Glyme−Lithium Bis(trifluoromethanesulfonyl)imide and Glyme−Lithium Bis(perfluoroethanesulfonyl)imide Phase Behavior and Solvate Structures

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Crystal structures of glyme solvates with LiTFSI and LiBETI ($TFSI^-$ = bis(trifluoromethanesulfonyl)-imide, $BETI^-$ = bis(perfluoroethanesulfonyl)imide) have been determined including $(monoglyme)_1$:LiBETI, $(diglyme)_2$:LiTFSI, $(diglyme)_{1/2}$:LiTFSI, and low-temperature $(triglyme)_1$:LiBETI. These solvates, combined with the phase behavior of the salts with various glymes from DSC analysis, provide insight into the molecular interactions of lithium salts in ethoxy solvents commonly used for solid polymer and liquid electrolytes. Many of the solvates appear to undergo order−disorder solid phase transitions. These are the first reported crystal structures containing the $BETI^-$ anion.

Introduction

In recent years, widespread attention has been devoted to several classes of salts based on fluorinated sulfonylimide anions, $N(SO_2C_nF_{2n+1})(SO_2C_mF_{2m+1})^-$, including lithium salts and room temperature ionic liquids (RTILs). Bis(trifluoromethanesulfonyl)imide, $N(SO_2CF_3)_2^-$ (or $TFSI^-$), the simplest and most widely studied of the anions, has been found to have both high flexibility and extensive charge delocalization over the $-SO_2-N-SO_2-$ backbone.[1−4] Bis(perfluoroethanesulfonyl)imide, $N(SO_2C_2F_5)_2^-$ (or $BETI^-$ or $PFSI^-$), is a newer, much less scrutinized, addition to this group of anions with equally interesting properties.[5]

Lithium salts with $TFSI^-$ and $BETI^-$ anions are being widely explored for both liquid and solid polymer electrolyte applications. Such electrolytes may find use in high-energy lithium batteries, dye-sensitized solar cells, light-emitting electrochemical cells, and other electrochemical devices.[6−15] Electrolytes with these salts have high ionic conductivities, high electrochemical and thermal stabilities, and other desirable properties. One unique feature of these salts is the presence of a "crystallinity gap" in PEO−LiTFSI and −LiBETI electrolytes at certain salt concentrations in which crystallization of polymer−salt solvates and excess PEO is extremely sluggish or hindered altogether.[16−20] Such an effect is not observed with more traditional electrolyte salts such as $LiCF_3SO_3$, $LiPF_6$, and $LiAsF_6$. This "plasticizing" effect is very useful as it is well-known that the ionic conductivity predominates in the amorphous phase of such electrolytes.[21−23] The origin of the crystallinity gaps, however, remains uncertain.

Salts with organic cations and $TFSI^-$ and $BETI^-$ anions often form plastic crystalline phases or are RTILs.[24−27]

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Interestingly, such salts often phase separate from aqueous mixtures. These salts have been suggested as useful electrolyte materials for metal deposition,[28] fuel cell,[29,30] and lithium battery[31−33] applications.

Intriguing questions remain regarding the novel properties of materials containing anions such as TFSI$^-$ and BETI$^-$. In this work, the solvate structures of LiTFSI and LiBETI with glymes, $CH_3O-(CH_2CH_2O)_n-CH_3$, where $n = 1-3$ for G1−G3 (monoglyme−triglyme), respectively, are examined. The solvated Li$^+$ cations and their interaction or lack of interaction with these anions serve as useful models for both RTILs and amorphous ether electrolytes. Numerous glyme−LiTFSI and −LiBETI crystalline solvates form, and many of these undergo solid phase changes. The data suggest that these are order−disorder transitions. Four crystalline solvate structures were determined to aid in understanding the phase behavior observed. Similar glyme−LiX (X = $CF_3SO_3^-$, ClO_4^-, TFSI$^-$, and SbF_6^-) solvate structures have been found to greatly aid in the vibrational spectroscopic characterization of ionic association in such mixtures.[34−38]

Experimental Section

The salts LiTFSI and LiBETI were kindly provided by 3M. G1 (monoglyme, 1,2-dimethoxyethane (DME), or ethylene glycol dimethyl ether) (Aldrich) and G2 (diglyme or 2-methoxyethyl ether) (Aldrich) were purchased as anhydrous and used as received. G3 (triglyme or tri(ethylene glycol) dimethyl ether) (Aldrich) was dried over 4 Å molecular sieves and used without further purification. Sample preparation occurred in either a dry room (<0.1% relative humidity) or a nitrogen glovebox. The preparation procedures for the single crystals and DSC samples are given in the Supporting Information along with information regarding the X-ray diffraction characterization. Structures were drawn using Mercury 1.2.1.

