Phase Transitions in Higher-Melting Ionic Liquids: Thermal Storage Materials or Liquid Crystals?

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To assess the application potential of a material in thermal energy storage, the knowledge of their thermophysical properties is of key importance. Specifically, an efficient material has to show, among others, large enthalpies of phase change and a sufficiently large thermal conductivity.

In this work, imidazolium-based ionic liquids (ILs) with long alkyl chain substituents 1-hexadecyl-3-methylimidazolium chloride and 1-hexadecyl-3-methylimidazolium saccharinate were studied in view of their possible use as phase-change materials. Differential scanning calorimetry (DSC) and the heat-leak modulus methods were used to determine the temperatures and the enthalpies of phase transitions in the studied ILs, enabling us to study the influence of the heating rates on the measured properties. Enthalpies of fusion near to or larger than 100 J·g–1 were found in the studied ionic liquids, making them promising candidates for thermal energy storage. Furthermore, peaks corresponding to possible liquid crystalline phases in the DSC traces of 1-hexadecyl-3-methylimidazolium saccharinate were observed.

The measured properties are not only essential characteristics of a thermal storage material, temperatures and enthalpies of melting are necessary in thermodynamic description and modelling of solid-liquid phase behavior and thus in the possible utilization of the material in separation and crystallization processes.

1. Introduction

Limited supplies of fossil fuels along with the strife towards decreasing the emissions of greenhouse gases lead to an increasing demand for economically viable sustainable sources of energy. However, one of the disadvantages of renewable energies is their intermittent supply. Therefore, meaningful ways of storing energy have to be investigated. In thermal energy storage, utilization of phase-change materials (PCM) is one of the currently explored options (Zhang et al., 2016). These materials allow for storing heat thanks to their sufficiently high enthalpy of phase change (>100 J·g–1); the material melts during the charging period, absorbing the heat at a higher temperature, releasing it on crystallization during the discharging period at a lower temperature. Conventional paraffins, inorganic salts, or inorganic salt hydrates are the most often used materials (Pielichowska and Pielichowski, 2014), ionic liquids are however also considered in energy storage in general for their rather multipurpose character (MacFarlane et al., 2016).

Ionic liquids (ILs) are broadly defined by a melting temperature lower than 100 °C. Even though ILs showing a large liquid range seem to be of the greatest interest to both fundamental and applied research, there is a number of higher-melting ILs solid at room temperature that show a wealth of interesting thermodynamic and phase transition behavior, for instance liquid crystalline phases (see e.g. (Zurner et al., 2016) and (Lava et al., 2009)). Some of these ILs even show sufficiently large enthalpies of melting to be considered for use as phase-change materials (PCMs) (Zhu et al., 2009]. All this suggests that they could find their use as even more versatile task-specific materials. In this work, thermal properties of higher-melting ionic liquids with a common 1-methyl-3-hexadecylimidazolium cation are therefore studied by means of the differential scanning calorimetry (DSC) and heat-leak modulus method (HLM) (Quirion et al., 1992) to determine the influence of

the anion on their phase transitions. As a result of the presence of a long alkyl chain substituent on the cation, the studied ionic liquids are solids at room temperature, typically showing melting temperatures higher than 50 °C and enthalpies of melting close to or larger than 100 J·g^{-1}. Also, as expected, the DSC experiments point towards the occurrence of a liquid crystalline phase. In addition, heat capacity as a function of temperature was measured by means of the DSC in the liquid and solid phase for the studied ionic liquids. Finally, the experimental data were analyzed by means of methods based on mathematical gnostics (Kovanic and Humber, 2015).

2. Experimental section

2.1.Chemicals used

To synthesize the studied ionic liquids, 1-methylimidazole (99% ReagentPlus, Sigma Aldrich), 1-hexadecylchloride (95%, Sigma Aldrich), sodium saccharinate dihydrate (>99.0%, Merck), N,N-dimethylformamide anhydrous (99.8%, Sigma Aldrich), acetone anhydrous (≥99.9%, Merck), ethylacetate (p.a., LachNer), and in-house doubly-distilled water were used.

