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Low temperature glass/crystal transition in ionic liquids determined by H-bond vs. coulombic strength†

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Self-assembled ionic liquid crystals are anisotropic ionic conductors, with potential applications in areas as important as solar cells, battery electrolytes and catalysis. However, many of these applications are still limited by the lack of precise control over the variety of phases that can be formed (nematic, smectic, or semi/fully crystalline), determined by a complex pattern of different intermolecular interactions. Here we report the results of a systematic study of crystallization of several imidazolium salts in which the relative contribution of isotropic coulombic and directional H-bond interactions is carefully tuned. Our results demonstrate that the relative strength of directional H-bonds with respect to the isotropic Coulomb interaction determines the formation of a crystalline, semi-crystalline or glassy phase at low temperature. The possibility of pinpointing H-bonding directionality in ionic liquids make them model systems to study the crystallization of an ionic solid under a perturbed Coulomb potential.

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Introduction

Many properties of ionic liquids (ILs), such as their vapor pressure, viscosity, or melting point reflect the nature and magnitude of their intermolecular interactions. Although, to a large extent, Coulomb interactions are responsible for this phenomenology, it has become increasingly evident that (doubly ionic) H-bonds play an important role in their understanding.^{1–11} For example, Fumino *et al.*⁴ pointed out that directional H-bonds can be regarded as defects on the Coulomb potential of Imidazole-based ionic liquids (Im-ILs), leading to a counter-intuitive decrease of their viscosity with increasing H-bond strength. Molecular dynamics calculations by Zahn *et al.*¹²

revealed an scenario in which induction/dispersive intermolecular forces flatten the interaction potential, allowing the ions to explore different configurations separated by low energy barriers. On the other hand, deactivation of the more acidic H-bonds on the imidazole cation restricts the movement of anions around the aromatic ring, resulting in higher viscosities and melting points. However, the presence of long alkyl chains in Im-ILs also adds van der Waals interactions to the Coulomb potential, which if sufficiently strong (typically for > 12 carbon atoms) results in the formation of lamellar mesophases below a certain temperature.¹³ Hence, given the important applications derived from these materials,^{14–21} a complete understanding of the effect of different interactions on the formation and properties of crystalline and mesomorphic ionic solids is crucial.

In this paper we report a systematic study of a series of Im-ILs, selected to probe the effect of the H-bond strength on the nature of the solid phase stabilized at low temperature. The structural changes occurring across the liquid-to-solid transition were studied through the temperature dependence of the X-ray diffraction, polarized optical microscopy, electrical and thermal conductivities, infrared absorption, and differential scanning calorimetry experiments. Our main findings can be summarized as follows: (i) increasing the strength of H-bonds frustrates the crystallization of a 3D ionic solid, leading to a progressive loss of the 3D crystalline order and, for sufficiently strong H-bonds, the formation of a glass. (ii) The glass is thermodynamically unstable upon further cooling and small

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† Electronic supplementary information (ESI) available: Additional information about materials and methods, as well as additional IR, DSC, POM, X-Ray Diffraction, thermal conductivity and heat capacity analysis. See DOI: 10.1039/d0cp02633f

Fig. 1 Proposed phase diagram for Im-ILs, presenting the progressive loss of 3D crystalline order as the frequency of the intermolecular H-bonds increases. This is the consequence of the larger contribution of directional bonds with respect to the isotropic Coulomb potential. The frequency along the abscissa directly mirrors to the strength of intermolecular sH-bonds, as discussed in the text. Solid squares and circles represent the liquid-to-crystal phase transition, while the triangles represent the liquid-to-glass. Empty circles mark the temperature of formation of crystalline nuclei within the glassy phase. The nature of these transitions was deduced from a combination of different spectroscopic, calorimetric and transport experiments, and are explained in detail in the text. A summary of these temperatures can be found in Table S1 in the ESI.†

crystallization nuclei are spontaneously formed, resulting in a substantial enhancement of the thermal conductivity. (iii) Large alkyl chains produce similar effects as H-bonds, suggesting a common mechanism in which anisotropic interactions in addition to the Coulomb potential hinder the formation of an ionic crystal. These findings are condensed in a phase diagram of ILs (Fig. 1) in which the effect of directional H-bonds on the dominant isotropic Coulomb interaction is considered.