Note that the crystals of $(G3)_1$:LiBETI undergo a solid−solid phase transition on cooling. Rapid cooling of these crystals leads to poor diffraction data. To prevent water contamination when a single crystal was slowly cooled, it was necessary to cover the crystal with epoxy and seal it in a 0.4 mm capillary tube.

Results and Discussion

Ab initio calculations for the uncoordinated TFSI$^-$ and BETI$^-$ anions[1,2,4,5] have indicated that two low-energy conformations exist for both anions with *cisoid* and *transoid* C−S−S−C torsional angles, respectively. In the *cisoid* form (C_1), the perfluoroalkyl groups lie on the same side of the S−N−S plane, while in the *transoid* form (C_2) they are on opposite sides. Such studies suggest that low-energy barriers exist between these two conformations and the highly flexible nature of the anions is mainly due to rotations about the two N−S bonds and not to changes of the S−N−S angle.[1] The charge distribution for both conformations is approximately the same. Both TFSI$^-$ conformations are found in salt crystal structures.[3]

Vibrational spectroscopic characterization of ionic association in glyme and PEO mixtures with LiTFSI or LiBETI indicates that the Li$^+$ cations tend to be fully solvated by the ether oxygens (EOs) as solvent-separated ion pairs (SSIPs) when enough EOs (typically five or six) are present.[39−41] These coordinating EOs may originate from one to three glyme molecules or PEO polymer chains. Contact ion pair (CIP) and aggregate (AGG) solvates form predominantly only when fewer EOs are available for Li$^+$ cation coordination. No direct coordination occurs in SSIPs between the anions and Li$^+$ cations, whereas for CIP and AGG solvates the anions are coordinated to one and two or more cations, respectively.

The crystal structure of LiTFSI is known.[42] In the crystalline salt, the TFSI$^-$ anions have a C_2 conformation and are coordinated to four Li$^+$ cations. Each anion oxygen coordinates a single cation. Each four-coordinate Li$^+$ cation is coordinated by four oxygens (one each from four anions). In contrast, the TFSI$^-$ anions in the $(H_2O)_1$:LiTFSI monohydrate solvate have a C_1 conformation in which each anion is coordinated to four Li$^+$ cations.[3]

AGG $(G1)_1$:LiBETI Crystal Structure. The cation coordination in the AGG $(G1)_1$:LiBETI solvate is shown in Figure 1a. The five-coordinate Li$^+$ cations are coordinated by two EOs from a single G1 molecule and three anion oxygens, one from one BETI$^-$ anion and two from another. The BETI$^-$ anions adopt a C_2 conformation and are coordinated to two Li$^+$ cations with three oxygens, forming one-dimensional, polymeric chains. One of the oxygen atoms of each anion remains uncoordinated. The end $-CF_3$ groups of the side of the anions coordinated to a single Li$^+$ cation are disordered (not shown).

The $(G1)_1$:LiBETI solvate crystal structure bears a striking resemblance to the $(G1)_1$:LiTFSI solvate structure.[38] The same form of Li$^+$···anion coordination is observed in both structures. In fact, a comparison of the bond distances in the two solvates finds that the TFSI$^-$ and BETI$^-$ anions are very close in structure (see the Supporting Information).

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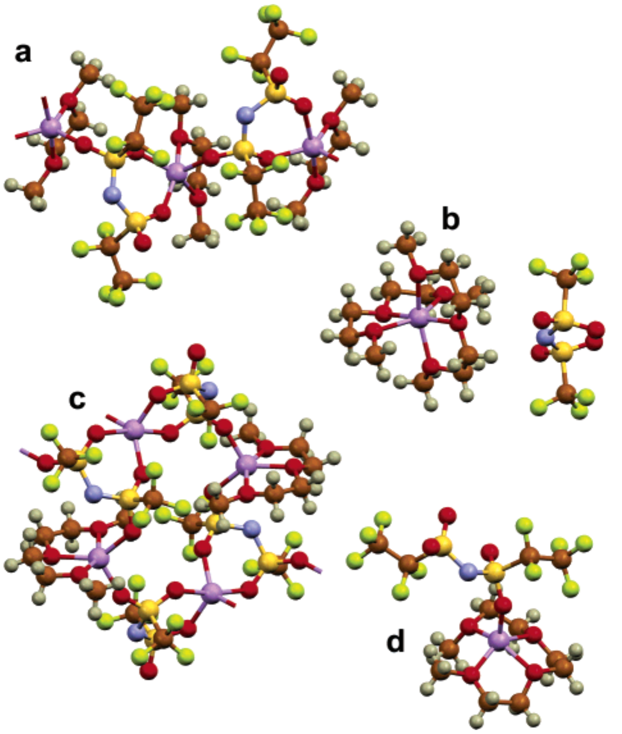

