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Structural and aggregate analyses of (Li salt + glyme) mixtures: The complex nature of solvate ionic liquids

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Abstract

The structure and interactions of different (Li salt-glyme) mixtures, namely equimolar mixtures of lithium bis(trifluoromethylsulfonyl)imide, nitrate or trifluoroacetate salts combined with either triglyme or tetraglyme molecules, are probed using Molecular Dynamics simulations.

Structure Factor functions, calculated from the MD trajectories, confirmed the presence of different amounts of lithium-glyme solvates in the aforementioned systems. The MD results are corroborated by $S(q)$ functions derived from diffraction and scattering data (HEXRD and SAXS/WAXS). The competition between the glyme molecules and the salt anions for the coordination to the lithium cations is quantified by comprehensive aggregate analyses. Lithium-glyme solvates are dominant in the lithium bis(trifluoromethylsulfonyl)imide systems and much less so in systems based on the other two salts. The aggregation studies also emphasize the existence of complex coordination patterns between the different species (cations, anions, glyme molecules) present in the studied fluid media. The analysis of such complex behavior is extended to the conformational landscape of the anions and glyme molecules and to the dynamics (solvate diffusion) of the bis(trifluoromethylsulfonyl)imide plus triglyme system.

Introduction

Room-temperature ionic liquids —pure salts with unusually low melting-points— have great potential as solvents in capacitors, fuel cells, dye-sensitized solar cells and rechargeable batteries.¹⁻⁶ Lithium compounds are critical for electrochemical devices such as lithium-ion batteries, but unfortunately, most common lithium salts have melting-point temperatures well above 373 K and do not fall within the ionic-liquid class. One way to circumvent this issue is to

consider (ionic liquid + Li salt) mixtures with a common anion.⁷ Many of these mixtures have a wide solubility window and eutectic points that produce ionic liquid mixtures at room temperature.

Alternatively, the lithium salt can be mixed with a molecular solvent that is also capable of forming a single liquid phase at room temperature. A particularly interesting and successful example of this route are equimolar mixtures of lithium salts with oligoethers (glymes)⁸. Such mixtures have been proposed as a new ionic liquid sub-class⁹⁻¹⁰ known as solvate ionic liquids due to the specific interactions between the lithium ions and the glyme molecules, which can yield lithium-glyme coordination complexes¹¹.

In this study we will probe the structure and interactions of different (Li salt-glyme) mixtures using Molecular Dynamics simulations. The results are validated against experimental diffraction results (wide-angle x-ray scattering data) and also very recent structural analyses on the same type of systems performed by the combination of Raman spectroscopy, *ab-initio* calculations and MD simulations^{12,13}.

The focus of this work is MD simulations of equimolar mixtures of lithium bis(trifluoromethylsulfonyl)imide, nitrate or trifluoroacetate salts (Li[Ntf₂], Li[NO₃] or Li[CF₃CO₂], respectively) combined with either triglyme or tetraglyme molecules (G3 or G4, respectively). The solvate ionic liquid structures will be contrasted with simulations of the pure components.

Experimental

1. High-Energy X-Ray Diffraction; Small- and Wide-Angle X-Ray Scattering

High-energy X-ray diffraction (HEXRD) measurements were carried out at 298 K using the BL04B2 beam-line of the SPring-8 facility at the Japan Synchrotron Radiation Research Institute (JASRI)^{14,15}.

All glyme molecules (stabilizer free, water content < 50 ppm), namely triglyme (G3) and tetraglyme (G4), were obtained from Nippon Nyukazai. Li[Ntf₂] (battery-grade, water content < 50 ppm) was kindly supplied by Solvay Chemicals. Lithium nitrate (Li[NO₃]) and lithium trifluoroacetate (Li[CF₃CO₂]) from Sigma-Aldrich, were dried under high vacuum at an elevated temperature prior to use. Equimolar glyme-Li salt mixtures were prepared by mixing appropriate amounts of the lithium salt and glyme in an Ar-filled glove box (VAC, [H₂O] < 1 ppm). The lithium salt and glyme were mixed and magnetically stirred in a vial, at 60 °C overnight. The water content of the mixtures was determined by Karl-Fischer titration using a Mitsubishi Chemical CA-07 moisture meter and found to be less than 100 ppm.

Samples of equimolar mixtures of Li[Ntf₂]+G3, Li[Ntf₂]+G4 and Li[NO₃]+G3 were placed in 2 mm-thick polyetheretherketone (PEEK) cells equipped with Kapton®-film X-ray windows hermetically sealed with Kalrez® O-rings and stainless steel cover plates. Monochrome 61.6 keV X-rays were obtained using a Si (220) monochromator.

The observed X-ray intensity was corrected for absorption¹⁶ and polarization. Incoherent scatterings¹⁷ were subtracted to obtain coherent scatterings, $I_{\text{coh}}(q)$, where q represents a scattering vector $q = 4\pi\sin(\theta)/\lambda$ (θ and λ stand for the

scattering angle and the irradiated X-ray wavelength, respectively). The X-ray structure factor $S(q)$ per stoichiometric volume were respectively obtained according to

$$S(q) = \frac{I_{\text{coh}}(q) - \sum n_i f_i(q)^2}{(\sum n_i f_i(q))^2} + 1 \quad (1)$$

where n_i and $f_i(q)$ denote the number and the atomic scattering factor of atom i ¹⁸, respectively. All data treatment was carried out using the program KURVLR¹⁹.

Small- and Wide-angle scattering (SAXS/WAXS) was performed on a point collimated Anton Paar SAXSess. The scattering intensity was collected on image plates, which were read with a Perkin-Elmer Cyclone phosphor storage system using standard OptiQuant software. The 2D intensity profiles were integrated using SAXSquant 2D software to yield the radial average intensity, $I(q)$, and normalized to a direct beam intensity of 1 before subtraction of the empty cell scattering. Scattering was measured at 298 K from 1 mm quartz capillaries for all samples except Li[CF₃CO₂] + G3, which was measured in a paste cell with amorphous poly(methylmethacrylate) windows, due to its high viscosity. All data sets were accumulated for 10 minutes per sample. The samples were from similar batches as those used in the HEXRD experiments. Water content, checked by Karl Fischer titration prior to the experiments in Australia, was similar to that reported by the Japanese groups.

2. Simulation Details

A. Model and Molecular Dynamics runs.

The molecular solutes, triglyme (G3) and tetraglyme (G4), were modeled using the OPLS force field²⁰.

Li[Ntf₂], Li[NO₃] and Li[CF₃CO₂] were modeled within the framework of the CL&P atomistic force field²¹⁻²³, which is an extension of the AMBER and OPLS force fields²⁰ specially designed to study ions that usually compose ionic liquids and other ionic compounds with low melting points. Moreover, in the context of the present work, all simulations were carried out using a modification of the original model: the attributed atomic point charges (APCs) directly taken from the CL&P force field were all scaled down with a charge scaling factor of 0.8. Such factor is incorporated in the model in order to take into account the reduction of the electrostatic interactions between ions due to polarization effects²⁴⁻²⁷.

The necessity of such correction in the model is corroborated by two distinct pieces of evidence: i) it is known that the cohesive energy of pure ionic liquids modeled using full APCs and non-polarizable atomistic force-fields is in general over-predicted by as much as 50%^{28, 29}. The effect of polarization (or the lack of it in the model) can be compensated by scaling down the intensity of the electrostatic interactions between ions through the use of reduced APCs; ii) When two of the salt-glyme systems (Li[CF₃CO₂]-G3 and Li[NO₃]-G4 equimolar mixtures) were modeled using full APCs we have witnessed a clear demixing between a glyme-rich and a salt-rich sub-phase. Evidently the modeled interactions between the salt ions were too strong to allow for some

coordination of the lithium ions to the glyme molecules and allow the mixing of the two components of the mixture. Although it is true that in both Li[CF₃CO₂] and Li[NO₃] systems the stronger interionic interactions suppress the formation of lithium-glyme complexes, such phase separation was not obvious in the experimental studies¹¹. When the APCs were scaled down the miscibility of the two components in the Li[CF₃CO₂]-G3 and Li[NO₃]-G4 systems increased. In order to have a general model, we have decided to use the same charge reduction scheme in all systems, including those based on the Li[Ntf₂] salt, where the need for the correction was not so obvious.

Molecular dynamics simulations were carried out using the DL_POLY 2.20 package³⁰. The runs were performed with 2 fs time steps. It must be noted that within the framework of the OPLS and CL&P force-fields it is possible to constrain the stretching vibrations of bonds that include hydrogen atoms in order to be able to use time steps above 1 fs. Cutoff distances of 1.6 nm were used, with Ewald summation corrections performed beyond such threshold. The simulations were performed using cubic boxes with 500 ion pairs of the molten salts and 500 glyme molecules. The number of ion pairs and size of the box for all systems are presented in Table 1. Due to the slow dynamics of this type of system, special care was taken to ensure the attainment of equilibrium conditions, including the proper diffusion of the solutes in the molten salt media: (i) equilibrations started from low-density initial configurations; (ii) reduced charges were applied for the molten salts; (iii) typical equilibrations were implemented in succession for more than 1 ns each at constant NpT; (iv) multiple re-equilibrations through the use of temperature annealing were performed; (v) further simulation runs were used to produce equilibrated systems at 303 K. Production runs typically lasted for at least 6 ns. Finally, the evolution of the equilibrated systems was monitored during long simulation runs (cf. Results and Discussion, sub-section F) where we could observe the interchange between glyme- and anion-complexed lithium atoms. The simulations results were confronted with experimental density data at 303 K¹¹, yielding deviations in the 1-3% range, compatible with the degree of accuracy obtained in this type of model.

