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New Disordering Mode for TFSI$^-$ Anions: The Nonequilibrium, Plastic Crystalline Structure of Et_4NTFSI

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A new TFSI$^-$ anion disordering mode has been discovered in a supercooled plastic crystalline phase of Et_4NTFSI, which may, in part, account for the low melting points of TFSI$^-$ salts with organic cations, thereby forming ionic liquids, and the intriguing properties of LiTFSI for lithium battery applications.

The factors that determine the melting point of a salt, and thus the formation of room-temperature ionic liquids, remain poorly understood. Figure 1 displays the melting points of salts with commonly utilized cations and varying anions.[1] It is intriguing that the $N(SO_2CF_3)_2^-$ (TFSI$^-$) anion is so effective at reducing a salt's melting point, whereas the same effect is not found for other charge-delocalized anions. This has been attributed to the lower symmetry and bulky nature of the anion (relative to, for example, BF_4^-), as well as its extensive charge delocalization[2] and flexibility.[3] In particular, two low-energy conformations are known with C_2 and C_1 symmetry (Figure 2a). Here we report a nonequilibrium, disordered structure for Et_4NTFSI, which reveals a new disordering mode for the TFSI$^-$ anion.[4] This disordering mode may help explain both the "crystallinity gap" in poly(ethylene oxide)−LiTFSI electrolytes[5] and the low melting points of organic salts with TFSI$^-$ anions (Figure 1).

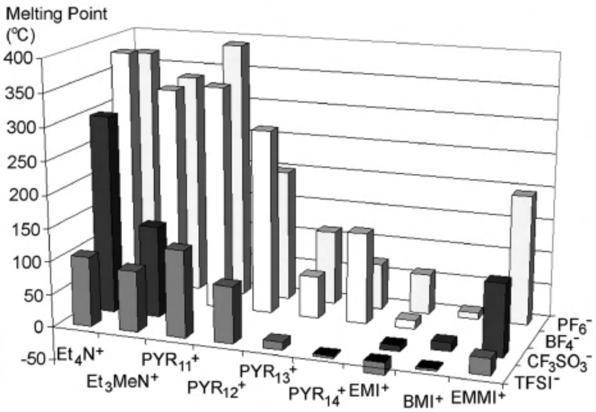

Figure 1. Melting points of various salts (PYR_{13}^+ = *N*-methyl-*N*-propylpyrrolidinium, EMI^+ = 1-ethyl-3-methylimidazolium, BMI^+ = 1-butyl-3-methylimidazolium, and $EMMI^+$ = 1-ethyl-2,3-dimethylimidazolium).

Et_4NTFSI exhibits two solid-phase transitions at 277 and 322 K prior to melting at 377 K (Figure 2b). There is a strong hysteresis in the phase III → II transition near 277 K, which enabled a single crystal in the room-temperature phase II configuration to be supercooled to 100 K and the structure

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(1) (a) Xu, K.; Ding, M. S.; Jow, T. R. *J. Electrochem. Soc.* **2001**, *148*, A267. (b) Golding, J.; Hamid, N.; MacFarlane, D. R.; Forsyth, M.; Forsyth, C.; Collins, C.; Huang, J. *Chem. Mater.* **2001**, *13*, 558. (c) Forsyth, S.; Golding, J.; MacFarlane, D. R.; Forsyth, M. *Electrochim. Acta* **2001**, *46*, 1753. (d) MacFarlane, D. R.; Meakin, P.; Sun, J.; Amini, N.; Forsyth, M. *J. Phys. Chem. B* **1999**, *103*, 4164. (e) Henderson, W. A.; Passerini, S. *Chem. Mater.* **2004**, *16*, 2881. (f) Matsumoto, K.; Hagiwara, R.; Yoshida, R.; Ito, Y.; Mazej, Z.; Benkić, P.; Žemva, B.; Tamada, O.; Yoshino, H.; Matsubara, S. *Dalton. Trans.* **2004**, 144. (g) Ngo, H. L.; LeCompte, K.; Hargens, L.; McEwen, A. B. *Thermochim. Acta* **2000**, *357*−*358*, 97. (h) Bonhôte, P.; Dias, A.-P.; Armand, M.; Papageorgiou, N.; Kalyanasundaram, K.; Grätzel, M. *Inorg. Chem.* **1996**, *35*, 1168. (i) Huddleston, J. G.; Visser, A. E.; Reichert, W. M.; Willauer, H. D.; Broker, G. A.; Rogers, R. D. *Green Chem.* **2001**, *3*, 156. (j) Fredlake, C. P.; Crosthwaite, J. M.; Hert, D. G.; Aki, S. N. V. K.; Brennecke, J. F. *J. Chem. Eng. Data* **2004**, *49*, 954.

