Supplementary Information

Origin of Low Melting Point of Ionic Liquids: Dominant Role of Entropy

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Details of IL synthesis.
1,3-dimethylimidazolium iodide ([C$_{1}$mim]I): 1-Methylimidazole (0.268 mol, 22.0 g) and a slight excess amount of iodomethane (0.295 mol, 41.9 g) were dissolved in ethyl acetate. The solution was stirred under an inert atmosphere for 1 hour in an ice bath. The precipitate was washed with ethyl acetate five times, and subsequently recrystallized with acetone. A colorless crystal of [C$_{1}$mim]I was obtained via filtration (yield: 94%).
$^1$H-NMR (DMSO-d$_6$): $\delta$ (in ppm) = 9.07 (1H, s, NCH$_2$N), 7.69 (2H, t, NCH$_2$CH), 3.82 (6H, s, (NCH$_3$)$_2$)
$^{13}$C-NMR (DMSO-d$_6$): $\delta$ (in ppm) = 137.5 (s, NCHN), 123.9 (s, NCH$_2$CH), 36.4 (s, NCH$_3$) Water content: 20 ppm

1,3-dimethylimidazolium nitrate ([C$_{1}$mim]NO$_3$): AgNO$_3$ (0.031 mol, 5.27 g) was added into [C$_{1}$mim]I (0.034 mol, 7.62 g) aqueous solution. The solution was stirred for 2 hours with light shielding. After the reaction, the precipitant (AgI) was removed by filtration, and the solvent was removed by evaporation. The obtained solid was dissolved in dichloromethane, which produces white precipitant (residual AgI). The precipitant and dichloromethane were removed by filtration and evaporation, respectively. This residual byproduct-removing process was repeated until no precipitant was observed. After the final evaporation, the obtained solid was recrystallized with acetonitrile. A colorless crystal was then obtained via filtration (yield: 64%).
$^1$H-NMR (DMSO-d$_6$): $\delta$ (in ppm) = 9.08 (1H, s, NCH$_2$N), 7.67 (2H, t, NCH$_2$CH), 3.82 (6H, s, (NCH$_3$)$_2$)
$^{13}$C-NMR (DMSO-d$_6$): $\delta$ (in ppm) = 137.7 (s, NCHN), 123.9 (s, NCH$_2$CH), 36.1 (s, NCH$_3$) Water content: 60 ppm I' content: 320 ppm

1,3-dimethylimidazolium acetate ([C$_{1}$mim]CH$_3$CO$_2$): By passing acetic acid (0.235 mol, 14.1 g) aqueous solution through a column filled with the ion exchange resin (Amberlite IRN78, hydroxide form, 55 ml), the ion exchange resin of CH$_3$CO$_2$ form was obtained. Subsequently, [C$_{1}$mim]I (0.031 mol, 6.95 g) dissolved in distilled water was passed through the column to produce [C$_{1}$mim]CH$_3$CO$_2$ aqueous solution. No detectable iodide salt was confirmed in the solution by the AgNO$_3$ test. Water was removed from the solution by evaporation and subsequent vacuuming. After washing with ethyl acetate, the obtained solid was recrystallized with acetonitrile to give a colorless crystal (yield: 90%).
$^1$H-NMR (DMSO-d$_6$): $\delta$ (in ppm) = 10.18 (1H, s, NCH$_2$N), 7.83 (2H, t, NCH$_2$CH), 3.84 (6H, s, (NCH$_3$)$_2$), 1.54 (3H, s, CH$_3$COO)
$^{13}$C-NMR (DMSO-d$_6$): $\delta$ (in ppm) = 173.7 (s, CH$_3$COO), 139.1 (s, NCHN), 123.9 (s, NCH$_2$CH), 35.8 (s, NCH$_3$), 26.9 (s, CH$_3$COO) Water content: 530 ppm

1,3-dimethylimidazolium trifluoroacetate ([C$_{1}$mim]CF$_3$CO$_2$): 1-Methylimidazole (0.050 mol, 4.11 g) and a slight excess amount of methyl trifluoroacetate (0.055 mol, 7.04 g) were dissolved in ethyl acetate. The solution was stirred under an inert atmosphere for 1 day at 373 K. The obtained solid was washed with ethyl acetate five times, and subsequently recrystallized with acetonitrile. A colorless crystal of [C$_{1}$mim]CF$_3$CO$_2$ was obtained via filtration (yield: 61%).
$^1$H-NMR (DMSO-d$_6$): $\delta$ (in ppm) = 9.16 (1H, s, NCH$_2$N), 7.69 (2H, t, NCH$_2$CH), 3.82 (6H, s, (NCH$_3$)$_2$)
$^{13}$C-NMR (DMSO-d$_6$): $\delta$ (in ppm) = 158.5 (q, CF$_3$COO), 137.7 (s, NCHN), 124.0 (s, NCH$_2$CH), 115.9 (s, CF$_3$COO), 36.1 (s, NCH$_3$)
$^{19}$F-NMR (DMSO-d$_6$): $\delta$ (in ppm) = -73.5 (3F, s, CF$_3$COO) Water content: 40 ppm

1,3-dimethylimidazolium mesylate ([C$_{1}$mim]CH$_3$SO$_3$): 1-Methylimidazole (0.100 mol, 8.21 g) and a slight excess amount of methyl methanesulfonate (0.110 mol, 12.1 g) were dissolved in ethyl acetate. The solution was stirred under an inert atmosphere for 1 day in an ice bath. The obtained
solid was washed with ethyl acetate five times, and subsequently recrystallized with acetonitrile. A colorless crystal of \([\text{C}_{3}\text{mim}]\text{CH}_3\text{SO}_3\) was obtained via filtration (yield: 94%).

\(^1\text{H}-\text{NMR (DMSO-}d_6\text{)}: \delta (\text{in ppm}) = 9.13 (1\text{H, s, NCHN}), 7.69 (2\text{H, t, NCHCH}), 3.82 (6\text{H, s, (NCH}_3)_2\text{)}, 2.32 (3\text{H, s, CH}_3\text{SO}_3)\)

\(^1\text{C}-\text{NMR (DMSO-}d_6\text{)}: \delta (\text{in ppm}) = 137.8 (\text{s, NCHN}), 124.0 (\text{s, NCHCH}), 40.4 (\text{s, CH}_2\text{SO}_3), 36.1 (\text{s, NCH}_3)\)

Water content: 120 ppm.