Table 1: Simulation conditions and size of the equilibrated boxes.

System	<i>N</i> ion pairs	<i>N</i> solute	<i>V</i> _{box} /nm ³	<i>l</i> _{box} /nm	<i>T</i> /K
Li[Ntf ₂]	500		127.7	5.04	530
Li[NO ₃]	500		27.1	3.01	530
Li[CF ₃ CO ₂]	500		59.2	3.90	530
G3	500		151.1	5.33	303
G4	500		182.5	5.67	303
Li[Ntf ₂] + G3	500	500	262.4	6.40	303
Li[NO ₃] + G3	500	500	294.4	6.65	303
Li[CF ₃ CO ₂] + G3	500	500	174.7	5.59	303
Li[Ntf ₂] + G4	500	500	207.1	5.92	303
Li[NO ₃] + G4	500	500	202.9	5.88	303
Li[CF ₃ CO ₂] + G4	500	500	235.2	6.17	303

B. Structural and Aggregate Analyses.

The pair radial distribution functions $g_{ij}(r)$ between selected pairs of atoms or interaction centers were calculated in the usual way³¹. The $g_{ij}(r)$ functions were calculated up to $r = 2.5$ nm distances.

The total static structure factors, $S(q)$, were calculated using a previously described methodology³². In brief, $S(q)$ was obtained from

$$S(q) = \sum_i \sum_j S_{ij}(q) \quad (2)$$

$$S_{ij}(q) = \frac{\rho_0 x_i x_j b_i(q) b_j(q) \int_0^R 4\pi r^2 [g_{ij}(r) - 1] \frac{\sin(qr)}{qr} \frac{\sin(\pi R)}{\pi r/R} dr}{\left(\sum_i x_i b_i(q) \right)^2} \quad (3)$$

where $S_{ij}(q)$ is the partial static structure factor between atoms of type i and j (e.g., carbon, hydrogen, or nitrogen), calculated from the corresponding Fourier transform of the partial radial distribution function $g_{ij}(r)$; q is the scattering vector; ρ_0 is the average atom number density; R is the cutoff used in the calculation of $g_{ij}(r)$, established to half the side of the simulation box (in this case at least 5.2 nm for any of the studied ionic liquids); x_i and x_j are the atomic fractions of i and j ; and $b_i(q)$ and $b_j(q)$ are either the X-ray scattering factors or the coherent bound neutron scattering lengths of the corresponding atom type, interpolated from recommended values in the International Tables for Crystallography³³. The term $\sin(\pi R)/(\pi r/R)$ in eq 2 is a Lorch-type window function used to reduce the effect of using a finite cutoff in the radial distribution function calculation³⁴.

The aggregation analyses of all salt-glyme systems focused on the calculation of the connectivity between the lithium ions and oxygen atoms of the anion or of the molecular solutes. A connectivity threshold for each case is established by considering the corresponding $g_{ij}(r)$ data. The lithium–oxygen interionic distance has been set to 0.275 nm, corresponding to the first coordination shell limit of the $g_{ij}(r)$ data. The use of the threshold criteria allows the computation of closest-neighbor lists for each interaction center for all recorded configurations in the production runs. The connectivity is stipulated as always being between a lithium ion and an oxygen atom.

Results and Discussion

A. The structure of pure liquid Li[Ntf₂]

Simulations of pure liquid Li[Ntf₂] were conducted at 530 K which is slightly above its melting point. The Structure Factor function, $S(q)$ —calculated *via* the appropriate Fourier transforms of the correlation functions obtained from the simulated MD trajectories (see experimental section)— shows three peaks/shoulders in the low- q region, for $q < 20$ nm⁻¹. Fig. 1 shows the global $S(q)$ along with the resulting multi-peak fitting in the $3 < q/\text{nm}^{-1} < 20$ region that

yielded three Gaussian curves centered at 6.2, 11.9 and 15.5 nm⁻¹. These three peaks correspond to intermolecular structural features of the liquid. As in diffraction spectra, the heavier sulfur atoms present in the anions contribute significantly to the intensity of those peaks.

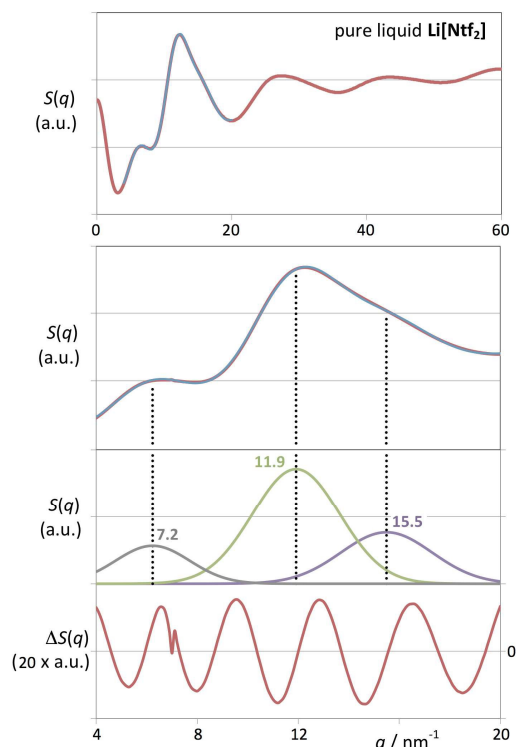


Fig. 1 Total Structure Factor Function, $S(q)$, of liquid Li[Ntf₂] at 530 K. The graphs in the bottom show the deconvolution of $S(q)$ in the $4 < q/\text{nm}^{-1} < 20$ region, yielding three Gaussian functions. The residues of the fitting process are shown at the bottom.

The shoulder fitted to the Gaussian curve centered at 15.5 nm⁻¹ is known as the contact peak and corresponds to distances between neighboring atoms of different ions. It therefore broadly defines the boundary between intra- and intermolecular structural features of the liquid.

The prominent peak at 11.9 nm⁻¹ is the charge-ordering peak (COP) and is a distinctive feature of ionic liquids and molten salts^{32, 35-39}. In order to establish local electro-neutrality each ion in an ionic liquid or molten salt must be surrounded by counter-ions. Such three-dimensional networks of alternate ions are often referred to as the so-called polar network. The space correlation functions between pairs of ions with opposite charge and pairs of ions with the same charge have a unique characteristic wavelength and are opposite in phase (Fig. 2). In reciprocal space the polar network wave length (around 0.53 nm for the Li[Ntf₂]) corresponds to the q value of the COP peak ($0.53 = 2\pi/11.9$). It must be stressed that the correlations between same-charged ions and opposite-charged ions contribute with different signs for the emergence of the COP peak. In some ionic liquids^{37,38,40}, even though the polar network is present the COP can be absent because the contributions from the different charge-charge correlations cancel each other. Such situation is obviously linked to different

charge distributions and how their correlations are dampened by the fact that we have a fluid media with no ultimate long-range order.

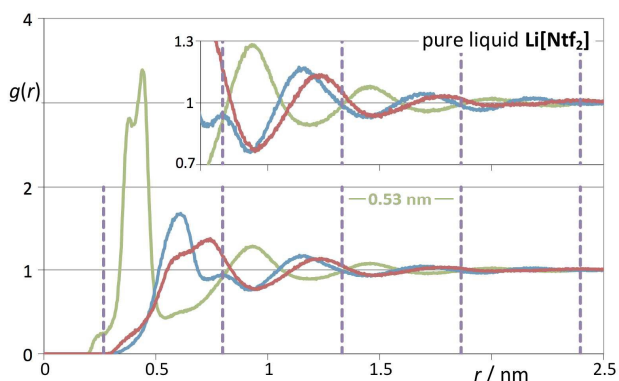


Fig. 2 Three selected radial distribution functions (RDFs), $g(r)$, as a function of distance, r , for liquid $\text{Li}[\text{Ntf}_2]$ at 530 K. Green lines: RDFs between the lithium cation and the nitrogen atom of the anion (NBT); blue lines: Li-Li RDFs; red lines: NBT-NBT RDFs. The purple dashed lines indicate the characteristic wavelength of all RDFs and are related to the position of the corresponding COP peak (green Gaussian) in Figure 1. The inset magnifies the 0.7-2.5 nm region.

Finally, the weak shoulder centered at 6.2 nm^{-1} (1.01 nm in direct space) probably corresponds to distances between sulfur atoms belonging to two $[\text{Ntf}_2]^-$ ions that instead of being separated by an intercalated lithium cation are orientated side-by-side. The existence of adjoining anions that touch *via* their less charged moieties, i.e., the CF_3 groups, is a direct consequence of the very large size difference between the Li cation and the $[\text{Ntf}_2]^-$ ion. One can have a better idea of the two types of S-S distances that correspond to the two low- q peaks just discussed (0.53 nm for $[\text{Ntf}_2]^-$ ions intercalated by a lithium cation; 1.01 nm for side-by-side $[\text{Ntf}_2]^-$ ions) if one considers the structure of crystalline $\text{Li}[\text{Ntf}_2]$ ⁴¹, Fig. 3. In the case of the more compact and ordered crystal, those two distances are approximately 0.52 and 0.86 nm , respectively.