2.1.1 Synthesis of 1-hexadecyl-3-methylimidazolium chloride (abbrev. [C$_{16}$C$_1$im]Cl)

For the preparation of [C$_{16}$C$_1$im]Cl (Seddon et al., 2000), 23.81 g (0.29 mol) of 1-methylimidazole and 91.31 g (0.35 mol) of 1-hexadecylchloride were dissolved in 50 mL *N,N*-dimethylformamide in a round-bottomed flask equipped with a reflux condenser. The mixture was continuously stirred and heated at 90 °C for 70 h under inert argon atmosphere. The resulting brownish viscous liquid readily crystallized upon cooling giving pale yellow crystals; however, in order to obtain IL of higher purity, the solvents were evaporated under reduced pressure and the resulting residue was crystallized several times from ethyl acetate. The final product was obtained as white crystals in 86% yield and was further dried *in vacuo* (3 mbar) for 48 h. The water content after drying was typically 1% (mass). Its structure was confirmed by means of NMR spectroscopy (Thomas et al., 2018).

2.1.2 Synthesis of 1-hexadecyl-3-methylimidazolium saccharinate (abbrev. [C$_{16}$C$_1$im][Sac])

 [C$_{16}$C$_1$im][Sac] was prepared by ion exchange reaction from [C$_{16}$C$_1$im]Cl and sodium saccharinate (NaSac) as precursors. A methanol solution of [C$_{16}$C$_1$im]Cl (20 g, 0.058 mol, in 109 mL) was slowly added (dropwise) to a stirred solution of NaSac (22 g, 0.099 mol) in 20 mL of methanol at 60 °C. The flask was equipped with a magnetic stirrer, a dropping funnel, a reflux condenser and a calcium chloride tube. The reaction mixture was stirred for 24 h under reflux. The solvent was then evaporated under reduced pressure giving a suspension. This residue was treated with acetone in order to precipitate the NaCl and NaSac, while keeping [C$_{16}$C$_1$im][Sac] in solution. The inorganic solids were further filtered off and the organic solvent was removed under reduced pressure. The above procedure was repeated several times until no inorganic precipitates in the acetone were observed. The IL obtained, [C$_{16}$C$_1$im]Sac], was subsequently crystallized from ethyl acetate (yield 90%) and dried *in vacuo* (approx. 3 mbar) for 48 h. The water content after drying was typically 1% (mass). Its structure was confirmed by NMR spectroscopy – 1H NMR (400.13 MHz, CD3OD): δ= 0.88 (3H, t, J = 7.3, CH2CH3), 1.23–1.34 (26H, m, CH2), 1.82–1.90 (2H, m, CH2), 3.91 (3H, s, N–CH3), 4.18 (2H, t, J = 7.4, N–CH2), 7.54 (1H, t, J = 1.8, CH/im), 7.61 (1H, t, J = 1.8, CH/im), 7.64–7.69 (2H, m, CH/Sac), 7.72–7.82 (2H, m, CH/ Sac), 8.91 (1H, bs, N–CH=N).

2.2 Experimental methods used

Phase transition temperatures and enthalpies were determined by means of a Setaram DSCIII evo micro-calorimeter under N$_2$ atmosphere. Temperature calibration of the calorimeter was performed using the melting points of water and naphthalene, the energetic calibration was carried out using the Joule effect. Tap water was used as calibration standard, according to the recommendation of the calorimeter manufacturer, to avoid subcooling that often occurs in distilled water. The naphthalene standard was provided by the manufacturer. Cooling was carried out at 0.6 K·min^{-1}. Heating was carried out at 0.2, 0.5, and 1 K·min^{-1}, respectively. The temperature ranges in which the experiments were performed were determined for each sample individually according to the temperatures at which crystallization, fusion, or other phase transitions occurred. The uncertainty in phase transition determination was found to be better than 0.3 K and in enthalpy of phase transition better than 1.7 J·g^{-1}.

To investigate the influence of the heating rate on the measured phase transitions, the temperatures and enthalpies of fusion for [C$_{16}$C$_1$im]Cl were also determined by the Heat-Leak Modulus (HLM) method (Quirion et al., 1992) using an AT-HLM prototype provided by François Quirion. The HLM is a measure of the heat

transfer between the environment and the sample. The sample is mounted on a temperature probe and inserted into a one of the reservoirs with a constant temperature T_R. The temperature of the sample, T_S, is then determined as a function of time. From this dependence the HLM is calculated from Eq.1:

$$HLM = \frac{(dT_c/dt)}{T_R - T_S} \qquad (1)$$

The HLM can be determined both on heating ($T_R > T_S$) or cooling ($T_S > T_R$). In the absence of an enthalpic transitions, the HLM is a monotonous function of T_S. An enthalpic transition results in a peak from which the temperature and enthalpy of the transition can be determined.