1,3-dimethylimidazolium trifluoromethanesulfonate ([C\text{\textsubscript{1}}\text{mim}]\text{CF}_3\text{SO}_3\text{}): 1-Methylimidazole (0.050 mol, 4.11 g) and a slight excess amount of methyl trifluoromethanesulfonate (0.055 mol, 9.03 g) were dissolved in ethyl acetate. The solution was stirred under an inert atmosphere for 1 day in an ice bath. The solution was evaporated to remove ethyl acetate. The obtained solid was washed with diethyl ether five times, and subsequently recrystallized with acetonitrile. A colorless crystal was obtained as the final product (yield: 95%).

\(^1\text{H}-\text{NMR (DMSO-}d_6\text{)}: \delta (\text{in ppm}) = 8.97 (1\text{H, s, NCHN}), 7.63 (2\text{H, t, NCHCH}), 3.81 (6\text{H, s, (NCH}_3)_2\text{)}\)

\(^1\text{C}-\text{NMR (DMSO-}d_6\text{)}: \delta (\text{in ppm}) = 137.5 (\text{s, NCHN}), 123.9 (\text{s, NCHCH}), 119.1 (\text{s, CF}_3\text{SO}_3), 36.1 (\text{s, NCH}_3)\)

Water content: 30 ppm.

1,3-dimethylimidazolium tosylate ([C\text{\textsubscript{1}}\text{mim}]\text{OTs}\text{}): 1-Methylimidazole (0.050 mol, 4.11 g) and a slight excess amount of methyl 4-toluene- sulphonate (0.055 mol, 10.2 g) were dissolved in ethyl acetate. The solution was stirred under an inert atmosphere for 1 day at room temperature. The obtained solid was washed with ethyl acetate five times, and subsequently recrystallized with acetonitrile. A colorless crystal of [C\text{\textsubscript{1}}\text{mim}]\text{OTs}\text{} was obtained via filtration (yield: > 99 %).

\(^1\text{H}-\text{NMR (DMSO-}d_6\text{)}: \delta (\text{in ppm}) = 9.04 (1\text{H, s, NCHN}), 7.65 (2\text{H, t, NCHCH}), 7.48 (2\text{H, d, CH}_3\text{CCCH}), 7.09 (2\text{H, d, CHCSO}_3), 3.78 (6\text{H, s, (NCH}_3)_2\text{)}, 2.25 (3\text{H, s, CH}_3\text{)}\)

\(^1\text{C}-\text{NMR (DMSO-}d_6\text{)}: \delta (\text{in ppm}) = 146.1 (\text{s, CH}_3\text{)}, 138.3 (\text{s, CHCH}_3\text{)}, 137.7 (\text{s, NCHN}), 128.7 (\text{d, CH}_2\text{CCCH}), 126.0 (\text{d, CHCSO}_3\text{)}, 123.9 (\text{s, NCHCH}), 36.1 (\text{s, NCH}_3\text{)}, 21.3 (\text{q, CH}_3\text{)}\)

Water content: 160 ppm.

1,3-dimethylimidazolium thiocyanate ([C\text{\textsubscript{1}}\text{mim}]\text{SCN}\text{): Anion exchange from [C\text{\textsubscript{1}}\text{mim}]\text{Cl}\text{ aqueous solution. Water in the solution was removed by evaporation and subsequent vacuuming. After recrystallization with acetonitrile, a colorless crystal of [C\text{\textsubscript{1}}\text{mim}]\text{Cl}\text{ was obtained via filtration (yield: 68%). Then, NaSCN (0.024 mol, 1.95 g) and [C\text{\textsubscript{1}}\text{mim}]\text{Cl}\text{ (0.022 mol, 2.92 g) were dissolved into distilled water, and stirred at room temperature for 1 day. After evaporation of the solution, dichloromethane was added into crude [C\text{\textsubscript{1}}\text{mim}]\text{SCN}\text{ to produce white precipitant (NaCl). The precipitant and dichloromethane were removed by filtration and evaporation, respectively. This process was repeated until no precipitant was obtained. After the final evaporation, [C\text{\textsubscript{1}}\text{mim}]\text{SCN}\text{ was obtained as a pale yellow liquid (yield: 64%).

\(^1\text{H}-\text{NMR (DMSO-}d_6\text{)}: \delta (\text{in ppm}) = 8.96 (1\text{H, s, NCHN}), 7.62 (2\text{H, t, NCHCH}), 3.83 (6\text{H, s, (NCH}_3)_2\text{)}\)

\(^1\text{C}-\text{NMR (DMSO-}d_6\text{)}: \delta (\text{in ppm}) = 137.5 (\text{s, NCHN}), 130.5 (\text{s, SCN}), 123.9 (\text{s, NCHCH}), 36.3 (\text{s, NCH}_3\text{)}\)

Water content: 140 ppm.

Na\textsuperscript{+} content: 400 ppm.

1,3-dimethylimidazolium dicyanamide ([C\text{\textsubscript{1}}\text{mim}]N(CN\textsubscript{2})\text{): The synthetic procedure was the same as that of [C\text{\textsubscript{1}}\text{mim}]\text{SCN} except that NaN(CN\textsubscript{2})\text{ was used instead of NaSCN. The [C\text{\textsubscript{1}}\text{mim}]N(CN\textsubscript{2})\text{ was recrystallized with acetonitrile. After filtration and subsequent evaporation, [C\text{\textsubscript{1}}\text{mim}]N(CN\textsubscript{2})\text{ was obtained as a pale yellow liquid (supercooled liquid) at room temperature (yield: 73%).}}

Water content: 400 ppm.
\[ ^1H-NMR \text{ (DMSO-d}_6\text{): } \delta \text{ (in ppm) } = 8.98 \text{ (1H, s, NCHN), 7.61 (2H, t, NCHCH), 3.81 (6H, s, (NCH}_3\text{)}_2\text{)} \]

\[ ^{13}C\text{-NMR (DMSO-d}_6\text{): } \delta \text{ (in ppm) } = 137.5 \text{ (s, NCHN), 123.9 (s, NCHCH), 119.6 (s, NCN), 36.2 (s, NCH}_3\text{)} \]

Water content: 90 ppm.
Na\textsuperscript{+} content: 320 ppm.

