed before,<sup>12</sup> and these will be discussed below.

In Fig. 4B, all the data points are linear with approximately equal slopes at temperatures lower than 25–35 °C. Below these temperatures, the Vis-spectra are clearly different as can be seen by comparing Fig. 3A and B. However, at higher temperatures ( $>25$ –35 °C), the Vis-spectra in Fig. 3A and B become increasingly similar to each other, whilst downward deviation occurs in Fig. 4B which also shows clearly that the temperature at which

the deviation begins decreases with increasing the amount of added  $\text{Cl}^-$ .

A comparison between Fig. 2–4 suggests that all the high temperature deviations shown in Fig. 4 start to appear soon after the green-to-blue colour change has completed. Particularly, the shift of CCTR shown by Fig. 2 matches very well with the inflection point (temperature) where the downward deviation begins in Fig. 4B. In principle, above the CCTR, the solution is dominated by the  $\text{NiCl}_4^{2-}$  ion, and further raising the temperature will only cause relatively small increases to the  $\text{NiCl}_4^{2-}$  concentration, which can become too small to be detected by the Vis-absorbance, leading to underestimation. This understanding seems to reflect well the almost identical Vis-spectra recorded at 45, 55 and 75 °C as shown in Fig. 3B. On the other hand, Fig. 4 is presented according to eqn (3) which assumes both the enthalpy and entropy changes to be sufficiently constant in the temperature range of measurement. It is then likely that the van't Hoff Equation itself may become invalid at temperatures much higher (or lower) than the CCTR, which can also account for the deviations shown in Fig. 4B.

In summary, we have demonstrated the first example of cryo-solvatochromism in ionic liquids, utilising the donor anion induced decrease of the colour changing temperature of chloro-nickel complexes in a hydroxyl substituted ionic liquid to well below 0 °C. Preliminary investigations of the phenomena by differential scanning calorimetry and Vis-spectrometry produced further evidence supporting the proposed cryo-solvatochromism. Incorporation of this ionic liquid based cryochromism into a PVDF membrane has also been confirmed to function in the same temperature range. We hope the new concept of cryochromism in ionic liquids and the fundamental science communicated here may stimulate further development for technological explorations. These may include, but not limited to, temperature sensors under critical conditions, smart packaging for cryo-storage of foods and medicines, anti-fraud ink and security printing, and heat collection from low temperature sources. We also look forward to observations of cryochromisms in other solutions and materials, and expect challenges such as solubility of the donor anion/salt, evaporation of the organic solvent, and freezing of the aqueous solution at sub-zero temperatures.

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