

Supporting Information:

Phase Behavior and Crystalline Phases of Ionic Liquid-Lithium Salt Mixtures with 1-Alkyl-3-methylimidazolium Salts

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Experimental Details:

NMR Measurements. All NMR spectra were measured at room temperature on a Varian Gemini 200 MHz spectrometer. Deuterated acetonitrile (CD_3CN , 99.8 atom% D, containing 1% v/v TMS) was used as the solvent (Fig. S-1). ^1H NMR data for the clear, colorless $\text{IM}_{10\text{R}}\text{TFSI}$ (Table S-1 and Fig. S-2) salts indicate that the ILs are all of high purity (>99%).

IL-LiX Crystal Structures. Fig. S-3 shows two views of a portion of the polymeric ionic chains formed in the 1/1 ($x = 0.50$) $\text{IM}_{101}\text{CF}_3\text{SO}_3/\text{LiCF}_3\text{SO}_3$ crystalline phase by the Li^+ cations and CF_3SO_3^- anions. Each anion coordinates two Li^+ cations. The third anion oxygen atom forms a single hydrogen bond with one of the neighboring IM_{102}^+ cations. The Li^+ cations are coordinated by a total of four anion oxygen atoms (one each from four anions). The IM_{102}^+ cations reside between the polymeric ionic chains.

Fig. S-4 shows two views of a portion of the ionic planar sheets formed in the 1/2 ($x = 0.67$) $\text{IM}_{102}\text{TFSI}/\text{LiTFSI}$ crystalline phase by the Li^+ cations and TFSI anions. Each anion coordinates either two or three Li^+ cations. The anions have either C_2 or C_1 symmetry³⁻⁷ with twice as many of the latter present. The anions with C_1 symmetry are the ones coordinated to three Li^+ cations. The Li^+ cations are coordinated by five anion oxygens. The IM_{102}^+ cations reside in cavities formed by these sheets. The Li^+ cation coordination to the anions in this structure is shown in Fig. S-5.

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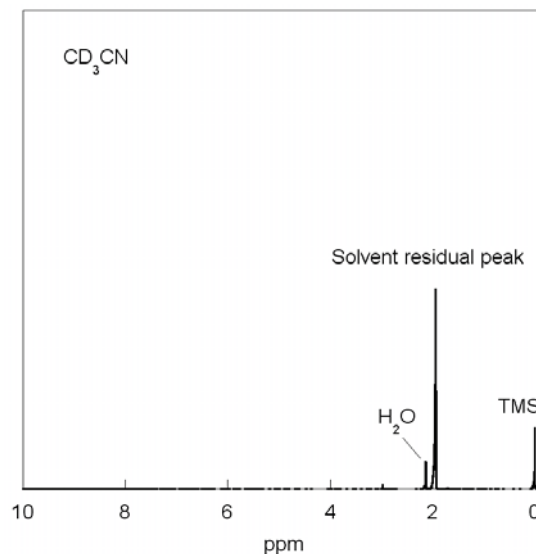


Figure S-1. ^1H NMR spectrum for CD_3CN .

Table S-1. ^1H NMR data for $\text{IM}_{10\text{R}}\text{TFSI}$ ($R = 1, 2$ or 4), δ_{H} (200 MHz, CD_3CN).

| | |
|------------------------------|---|
| $\text{IM}_{101}\text{TFSI}$ | 8.37 (s, 1H), 7.32 (d, 2H), 3.82 (s, 6H) |
| $\text{IM}_{102}\text{TFSI}$ | 8.40 (s, 1H), 7.38 (s, 1H), 7.32 (s, 1H), 4.16 (q, 2H), 3.81 (s, 3H), 1.45 (t, 3H) |
| $\text{IM}_{104}\text{TFSI}$ | 8.42 (s, 1H), 7.38 (t, 1H), 7.34 (t, 1H), 4.13 (t, 2H), 3.83 (s, 3H), 1.79 (qnt, 2H), 1.32 (sext, 2H), 0.94 (t, 3H) |