1,3-dimethylimidazolium tricyanomethanide ([C\textsubscript{1}mim]C(CN))\textsubscript{3}: The synthetic procedure was the same as that of [C\textsubscript{1}mim]SCN except that NaC(CN)\textsubscript{3} was used instead of NaSCN. The final product was a pale yellow liquid (supercooled liquid) at room temperature (yield: 68%).

\[ ^1H-NMR \text{ (DMSO-d}_6\text{): } \delta \text{ (in ppm) } = 8.97 \text{ (1H, s, NCHN), 7.59 (2H, t, NCHCH), 3.80 (6H, s, (NCH}_3\text{)}_2\text{)} \]

\[ ^{13}C\text{-NMR (DMSO-d}_6\text{): } \delta \text{ (in ppm) } = 137.5 \text{ (s, NCHN), 123.9 (s, NCHCH), 121.0 (s, C}_C\text{N), 36.2 (s, NCH}_3\text{), 5.3 (s, CCN) \]

Water content: 40 ppm.
Na\textsuperscript{+} content: 70 ppm.

Brief Theoretical background of two-phase thermodynamic (2PT) approach. The theory of 2PT is briefly described as follows (for details, please see the references\textsuperscript{1,2}). The total kinetic entropy of a molecule in a liquid state can be divided into translational (\( S\text{\textsubscript{tra}} \)), rotational (\( S\text{\textsubscript{rot}} \)), and intramolecular vibrational (\( S\text{\textsubscript{vib}} \)) contributions.

\[ S = S\text{\textsubscript{tra}} + S\text{\textsubscript{rot}} + S\text{\textsubscript{vib}} \quad (S1) \]

In 2PT, \( S\text{\textsubscript{tra}} \) and \( S\text{\textsubscript{rot}} \) where diffusive motions are included are considered as a sum of gaseous and solid components.

\[ S\text{\textsubscript{tra}} = S\text{\textsubscript{tra}}^g + S\text{\textsubscript{tra}}^s \quad (S2) \]

\[ S\text{\textsubscript{rot}} = S\text{\textsubscript{rot}}^g + S\text{\textsubscript{rot}}^s \quad (S3) \]

The estimation of these entropies is based on density of states function \( g(v) \) which is the Fourier transform of the velocity autocorrelation function \( C(t) \) of a molecule,

\[ g(v) = \frac{2}{kT} \lim_{r \to +\infty} \int_{-r}^{r} C(t) e^{-r^2\pi r t} dt \quad (S4) \]

where \( k \) is the Boltzmann constant, \( T \) is temperature, and \( v \) is the frequency. \( C(t) \) is the sum of the mass-weighted velocity autocorrelation function of atoms,

\[ C(t) = \sum_{j=1}^{N} \sum_{k=1}^{3} m c_j^k (t) \quad (S5) \]

where \( m \) is the mass of an atom \( j \) and \( N \) is the total number of atoms of the systems. Same as the entropy, \( g(v) \) is divided into translational (\( g\text{\textsubscript{tra}}(v) \)), rotational (\( g\text{\textsubscript{rot}}(v) \)), and intramolecular vibrational (\( g\text{\textsubscript{vib}}(v) \)) components.

\[ g(v) = g\text{\textsubscript{tra}}(v) + g\text{\textsubscript{rot}}(v) + g\text{\textsubscript{vib}}(v) \quad (S6) \]

The functions \( g\text{\textsubscript{tra}}(v) \) and \( g\text{\textsubscript{rot}}(v) \) are determined from autocorrelation functions of center-of-mass velocity and angular velocity of the molecule of interest, respectively. \( g\text{\textsubscript{vib}}(v) \) is obtained by the deduction of \( g\text{\textsubscript{tra}}(v) \) and \( g\text{\textsubscript{rot}}(v) \) from the total density of states function. \( g\text{\textsubscript{tra}}(v) \) contains gaseous and solid components.

\[ g\text{\textsubscript{tra}}(v) = g\text{\textsubscript{tra}}^g(v) + g\text{\textsubscript{tra}}^s(v) \quad (S7) \]

\( g\text{\textsubscript{tra}}(v) \) is expressed by employing a hard-sphere model as,
Entropy is expressed as, 

\[ S = \frac{g_{\text{tra}}(0)}{1 + \left( \frac{\pi g_{\text{tra}}(0) \nu}{6 f_{\text{tra}} N} \right)^2} \]  

(S8)

where \( f_{\text{tra}} \) is the translational “fluidity”. Because “fluidity” expresses the fraction of the hard-sphere (gaseous) component in the overall system, the integral of \( g_{\text{tra}}(\nu) \) corresponds to \( 3Nf_{\text{tra}} \).

\( f_{\text{tra}} \) can be numerically derived with the following equations,

\[ 2\Delta^{9/2} f_{\text{tra}}^{5/2} - 6 \Delta^{-3/2} f_{\text{tra}}^3 - \Delta^{-3/2} f_{\text{tra}}^{7/2} + 6 \Delta^{-3/2} f_{\text{tra}}^{5/2} + 2 \Delta_{\text{tra}} - 2 = 0 \]  

(S9)

\[ \Delta_{\text{tra}} = \frac{2g_{\text{tra}}(0)}{9N} \left( \frac{\pi kT}{m} \right)^{1/2} \left( \frac{N}{V} \right)^{1/3} \left( \frac{6}{\pi} \right)^{2/3} \]  

(S10)

where \( \Delta \) is the dimensionless diffusivity constant and \( V \) is the system volume. The density of states at zero frequency \( g_{\text{tra}}(0) \) can be determined directly from \( g_{\text{tra}}(\nu) \) or via diffusion coefficient \( D \) of molecule.

\[ g_{\text{tra}}(0) = \frac{12mND}{kT} \]  

(S11)

Based on the Carnahan-Starling equation of state, the analytical form of the gaseous translational entropy is expressed as,

\[ S_{\text{tra}}^g = \frac{5}{2k} + k \ln \left[ \left( \frac{2\pi mkT}{\hbar^2} \right)^{3/2} \frac{V}{f_{\text{tra}} N} Z \right] + \frac{y(3y-4)}{(1-y)^2} \]  

(S12)

\[ Z = \frac{1 + y + y^2 - y^3}{(1-y)^3} \]  