Our study also demonstrates that thermal conductivity is an extremely sensitive tool to explore the dynamics of the ILs in the solid phase, either glass or crystal. The study of the low temperature crystallization of the Im-ILs upon systematically increasing the strength of directional H-bonds provides an ideal framework to study the crystallization of an ionic crystal under a perturbed Coulomb potential, as well as, to design effective thermal regulators.

Materials and methods

Ionic liquids were purchased from Sigma Aldrich and Iolitec. The liquids were dried under vacuum at 100 °C for several hours to remove any water which could affect the crystallization, as will be discussed below. Thermal conductivity was measured using a variation of the 3ω method described previously.²² We added two independent electrodes in order to measure the electrical conductivity under the same conditions. Far-FTIR measurements were performed with a Bruker Vertex 70v FTIR spectrometer, equipped with a DLATGS detector. Samples were mixed with polyethylene powder and pressed into 13 mm

diameter pellets, and the spectra (32 scans, resolution 2 cm⁻¹) were collected under vacuum (0.2 mbar) to reduce water and CO₂ adsorption. Mid-FTIR measurements were performed using a Nicolet 6700 FTIR spectrometer (resolution 1 cm⁻¹).

For cryogenic FTIR measurements the sample is inside CaF₂ cells (15 μm spacer) mounted in a brass holder in thermal contact with the heat exchanger of a liquid-N₂ cryostat (DN1704, Oxford Instruments). Temperature scans (2 K min⁻¹) were made using an Oxford Instruments ITC4 temperature controller, while the temperature is measured through a type K thermocouple mounted close to the sample. The infrared spectra were recorded approximately every 18 seconds using a Perkin Spectrum Two FTIR spectrometer (spectral resolution 1 cm⁻¹).

The liquids were placed between two KBr windows for these measurements. Differential Scanning Calorimetry experiments were carried out using a Mettler Toledo DSC/821. Heat capacity was measured in a PPMS from Quantum Design. X-Ray diffraction was performed in a Bruker D8 Venture Photon III 14 κ-geometry diffractometer (Cu Kα radiation). Liquids were sealed inside capillary tubes for these measurements (diameter 400 μm, wall thickness 10 μm). Each experiment was taken at a sample-detector distance of 50 mm, 100 s per image, and with the capillary perpendicular to the direction of the incident beam.

Results and discussion

We have selected for this study a series of Im-ILs in which the availability of the most acidic C(2) and N(1) positions at the cation, and different anions, were systematically varied to increase the strength of the intermolecular C-H...A-hydrogen bonds (see the molecular structure in Fig. 1). The strength of the H-bonds on the different Im-ILs studied in this work was probed by FTIR spectroscopy, Fig. 2.⁴ The suitability of IR spectroscopy to characterize the intermolecular H-bond strength in Im-ILs was previously corroborated by comparison with NMR.^{23,24}

Im-ILs show characteristic bands in the mid-IR spectra associated with the intramolecular vibrational modes, while the low frequency (far-IR) bands are characteristic of the stretching and bending H-bonds between the anion and cation.^{4,5,25} The progressive increase of the frequency of the broad band at ~70–130 cm⁻¹, and the shift of the stretching mode of intramolecular C(2)-H to lower frequencies observed in the mid-FTIR spectrum confirm the increasing H-bond strength along this series of Im-ILs (Fig. 2).⁵

It should be noted that the decreasing reduced mass, μ , will also contribute to the observed frequency shifts.^{6,26,27} Previous experimental and theoretical analysis by Fumino *et al.*²⁷ showed that a simple calculation based on the harmonic oscillator approximation can provide a correct estimation of the contribution from μ , independent from the changes in the intermolecular force constant. Such approximation predicts a frequency shift $\Delta\nu(1 \rightarrow 2) \approx (\mu_2/\mu_1)^{1/2}$, which is much smaller than the experimental observations. For instance, the decrease