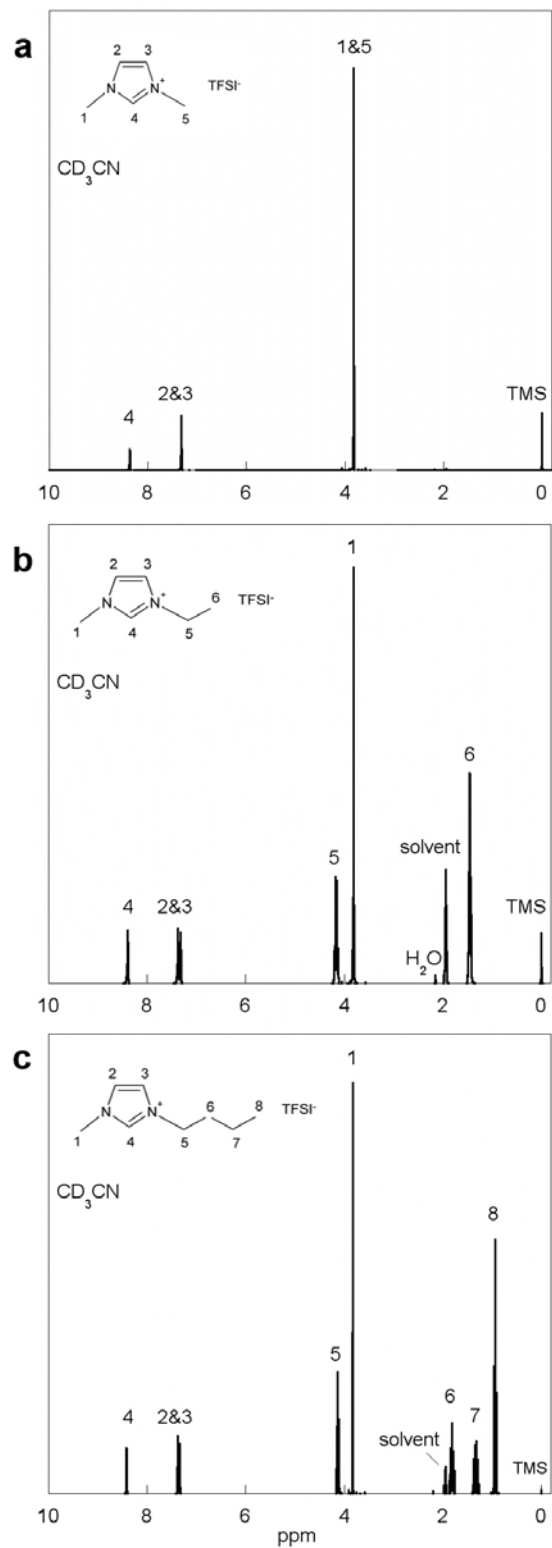


Figure S-2. ^1H NMR spectrum for $\text{IM}_{10\text{R}}$ TFSI (a) $\text{R} = 1$, (b) $\text{R} = 2$ and (c) $\text{R} = 4$.