(S13)

\[ y = \frac{f_{\text{tra}}^{5/2}}{\Delta^{3/2}} \]  

(S14)

where \( \hbar \) is the Planck constant, \( y \) is the hard-sphere packing fraction, and \( Z \) is the compressibility. The estimation of solid translational entropy is based on the harmonic oscillator model.

\[ S_{\text{tra}}^s = k \ln Q_{\text{tra}} + \frac{1}{\beta} \left( \frac{\partial \ln Q_{\text{tra}}}{\partial T} \right)_{N,y} \]  

(S15)

\[ \beta = \frac{1}{kT} \]  

(S16)

In the harmonic oscillator model, the canonical partition function of translation \( Q_{\text{tra}} \) was expressed as,

\[ \ln Q_{\text{tra}} = \int_0^\infty g_{\text{tra}}(\nu) \ln q_{\text{HO}}(\nu) d\nu \]  

(S17)

\[ q_{\text{HO}}(\nu) = \frac{e^{-\beta \hbar \nu/2}}{1 - e^{-\beta \hbar \nu}} \]  

(S18)

\( S_{\text{rot}} \) was estimated in a similar manner as \( S_{\text{tra}} \). Since \( S_{\text{vib}} \) contains no diffusive motion, it is determined only in the harmonic oscillator framework.

**Melting point \( (T_m) \), fusion enthalpy \( (\Delta_{\text{fus}} H) \), and fusion entropy \( (\Delta_{\text{fus}} S) \) estimations.** To estimate \( T_m \), \( \Delta_{\text{fus}} H \), and \( \Delta_{\text{fus}} S \), first, Helmholtz energy difference between liquid and crystal \( (\Delta_{\text{vib}} A) \) at a certain reference temperature \( T_{\text{ref}} \) is required. \( T_{\text{ref}} \) of NaCl, \([\text{C}_2\text{mim}]\text{PF}_6\), and \([\text{C}_4\text{mim}]\text{PF}_6\) were
was derived as the sum of four simulations at various temperatures were fitted with a second-degree polynomial function. Then, equation (S27) becomes, 

\[
\Delta_r A = \Delta_1 A + \Delta_2 A + \Delta_3 A + \Delta_4 A \tag{S19}
\]

Except for \(\Delta_r A\), the Helmholtz energy difference in the PSCP cycle is expressed as,

\[
\Delta A = \int_0^1 \left\{ \frac{dU}{d\lambda} \right\}_\lambda d\lambda \tag{S20}
\]

where \(\lambda\) is the alchemical variable ranging from 0 to 1 and \(U\) is the potential energy. Starting from the “crystal” state, it is first transformed to the “weak crystal” state. In this step, both \(LJ (U_{LJ})\) and Coulombic \(U_{Coul}\) potentials are weakened, and a tether potential \((U_{tether})\) emerges.

\[
U_1 = (1 - 0.9\lambda)U_{LJ} + (1 - 0.9\lambda)^2 U_{Coul} + \lambda U_{tether} + U_{bonded} \tag{S21}
\]

\[
U_{tether} = \sum_i \sum_j a_{ij} e^{-b_{ij}r_{ij}^2} \tag{S22}
\]

The tether potential that binds atoms to lattice points has the Gaussian function form. It was applied for both Na\(^+\) and Cl\(^-\) of NaCl. For ILs, the C and N atoms of the cation and the P atom of the anion were used for \(U_{tether}\). The constant \(a\) of the cation atoms was 16.0254 kJ mol\(^{-1}\), and that of the anion atom was 14.0789 kJ mol\(^{-1}\). The value of 90 nm\(^{-2}\) was used for the constant \(b\) of every atom. \(U_{bonded}\) is the potential for intramolecular bonds, angles, dihedral angles, and improper angles, which are constant during the PSCP cycle.

In step 2, the “weak crystal” is transformed into “weak dense fluid” by removing the tether potential

\[
U_2 = 0.1U_{LJ} + 0.01U_{Coul} + (1 - \lambda)U_{tether} + U_{bonded} \tag{S23}
\]

The “weak dense fluid” is then transformed into the “weak liquid”. In this step, the cell volume is changed from that of crystal \((V_{cry})\) to liquid \((V_{liq})\) while the potential is not varied. Therefore, the Helmholtz energy difference \(\Delta_3 A\) is,

\[
\Delta_3 A = \int_{V_{cry}}^{V_{liq}} p dV \tag{S24}
\]

In step 4, intermolecular potentials are retrieved to the original one, corresponding to the transformation from the “weak liquid” to the normal “liquid” states, as

\[
U_4 = (0.1 + 0.9\lambda)U_{LJ} + (0.1 + 0.9\lambda)^2 U_{Coul} + U_{bonded} \tag{S25}
\]

The results from the PSCP cycle for NaCl, \([C_2\text{mim}]\text{PF}_6\), and \([C_4\text{mim}]\text{PF}_6\) are displayed in Figures S4–S6 and Table S6. The Gibbs energy difference at the reference temperature in the NPT ensemble was obtained from \(\Delta_{ref} A\),

\[
\Delta_{ref} G = \Delta_{ref} A + p\Delta V \tag{S26}
\]

With the \(\Delta_{ref} G\) value, it is now possible to estimate \(T_m\) where \(\Delta G = 0\) via the Gibbs-Helmholtz equation

\[
\int_{\Delta_{ref} G}^{\Delta G} \frac{dG}{T} = \int_{T_{ref}}^{T} \frac{\Delta H}{T^2} dT \tag{S27}
\]

The enthalpy differences between the crystal and liquid states obtained from the NPT MD simulations at various temperatures were fitted with a second-degree polynomial function. Then, equation (S27) becomes,

\[
\frac{\Delta G}{T} - \frac{\Delta_{ref} G}{T_{ref}} = a \left( \frac{1}{T} - \frac{1}{T_{ref}} \right) - b \ln \frac{T}{T_{ref}} - c \left( T - T_{ref} \right) \tag{S28}
\]

where \(a\), \(b\), and \(c\) are the fitting constant. With \(T_m\) value where \(\Delta G = 0\) (Figure S7) and \(\Delta_{ref} H\) at the same temperature, \(\Delta_{us} S\) is obtained based on equation (1) in the main text. Obtained \(T_m\)
Δ\text{fus}^H, and Δ\text{fus}^S are summarized in Table S7 with reported experimental and MD values. A production run of 2 ns was applied for these simulations with 0.1 ps data accumulations.