A plastic tube was used to mount the sample to the temperature probe. This assembly was calibrated with water as standard. To obtain high heating rates, a sample of 70 mg was exposed to an oven temperature around 200 °C. It was taken out of the oven at temperatures above 90 °C and transferred into a cold chamber around -70 °C. The sample was removed as it reached about 0°C and the cycle was repeated. Under the conditions described above, the heating and cooling rates were about 55 °C/min when the sample was at 60°C. These rates are much higher than the rates investigated by DSC (heating at 1, 0.5 and 0.2 °C·min^{-1} and cooling at 0.6 °C·min^{-1}). In this way, the experiments of four heating and four cooling runs took only 20 minutes as opposed to more than 24 hours of the same number of experiments in a DSC.

2.3 Data Analysis

Mathematical gnostics (MG) (Kovanic et al., 2015) provides us with a non-statistical approach towards the uncertainty treatment. In statistics, the measurement uncertainty is estimated from a series of repeated measurements using an *a priori* assumption of the error distribution function. Since the underlying theory of MG was derived considering the uncertainty of every single measurement, the properties of a data sample are then evaluated by aggregation of properties of each measurement with no need for such an assumption. The uncertainty is then a property of each data point. Small data samples can thus be analyzed and a sound estimate of the experimental uncertainty obtained. In this work, the repeatability of the experimental data was thus determined from the parameters of the local distribution function as

$$u = \frac{(Z_{0U} - Z_{0L})}{2} \qquad (2)$$

where Z_{0U} and Z_{0L} are the upper and lower bounds of the tolerance interval, respectively (Andresová et al., 2017).

3. Results and Discussion

Table 1 lists the temperatures and enthalpies of transitions determined by means of DSC for the two studied ionic liquids. Figure 1 shows examples of the DSC traces obtained on heating at a rate of 0.2 K·min^{-1} for [C$_{16}$C$_1$im]Cl and [C$_{16}$C$_1$im][Sac]. Figure 2 shows examples of the DSC traces for the studied ionic liquids obtained on cooling at a rate of 0.6 K·min^{-1}. The ionic liquid [C$_{16}$C$_1$im]Cl shows a single endothermic peak in the temperature range of temperatures (18–90) °C. As shown in (Zhao et al., 2009) and (Thomas et al., 2018), this ionic liquid also shows a transition from lamellar liquid crystalline phase to isotropic phase at about 250 °C, however, the temperature range of the DSC device used in this work did not allow for the determination of this transition.

Table 1: Temperatures and enthalpies of transition for the ionic liquids [C$_{16}$C$_1$im]Cl and [C$_{16}$C$_1$im][Sac] determined by DSC. Repeatability ranges were determined by means of marginal analysis (Eq. 2)

ionic liquid	t_{fus} / °C	ΔH_{fus} / J·g^{-1}	$t_{LC\text{-}iso}$ / °C	$\Delta H_{LC\text{-}iso}$ / J·g^{-1}	t_{cr} / °C	ΔH_{cr} / J·g^{-1}
[C$_{16}$C$_1$im]Cl	63.43±0.05 [a]	159±2 [a]			52.0±0.5 [a]	-151.2±0.6 [a]
[C$_{16}$C$_1$im][Sac]	50.99±0.07 [b]	98±2 [b]	87.4±0.3 [b]	0.930±0.004 [b]	38.88±0.06 [b]	-91.2±0.6 [b]
	53.2±0.2 [c]	108.3±0.7 [c]	95.5±0.1 [d]	1.005±0.003 [d]	41.00±0.03 [c]	-105.2±0.1 [c]

[a] measured in the temperature range (25—90) °C, [b] measured in the temperature range (10–115)°C, [c] measured in the temperature range (10–80)°C,, [d] measured in the temperature range (60–115) °C