Figure 1. (Glyme)$_n$:LiX crystalline solvate structures: (a) AGG $(G1)_1$:LiBETI, (b) SSIP $(G2)_2$:LiTFSI, (c) AGG $(G2)_{1/2}$:LiTFSI, and (d) CIP $(G3)_1$:LiBETI (low temperature structure) (Li, purple; O, red; N, blue; S, gold; F, green).

Despite the similarities, the melting points (T_m) of the two solvates differ noticeably (56 °C for $(G1)_1$:LiTFSI and 74 °C for $(G1)_1$:LiBETI).

SSIP $(G2)_2$:LiTFSI Crystal Structure. The cation coordination in the SSIP $(G2)_2$:LiTFSI solvate is shown in Figure 1b. The six-coordinate Li^+ cations are coordinated by six EOs from two G2 molecules. The $TFSI^-$ anions remain uncoordinated between the $[(G2)_2Li]^+$ solvates. This form of SSIP $(G2)_2$:LiX crystalline solvate is relatively common for LiX salts containing anions with sterically hindered or delocalized charge.[35,38,43−47] All four of the $TFSI^-$ anions in the asymmetric unit have C_2 conformations.

AGG $(G2)_{1/2}$:LiTFSI Crystal Structure. The cation coordination in the AGG $(G2)_{1/2}$:LiTFSI solvate is shown in Figure 1c. Two different cation coordination sites exist. In the first site, the five-coordinate Li^+ cations are coordinated by three EOs from a single G2 molecule and two anion oxygens (one each from two different anions). In the second site, the five-coordinate Li^+ cations are coordinated by five anion oxygens (two each from two different anions and one from a third anion). One of the two $TFSI^-$ anions in the asymmetric unit has a C_2 conformation and is coordinated to two Li^+ cations through three oxygens. The second $TFSI^-$ anion in the asymmetric unit has a C_1 conformation and is coordinated to three Li^+ cations through all four oxygens.

CIP $(G3)_1$:LiBETI Crystal Structure. The Li^+ cation coordination in the CIP $(G3)_1$:LiBETI solvate is shown in Figure 1d. The reported crystal structure is a low-temperature structure as the $(G3)_1$:LiBETI crystalline solvate undergoes a solid−solid phase change on cooling from room temperature. The asymmetric unit contains two G3 molecules, two Li^+ cations, and two $BETI^-$ anions related by a pseudoglide operation with $Z = 4$ and $Z' = 2$. The low-temperature $(G3)_1$:LiBETI structure is truly triclinic and a two-component, nonmerohedral twin.

At approximately −30 to −35 °C, there is an abrupt change that occurs in the XRD spot patterns of $(G3)_1$:LiBETI single crystals. The diffraction patterns strongly suggest that this is an order−disorder phase change. In similar twins, the space group for the low-temperature phase twin components is "$P\bar{1}$", where the low-temperature phase is related to a distortion of the reduced cell of $C2/c$ for the high-temperature phase. Indexing of the high-temperature phase leads to a C-centered monoclinic cell with approximately 3 times the volume of the low-temperature phase with cell constants $a = 14.7311$ Å, $b = 52.4008$ Å, $c = 9.1987$ Å, $\beta = 104.392°$, and $V = 6877.84$ Å^3. The phase change is nondestructive. The data from the high-temperature phase have not provided a structural solution.

The five-coordinate Li^+ cations are coordinated by four EOs from a single G3 molecule and one anion oxygen. The G3 molecules adopt a conformation similar to that of a Li^+ cation coordinated crown ether 12-crown-4 molecule. The $BETI^-$ anions adopt a C_2 conformation and are coordinated to only a single Li^+ cation through one oxygen.