(2) Benrabah, D.; Arnaud, R.; Sanchez, J.-Y. *Electrochim. Acta* **1995**, *40*, 2437.

(3) (a) Johansson, P.; Gejji, S. P.; Tegenfeldt, J.; Lindgren, J. *Electrochim. Acta* **1998**, *43*, 1375. (b) Arnaud, R.; Benrabah, B.; Sanchez, J.-Y. *J. Phys. Chem.* **1996**, *100*, 10882. (c) Foropoulos, J., Jr.; DesMarteau, D. D. *Inorg. Chem.* **1984**, *23*, 3720.

(4) There is one previous report of similar TFSI$^-$ anion disordering: Schlueter, J. A.; Geiser, U.; Wang, H. H.; Kini, A. M.; Ward, B. H.; Parakka, J. P.; Daugherty, R. G.; Kelly, M. E.; Nixon, P. G.; Winter, R. W.; Gard, G. L.; Montgomery, L. K.; Koo, H.-J.; Whangbo, M.-H. *J. Solid State Chem.* **2002**, *168*, 524.

(5) (a) Vallée, A.; Besner, S.; Prud'homme, J. *Electrochim. Acta* **1992**, *37*, 1579. (b) Edman, L.; Ferry, A.; Doeff, M. M. *J. Mater. Res.* **2000**, *15*, 1950. (c) Tarascon, J.-M.; Armand, M. *Nature* **2001**, *414*, 359.

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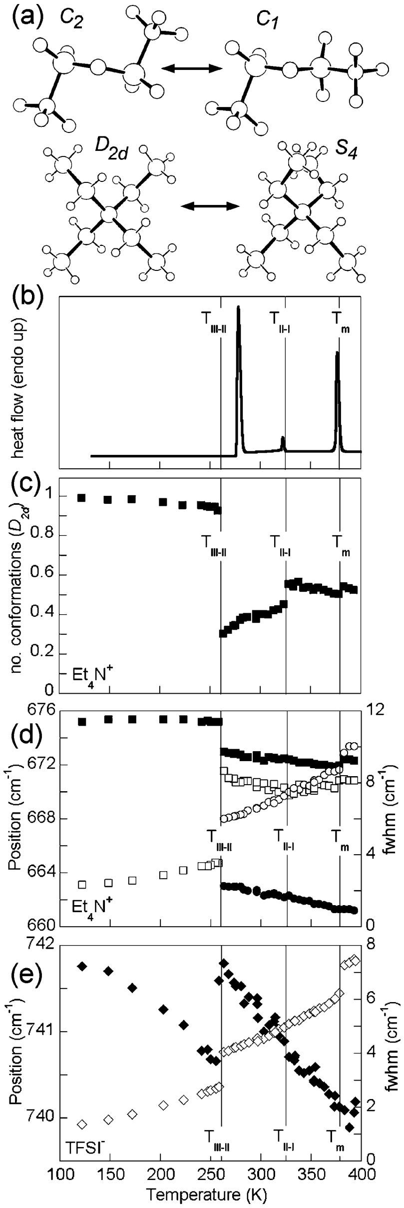

Figure 2. (a) Low-energy TFSI$^-$ anion and Et$_4$N$^+$ cation conformations. (b) DSC heating trace of Et$_4$NTFSI. (c) Fraction of Et$_4$N$^+$ cation D_{2d} conformers calculated from the 675 (D_{2d}) and 663 (S_4) cm^{-1} Raman doublet. (d) Band position (filled symbols) and fwhm (open symbols) changes for the Et$_4$N$^+$ cations (D_{2d}, squares; S_4, circles). (e) Band position (filled diamonds) and fwhm (open diamonds) changes for the TFSI$^-$ Raman band as a function of temperature.

of this nonequilibrium phase determined. The hysteresis and shape of the differential scanning calorimetry (DSC) endothermic peak of Et$_4$NTFSI at 277 K indicate that this is a first-order phase transition that results in a considerable structural change from the low-temperature phase III structure. The energy associated with this transition is greater than that of the fusion transition ($\Delta_{\text{III-II}}H = 18.3$ kJ mol^{-1}, $\Delta_{\text{III-II}}S = 65.6$ J K^{-1} mol^{-1}; $\Delta_{\text{I-fus}}H = 9.0$ kJ mol^{-1}, $\Delta_{\text{I-fus}}S = 24.0$ J K^{-1} mol^{-1}), suggesting that the ions become highly disordered at room temperature. Both the Et$_4$N$^+$ cations and TFSI$^-$ anions may be examined by Raman spectroscopy to glean insight into the variations in ion conformations, disorder, and interactions with neighboring ions.[6] The hysteresis in the phase III → II transition is evident in the discrepancy between the DSC and Raman transition onsets (Figure 2).