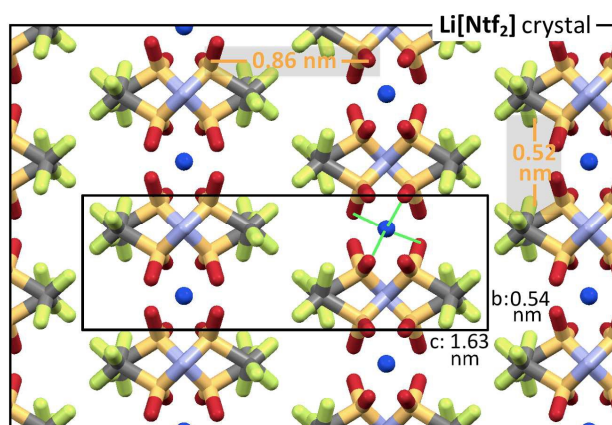


Fig. 3 Molecular rendering of a slab of a $\text{Li}[\text{Ntf}_2]$ orthorhombic $Pnaa$ crystal⁴¹. The figure shows the dimensions of the crystalline unit cell in the two directions (b and c) parallel to the slab ($a = 0.96 \text{ nm}$), two characteristic distances between sulfur atoms in the lattice, and the connectivity of the lithium anion —coordination to four oxygen atoms belonging to four different $[\text{Ntf}_2]^-$ ions.

B. The structure factor functions of equimolar Li[Ntf₂] – glyme mixtures

The $S(q)$ functions for two different glymes (G3 and G4) mixed with equimolar concentrations of the Li[Ntf₂] that form the solvate ionic liquid are shown in Fig. 4. These were obtained from MD runs performed at room temperature. For comparison purposes, the $S(q)$ function of pure liquid Li[Ntf₂] at 530 K is also shown. The figure shows that i) the contact peaks of the mixtures are more prominent and shifted to lower q -values (maxima at 15.0 nm⁻¹) relative to those of pure liquid Li[Ntf₂] (weak shoulder at 15.5 nm⁻¹); ii) the prominent COP (11.9 nm⁻¹) present in liquid Li[Ntf₂] becomes very weak in the solvate ionic liquids at around 11.5 nm⁻¹; and iii) the solvate ionic liquids exhibit prominent low- q peaks at around 8.1 nm⁻¹ as opposed to the weak low- q shoulder of pure liquid Li[Ntf₂] at 7.2 nm⁻¹.

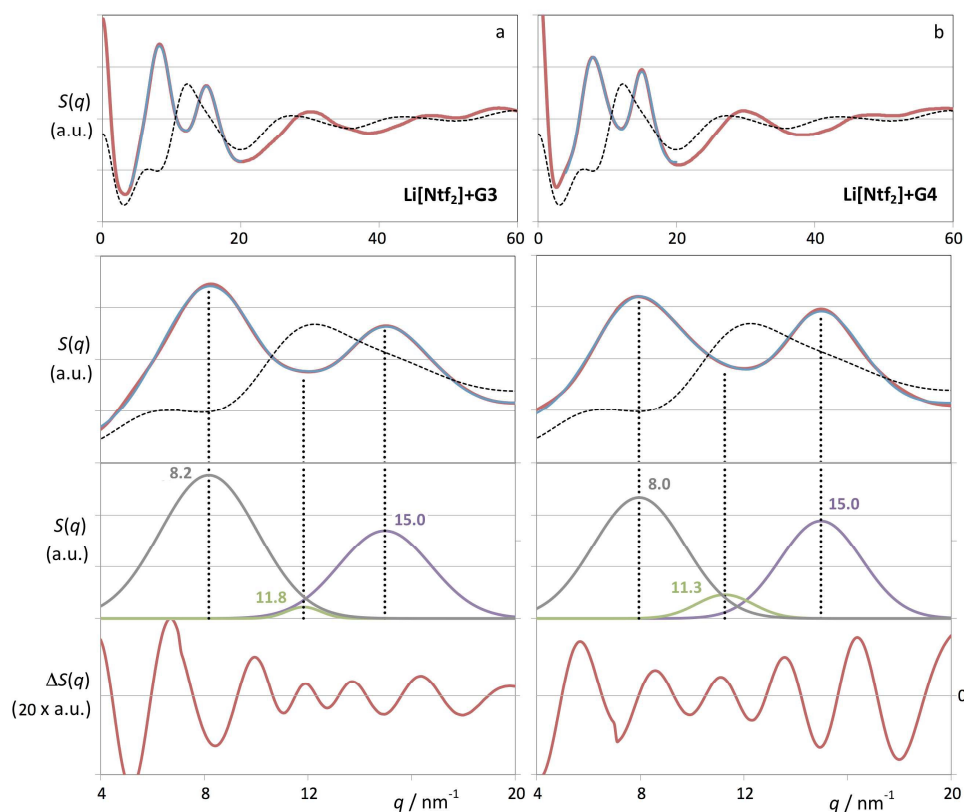


Fig. 4 Total Structure Factor Functions, $S(q)$, of (a) Li[Ntf₂]+G3 and (b) Li[Ntf₂]+G4 mixtures at 303 K. The graphs in the bottom show $S(q)$ Gaussian deconvolutions in the $4 < q/\text{nm}^{-1} < 20$ region. The residues of the fitting process are shown at the bottom. The dashed black curves depict the $S(q)$ of pure liquid Li[Ntf₂] (as in Fig. 1) and are used for comparison purposes.

The shifts of the contact peaks are justified by the presence of the methylene and methyl groups of the glyme molecules that promote intermolecular contacts between atoms heavier than hydrogen at slightly larger distances (lower q values). Moreover, the absence of a prominent COP peak in the q -region above 11 nm⁻¹ allows the contact peaks of the mixtures to appear as distinct peaks rather than the contact shoulder-peaks in the pure salt.

The conspicuous peaks at $\sim 8.1 \text{ nm}^{-1}$ in the solvate ionic liquids must be a consequence of characteristic separations between the anions consistent with glyme-solvated lithium ions.

If the glyme molecules form stable solvates with the lithium ions that effectively destroy all its direct contacts with the anion, then the system becomes a mixture of solvent-separated ion pairs (SSIP): the lithium solvate would become a larger cationic entity interacting with the $[\text{Ntf}_2]^-$ ions. The corresponding polar network would then exhibit longer characteristic wavelength distances and the COP peak would shift to lower q .

An example of a crystalline structure based on Li-glyme SSIPs has been experimentally determined by Henderson et al.⁴³ for the diglyme-Li $[\text{Ntf}_2]$ system. However, the proportion of diglyme and salt used in this mixed crystal was 2:1 because each lithium ion was solvated by two diglyme molecules (six oxygen-lithium bonds) in order to form a stable SSIP.

When the proportion of diglyme:salt is the opposite (1:2) a more complex situation emerges where only part of the lithium-anion interactions present in the pure salt are replaced by glyme-lithium contacts⁴³. In that case large lithium-glyme- $[\text{Ntf}_2]$ aggregates are formed where some lithium cations are still surrounded by $[\text{Ntf}_2]^-$ ions and others are partially coordinated to one diglyme molecule. The typical Li-Li distances in these mixed crystals, cf. Fig. 5, vary from around 0.5 nm—the distances already discussed for pure Li $[\text{Ntf}_2]$ —to around 0.9 nm, when the lithium ions are solvated (or partially solvated) by glyme molecules.

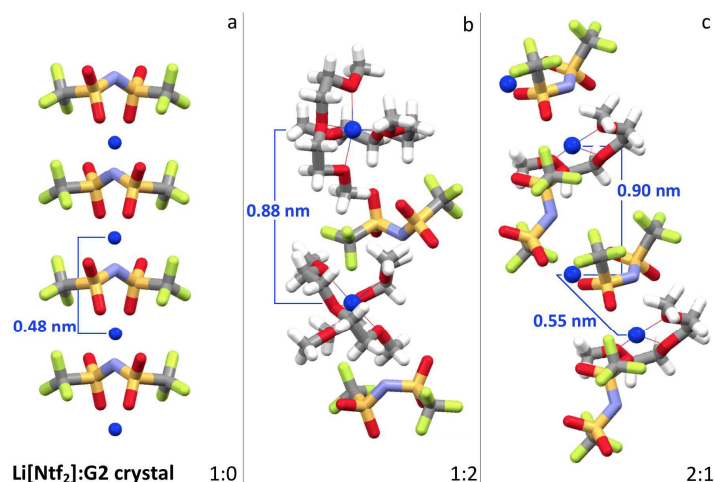


Fig. 5 Molecular rendering of selected sections of (a) a Li $[\text{Ntf}_2]$ orthorhombic $Pnna$ crystal⁴¹, (b) a 1:2 Li $[\text{Ntf}_2]$:G2 monoclinic Cc mixed crystal⁴³, (c) a 2:1 Li $[\text{Ntf}_2]$:G2 monoclinic $P2_1/c$ crystal⁴³. Different Li-Li distances are shown: (a) between anion-intercalated cations; (b) between cations contained in solvent separated ion pairs (SSIPs); (c) between partially solvated cations.