Phase Behavior of G1−LiTFSI and −LiBETI Mixtures. The previously reported phase diagram for G1−LiTFSI mixtures indicated the formation of 3/1 ($T_m = 29$ °C) and 1/1 ($T_m = 56$ °C) crystalline phases.[48] The DSC traces reported in Figure 2 indicate that the 3/1 solvate undergoes solid−solid phase transitions at approximately −92, −86, and −67 °C. Vibrational spectroscopy suggests that the 3/1 solvate contains SSIPs[37] and thus consists of solvated $[(G1)_3Li]^+$ cations and uncoordinated $TFSI^-$ anions. This form of 3/1 G1/LiX solvate structure has been widely reported.[49−54] The crystal structure of the AGG 1/1 solvate is known[37] and is similiar to that of $(G1)_1$:LiBETI as noted above. The DSC trace for the $n = 2$ sample shows a single endothermic peak. This suggests that a 2/1 ($T_m = 20$ °C) crystalline solvate also forms in addition to the 3/1 and 1/1 solvates. A small peak is also present for the largest solid−

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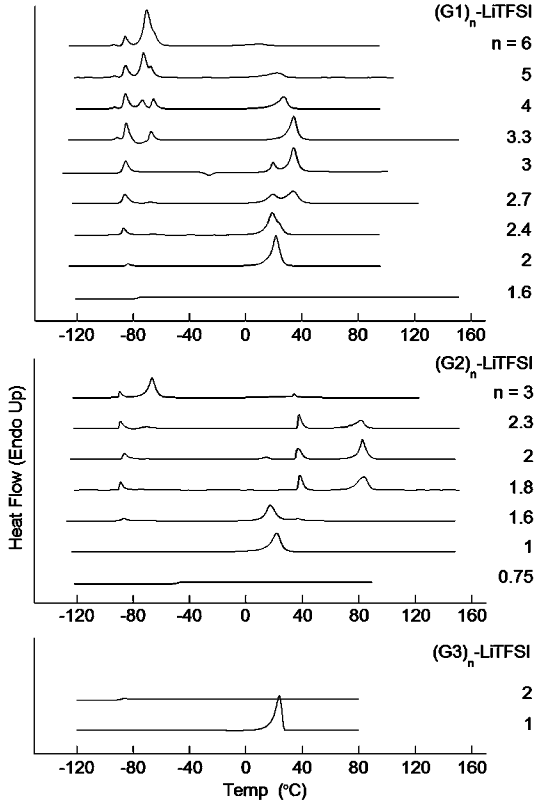

Figure 2. DSC heating traces for (glyme)$_n$−LiTFSI (G1−G3) mixtures.

solid phase transition of the 3/1 phase, which may be due to a small amount of sample inhomogeneity. The disappearance of the solid−solid phase transition peaks for the 3/1 phase at an $n = 2$ concentration indicates that this is not a eutectic. CIP 2/1 crystalline solvates with LiX salts are well-known in which the Li^+ cations are coordinated by four EOs from two G1 molecules and a single anion.[35,55−59] In contrast, vibrational spectroscopy of $1 < n < 3$ mixtures indicates a continuous transition between AGG and SSIP solvates with very few CIPs present.[37] This study, however, was conducted at room temperature, which is above the T_m of the suggested 2/1 solvate. Low-temperature Raman spectroscopic characterization should be conducted with carefully controlled crystallization conditions to determine if a CIP 2/1 solvate does indeed form. The $n = 1.6$ sample remained amorphous (with a T_g near −77 °C) despite attempts to crystallize the sample by storage in a freezer and slow thermal cycling in the DSC instrument at low temperatures.

The DSC traces for G1−LiBETI mixtures (Figure 3) suggest that 3/1 (T_m = 38 °C), 2/1 (T_m = 2 °C), and 1/1 (T_m = 74 °C) crystalline solvates also form. The 3/1 and 2/1 phases are likely to be SSIP and CIP solvates, respectively. The crystal structure of the AGG 1/1 solvate is reported above. The 3/1 solvate undergoes a solid−solid phase transition at −56 °C. The 2/1 solvate appears to have a solid−solid phase transition at −3 °C. Note that the solid−solid phase transitions for the 3/1 solvate disappear at the $n = 2$ composition, again indicating that a 2/1 solvate forms rather than this being a eutectic.