As is evident from Table 1, the temperature of fusion of [$C_{16}C_1$im]Cl is of 63.43 °C while its enthalpy of fusion is of 159 J·g^{-1}. Both the temperature and enthalpy of fusion found in this work are larger than those in (Thomas et al., 2018) who report the temperature of fusion of 56.9°C and the enthalpy of fusion in the range of 58 to 145 J·g^{-1}, however, no information is given in their study e.g. on the water content in the studied ionic liquid or its purity. It should also be noted that the enthalpies of fusion and solidification measured by the DSC were well balanced for [$C_{16}C_1$im]Cl (ΔH_{fus}=159±2 J·g^{-1} vs. ΔH_{cr}=-151±2 J·g^{-1}), suggesting that the solid that formed is the one that melts.
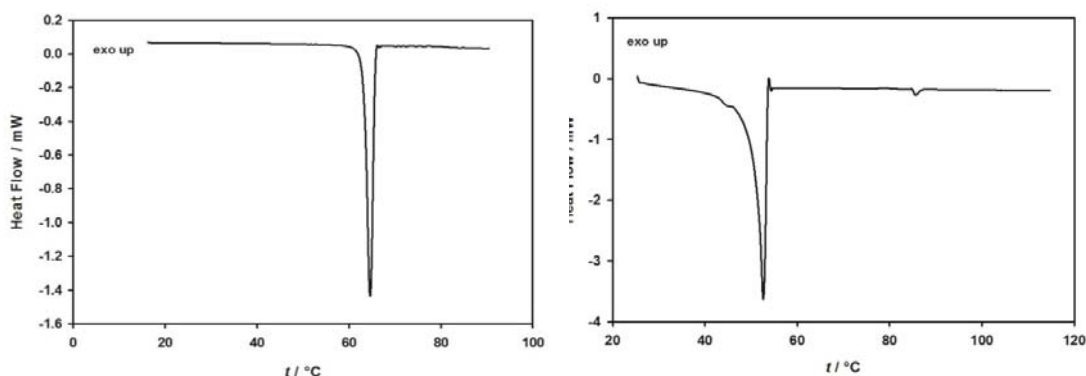

Figure 1: Examples of DSC traces on heating for [$C_{16}C_1$im]Cl (left) and [$C_{16}C_1$im][Sac] (right). Large endothermic transition: melting of the ionic liquid. Small endothermic transition for [$C_{16}C_1$im][Sac]: transition from the liquid crystal mesophase to isotropic liquid.
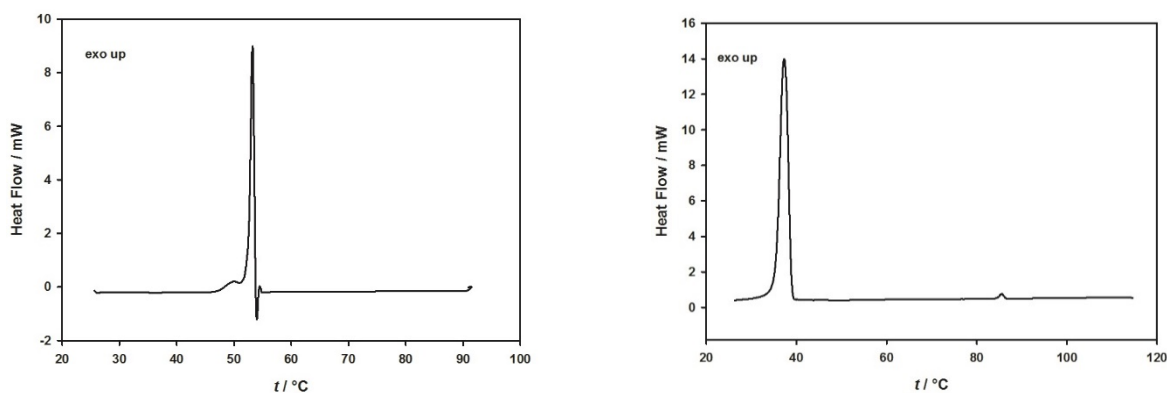

Figure 2: Examples of a DSC traces on cooling for [$C_{16}C_1$im]Cl (left) and [$C_{16}C_1$im][Sac] (right). Large exothermic transitions: solidification of the ionic liquids. Small exothermic transition for [$C_{16}C_1$im][Sac]: transition from the isotropic liquid to the liquid crystal mesophase.