Fig. 2 Far-FTIR (a) and mid-FTIR (b) spectra of the different Im-ILs studied in this work. (1) 1-Ethyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide (EBisMIM-NTF₂); (2) 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIM-NTF₂); (3) 1-butyl-3-methylimidazolium triflate (BMIM-TFO); (4) 1-ethylimidazolium bis(trifluoromethylsulfonyl)imide (EIM-NTF₂); (5) 1-butyl-3-methylimidazolium nitrate (BMIM-NO₃); (6) 1-ethyl-3-methylimidazolium acetate (EMIM-Ac). The broad band around $\approx 70\text{--}130\text{ cm}^{-1}$ in (a) corresponds to the stretching of intermolecular C–H...A-hydrogen-bonds. The dashed-arrow in (b) marks the frequency dependent of the intramolecular C–H bond at carbon (2) of the imidazole ring. The imidazolium ring shows four possible positions for H-bonding, numbered as C(2), C(4), C(5) and N(1) in the chemical formula of Fig. 2(b).

of μ from (1) to (4) accounts for a $\approx 10\%$ displacement of the far-IR broad band, while the experimental observation shows a frequency change $\approx 30\%$. For ILs (5) and (6), which much lighter anions, the predicted $\Delta\nu(5 \rightarrow 6) \approx (\mu_6/\mu_5)^{1/2} \approx 5\%$ is much smaller than the 15% observed experimentally (see also Fig. S2 in the ESI†).

Therefore, we conclude that the change in H-bond strength is the main contribution to the frequency shift of the far-IR absorption band of the ILs studied in this work.

This conclusion is further supported by the behavior of other intramolecular modes in the low frequency region; for instance, the vibrational band between $290\text{--}310\text{ cm}^{-1}$ corresponds to the out-of-plane bending of the CH₃–N groups in the imidazolium cation, and it is present in all the ILs with different intensities (the data have been normalized to the lowest frequency peak, for clarity). The vibrational band at about 270 cm^{-1} in (1) corresponds to the out-of-plane bending mode of the CH₃ methyl group at C(2) position of the imidazolium cation. The wagging modes of the NTF₂ anion give place to the double peak absorption at 200 cm^{-1} , that represents the wagging modes of O=S=O groups (also present as a single peak in TFO).⁵ The intensity ratio between both peaks decreases $\approx 10\%$ from (1) to (3), as the number of sites available for H-bonding increases.

The red-shift of the C(2)–H stretching mode along this series, as shown in (Fig. 2b), also supports the hypothesis of an increasing H-bond strength along the series. Although in this case the absorption between $\approx 3100\text{--}3150\text{ cm}^{-1}$ contains a

contribution from a fundamental C–H stretching mode and overtones of the Im-ring (a Fermi resonance),²⁸ it was firmly established that H-bonding is the main responsible of the displacement of this absorption to lower frequencies.²⁹

Fig. 3 shows the temperature dependence of the electrical conductivity, $\sigma(T)$, of the Im-ILs across their liquid-to-solid transition. Liquids (1) to (4) show a large thermal hysteresis, consistent with crystallization and melting at T_C and T_m , respectively. These phase transitions were corroborated by the observation of endothermic/exothermic peaks in differential scanning calorimetric (DSC) experiments (Fig. S3 in ESI†). The hysteresis is reduced on (4), and partially suppressed on (5). For these liquids, DSC experiments show a glass transition on cooling, and a recrystallization peak at T_C' during heating, which (partially) induces a thermal hysteresis in the $\sigma(T)$ curve. Finally, liquid (6) shows a completely reversible transition at T_g , coincident with the glass transition observed in the DSC experiments. Thus, the results analyzed so far suggest a correlation between the H-bond strength and the propensity to form a glass on cooling from the liquid (see Table S1 in the ESI† for the list of transition temperatures reported in this work).

Note also that although nanometer-scale segregation was observed in the liquid phase of Im-ILs with alkyl side chains as short as 4–6 carbon atoms,^{10,30–32} the comparison of $\sigma(T)$, in liquids (1)–to–(4) shows that this is not a relevant effect for the crystallization of the liquids studied in this work. Therefore, our hypothesis is that directional H-bonds can be treated as defects in the isotropic Coulomb potential, which frustrate the

Fig. 3 Temperature dependence (cooling/heating) of the electrical conductivity of the Im-ILs studied in this work (1)–(8). The scan rate is 1 K min^{−1} for all curves. The curves have been multiplied by a factor (indicated), to fit in the same scale.

formation of the thermodynamically stable ionic crystals at low temperature.