**Conformational entropy (S_{\text{confor}}) estimation.** \([\text{C}_2\text{mim}]^+\) is known to possess non-planar (n) and planar (p) conformations along the C-N-C-C dihedral angle (Figure S8A).\(^8\) By including the mirror-inverted conformation of the non-planar (n'), the cation has three conformers, which were also observed in our simulations (Figure S8B). In addition to the C-N-C-C dihedral angle, the N-C-C-C and C-C-C-C dihedral angles are present in [Cmim]^+, which produce additional three conformers each, i.e., trans (t), gauche (g), and gauche' (g') (Figure S9A).\(^8\) In total, this cation has 3 × 3 × 3 = 27 conformations. Hereafter, for example, the conformation for \([\text{C}_4\text{mim}]^+\) with non-planar (C-N-C-C), gauche (N-C-C-C), and trans (C-C-C-C) is abbreviated as ngt. Conformational analyses were performed on the cations in [C_2mim]PF_6 or [C_4mim]PF_6 via 20 ns simulations with 2 ps data accumulations in the NVT ensemble. Once a population of each conformer is estimated from MD trajectories, conformational entropy (S_{\text{confor}}) was calculated,

\[
S_{\text{confor}} = -R \sum_i p_i \ln p_i
\]

(S29)

where \(R\) is the gas constant and \(p_i\) is the population of the conformer \(i\). The results are summarized in Tables S8 and S9.

**Kinetic entropy (S_{\text{kin}}) estimation.** The production runs for 2PT were executed with the velocity Verlet algorithm for 1 ns (a simulation time of 250 ps for 1 block) with 2 fs data acquisition in the NVT ensemble. The convergence of the 2PT method is known to fast (typically ca. 20 ps),\(^2\) and we confirmed that 250 ps is long enough for \([\text{C}_4\text{mim}]\text{PF}_6\) (Figure S10). Translational, rotational, and vibrational density of states functions were obtained using the DoSPT program\(^13\). The results are displayed in Figures S11–S14, and the obtained numerical values are in Tables S10 and S11.

**Diffusion coefficient (D) estimation.** For diffusion coefficient (D) estimations, production runs of 200 ns with 0.1 ps data acquisition were performed in the NVT ensemble. The diffusion coefficients of the ions were calculated from mean square displacement (MSD) with the Einstein’s equation (Figure S15). The D values are listed in Table S12.

\[
D = \left[ \frac{1}{6t} \text{MSD} \right]_{t \to \infty}
\]

(S30)
Fig. S1. DSC traces of [C$_1$ mim]X.
Fig. S2. Optimized local minima for ion pairs of $[C_2\text{mim}]PF_6$ (left) and $[C_4\text{mim}]PF_6$ (right) in the gas phase.
Fig. S3. Schematic of the PSCP cycle.
Fig. S4. Derivatives of the potential energy per ion pair of NaCl in (A) step 1, (B) step 2, and (D) step 4 along the PSCP cycle. (C) Pressure as a function of volume for step 3.
Fig. S5. Derivatives of the potential energy per ion pair of [C$_2$ mim]PF$_6$ in (A) step 1, (B) step 2, and (D) step 3 along the PSCP cycle. (C) Pressure as a function of volume for step 3.
Fig. S6. Derivatives of the potential energy per ion pair of [C₄mim]PF₆ in (A) step 1, (B) step 2, and (D) step 3 along the PSCP cycle. (C) Pressure as a function of volume for step 3.
Fig. S7. Calculated ΔG versus temperature. (A) NaCl, (B) [C$_2$mim]PF$_6$, and (C) [C$_4$mim]PF$_6$. 
Fig. S8. (A) Structure of three conformers for [C\textsubscript{2}mim]\textsuperscript{+}. (B) Dihedral angle distribution of C-N-C-C of [C\textsubscript{2}mim]\textsuperscript{+} in [C\textsubscript{2}mim]PF\textsubscript{6} in the liquid state at 338 K.
Fig. S9. (A) Newman projection for the trans, gauche, and gauche’ conformers. Dihedral angle distributions of (B) C-N-C-C, (C) N-C-C-C, and (D) C-C-C-C of [C₄mim]+ in [C₄mim]PF₆ in the liquid state at 275 K.
Fig. S10. Kinetic entropies estimated from the 2PT method for [C₄mim]PF₆ at 275 K as a function of simulation time.
Fig. S11. Density of states functions of NaCl at 1089 K in the (A) crystal and (B) liquid states.
Fig. S12. Density of states functions of \([\text{C}_2\text{mim}]\text{PF}_6\) at 338 K in the (A–C) crystal and (D–F) liquid states.
Fig. S13. Density of states functions of [C_4 mim]PF_6 at 275 K in the (A–C) crystal and (D–F) liquid states.
Fig. S14. Absolute kinetic entropies of NaCl (1089 K), [C_2 mim]PF_6 (338 K), and [C_4 mim]PF_6 (275 K). The results in the (A) crystal and (B) liquid states were obtained from the MD simulations (Tables S10 and S11) while that in the (C) gas state was estimated by the DFT calculations (Table S5) as the sum of the entropies of the isolated ions. The same symbols are used through (A–C).
Fig. S15. Mean square displacements of the ions in (A) NaCl (1089 K), (B) [C$_2$mim]PF$_6$ (338 K), and (C) [C$_4$mim]PF$_6$ (275 K). Black lines are the linear fit from 10 ns to 30 ns.
Table S1. $T_m$, $\Delta_{fus}H$, and $\Delta_{fus}S$ data for ILs from the ILThermo database.\textsuperscript{14, 15}