The crucial point is to know what happens in a 1:1 glyme-salt *liquid* mixture. Unlike the mixed crystals, one does not have lithium ions coordinated in just one or two types of way (SSIPs in the 2:1 crystal, partial SSIPs or Li- $[\text{Ntf}_2]$ complexes in the 1:2 crystal). Rather, lithium cations can be connected in various interchangeable ways with competing glyme molecules and $[\text{Ntf}_2]^-$ ions. Indeed, Henderson et al. studied a 1:1 Li- $[\text{Ntf}_2]$:G3 mixture and although they reported a

1:1 crystalline solvate with a melting point temperature of 296 K, the corresponding structure showed a high level of disorder (triclinic $P1$ crystal), with the lithium ions coordinating to the four oxygen atoms of a G3 molecule while maintaining a fifth direct link to one oxygen atom of a neighbouring $[\text{Ntf}_2]^-$ ion⁴³. Raman spectroscopy confirmed that at room temperature (in the liquid state) half of the solvates in the mixture were SSIPs and half were aggregates including direct cation-anion connections⁴³, confirming the original Raman data reported by Brouillette et al.⁴⁴. More recently, Henderson and co-workers⁴⁵ updated the data on solvate structures of $\text{Li}-[\text{Ntf}_2]:\text{G3}$ electrolytes and reported that in the corresponding crystal, the six possible coordination positions of the lithium cation are filled by four oxygen atoms from G3 molecules and two oxygen atoms from $[\text{Ntf}_2]^-$ ions.

Figure 6 shows selected pair radial distribution functions, RDFs, corresponding to different atomic correlations within the polar network of the $\text{Li}[\text{Ntf}_2]-\text{G3}$ mixture.

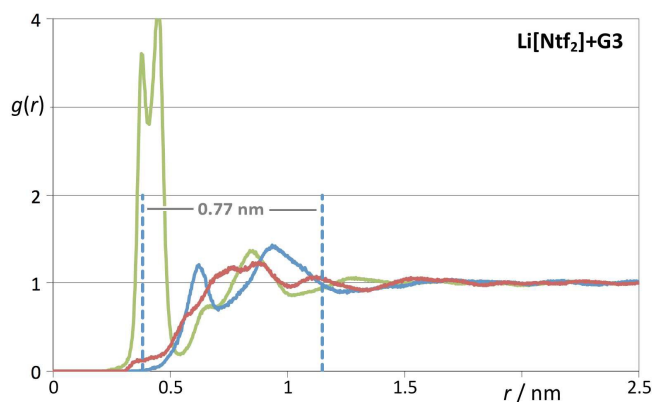


Fig. 6 Three selected radial distribution functions (RDFs), $g(r)$, as a function of distance, r , for the $\text{Li}[\text{Ntf}_2]-\text{G3}$ mixture at 303 K. Green lines: RDFs between the lithium cation and the nitrogen atom of the anion (NBT); blue lines: Li-Li RDFs; red lines: NBT-NBT RDFs. The blue dashed lines indicate the characteristic wavelength of the Li-Li RDF and are related to the position of the corresponding low- q peak (grey Gaussian) in Figure 4a.

Comparison of Fig. 6 with Fig. 2 reveals that the $\text{Li}-[\text{Ntf}_2]$ first peak is stronger in the mixture due to the dilution of the ions and normalization of the RDFs. This means that most $[\text{Ntf}_2]^-$ ions still maintain at least one direct contact with the lithium ions. However, the oscillatory and opposition-of-phase behavior present in the pure $\text{Li}-[\text{Ntf}_2]$ liquid RDFs has been suppressed. This means that the glyme molecules have disrupted the polar network by partially solvating the lithium ions.

Such solvation can be discussed in terms of the Li-Li RDFs presented in Fig. 2 and 6. The first peak of these RDFs, centered around 0.59 nm, is much more prominent in the pure liquid than in the mixture. These distances correspond to Li-Li distances where the two ions are intercalated by a $[\text{Ntf}_2]^-$ ion (cf. Fig 5a and 5c for a comparison with the known structure of analogous salts). On the other hand, the RDF of the mixture has a second peak around 0.9 nm that is absent in the pure liquid. Such peak relates to Li-Li distances between glyme-solvated lithium cations (cf. Fig. 5b and 5c). The position of this second peak of the mixture can be correlated with the low- q peak in the corresponding $S(q)$ function: if one measures one wave length from the onset of the Li-Li RDF to the

first $g(r)=1$ crossing of the Li-Li RDF (blue dashed lines in Fig. 6), the distance (0.77 nm) corresponds to the low- q peak: $8.2 \text{ nm}^{-1} = 2\pi/0.77$.

The structure factor functions corresponding to the complex structure of these liquid mixtures make it possible to analyze the connectivity of the lithium ions. However, before performing such aggregate analysis we will validate the calculated $S(q)$ functions of the present model against experimental results obtained from HEXRD and WAXS data.

C. Validation of $S(q)$ data: WAXS and HEXRD versus MD data.

Figs. 7 and 8 show comparisons between experimental (WAXS and HEXRD data) and simulated $S(q)$ functions of Li[Ntf₂]-G3, Li[CF₃CO₂]-G3, Li[Ntf₂]-G4 and Li[NO₃]-G4 equimolar mixtures. Since the intensity of the peaks in Figs. 7 and 8 are in arbitrary scales, the different functions were shifted in the vertical direction for clarity.

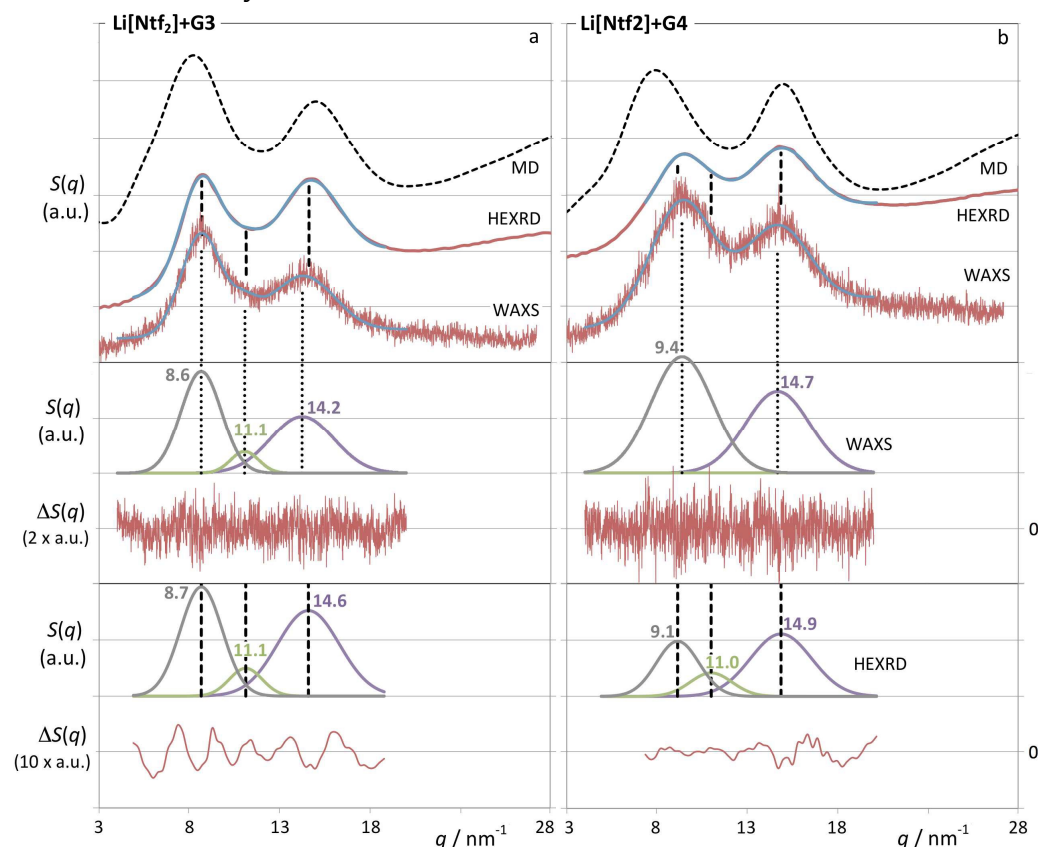


Fig. 7 WAXS and HEXRD Structure Factor Functions, $S(q)$, of (a) Li[Ntf₂]+G3, and (b) Li[Ntf₂]+G4, mixtures at 303 K. The graphs also show the $S(q)$ Gaussian deconvolutions in the $5 < q/\text{nm}^{-1} < 20$ region and the residues of the fitting process. The dashed black curves depict the corresponding simulated $S(q)$ functions (cf. Fig. 4).