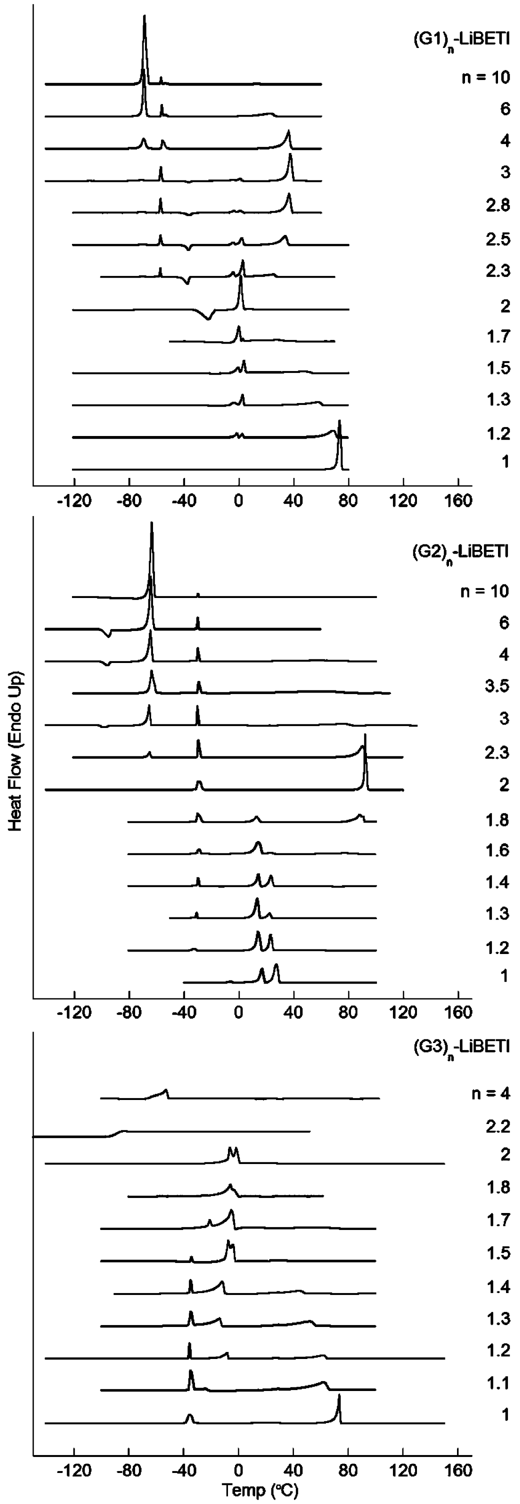

Figure 3. DSC heating traces for (glyme)$_n$:LiBETI (G1−G3) mixtures.

Phase Behavior of G2−LiTFSI and −LiBETI Mixtures. The previously reported phase diagram for G2−LiTFSI mixtures indicated the formation of a 2/1 (T_m = 83 °C) crystalline phase.[48] The crystal structure of the SSIP 2/1 solvate is reported above. Raman spectroscopy also

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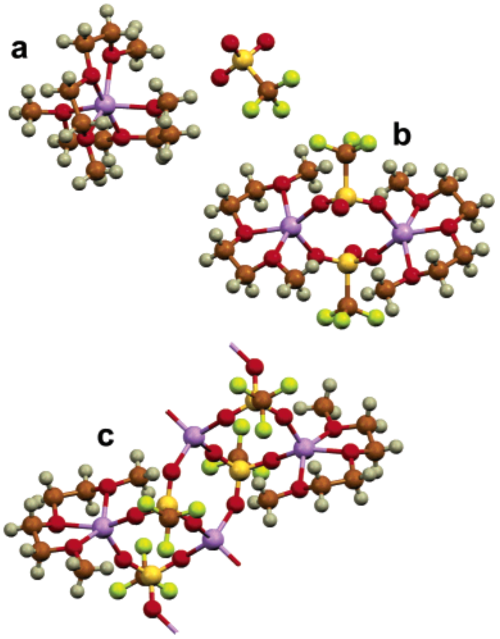

Figure 4. $(G2)_n$:$LiCF_3SO_3$ crystalline solvate structures: (a) SSIP $(G2)_2$:$LiCF_3SO_3$ (speculative), (b) AGG $(G2)_1$:$LiCF_3SO_3$, and (c) AGG $(G2)_{1/2}$:$LiCF_3SO_3$ (Li, purple; O, red; N, blue; S, gold; F, green).