To prove the validity of this scenario, we measured $\sigma(T)$ of Im-ILs (7) (1-octyl-3-methylimidazolium hexafluorophosphate, MOIM-PF₆) and (8) (1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, MOIM-NTF₂), both with moderate H-bonding strength ($\nu = 85$ cm^{−1}, Fig. S4 in ESI[†]), but with a long alkyl chain. The long lateral chain at the Im-cation introduces a steric hindrance, which can also be treated as a

defect on the isotropic potential. Consistent with this hypothesis, the conductivity $\sigma(T)$ of (7) and (8) is completely reversible across their liquid-to-solid transition (see Fig. 3c), and the DSC curves show the change of slope characteristic of formation of a glass on cooling (Fig. S3c, ESI[†]).

To show how H-bond frustrates the 3D ionic arrangements in more detail, the nature of the different phases appearing at low temperature was studied by X-ray diffraction and polarized optical microscopy (POM); see Fig. 4. For liquid (1), with the

Fig. 4 Top: Low temperature X-ray diffraction patterns of (a) EBisMIM-NTF₂ (1), (b) BMIM-TfO (3), (c) BMIM-NO₃ (5), and (d) MOIM-PF₆ (7). The lower panels show the polarized optical microscope images taken at approximately the same temperatures as the X-ray patterns above. The X-ray and optical images are compatible with a single crystal in (a), a partially crystalline phase in (b), and amorphous, isotropic phases in (c) and (d). The polarized optical microscopy image in (b) shows a straight wall between two domains with different orientation. The images in (c) and (d) show the tension fracture lines in the glass appearing below T_{NC} (see also the text, Fig. S5 and S6, and the corresponding videos in the ESI[†]).

weakest H-bond interaction, the diffraction pattern is characteristic of a fully ordered 3D ionic crystal below $T_C \approx 230$ K. The texture observed in the POM and the kinetics of the process (see ESI†, video 1) suggest crystallization by conventional nucleation and growth kinetics. As the strength of the H-bonds increases, the 3D order is progressively lost; for instance, the X-Ray diffraction pattern and POM images of liquids (2)–(4) suggest the formation of different semi-crystalline or liquid crystal phases below $T_C \approx 230$ K (see also the corresponding videos in the ESI† and Fig. S5 and S6).³³ The precise crystalline structure of these phases is not relevant for the discussion or conclusions of this paper (as it will be further discussed below); its elucidation is thus beyond the scope of our work.

Niemann *et al.*³⁴ and Khudozhitkov *et al.*³⁵ also showed that the delocalization of the positive charge in the imidazole ring promotes the formation of cationic clusters (tetramers) by enhanced cation-cation H-bonding. This effect suppresses the tendency of these systems to form 3D crystals, resulting in low temperature liquid-to-glass transitions. These observations are in perfect agreement with our results.

Upon further increasing the H-bond strength the crystalline or semi-crystalline phases are replaced by an isotropic glass. This is the case for liquids (5) and (6), which only show an amorphous signal in the X-ray diffraction pattern down to the lowest temperature studied in this work, ≈ 110 K. However, despite the absence of any signal of crystal ordering in the X-ray diffraction pattern of these liquids, POM images show the sudden appearance of fracture lines throughout the entire system below a temperature which we have called T_{NC} (nucleation temperature) which varies between 110–150 K, depending on the liquid. This effect is totally reproducible and independent on the cooling rate, demonstrating that it is a thermodynamically (and not kinetically) driven process (see the corresponding

videos in the ESI†). The same effect is observed in liquids (7) and (8), with weaker H-bonds but with long alkyl chains.

To probe whether the effects observed in POM at T_{NC} imply an actual rearrangement of the molecular packing in the glass, we studied the temperature dependence of the thermal conductivity, $\kappa(T)$. Note that κ is the only transport coefficient that does not depend on ionic diffusivity in a condensed phase, and therefore can be monitored continuously across the different phase transitions. Moreover, as heat is propagated through anharmonic coupling of intermolecular vibrations, κ should be very sensitive to subtle changes in the molecular order of the system, both in the liquid and the solid state.