The Et$_4$N$^+$ cations are known to be flexible, adopting either an all-*trans* (tt,tt or D_{2d}) Greek cross or *trans*−*gauche* (tg,tg or S_4) Nordic cross conformation in crystalline salts (Figure 2a).[7,8] A ν_s(C$_4$N) stretching Raman vibrational band near 675 cm^{-1} originates from the D_{2d} conformation, whereas the S_4 conformation gives a band near 663 cm^{-1}.[8] Figure 2c shows the variation with temperature of the fraction of the Et$_4$N$^+$ cations with the D_{2d} conformation. At temperatures below the phase III → II transition, nearly all of the Et$_4$N$^+$ cations are ordered in the D_{2d} conformation. After the transition (to the disordered phase II), however, only 30% of the cations adopt the D_{2d} conformation (the remainder adopt the S_4 conformation). Figure 2d shows the variation with temperature of the ν_s(C$_4$N) stretching band positions and full-width at half-maximum (fwhm). The fwhm gives an indication of the distribution of ion conformations and thus of the disorder of the system. The position of the D_{2d} band in the low-temperature phase III is constant with increasing temperature, but the fwhm increases somewhat. At the first phase transition (phase III → II), the position of the D_{2d} band decreases sharply and thereafter decreases slightly with increasing temperature. The fwhm increases sharply at this transition, indicating a large disordering of the cations. Thereafter, the fwhm of this band also decreases slightly with increasing temperature. The 663-cm^{-1} band appears after the first phase transition, indicating the presence of cations with the S_4 conformation. The band position decreases steadily with temperature, but the fwhm increases strongly. The Et$_4$N$^+$ cations are thus ordered in the D_{2d} conformation in the low-temperature phase III, but become highly disordered in phase II.

As mentioned above, TFSI$^-$ anions are also highly flexible, with two low-energy transoid and cisoid conformations with C_2 and C_1 symmetry, respectively.[3,9] In this case, the Raman spectra aid in determining the degree of interaction between the TFSI$^-$ anions and neighboring cations. The TFSI$^-$ anion has a strong Raman band near 740 cm^{-1} associated with the expansion and contraction of the entire anion.[10] This band is often used to identify coordination of the TFSI$^-$ anions with Li$^+$ cations.[11] Figure 2e shows the variation with temperature of the position and fwhm of this band. With increasing temperature, the band position decreases and the fwhm increases until the phase III → II transition, at which point a dramatic upward shift occurs for both the anion band

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(6) Herstedt, M.; Henderson, W. A.; Smirnov, M.; Ducasse, L.; Servant, L.; Talaga, D.; Lassègues, J. C. *J. Raman Spectrosc.* **2006**, in press.

(7) Brand, H. V.; Curtiss, L. A.; Iton, L. E.; Trouw, F. R.; Brun, T. O. *J. Phys. Chem.* **1994**, *98*, 1293.

(8) Naudin, C.; Bonhomme, F.; Bruneel, J. L.; Ducasse, L.; Grondin, J.; Lassègues, J.-C.; Servant, L. *J. Raman Spectrosc.* **2000**, *31*, 979.

(9) Holbrey, J. D.; Reichert, W. M.; Rogers, R. D. *Dalton Trans.* **2004**, 2267.

(10) (a) Rey, I.; Johansson, P.; Lindgren, J.; Lassègues, J. C.; Grondin, J.; Servant, L. *J. Phys. Chem. A* **1998**, *102*, 3249. (b) Herstedt, M.; Smirnov, M.; Johansson, P.; Chami, M.; Grondin, J.; Servant, L.; Lassègues, J. C. *J. Raman Spectrosc.* **2005**, *36*, 762.

(11) (a) Rey, I.; Lassègues, J. C.; Grondin, J.; Servant, L. *Electrochim. Acta* **1998**, *43*, 1505. (b) Brouillette, D.; Irish, D. E.; Taylor, N. J.; Perron, G.; Odziemkowski, M.; Desnoyers, J. E. *Phys. Chem. Chem. Phys.* **2002**, *4*, 6063. (c) Edman, L. *J. Phys. Chem. B* **2000**, *104*, 7254.