confirms that this solvate consists of SSIPs.[37] The DSC traces in Figure 2 indicate that this solvate undergoes solid−solid phase transitions at −88 and 38 °C. The DSC trace for the $n = 1$ sample suggests that a 1/1 ($T_m = 22$ °C) crystalline solvate also forms. Note that the solid−solid phase transitions for the 2/1 solvate disappear at the $n = 1$ composition. The crystal structure for an AGG 1/2 crystalline solvate is reported above. The $n = 0.75$ sample remained amorphous (with a T_g near −50 °C) despite attempts to crystallize the sample by storage in a freezer and slow thermal cycling in the DSC instrument at low temperatures.

It is interesting to compare the G2−LiX phase behavior with $LiCF_3SO_3$ and LiTFSI. G2−$LiCF_3SO_3$ mixtures also form 2/1 ($T_m = -6$ °C), 1/1 ($T_m = 46$ °C), and 1/2 ($T_m = 150$ °C) crystalline solvates. The structure of the 2/1 solvate is not known, but vibrational spectroscopy indicates that it contains SSIPs[59−61] and thus consists of solvated $[(G2)_2Li]^+$ cations and uncoordinated $CF_3SO_3^-$ anions (Figure 4a). The crystal structures for the 1/1[34] and 1/2[62] solvates are known. The AGG 1/1 solvate consists of Li^+ cations coordinated by three EOs from a single G2 molecule and two anion oxygens (one each from two anions). Each $CF_3SO_3^-$ anion is coordinated to two Li^+ cations, forming dimers (Figure 4b). Half of the Li^+ cations in the AGG 1/2 solvate have the same form of coordination, while the other half are coordinated solely by (four) anions (Figure 4c). The 2/1 and 1/2 solvates with $LiCF_3SO_3$ and LiTFSI are thus very similiar. It is therefore reasonable to assume that the 1/1 solvate with LiTFSI consists of AGG dimers in which the Li^+ cations are coordinated by three EOs from a single G2 molecule and two anion oxygens (one each from two anions). The $TFSI^-$ anions may coordinate the two Li^+ cations with the oxygens from a single sulfonyl group as in the $P(EO)_3$:LiTFSI crystal structure,[63,64] leaving half of the anion uncoordinated. Similar $(G2)_1$:LiX crystalline solvates are known.[65−67] Raman spectroscopy of a $(G2)_n$−LiTFSI ($n = 1$) sample at room temperature (above the solvate T_m) indicates that this mixture consists of AGGs.[37]

The DSC traces for G2−LiBETI mixtures (Figure 3) suggest that 2/1 ($T_m = 92$ °C) and 1/1 ($T_m = 27$ °C) crystalline solvates also form. The 2/1 and 1/1 phases are likely to be SSIP and AGG solvates, respectively. The 2/1 and 1/1 solvates undergo solid−solid phase transitions at −29 and 14 °C, respectively. Note that the former solid−solid phase transition disappears at an $n = 1$ composition.

Phase Behavior of G3−LiTFSI and −LiBETI Mixtures. No crystalline solvates were noted in the previously reported phase diagram for G3−LiTFSI mixtures.[37] The DSC trace (Figure 2) for the $n = 1$ sample, however, indicates that a 1/1 ($T_m = 23$ °C) crystalline solvate does form. Raman spectroscopy of an $n = 1$ sample at room temperature (in the melt state) indicates that half of the solvates are SSIPs and half are AGGs. CIP 1/1 G3/LiX crystalline solvates have been reported (X = BH_4^-, BF_4^-, ClO_4^-, $CF_3SO_3^-$, and AsF_6^-).[68,69] An SSIP 1/1 G3/LiX crystalline solvate has also been reported (X = BPh_4^-).[69] Which type of 1/1 solvate is found with LiTFSI can be determined with low-temperature vibrational spectroscopy. The $n = 2$ sample remained amorphous (T_g near −90 °C) despite attempts to crystallize the sample by storage in a freezer and slow thermal cycling in the DSC instrument at low temperatures.