| IL                                      | $T_m$ / K | $\Delta_{fus}H$ / kJ mol\textsuperscript{-1} | $\Delta_{fus}S$ / J K\textsuperscript{-1} mol\textsuperscript{-1} |
|----------------------------------------|-----------|-----------------------------------------------|---------------------------------------------------------------|
| 1-Methylimidazolium nitrate\textsuperscript{16} | 343.6     | 19.24                                         | 56.00                                                         |
| 1,3-Dimethylimidazolium methylsulfate\textsuperscript{17} | 308.9     | 16.58                                         | 53.67                                                         |
| 1,3-Dimethylimidazolium bis(trifluoromethylsulfonyl)imide\textsuperscript{18} | 299       | 24.5                                          | 81.7                                                          |
| 1-Ethyl-3-methylimidazolium chloride\textsuperscript{19} | 370.1     | 15.1                                          | 40.8                                                          |
| 1-Ethyl-3-methylimidazolium thiocyanate\textsuperscript{20} | 267       | 27.0                                          | 101                                                           |
| 1-Ethyl-3-methylimidazolium acetate\textsuperscript{21} | 370.85    | 30.2                                          | 81.4                                                          |
| 1-Ethyl-3-methylimidazolium nitrate\textsuperscript{22} | 316.4     | 17.6                                          | 55.6                                                          |
| 1-Ethyl-3-methylimidazolium bromide\textsuperscript{23} | 349.91    | 18.26                                         | 52.18                                                         |
| 1-Ethyl-3-methylimidazolium tetrafluoroborate\textsuperscript{24} | 287.6     | 9.5                                           | 33.0                                                          |
| 1-Ethyl-3-methylimidazolium tricyanomethanide\textsuperscript{22} | 274.9     | 12.6                                          | 45.8                                                          |
| 1-Ethyl-3-methylimidazolium iodide\textsuperscript{25} | 351       | 15.488                                        | 44.125                                                        |
| 1-Ethyl-3-methylimidazolium hexafluorophosphate\textsuperscript{26} | 334.2     | 17.7                                          | 53.2                                                          |
| 1-Ethyl-3-methylimidazolium tetrachloroaluminate\textsuperscript{19} | 279.6     | 13.8                                          | 49.4                                                          |
| 1-Ethyl-3-methylimidazolium 4-methylbenzenesulfonate\textsuperscript{22} | 328.2     | 20.1                                          | 61.2                                                          |
| 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide\textsuperscript{27} | 271.44    | 21.89                                         | 80.64                                                         |
| 1-Ethyl-3-methylimidazolium dimethylphosphate\textsuperscript{22} | 312.9     | 21.5                                          | 68.7                                                          |
| 1-Ethyl-3-methylimidazolium 1,1,2,2-tetrafluoroethanesulfonate\textsuperscript{28} | 317.6     | 20.2                                          | 63.6                                                          |
| 1-Ethyl-3-methylimidazolium trifluoromethanesulfonate\textsuperscript{22} | 262.6     | 11.7                                          | 44.6                                                          |
| 1-Ethyl-3-methylimidazolium bis(fluorosulfonyl)imide\textsuperscript{29} | 260       | 9.3                                           | 35.8                                                          |
| 1-Methyl-3-propylimidazolium bromide\textsuperscript{30} | 312.93    | 19.11                                         | 61.75                                                         |
| 1-Methyl-3-propylimidazolium hexafluorophosphate\textsuperscript{26} | 311.8     | 14.1                                          | 45.2                                                          |
| 1-Butyl-3-methylimidazolium chloride\textsuperscript{31} | 347.1     | 18                                            | 52                                                            |
| 1-Butyl-3-methylimidazolium nitrate\textsuperscript{32} | 309.18    | 17.991                                        | 58.19                                                         |
| 1-Butyl-3-methylimidazolium dicyanamide\textsuperscript{33} | 270.83    | 17.8                                          | 65.7                                                          |
| 1-Butyl-3-methylimidazolium bromide\textsuperscript{23} | 351.35    | 22.88                                         | 65.12                                                         |
| 1-Butyl-3-methylimidazolium trifluoroacetate\textsuperscript{34} | 296.41    | 19.14                                         | 64.59                                                         |
| 1-Butyl-3-methylimidazolium iodide\textsuperscript{30} | 291.92    | 18.99                                         | 65.05                                                         |
| 1-Butyl-3-methylimidazolium hexafluorophosphate\textsuperscript{35} | 283.5     | 19.601                                        | 69.139                                                        |
| 1-Butyl-3-methylimidazolium trifluoromethanesulfonate\textsuperscript{36} | 291.46    | 20.18                                         | 69.24                                                         |
| 1-Butyl-3-methylimidazolium tosylate\textsuperscript{37} | 343.89    | 21.573                                        | 62.732                                                        |
| 1-Butyl-3-methylimidazolium octylsulfate\textsuperscript{38} | 307.6     | 12.7                                          | 41.3                                                          |
| 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide\textsuperscript{39} | 270.35    | 23.8                                          | 88                                                            |
| 1-Butyl-3-methylimidazolium 2-methoxy-2-oxoacetate\textsuperscript{40} | 330.2     | 9                                             | 27                                                            |
| 1-Hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide\textsuperscript{41} | 272.11    | 27.825                                        | 102.256                                                       |
| 1-Methyl-3-octylimidazolium tetrafluoroborate\textsuperscript{42} | 245.81    | 15.31                                         | 62.27                                                         |
| 1-Methyl-3-octylimidazolium hexafluorophosphate\textsuperscript{43} | 272.3     | 12.9                                          | 47.4                                                          |
| 1-Methyl-3-octylimidazolium bis(trifluoromethylsulfonyl)imide\textsuperscript{27} | 263.96    | 25.18                                         | 95.39                                                         |
| 1-Methyl-3-octylimidazolium trifluoromethanesulfonate\textsuperscript{36} | 285.98    | 16.54                                         | 57.84                                                         |
| 1-Nonyl-3-methylimidazolium hexafluorophosphate\textsuperscript{26} | 293       | 16.5                                          | 56.4                                                          |