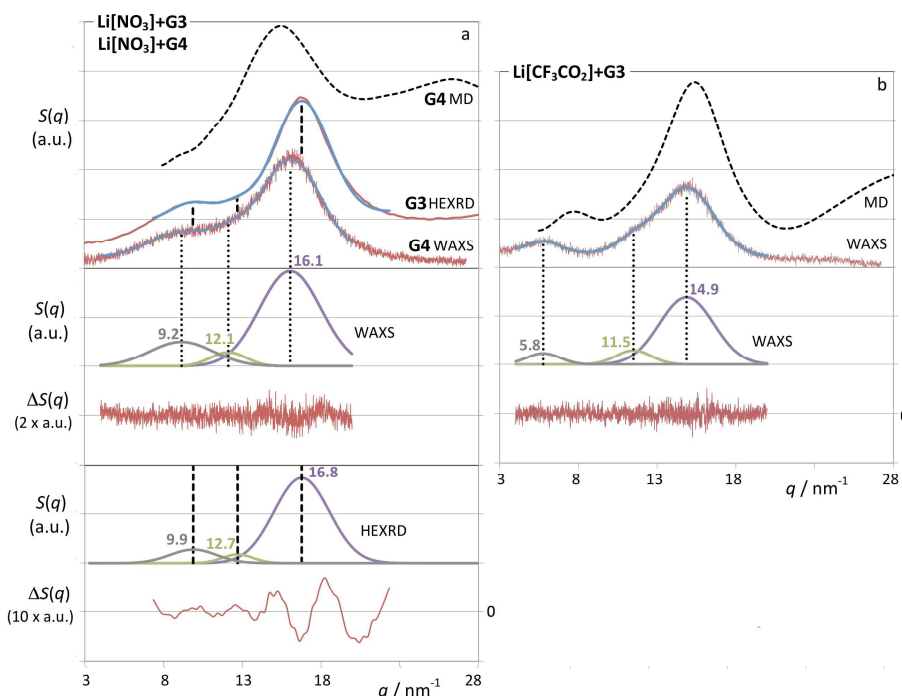


Fig. 8 WAXS and HEXRD Structure Factor Functions, $S(q)$, of (a) $\text{Li}[\text{NO}_3]+\text{G3}$ and $+\text{G4}$, and (b) $\text{Li}[\text{CF}_3\text{CO}_2]+\text{G3}$, mixtures at 303 K. The graphs also show the $S(q)$ Gaussian deconvolutions in the $5 < q/\text{nm}^{-1} < 20$ region and the residues of the fitting process. The dashed black curves depict the corresponding simulated $S(q)$ functions.

Figs. 7a and 7b show that the two low- q prominent bands in the WAXS and HEXRD spectra of the two $\text{Li}[\text{Ntf}_2]$ -glyme mixtures are reproduced in the MD-calculated $S(q)$ functions. Deconvolution of the experimental spectra yields three Gaussian peaks in all cases except for the WAXS $\text{Li}[\text{Ntf}_2]$ -G4 data; this data has the lowest signal-to-noise ratio, which may mask the presence of the small intermediate peak. The three Gaussian curves correspond to: large contact peaks in the 14-15 nm^{-1} region; small COP peaks in the 11-12 nm^{-1} region; and large low- q peaks in the 8-9 nm^{-1} region. The relatively high q -value of the low- q peak in the WAXS $\text{Li}[\text{Ntf}_2]$ -G4 data (9.5 nm^{-1}) is probably due to failed deconvolution of the low- q band into two peaks, as mentioned above.

The corresponding MD spectra (Fig. 4) show the same type of deconvolution. The MD peaks exhibit small q -value shifts relative to the x-ray data which are well within the precision of the modeling. In general, the MD data is in better agreement with the HEXRD data, which has a higher signal-to-noise ratio. The largest departure between the MD and the experimental data can be seen in the low- q peak of the $\text{Li}[\text{Ntf}_2]$ -G4 system (the MD peak is around 8.0 nm^{-1} , Fig. 4b, whereas the HEXRD data show a low- q peak centered at 9.1 nm^{-1} , Fig 7b). This difference maybe attributed to the model predicting a relatively large proportion of loosely bound Li-G4 complexes —G4 molecules coordinated by only three or four of its five oxygen atoms— and uncoordinated G4 molecules (cf. next subsection). This will increase the average distance between anions in adjoining Li-G4 complexes and shift the low- q peak to lower q .

The $S(q)$ functions for the trifluoroacetate- and nitrate-based salts, presented in Figs. 8a and 8b, also agree qualitatively with the WAXS data and the HEXRD data in that the low- q peaks are suppressed. This could be a consequence of the

absence of 3rd period atoms in the $[\text{CF}_3\text{CO}_2]^-$ or $[\text{NO}_3]^-$ ions compared to the sulfur atoms of the $[\text{Ntf}_2]^-$ ion that contribute disproportionately to the low- q x-ray diffraction patterns. Alternatively, it is possible that the increasing difficulty of finding large numbers of lithium-glyme aggregates impacts the ordering of the (partial) polar network in these systems, discussed below. It must also be stressed that the eventual phase separation of the system can also influence the existence of spurious low- q peaks in the MD $S(q)$ functions, as shown in Figs. 8a and 8b.

D. Aggregation analyses of Li-glyme and Li-anion complexes.

Fig. 9 summarizes the clustering of glyme molecules around the lithium ions using cluster analysis. Six systems were considered: the $\text{Li}[\text{Ntf}_2]$, $\text{Li}[\text{CF}_3\text{CO}_2]$ and $\text{Li}[\text{NO}_3]$ salts combined in equimolar proportions with either G3 or G4. The Venn diagrams of the figure show, for each system, how many glyme molecules are directly attached to a lithium ion according to both the number and type of oxygen atom (O1 to O4 in G3, O1 to O5 in G4).

In the $\text{Li}[\text{Ntf}_2]$ +G3 system (Fig. 9a), 291 of the 500 glyme molecules are coordinated to the lithium ions using all four oxygen atoms. Only a few glyme molecules are attached by one of their terminal oxygen atoms (O1 or O4) to a lithium ion. According to the Venn diagram only 5 glyme molecules are not in contact with a lithium ion. However, if the same connectivity criteria used to count the connections is applied to the direct calculation of unattached glyme molecules the total is 20. This is because 15 glyme molecules bridge between two distinct lithium ions via its O1 and O4 oxygen atoms. The Venn diagrams also show that the attachment of the glyme molecules to the lithium ions in the $\text{Li}[\text{Ntf}_2]$ -glyme systems (Figs. 9a and 9b) is obtained via a wide range of possibilities, from completely complexed glyme molecules to some that are only attached by only one or two of its oxygen atoms. Moreover, since the MD simulations are probing the liquid phase, connectivity patterns evolve during the simulation.

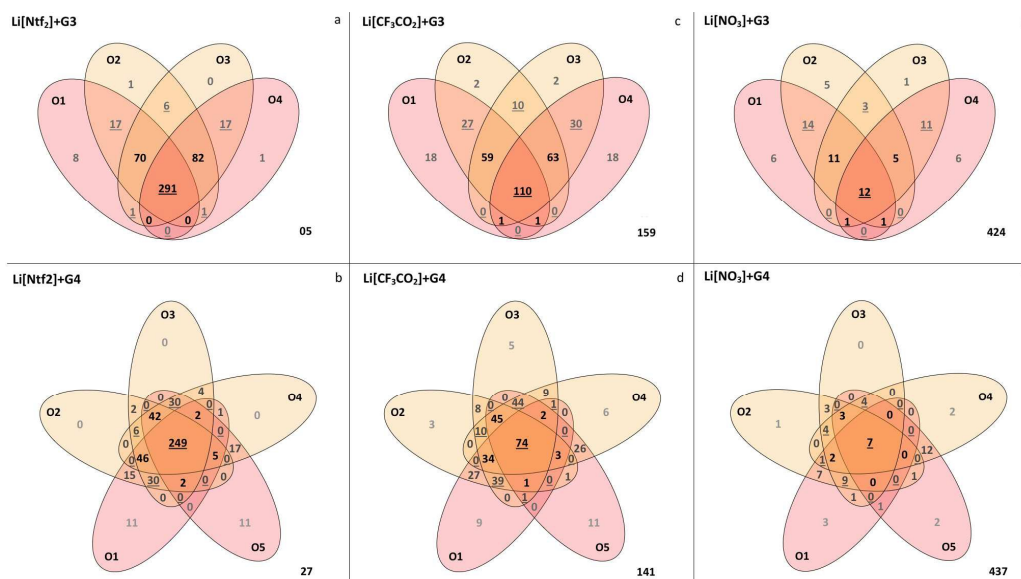


Fig. 9 Venn diagrams depicting the connectivity between lithium atoms and the oxygen atoms of G3 and G4 glyme molecules for equimolar mixtures of (a) Li[Ntf₂]+G3, (b) Li[Ntf₂]+G4, (c) Li[CF₃CO₂]+G3, (d) Li[CF₃CO₂]+G4, (e) Li[NO₃]+G3 and (f) Li[NO₃]+G4 mixtures at 303 K. The pink and yellow ellipses correspond to the outermost and inner oxygen atoms of the glyme molecules, respectively.

The six panels of Fig. 9 show that the number of glyme-lithium clusters decreases considerably—and the number of unattached glyme molecules increases—when changing from Li[Ntf₂] to Li[CF₃CO₂] or Li[NO₃]. The results mirror the experimental findings¹¹.