The results shown in Fig. 5 can be grouped in two different categories: (i) Im-ILs with weak H-bonding and no steric impediments (liquids (1) to (4)) show a large increase in the thermal conductivity below T_C , and a more pronounced temperature dependence in the solid phase. The hysteresis between T_C and T_m is consistent with the formation of an ordered phase at low temperatures. (ii) Im-ILs with stronger H-bond interactions or steric effects (liquids (5) to (8)) show a broad peak in κ at T_g characteristic of a glass transition,³⁶ and a flat liquid-like temperature dependence until T_{NC} . Below this temperature, both the temperature dependence of $\kappa(T)$ and the existence of a thermal hysteresis, are consistent with the existence of crystalline ordering. This phase persists up to T_g upon heating, before transforming again into the isotropic liquid. Different cooling/warming cycles resulted in very reproducible results of $\kappa(T)$, showing that the possible presence of different crystal polymorphs does not affect significantly the thermal conductivity, at least for the Im-ILs studied in this work.³⁷

The value of κ below T_{NC} does not depend on the cooling rate (see Fig. S7 in the ESI†), confirming the thermodynamic origin of this phase. The existence of the transition at T_{NC} and

Fig. 5 (a)–(c) Temperature dependence (cooling/heating) of the thermal conductivity of the Im-ILs studied in this work (1)–(8). Temperature ramps are fixed to 1 K min^{-1} for all curves. The curves have been multiplied by a factor (indicated) and displaced vertically, for clarity.

Fig. 6 Reversible variation of the thermal conductivity after continuous cycling across T_{NC} of liquid (7).

the associated hysteresis was also verified through heat capacity $C_p(T)$ measurements (see Fig. S8 in the ESI†). Therefore, both $\kappa(T)$ and $C_p(T)$ suggest the spontaneous nucleation of some ordered phase within the glass below T_{NC} . These are probably crystalline clusters, smaller than a few tens of nanometers for them to remain unobservable in X-ray diffraction (and on the IR of C-H vibrational modes; see Fig. S9, ESI†).

Nucleation of a local crystalline order more within the glass will introduce microscale strain fields, which propagate beyond nearest neighbor distances, thus affecting the thermal diffusivity of the whole system in spite of constituting a small fraction of the total volume. The strain fields will also lead to the fast propagation of cracks observed in the POM. Note also that these nanocrystals will grow upon reheating, acting as nucleation seeds that promote the recrystallization observed in the DSC (see Video 5b and Fig. S10 in the ESI†).

Importantly, the large thermal contrast across T_{NC} allows a surprisingly large reversible modulation of κ , of $\approx 35\%$ (see Fig. 6). Different from previous reports of temperature regulation using complex liquids across a metal-to-insulator electrical transition,³⁸ the data reported in Fig. 6 correspond to a transition between two electrically insulating states in a single phase material. This suggests a new approach for designing effective thermal regulators, through the careful tuning of the different interactions that govern the crystallization of ILCs. A phase diagram summarizing all these findings is shown in the Fig. 1 at the beginning of the paper.

Conclusions

In summary, we have shown that H-bonds act as defects in the isotropic Coulomb potential, and that the relative magnitude of the H-bond strength with respect to the Coulomb interaction determines whether the crystallization or vitrification occurs upon cooling down Im-ILs. The H-bonds act as perturbations that frustrate the 3D ionic ordering and if they are strong enough, the system forms a glassy phase. The spontaneous nucleation of small crystalline nuclei within the glass at low

temperature enhances the thermal conductivity upon further cooling. Our results show the very high sensitivity of the thermal conductivity to tiny changes in the molecular structure, which allows the detection of new phase transitions that cannot be followed by conventional electrical conductivity measurements and are barely observed in DSC experiments. The results presented also demonstrate the possibility to achieve large, reversible changes in the thermal conductivity of these materials, which could be of interest for effective thermal regulation. Finally, we want to remark that the tunability of H-bond strength make Im-ILs a good model system to study the process of crystallization of an ionic solid. Since a similar balancing between directional (H-bonding) and isotropic (Coulomb) contributions to the intermolecular potential should occur in other ionic liquids, we believe the phase behavior observed here should quite general, and we hope that our work will stimulate further experimental and theoretical work in this direction.

Conflicts of interest

There are no conflicts to declare.

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