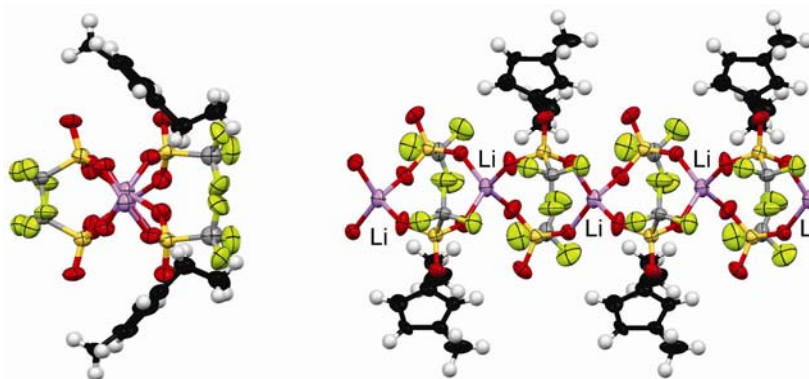


Figure S-3. Portion of the crystal structure of the 1/1 ($x = 0.50$) $\text{IM}_{101}\text{CF}_3\text{SO}_3/\text{LiCF}_3\text{SO}_3$ crystalline phase (two views—rotated 90°).¹ The C and N atoms of the IM_{102}^+ cations are colored black for clarity (Li-purple, O-red, S-yellow, F-green).

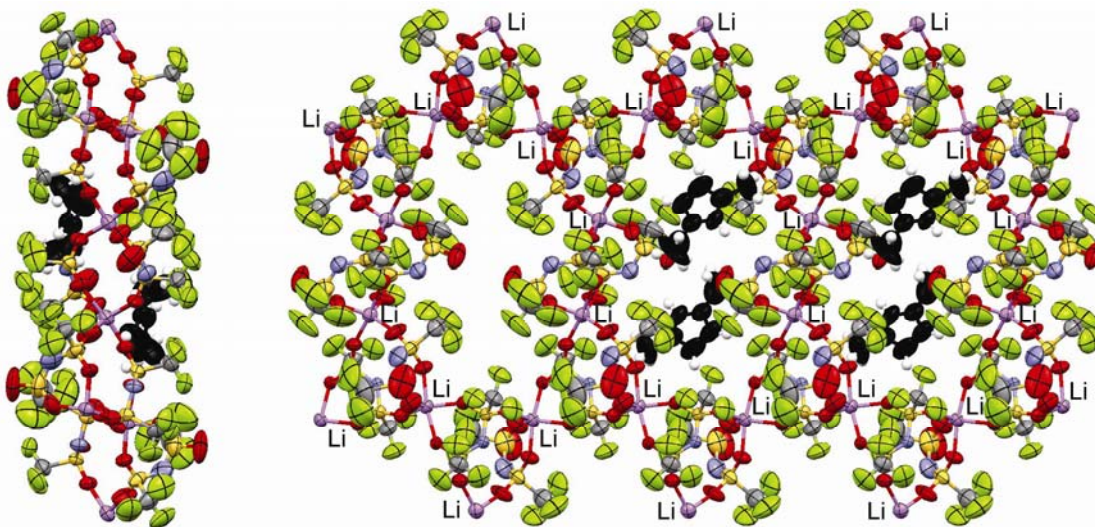


Figure S-4. Portion of the crystal structure of the 1/2 ($x = 0.67$) $\text{IM}_{102}\text{TFSI}/\text{LiTFSI}$ crystalline phase (two views—rotated 90°).² The C and N atoms of the IM_{102}^+ cations are colored black and the two cations have been removed from the left cavity for clarity (Li-purple, O-red, S-yellow, F-green).

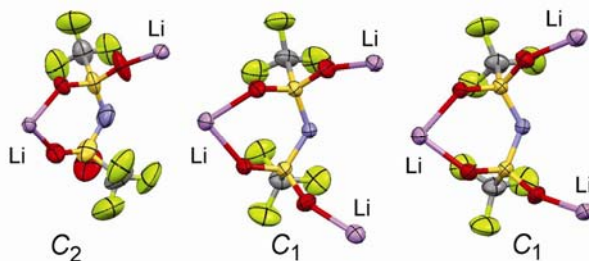


Figure S-5. $\text{Li}^+ \dots \text{TFSI}^-$ coordination in the 1/2 ($x = 0.67$) $\text{IM}_{102}\text{TFSI}/\text{LiTFSI}$ crystalline phase. The asymmetric unit contains two anions each with this coordination (6 total) (Li-purple, O-red, S-yellow, F-green).