Changing from G3 to G4 affects the system less strongly. The number of unattached glyme molecules in the Li[Ntf₂]-G4 system is larger than in the Li[Ntf₂]-G3 system (albeit the number of displaced [Ntf₂]⁻ ions is also higher, cf. below). This is because the extra G4 oxygen atom leads to interactions with Li cations via more sites but this more comprehensive complexation prevents attachment of more than one glyme molecule. On the other hand, since the G4 molecules are longer (and the two ends more independent of each other), the number of bridging glyme molecules increases from G3 to G4.

The same type of analysis for the lithium-anion direct contacts have also been performed. The results are given in Table 2 for the six systems under discussion along with data for the three pure liquid salts.

Table 2. Distribution of lithium-oxygen connections in the three pure molten salts (530 K) and six salt-glyme mixtures (303 K) under discussion. All numbers are given as average values per lithium cation.

Pure liquid	Li-O _{anion}	Li-anion	Mixture	Li-O _{anion}	Li-anion	Li-O _{glyme}	Li-glyme
Li[Ntf ₂]	3.72	3.21	Li[Ntf ₂]-G3	2.18	1.80	3.43	0.99
			Li[Ntf ₂]-G4	1.90	1.55	3.86	0.95
Li[CF ₃ CO ₂]	3.81	3.23	Li[Ntf ₂]-G3	3.07	2.55	1.97	0.68
			Li[Ntf ₂]-G4	2.78	2.31	2.34	0.72
Li[NO ₃]	5.70	4.76	Li[Ntf ₂]-G3	5.63	4.83	0.35	0.15
			Li[Ntf ₂]-G4	5.66	4.84	0.33	0.13

Since the number of oxygen atoms in the anion varies in the three salts, we have counted: (1) the number of total Li-oxygen contacts, Li-O(anion), regardless of a lithium ion can be directly attached to two or more oxygen atoms belonging to the same anion, and (2) the number of single Li-anion contacts, with double or triple Li-O connections between a given ion pair discounted.

In pure liquid Li[Ntf₂] the number of Li-anion contacts per lithium ion is 3.21 compared to 4 in the crystal solid, cf. Fig. 5. The total number of Li-O(anion) contacts per lithium ion is slightly higher (3.72) which means that around 14% of the anions are attached to a lithium ion by more than one oxygen atom (in the crystal they are all attached by just one oxygen atom). It is natural that the less dense and disordered liquid has fewer Li-anion contacts (3.72) than the corresponding crystal (4): the enthalpy loss caused by the reduction of the number of interactions is compensated by entropy gains.

When Li[Ntf₂] is mixed with G3 molecules in a 1:1 proportion, the number of total Li-anion and Li-O(anion) contacts per lithium ion become 1.80 and 2.18, respectively. This represents interactions losses of around 40% relative to pure liquid Li[Ntf₂]. Obviously, the presence of G3 molecules partially destroys the polar network of the liquid salt. Interestingly, the percentage of anions contacting the lithium ions by more than one oxygen atom of an anion (17%) increases relative to the value found in the pure liquid case (14%) — apparently more attached anions are less likely to be displaced by glyme molecules. It must also be stressed that the number of [Ntf₂]⁻ ions not connected to any lithium is quite low in the Li[Ntf₂]-G3 mixture: only 6 % of the anions. This can be easily explained by the fact that in the pure Li[Ntf₂] each anion contacts more than one lithium ion (4 in the case of the crystal). When the glyme molecules disrupt around 50% of the existing Li-anion contacts, most anions will lose some of their Li contacts but will be able to retain at least one of them.

In the case of the Li[Ntf₂]-glyme mixtures, the loss of Li-anion bonds are more than compensated by the formation of Li-glyme contacts. In fact, the results “per glyme oxygen type” given in the Venn diagrams of Fig. 9 can be summed up to yield the total numbers of Li-O(glyme) and Li-glyme contacts. The results are also included in Table 2. The total number of Li-O(glyme) and Li-glyme contacts per lithium ion is 3.43 and 0.99, respectively. The difference between the two numbers reflects the fact that, unlike the anions, each glyme molecule tends to interact with the lithium ions by more than one oxygen (e.g. 291 out of the 500 G3 molecules of the simulation boxes use their four oxygen atoms, cf. Fig. 7a). This means that instead of having the 4 Li-O(anion) contacts per Li ion present in the crystal, in the Li[Ntf₂]-G3 mixture one has 2.18 Li-O(anion) plus 3.43 Li-O(glyme) = 5.61 Li-O contacts. This increase in Li-O contacts reflects the more efficient complexation of the glyme molecules. In fact, a related case was already discussed: in 2:1 G3:Li[Ntf₂] crystals where SSIPs are formed, the number of Li-O(glyme) contacts per lithium ion is 6.⁴³ In the case of a 1:1 G3:Li[Ntf₂] crystal⁴⁵ the number of contacts per lithium ion is also six (four to oxygens in glyme molecules, two to oxygens in [Ntf₂]⁻ ions). Such numbers are in fact quite similar to those found for the liquid (3.43 instead of 4; 2.18 instead of 2). The lower connectivity of the glyme molecules in the liquid state relative to the crystal reflect the larger entropy of the system and the enhanced dynamics of the Li-glyme complex formation.

The rest of Table 2 shows the Li-O tradeoffs for all other systems.

When G3 is replaced by G4 in the Li[Ntf₂]-glyme systems, the number of Li-O(glyme) contacts per Li ion increases (from 3.43 to 3.86) and the number of Li-O(anion) contacts per Li ion decreases (from 2.18 to 1.90). This reflects the improved complexing power of the G4 molecules. The biggest difference between the two systems lies in the fact that the number of anions unattached to any lithium ion more than doubles, from 6% in the G3-based system to 12.2% in the G4-based system.

In the Li[CF₃CO₂]-G3 systems the number of Li-O(anion) and Li-anion contacts are 3.07 and 2.55, respectively (down from 3.81 and 3.23 in pure liquid Li[CF₃CO₂]). The number of Li-O(glyme) contacts per Li ion (1.97) still compensate the Li-O(anion) losses (1.97+3.07 = 5.04 > 3.88). However this positive trade-off between Li-O contacts does not negate the fact that, relative to the [Ntf₂]-based systems, there are many more unattached glyme molecules (41% instead of 5%) and no unattached anions (0% instead of 9.6%). This is a direct consequence of the stronger electrostatic interactions between the ions preventing more effective coordination of the glymes and lithium ions. For the corresponding G4 systems the results are consistent with the trends already discussed for the Li[Ntf₂]-glyme systems (more bridging glyme molecules, larger self-competition effect).

The Li[NO₃]-G3 systems show small decreases in the number of Li-O(anion) and Li-anion contacts per Li ion (from 5.70 and 4.76, respectively, in the pure salt to 5.63 and 4.83). These are compensated by the formation of Li-O(glyme) contacts (only 0.35 per Li ion). These connectivity numbers correspond to a situation where all anions remain connected to Li ions and almost 89% of the glyme molecules are uncoordinated to any Li ions.

The present MD simulation data agree with experimental results that show that the coordination of the glyme molecules to the lithium cations is much more efficient in the Li[Ntf₂]-glyme mixtures than in the Li[CF₃CO₂]- or Li[NO₃]-glyme systems. Recent atomic force microscopy studies of equimolar Li[Ntf₂]-glyme and Li[NO₃]-glyme mixtures on gold and graphite electrode surfaces produced similar findings.⁴⁶ However, the MD simulation results show more Li-glyme aggregation in the Li[CF₃CO₂]-glyme mixtures than in their Li[NO₃] counterparts, a fact that does not agree with experimental findings based on the diffusion of the different types of ion or molecule¹¹. Possible explanations include: i) All ions and molecules have been modeled using a non-polarizable force field. To minimize the effects of such approximation, the partial point charges of the ions were reduced by a factor of 0.8 (cf. Simulation Details section). Due to symmetry, size and resonance effects, the modeling of the nitrate anion is likely to be least exact. An inaccurate balance between the Li-nitrate and Li-glyme interactions could lead to the observed aggregation results, including the tendency for (micro-) phase separation in the Li[NO₃]-glyme systems; ii) The viscosity of the Li[NO₃]-glyme system is particularly high¹¹, a situation that is common in pure ionic liquids and their mixtures, when the ionic liquid ions are small and have high charge-densities. Non-polarizable force fields behave poorly under those conditions; iii) The very low Li-glyme aggregation numbers observed in the Li[NO₃]-glyme can just reflect the phase separation of the system. Since most of the glyme molecules are forming a separate sub-phase, only a few of them are effectively mixed with the ions and are thus able to form aggregates. It must be stressed that the simulated $S(q)$ function for the Li[NO₃]-G4 system (Fig. 8a,

dashed line) shows a small shoulder around the $9\text{-}10\text{ nm}^{-1}$ region that may correspond to these few Li-G4 aggregates. This is also corroborated by both the WAXS and HEXRD spectra.