A typical cooling/heating sequence of an HLM measurement is presented in Figure 3. The sample solidifies in two steps, a major exothermic peak around 55 °C and a minor peak (or shoulder) around 45 °C. As this sample is heated, it first undergoes what looks like cold crystallization around 42 °C immediately followed by the melting of the crystallized [$C_{16}C_1$im]Cl around 63°C. The average enthalpies for these transitions are summarized in Table 2.

The temperature and the enthalpy of fusion generated by the experiments at high heating rates are in very good agreement with the data obtained by DSC. This suggests that the fusion of [$C_{16}C_1$im]Cl is not much affected by the heating rate. This was also observed on a smaller scale during the DSC experiments at 1, 0.5 and 0.2 °C·min^{-1}, respectively.The situation is different at high cooling rates.

First, [$C_{16}C_1$im]Cl solidifies at 55 °C as opposed to 51.0 to 53.4 °C observed at low cooling rates. The enthalpy of solidification is also significantly less exothermic (ΔH_{cr} = -130±3 J·g−1) than at low cooling rates (ΔH_{cr} = -

151±2 J·g−1). Some of the IL could thus solidify as an amorphous solid when cooled at high rates. This could explain the exothermic transition observed at reheating the sample as a cold crystallization of the amorphous part of the sample.

Table 2: Temperatures and enthalpies of transition for the ionic liquid [C$_{16}$C$_1$im]Cl determined by HLM.

	Cold Crystallization	Fusion	Solidification
t /°C	42.3±0.6	63.4±0.3	54.9±0.2
ΔH_{tr}/J·g^{-1}	-40±6	157±7	-130±3

It should also be noted that both techniques identified two steps in the solidification of [C$_{16}$C$_1$im]Cl. The AT-HLM thermogrammes show a pronounced shoulder around 45 °C while the DSC thermogrammes show a tiny peak that grows progressively with the number of heating/cooling cycles to become a definite shoulder (see Figure 2, left). The reason for that transition is not yet understood. It could be solid state transition or simply the crystallization of an impurity or degradation product.
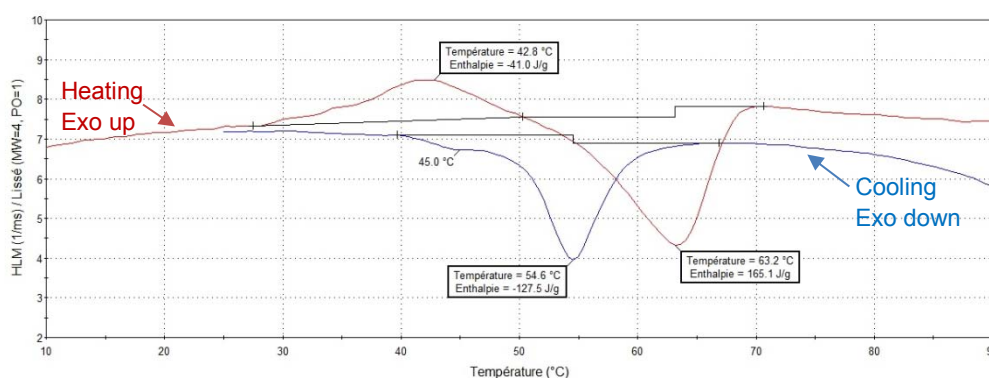

Figure 3: Example of HLM thermogrammes for [C$_{16}$C$_1$im]Cl

Figure 1 (right) shows an example of a DSC trace for [C16C1im][Sac]. On the first experiment carried out in the range of temperatures (10–115) °C two endothermic phenomena were observed, a large peak at 50.99 °C of 97.6 J·g−1 corresponding to the melting of the ionic liquid into a liquid crystal mesophase and a small peak at 87.4 °C of 0.93 J·g−1 corresponding to the transition from the liquid crystalline to isotropic phase.In comparison with [C16C1im]Cl, the bulkier saccharinate anion contributes to lower temperatures and enthalpies of fusion. The transition from the liquid crystalline phase to isotropic liquid also occurs at a lower temperature for the IL with the saccharinate anion than for the chloride.

In the second experiment, the DSC scans were divided into two shorter temperature ranges, (10–80) °C and (60–115) °C, respectively. These experiments showed two small endothermic peaks in the latter temperature region. The temperature of the endothermic transition from the liquid crystalline phase to the isotropic phase observed on the first set of experiments increased from 87.4 °C to 95.5 °C, showing the enthalpy of transition of about 1 J·g−1 and a new endothermic peak appeared at about 81 °C its enthalpy of transition gradually decreasing from approx. 0.7 J·g−1 to 0.2 J·g−1. This may indicate the presence of two liquid crystalline phases, a smectic and a nematic one. The latter transition however did not appear on cooling, further experiments by means of the polarized optical microscopy will be required to confirm or infirm this assumption.