The DSC traces for G3−LiBETI mixtures (Figure 3) suggest that 2/1 ($T_m = -2$ °C) and 1/1 ($T_m = 74$ °C) crystalline solvates form. The structure of the 2/1 solvate is unknown, but may resemble SSIP $(G3)_2$:NaX solvates, which consist of solvated $[(G3)_2Na]^+$ cations and uncoordinated anions.[70−74] The 2/1 solvate appears to undergo a solid−solid phase transition at −6 °C. The 1/1 solvate undergoes a solid−solid phase transition at −35 °C. The low-temperature structure of the CIP 1/1 crystalline solvate is reported above. The structure of this CIP 1/1 solvate is quite different from those of the CIP 1/1 solvates with $LiBH_4$, $LiBF_4$, $LiClO_4$, $LiCF_3SO_3$, and $LiAsF_6$.[68,69] In the latter solvates, the Li^+ cations are coordinated by a total of four EOs from two

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G3 molecules and one anion, resulting in polymeric chains, whereas the solvate with LiBETI consists of isolated Li^+ cations coordinated by all four EOs from a single G3 molecule and one anion. The G3 molecules adopt a conformation similar to that of 12-crown-4 molecules.[75,76] The difference is these solvates may originate from the large bulk of the $BETI^-$ anions, which hinders the close packing of the anions necessary for the polymeric solvate structures. It was not possible to crystallize the 2/1 phase for samples with concentrations of $n > 2$ despite extensive efforts to do so. Rather, these samples remain completely amorphous, or for the more dilute samples, some of the uncoordinated G3 is able to crystallize (Figure 3). This is analogous to the crystallinity gap behavior observed for PEO−LiTFSI mixtures.[16−20]

Order−Disorder Solid−Solid Phase Transitions. The disordering of ions within salts containing organic cations and $TFSI^-$ anions is frequently observed.[25,77] Such disordering leads to the formation of plastic crystalline solid phases[78] or lowers the T_m enough to form RTILs. The glyme-solvated Li^+ cations have many similarities to organic cations with delocalized and/or steric shielding of the positive charge. It is thus expected that the glyme−LiTFSI and −LiBETI solvates will also exhibit order−disorder solid−solid phase transitions. This is supported by visual observation. The glyme−LiTFSI and −LiBETI crystalline solvates which display subambient temperature phase changes appear as waxy solids at room temperature rather than white, brittle solids.

Several attempts by us to elucidate the structural solutions of the $(G1)_3$:LiBETI and $(G2)_2$:LiBETI solvates from single crystals failed. The crystals were rapidly cooled under nitrogen to −100 °C in the diffractometer to prevent water contamination. In all cases, poor quality diffraction data resulted. It is likely that the room temperature disordered phases were frozen into the quenched crystals.[79] Similar results were found for crystals of the $(G3)_1$:LiBETI solvate, and a structural solution was only obtained after a crystal was encapsulated in a capillary tube and slowly cooled/annealed. Note that the $(G1)_1$:LiBETI solvate, in which the anions are relatively rigidly fixed due to the coordination to two Li^+ cations, does not have an evident solid−solid phase transition.

A reversible phase change was previously noted for the $(G2)_2$:LiTFSI solvate at −63 °C.[37] This is in contrast to the phase changes noted by us at −88 and 38 °C (Figure 2). The low-temperature crystal structure reported above (determined at −175 °C) contains a substantial amount of disorder for the $TFSI^-$ anions. Poor-quality XRD data were previously found for these crystals above the low-temperature solid−solid phase transition.[37] The XRD data at −53 °C did permit the structure elucidation of six-coordinate Li^+ cations coordinated by six EOs from two G2 molecules. A satisfactory refinement of the XRD data, however, was not possible. This strongly suggests that it is the uncoordinated $TFSI^-$ anions which may be disordered above the first phase transition, rather than the solvated $[(G2)_2Li]^+$ cations.

Raman spectroscopic characterization of the $(\text{glyme})_n$−LiTFSI and −LiBETI mixtures is currently in progress to determine whether or not CIP $(G1)_2$:LiX and AGG $(G2)_1$:LiX crystalline solvates do form at low temperatures, as well as to determine the nature of the solid−solid phase transitions.

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Supporting Information Available: Sample preparation and X-ray diffraction characterization procedures (PDF) and X-ray crystallographic files (CIF) for $(G1)_1$:LiBETI, $(G2)_2$:LiTFSI, $(G2)_{1/2}$:LiTFSI, and $(G3)_1$:LiBETI (low temperature structure). This material is available free of charge via the Internet at http://pubs.acs.org.

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