In order to test the inadequacy of the used nitrate anion model, we have performed extra simulation with an alternative, ad-hoc model where the charges of the oxygen atoms of the anion were changed in order to approximately reflect the charge distribution of single nitrate-lithium ion pairs. Those were calculated from single-point ab-initio calculations performed on selected pair configurations taken from the MD trajectories of pure $\text{Li}[\text{NO}_3]$. Instead of three oxygen atoms with a -0.52 a.c.u. each, we have used charges of -0.40 , -0.50 and -0.66 a.c.u. that reflect the charge fluctuations induced by different types of coordination to the lithium cations and the ability of the nitrate anion to distribute the charge by resonance effects. Aggregation analysis on the modified $\text{Li}[\text{NO}_3]$ -G3 system yielded no phase separation and a much larger proportion of Li-G3 contacts than in the original Venn diagrams of Fig. 9e, with only ca. 20% of the G3 molecules uncoordinated to any Li cation. These results based on a quite crude and approximate model show that in order to model correctly the resonance effects in small and strongly binding symmetrical ions such as nitrate one must incorporate polarization or charge-fluctuation schemes. Those are beyond the scope of the present work.

Due to the issues outlined in the previous two paragraphs, we will focus the remainder of the study on the $\text{Li}[\text{Ntf}_2]$ -glyme systems. The diversity and dynamics of the lithium-oxygen contacts in the $\text{Li}[\text{Ntf}_2]$ -glyme based systems can be appreciated in figure 10, where one simulation snapshot highlights the connectivity between lithium ions with anion or glyme oxygen atoms and their interchange over time. The image is combined with data rendering the different types of connections that each individual cation experiencing during the simulation.

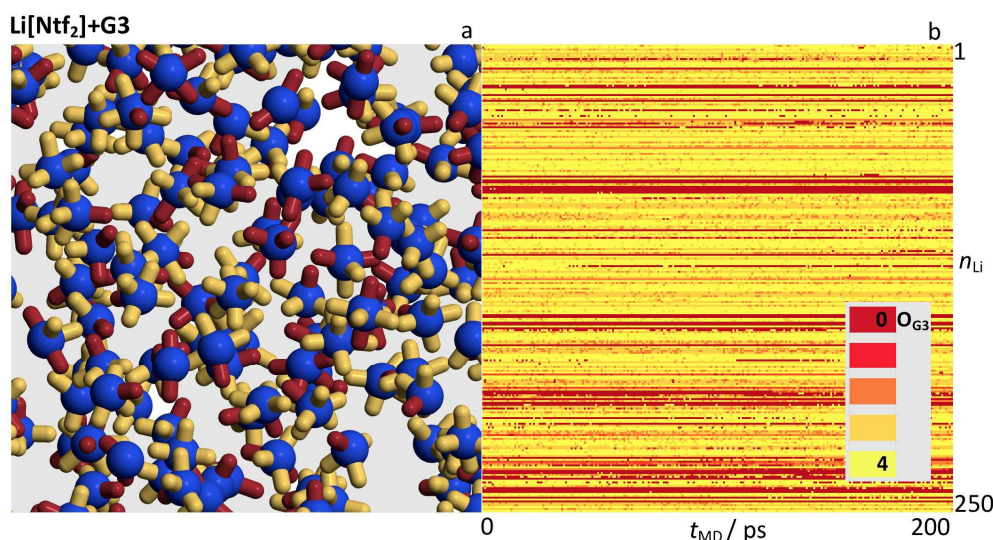


Fig. 10 (a) MD simulation snapshot of the $\text{Li}[\text{Ntf}_2]$ +G3 system at 303 K. The blue spheres depict the lithium ions, the red and yellow sticks correspond to Li-O(anion) and Li-O(G3) connections, respectively. (b) Visualization of the nature of connectivity in 250 Li cations during 0.2 ns of simulation. The color scale ranges from dark red pixels corresponding to lithium ions completely connected to anions (no G3 connections) to yellow points corresponding to lithium ions connected to glyme molecules *via* their 4 oxygen atoms.

E. Conformational analyses in the salt-glyme mixtures

If the anions present in the salt allow compete effectively with the glyme molecules for the coordination of lithium ions —as in the case of the $\text{Li}[\text{Ntf}_2]$ -based systems— then most of the glyme molecules will effectively act as poly-dentate ligands (Fig. 9a and 9b). This means that their internal conformation must match such behavior. Fig. 11 compares the O-C-C-O dihedral angles in pure G3 and in the equimolar $\text{Li}[\text{Ntf}_2]$ -G3 mixture, both obtained by MD simulation of the corresponding liquid phases at 303 K.

In pure G3 the chains adopt gauche-trans conformations around the O-C-C-O dihedral angles: the *transoid* (zig-zag) conformation of an alkyl chain has a large probability of developing a kink (a gauche conformation) each time methylene groups are replaced by oxygen atoms in order to form oligoether molecules (PEGs, glymes)^{32, 47, 48}. In the $\text{Li}[\text{Ntf}_2]$ -G3 mixture almost all O-C-C-O dihedral angles of the G3 molecules have gauche conformations (closer to a *cisoid* conformation). This allows the glyme molecules to bind to the lithium cation via multiple oxygen atoms. The difference between the two curves depicted in Fig. 11 illustrates how the flexible glyme molecules fulfill a multi-coordinating role.

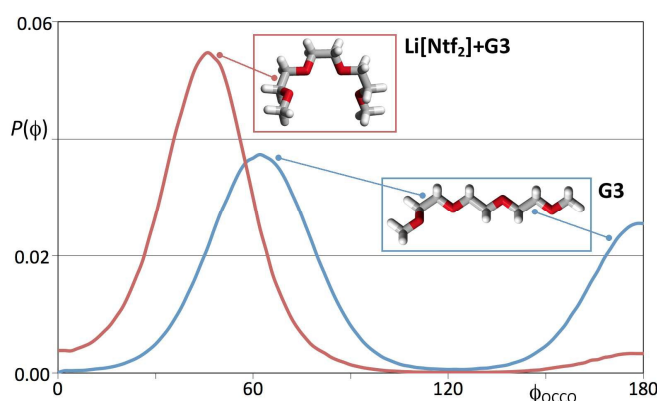


Fig. 11 Dihedral probability distribution functions of the OCCO dihedral angles of triglyme (G3) in pure G3 at 400 K (blue line) and in the $\text{Li}[\text{Ntf}_2]$ +G3 equimolar mixture at the same temperature (red line). The functions were calculated taking the average of the results for each of the three OCCO dihedral angles present in each G3 molecule. The insets show two examples of most probable conformations of the molecules displaying dihedral angles corresponding to maxima of the distribution functions. The all-gauche conformation in the (G3+Li) system corresponds to the wrapping of the G3 molecule around the lithium cation.

On the other hand, the $[\text{Ntf}_2]^-$ ion adopts a *anti* (C_2) conformation in the pure $\text{Li}[\text{Ntf}_2]$ crystal⁴¹. This is not always the case since it depends on packing considerations, including the volume ratios of the intervening ions —for instance in the pure $\text{Rb}[\text{CHTf}_2]$ crystal, the $[\text{CHTf}_2]^-$ ion adopts a *gauche* (C_1) form⁴². The *anti* conformation of $[\text{Ntf}_2]^-$ in the $\text{Li}[\text{Ntf}_2]$ crystal causes the oxygen atoms present in the two sulphonate groups of the ion to be further apart, which is an essential requirement for the binding (bridging) of one $[\text{Ntf}_2]^-$ ion to four distinct lithium cations. In the pure $\text{Li}[\text{Ntf}_2]$ liquid the stringency of such packing/binding considerations is relaxed and both forms (C_1 and C_2) can be present in the liquid phase, a situation that is common for most $[\text{Ntf}_2]$ -based ionic liquids⁴⁸⁻⁵².

In pure $\text{Li}[\text{Ntf}_2]$ liquid some anions interact with the same lithium cation *via* more than one oxygen atom, typically by the anion adopting a *gauche* form. Figure 12a shows the probability distribution surface of *gauche* and *anti* forms of the anion in the pure $\text{Li}[\text{Ntf}_2]$ liquid. The peaks corresponding to the *anti* forms are accompanied by *gauche* peaks, reflecting the possibility of co-existence and inter-conversion of the two forms in the liquid. The corresponding distribution surface for the $\text{Li}[\text{Ntf}_2]$ crystal would only show two narrow peaks corresponding to the *anti* forms at $(90^\circ, 90^\circ)$ and $(270^\circ, 270^\circ)$. Fig. 12b shows the same type representation for the $\text{Li}[\text{Ntf}_2]$ -G3 system. It is obvious that the *gauche* peaks get bigger at the expense of the *anti* ones. This confirms that the proportion of anions bonded to a single lithium cation by more than one oxygen atom is larger in the $\text{Li}[\text{Ntf}_2]$ -G3 mixtures (17%) than in the pure $\text{Li}[\text{Ntf}_2]$ liquid (14%).