4. Conclusion

Thermal properties of two higher melting ionic liquids with a common 1-hexyl-3-methylimidazolium cation and a chloride or saccharinate anion were investigated by means of the DSC and HLM methods in view of their possible use as phase-change materials. The enthalpies of melting of 159 J·g^{-1} and (98 and 108) J·g^{-1} for [C$_{16}$C$_1$im]Cl and [C$_{16}$C$_1$im][Sac], respectively, seem to indicate that both ILs could be considered as promising PCM materials. This, however, remains to be confirmed by further feasibility studies. The studied ILs also appear show a more complex phase behavior than simple melting/crystallization. Evidence of a liquid crystalline mesophase has already been given by other authors for [C$_{16}$C$_1$im]Cl. The [C$_{16}$C$_1$im][Sac] ionic liquid

also seems to form liquid crystals. Moreover, the mechanisms of melting and crystallization appear to be rather complex and will be investigated in further work along with the influence of the heating and cooling rates on the phase transitions in the studied ILs.

Acknowledgments

References

Andresová, A.; Bendová, M.; Schwarz, J.; Wagner, Z.; Feder-Kubis, J. Influence of the alkyl side chain length on the thermophysical properties of chiral ionic liquids with a (1 R ,2 S ,5 R)-(–)-menthol substituent and data analysis by means of mathematical gnostics, J. Mol. Liq. 2017, 242, 336-348.

Kovanic, P., Humber, M. B. The economics of information – mathematical gnostics for data analysis, book 717 pp, available online at http://www.math-gnostics.eu/books/, [cit 2017-10-13]

Lava, K., Binnemans, K., Cardinaels, T. Piperidinium, piperazinium and morpholinium ionic liquid crystals, J. Phys. Chem. B 113 (28) (2009) 9506-9511.

MacFarlane, D. R.; Forsyth, M.; Howlett, P. C.; Kar, M.; Passerini, S.; Pringle, J. M.; Ohno, H.; Watanabe, M.; Yan, F.; Zheng, W.; Zhang, S.; Zhang, J. Ionic liquids and their solid-state analogues as materials for energy generation and storage, Nature Reviews Materials 2016, 1, 15005+.

Pielichowska, K.; Pielichowski, K. Phase change materials for thermal energy storage, Prog. Mat. Sci. 2014, 65, 67-123.

Quirion, F., Lambert, D., Perron, G. The HLM method: a simple way to get the solid–liquid phase diagrams and enthalpies of transition of pure components and mixtures, Can. J. Chem. 70 (1992) 2745-2750.

Seddon, K. R., Stark, A., Torres, M. Influence of chloride, water, and organic solvents on the physical properties of ionic liquids J. Pure Appl. Chem. 72 (2000) 2275-2287.

Thomas, E.; Thomas, D.; Bhuvaneswari, S.; Vijayalakshmi, K. P.; George, B. K. 1-Hexadecyl-3-methylimidazolium chloride: Structure, thermal stability and decomposition mechanism, J.Mol. Liq. 2018, 249, 404-411.

Zhang, H.; Baeyens, J.; Cáceres, G.; Degrève, J.; Lv, Y. Thermal energy storage: Recent developments and practical aspects, Prog. Energy Combust. Sci. 2016, 53, 1-40.

Zhao, Y.; Chen, X.; Wang, X. Liquid Crystalline Phases Self-Organized from a Surfactant-like Ionic Liquid C16mimCl in Ethylammonium Nitrate, J. Phys. Chem. B 2009, 113, 2024-2030.

Zhu, J., Bai, L., Chen, B., Fei, W., Apr. 2009. Thermodynamical properties of phase change materials based on ionic liquids, Chem. Eng. J. 147 (1), 58-62.

Zurner, P., Schmidt, H., Bette, S., Wagler, J., Frisch, G. Ionic liquid, glass or crystalline solid? Structures and thermal behaviour of (C4mim)2CuCl3, Dalton Trans. 45 (8) (2016) 3327-3333.