| 1-Decyl-3-methylimidazolium chloride\textsuperscript{44} | 311.2     | 30.9                                          | 99.3                                                          |
| 1-Decyl-3-methylimidazolium bromide\textsuperscript{45} | 347.58    | 20.256                                        | 58.277                                                        |
| 1-Decyl-3-methylimidazolium hexafluorophosphate\textsuperscript{26} | 307.1     | 19.4                                          | 63.3                                                          |
| 1-Decyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide\textsuperscript{46} | 277.33    | 28.67                                         | 103.38                                                        |
| 1-Decyl-3-methylimidazolium trifluoromethanesulfate\textsuperscript{47} | 296.2     | 29.82                                         | 100.68                                                        |
| 1-Dodecyl-3-methylimidazolium hexafluorophosphate\textsuperscript{26} | 326.5     | 24.5                                          | 75.2                                                          |
| 1-Dodecyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide\textsuperscript{48} | 292.4     | 36                                            | 123                                                           |
| 1-Tetradecyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide\textsuperscript{46} | 308.77    | 45.18                                         | 146.32                                                        |
| 1-Hexadecyl-3-methylimidazolium bromide\textsuperscript{45} | 337.06    | 59.1                                          | 175.3                                                         |
| 1-Hexadecyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide\textsuperscript{46} | 319.25    | 51.28                                         | 160.63                                                        |
| Name                                                                 | Formula                                                                 | MW   | % 1  | % 2   |
|----------------------------------------------------------------------|--------------------------------------------------------------------------|------|------|-------|
| 1-Methyl-3-octadecylimidazolium bis(trifluoromethylsulfonyl)imide   | C23H47N2O2S2f                                                                 | 328  | 53   | 162   |
| 1-Methyl-3-octadecylimidazolium tris(pentafluoroethyl)trifluorophosphate | C35H59N3OS4Tr                                                                  | 319  | 54   | 169   |
| 1-Methyl-3-octadecylimidazolium bis(nonfluorobutanesulfonil)imide  | C23H47N2O2S3f                                                                  | 335  | 33   | 98    |
| 1-Docosyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide    | C35H59N3OS4f                                                                 | 341  | 67   | 197   |
| 1-Isopropyl-3-methylimidazolium bis( trifluorosulfonyl)imide       | C23H47N2O2SF                                                                  | 269.2| 14.3 | 53.3   |
| 1-Isopropyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide | C23H47N2O2S2f                                                                  | 283.5| 24.2 | 85.4   |
| 1-tert-Butyl-3-methylimidazolium bis(trifluorosulfonyl)imide       | C23H47N2O2S2f                                                                  | 326.6| 17.4 | 53.2   |
| 1-tert-Butyl-3-methylimidazolium bis(pentafluoroethylsulfonil)imide | C23H47N2O2S3p                                                                  | 280.4| 22.9 | 81.7   |
| 1,3-Diethylimidazolium bis(trifluoromethylsulfonyl)imide           | C23H47N2O2S2f                                                                  | 294.3| 16.7 | 56.6   |
| 1,2-Dimethyl-3-propylimidazolium bis(trifluoromethylsulfonyl)imide | C23H47N2O2S2f                                                                  | 262.6| 20.4 | 77.7   |
| 1-Butyl-2,3-dimethylimidazolium trifluoromethanesulfonate          |                                                                  | 318  | 15   | 47    |
| 1-Butyl-2,3-dimethylimidazolium chloride                          |                                                                  | 326.57| 14.413| 44.134 |
| 1-Butyl-2,3-dimethylimidazolium bromide                            |                                                                  | 349.66| 15.613| 46.613 |
| 1-Decyl-2,3-dimethylimidazolium bromide                            |                                                                  | 341.35| 23.923| 70.083 |
| 1-Hexadecyl-2,3-dimethylimidazolium bromide                        |                                                                  | 371.7 | 50.8 | 136.7  |
| 1-Benzyl-3-methylimidazolium 1,1,2,2-tetrafluoroethanesulfonate     |                                                                  | 315.4| 23.6 | 74.8   |
| 1-Methyl-3-(2-phenylethyl)imidazolium bis(trifluoromethylsulfonyl)imide | C23H47N2O2S2f                                                                  | 310.1| 5.4  | 17.4   |
| 1-Methyl-3-(3-phenylpropyl)imidazolium hexafluorophosphate        |                                                                  | 325.1| 9.5  | 29.2   |
| 1-Methyl-3-(3-phenylpropyl)imidazolium bis(trifluoromethylsulfonyl)imide | C23H47N2O2S2f                                                                  | 321.1| 14   | 44     |
| 1-(2-Naphthylmethyl)-3-methylimidazolium bis(trifluoromethylsulfonyl)imide | C23H47N2O2S2f                                                                  | 318.6| 34.1 | 107.0  |
| 1,3-Dibenzylimidazolium bis(trifluoromethylsulfonyl)imide          |                                                                  | 314.9| 23.6 | 74.9   |
| 1,3-Bis(butoxymethyl)imidazolium tetrafluoroborate                  |                                                                  | 281.4| 8.54 | 30.35  |
| 1,3-Bis((octyloxy)methyl)imidazolium bis(trifluoromethylsulfonyl)imide | C23H47N2O2S2f                                                                  | 287.7| 34.2 | 118.9  |
| 1,3-Dihexyloxymethylimidazolium bis(trifluoromethylsulfonyl)imide |                                                                  | 256.9| 6.8  | 26.5   |
| 1,3-Bis(hexyloxymethyl)imidazolium tetrafluoroborate               |                                                                  | 273.8| 16   | 58     |
| 1,3-Bis(hexyloxymethyl)imidazolium hexafluorophosphate             |                                                                  | 309.5| 12.8 | 41.4   |
| 1,3-Dibenzyloxymethylimidazolium dicyanamide                      |                                                                  | 350.8| 60.13| 171.41 |
| 1-(3-Cyanopropyl)-3-methylimidazolium chloride                     |                                                                  | 363.5| 19.1 | 52.6   |
| 1-Butynitrile-3-methylimidazolium hexafluorophosphate              |                                                                  | 345.2| 17.5 | 50.7   |
| 1,3-Bis(decyloxymethyl)imidazolium bis(trifluoromethylsulfonyl)imide | C23H47N2O2S2f                                                                  | 303.1| 79.36| 261.83 |
| 1-(2-Methoxyethyl)-3-ethylimidazolium perthenate                   |                                                                  | 211.82| 14.382| 67.93  |
| 1-(Methoxymethyl)-3-methylimidazolium bis(trifluoromethylsulfonyl)imide | C23H47N2O2S2f                                                                  | 273.0| 22   | 81     |
| 1-(2-Ethoxyethyl)-3-methylimidazolium bis(trifluoromethylsulfonyl)imide | C23H47N2O2S2f                                                                  | 265.6| 14.1 | 53.1   |