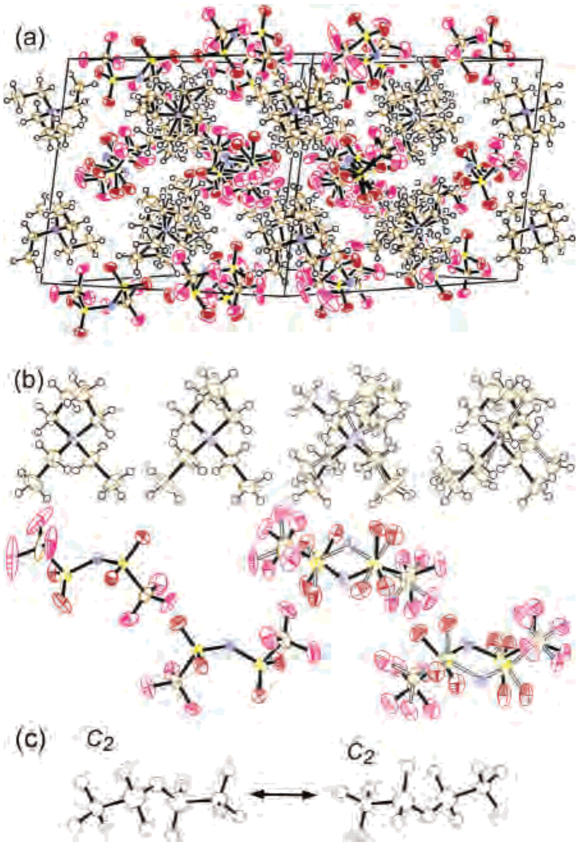

Figure 3. (a) Unit cell of the nonequilibrium, supercooled (phase II) crystal structure of Et_4NTFSI at 100 K. (b) Views of the ions found in the asymmetric unit. Two of the cations and two of the anions are disordered (N, blue; S, yellow; O, red; F, pink). (c) The two C_2 anion conformations for the disordered $TFSI^-$ anions in Et_4NTFSI.

position and fwhm. After the first transition, the wavenumber again decreases and the fwhm continues to increase until melting. This indicates that the $TFSI^-$ anions are also disordered in phase II. The variation in the 740-cm^{-1} band and fwhm below the phase III → II transition suggests that, as the temperature increases, approaching the transition temperature, the anions become increasingly disordered and the interaction of the anions with the neighboring cations becomes weaker. This may, in fact, be responsible for inducing the phase transition.

A single crystal of the salt was cooled at a rate of 0.5 K min^{-1} to 100 K, and the crystal structure was determined from the diffraction data. The structure at 100 K is both twinned and disordered (Figure 3a). The asymmetric unit consists of four Et_4N^+ cations and four $TFSI^-$ anions (Figure 3b). Two of the cations and two of the anions are disordered. The two ordered cations adopt the S_4 conformation. The first disordered cation adopts D_{2d} and S_4 conformations with 50.9% and 49.1% occupancy. The second disordered cation adopts the S_4 conformation with 83.0% occupancy and a second conformation of C_1 symmetry[7] with 17.0% occupancy. The structure is indeed the supercooled room-temperature phase II structure because the fraction of Et_4N^+ cations with the D_{2d} conformation is only 12.7% (rather than close to 100% for phase III). The supercooling of the phase II salt into a nonequilibrium, frozen-in disordered phase is analogous to the freezing of a disordered liquid into a disordered glassy solid. The phase II equilibrium between the Et_4N^+ cations with the D_{2d} and S_4 conformations changes continuously with temperature. If the data for the fraction of cations with the D_{2d} conformation (Figure 3c) are extrapolated from room temperature to about 200 K (near the expected glass transition), a value of about 13% is obtained. This indicates that, on cooling, the phase II structure is retained (becoming supercooled) and ionic motion is eventually completely frozen out, locking the ions into a particular conformation. All of the ions may be disordered at room temperature. The value of 200 K is close to the glass transition temperature of many $TFSI^-$ salts when they are quenched into supercooled amorphous phases.

Surprisingly, the anion disorder in the crystal structure does not consist of a mixture of the C_2 and C_1 conformations as expected.[3,9] Instead, all of the anions have a C_2 conformation, but two of the anions are disordered as two C_2 conformations with major occupancies of 60.8% and 77.5%, respectively, in which the nitrogen atom and SO_2CF_3 groups are rotated but the SCF_3 groups retain their approximate positions (though rotated about the C_3 axis) (Figure 3b). This indicates a new dynamic mode for the disordering of the $TFSI^-$ anions not previously modeled or observed experimentally in which the anions flex within the cage created by the neighboring cations (Figure 3c). The same disordering mode has also been observed by us in crystal structures of $PYR_{12}TFSI$,[12] PIP_{12}-TFSI (with *N*-ethyl-*N*-methylpyrrolidinium and -piperidinium cations, respectively), and Me_4NTFSI. This implies that the $C_2 \leftrightarrow C_2$ anion disordering mechanism reported here is the norm for plastic crystalline phases of salts with $TFSI^-$ anions.

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Supporting Information Available: Experimental procedures (PDF) and X-ray crystallographic data file for Et_4NTFSI (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) Henderson, W. A.; Young, V. G., Jr.; Passerini, S.; Trulove, P. C.; De Long, H. C. *Chem. Mater.* **2005**, in press.