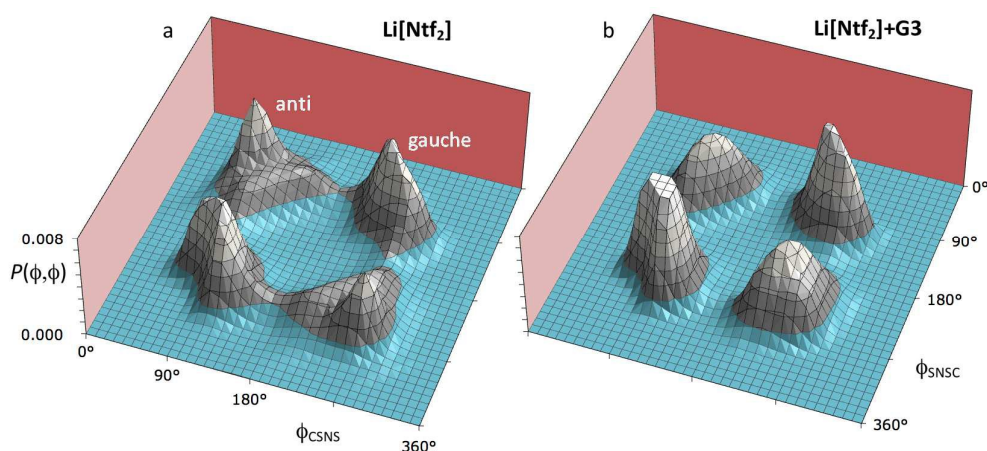


Fig. 12 Conformer probability distribution functions as a function of the two dihedral angles of the $[\text{Ntf}_2]$ - ion. Anion conformations present in (a) pure liquid $\text{Li}[\text{Ntf}_2]$ at 530 K and in (b) the equimolar $\text{Li}[\text{Ntf}_2]$ +G3 mixture at 400 K.

F. Dynamics of lithium ions

One of the major potential applications of salt-glyme mixtures is in the development of novel electrolytes for new electrochemical devices such as batteries.^{8,11,53-59} As such, the dynamics of the lithium ions in the liquid is crucial. In sub-section D it was shown that the number of Li-O intermolecular interactions in the $\text{Li}[\text{Ntf}_2]$ -glyme equimolar mixtures is larger than in pure $\text{Li}[\text{Ntf}_2]$. Nonetheless, experiments^{8,11,53-59} have shown that such mixtures can be used as effective electrolyte solutions in lithium secondary batteries, which is critical because the pure salt is a solid at room temperature.

The MD results can be reconciled with the experimental findings if one takes into consideration three facts: i) the mixture of the two components promotes the existence of a deep eutectic mixture, with much lower melting temperatures; ii) the nature of the Li-O(anion) and Li-O(glyme) interactions is quite diverse; iii) the poly-dentate nature of the glyme molecules enables their multicoordination to a single lithium ion. Fact i) means that the equimolar mixtures remain liquid at much lower temperatures simply because crystals are thermodynamically unstable; ii) means that if the Li-O interactions in a mixture are predominantly of

the Li-O(glyme) type, then those interactions will not contribute to the electrostatic cohesion forces of the polar network and the concomitant immobilization of the lithium ions; iii) means that more Li-O interactions do not entail a more interconnected network (multiple connections are established between one lithium ion and one glyme molecule). This lack of bridging connections also promotes the mobility of lithium ions.

Unfortunately MD simulations based on non-polarizable descriptions of ionic species are not suitable to yield quantitative information about the dynamics of the system (viscosity, diffusion coefficients). Nevertheless the MD runs can provide two important pieces of information: i) the auto-diffusion coefficients of glyme molecules (G3 or G4) in pure glyme at 303K are much larger than those of G3 or G4 molecules included in Li[Ntf₂]-glyme or Li[NO₃]-glyme equimolar mixtures at the same temperature; ii) The decrease in the glyme diffusion coefficients is more pronounced in the Li[Ntf₂]-glyme system than in the Li[NO₃]-glyme mixture.

This corroborates the experimental data reported by Ueno et al.¹¹ which shows that the diffusion coefficients of glyme molecules in Li[NO₃]-G3 mixtures are larger than in the Li[Ntf₂]-G3 system (1.09×10^{-7} and 0.84×10^{-7} cm².s⁻¹, respectively), even though the former system exhibits a larger viscosity (206 mPa.s) than the latter (169 mPa.s). In other words, the glyme molecules become closer to the diffusion regime of the lithium ions when the amount of Li-glyme aggregates is more important.

Finally, in a different set of simulation runs we have subjected the Li[Ntf₂]-based systems (pure liquid at 530 K and mixtures with G3 and G4 at 303 K) to an ad-hoc electrical field that induced the movement of the lithium ions in one direction and the movement of the [Ntf₂]⁻ ions in the other direction. Again we have calculated the flux of glyme molecules present in the system under different conditions. The results also show that the diffusion regime of the glyme molecules approaches that of the lithium ions, i.e., the diffusion of the lithium ions under the influence of an electrical field is achieved through the concerted movement of lithium-glyme aggregates, Fig. 13.

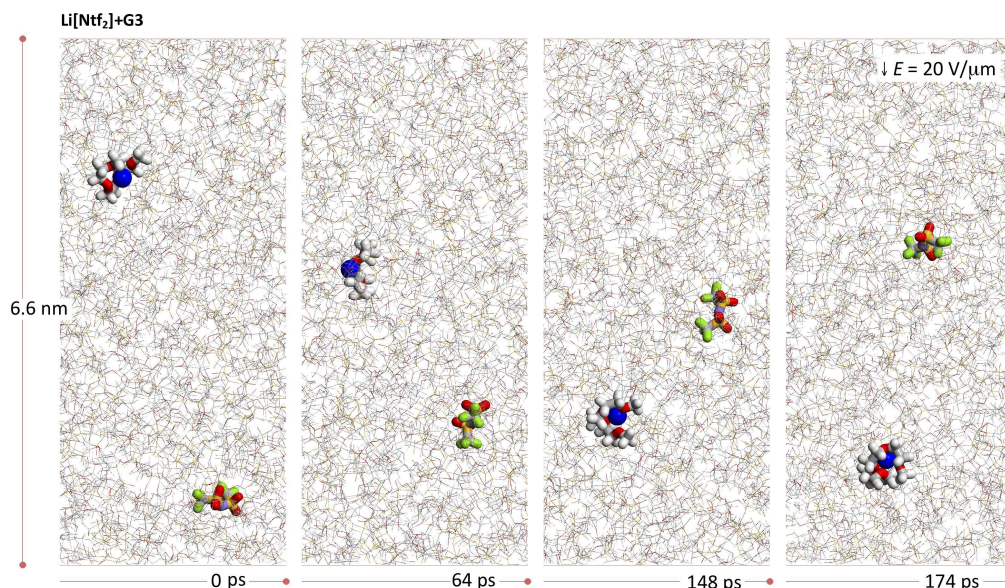


Fig. 13 Four MD simulation snapshots of a Li[Ntf₂]+G3 system at 303 K subjected to a vertical uniform electric field of 20 V/μm (the arrow in the figure indicates the direction of the field). All 1500 ion pairs plus G3 molecules are rendered in wireframe mode except one lithium-glyme aggregate and one [Ntf₂]⁻ ion (ball-and-stick representation). The four snapshots allow the visualization of the movement of the selected species under the influence of the strong electric field along ca. 0.2 ns of simulation time.

Conclusions

The nature at a molecular level of solvate ionic liquids can be probed effectively using a combination of Molecular Dynamics trajectories plus structural and aggregation analysis techniques.

The MD-calculated Structure Factor functions, $S(q)$, allowed the rationalization of the different intermolecular and interionic q -peaks found for pure lithium salts and solvate ionic liquid systems. The existence or absence of lithium-glyme complexes can be easily inferred from the $S(q)$ functions: the former case yields low- q peaks; the latter are dominated by intermediate- q (COP) peaks characteristic of the pure lithium salts. The MD results are corroborated by $S(q)$ functions derived from diffraction and scattering data (HEXRD and SAXS). Comprehensive aggregation analyses highlighted the competition between different glyme molecules (G3, G4) and ionic liquid anions ([Ntf₂]⁻, [CF₃CO₂]⁻, [NO₃]⁻) for the coordination to lithium cations. Lithium-glyme solvates are ubiquitous in the (Li[Ntf₂]+G3 or +G4) systems and much less so in systems based on the other two salts. On the other hand, the MD aggregation results failed to predict the proportion of lithium-glyme solvates in the lithium nitrate plus glyme system owing to a deficient modeling of the charge asymmetry in the coordinated nitrate ion caused by resonance effects. All aggregation studies emphasized the existence of complex distributions of uncoordinated, partially

coordinated and completely coordinated glyme molecules that are able to change their interaction status at different rates during the simulation runs. The same applies to the lithium-anion interactions, Conformational analyses of the MD trajectories in the (Li[Ntf₂]+G3) system show how the glyme molecules are able to change their internal dihedral angles in order to better coordinate to the lithium ions by their multiple interaction sites (the ether oxygen atoms). Conversely, the partial destruction of the Li-[Ntf₂] ionic network also changes the conformational landscape of the anions, shifting the balance between anti and gauche conformations in the benefit of the latter. Finally, the dynamics of (Li[Ntf₂]+G3 or +G4) systems were further explored by simulations where MD boxes are exposed to strong electrical fields. The obtained trajectories vividly capture the concurrent diffusion of the lithium ions and their coordinating glyme molecules, a result that is corroborated by experimental evidence.

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