**Pyridinium**

| Name                                                                 | Formula                                                                 | MW   | % 1  | % 2   |
|----------------------------------------------------------------------|--------------------------------------------------------------------------|------|------|-------|
| 1-Ethylpyridinium bis(trifluoromethylsulfonyl)imide                   | C23H47N2O2S2f                                                                   | 303.6| 18.9 | 62.3   |
| 1-Ethylpyridinium trifluoromethanesulfonate                           |                                                                  | 300.4| 11.5 | 38.3   |
| 1-Propylpyridinium hexafluorophosphate                                 |                                                                  | 370.99| 6.83 | 18.41  |
| 1-Propylpyridinium bromide                                            |                                                                  | 342.83| 10.97 | 32.00  |
| 1-Butylpyridinium bis(trifluoromethylsulfonyl)imide                   | C23H47N2O2S2f                                                                   | 299.1| 27.9 | 93.3   |
| 1-Butylpyridinium trifluoromethanesulfonate                           |                                                                  | 301.4| 12   | 40     |
| 1-Butylpyridinium tetrafluoroborate                                   |                                                                  | 272.5| 10.5 | 38.5   |
| 1-Pentylpyridinium hexafluorophosphate                                |                                                                  | 328.14| 5.9  | 17.98  |
| 1-Pentylpyridinium bis(trifluoromethylsulfonyl)imide                  | C23H47N2O2S2f                                                                   | 272.8| 22.8 | 83.6   |
| 1-Methyl-3-propylpyridinium hexafluorophosphate                       |                                                                  | 311.2| 15   | 48     |
| 1-Butyl-3-methylpyridinium 4-methylbenzenesulfonate                   |                                                                  | 323.7| 11.34| 35.03  |
| Compound                                                                 | MW  | LogP  | Tg     |
|-------------------------------------------------------------------------|-----|-------|--------|
| 1-Butyl-4-methylpyridinium tosylate                                       | 324.86 | 14.33 | 44.11  |
| 1-Butyl-4-methylpyridinium bis(trifluoromethylsulfonyl)imide             | 291.4 | 21.94 | 75.29  |
| 1-Hexyl-3-methylpyridinium chloride                                      | 355.1 | 19.7  | 55.5   |
| 1-Hexyl-3-methylpyridinium trifluoromethanesulfonate                     | 337.76 | 41.968 | 124.254 |
| 1-Hexyl-3-methylpyridinium 4-methylbenzenesulfonate                      | 329.3 | 10.094 | 30.653 |
| 1-Octyl-3-methylpyridinium chloride                                      | 352.3 | 14.9  | 42.3   |
| 1-Decyl-3-methylpyridinium chloride                                      | 352.5 | 14.4  | 40.9   |
| 1-Dodecyl-3-methylpyridinium chloride                                    | 360.8 | 37.1  | 102.8  |
| 1-Dodecyl-4-methylpyridinium chloride                                    | 323.9 | 44.4  | 137.1  |
| 1-Tetradecyl-3-methylpyridinium chloride                                 | 366.8 | 42.7  | 116.4  |
| 1-Butyl-3,5-dimethylpyridinium thiocyanate                               | 286.1 | 16.04 | 56.06  |
| 1-Butyl-3,5-dimethylpyridinium dicyanamide                               | 272.1 | 3.85  | 14.15  |
| 1-Butyl-3,5-dimethylpyridinium trifluoromethanesulfonate                 | 364.1 | 28.5  | 78.3   |
| N-Butyronitrile pyridinium chloride                                      | 342.4 | 13.9  | 40.6   |
| N-Butyronitrile pyridinium tetrafluoroborate                             | 342.4 | 12.4  | 36.2   |
| 3,5-Dimethyl-1-octylpyridinium thiocyanate                               | 235.1 | 6.39  | 27.18  |
| 3,5-Dimethyl-1-octylpyridinium tetrafluoroborate                         | 329.1 | 28.07 | 85.29  |
| 3,5-Dimethyl-1-octylpyridinium iodide                                    | 355.1 | 25.45 | 71.67  |
| 3,5-Dimethyl-1-octylpyridinium trifluoromethanesulfonate                 | 349.1 | 24.81 | 71.07  |
| 2,3,5-Trimethyl-1-octylpyridinium thiocyanate                            | 293.1 | 14.66 | 50.02  |
| 1-Butyl-2,3,5-trimethylpyridinium trifluoromethanesulfonate              | 290.1 | 16.88 | 58.19  |
| 1-Butyl-2,3,5-trimethylpyridinium tricyanomethanide                      | 347.1 | 20.97 | 60.41  |
| 5-Ethyl-2-methyl-1-octylpyridinium iodide                                 | 360.1 | 30.87 | 85.73  |
| 1-Hexyl-4-cyanopyridinium bis(trifluoromethylsulfonyl)imide               | 280.2 | 18.83 | 67.20  |
| 3-Cyano-1-octylpyridinium bis(trifluoromethylsulfonyl)imide               | 287.9 | 13.71 | 47.62  |
| 4-(1-Hexadecylheptadecyl)-1-methyl-pyridinium chloride                    | 337.1 | 56.9  | 168.8  |
| 1-Butyl-4-cyanopyridinium tricyanomethanide                              | 361.8 | 29.7  | 82.1   |
| 1-Decyloxymethyl-3-amido-pyridinium tetrafluoroborate                    | 361.9 | 51.26 | 141.64 |
| 1-(3-Cyanopropyl)pyridinium tricyanomethanide                            | 305.2 | 21.6  | 70.8   |
| 1-(Methoxymethyl)pyridinium bis(trifluoromethylsulfonyl)imide             | 268.8 | 16.7  | 62.1   |
| 1-(2-Ethoxyethyl)pyridinium bis(trifluoromethylsulfonyl)imide             | 259.2 | 19.5  | 75.2   |
| 1-(2-Propanoyl)pyridinium bis(trifluoromethylsulfonyl)imide               | 256.4 | 3.3   | 12.9   |
| **Pyrrolidinium**                                                        |     |       |        |
| 1,1-Dimethylpyrrolidinium thiocyanate                                    | 368  | 9.97  | 27.09  |
| 1-Ethyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide          | 363.1 | 9.1   | 25.1   |
| 1-Methyl-1-propylpyrrolidinium thiocyanate                               | 280  | 23.3  | 83.3   |
| 1-Methyl-1-propylpyrrolidinium trifluoromethanesulfonate                 | 350.7 | 37.2  | 106.1  |
| 1-Methyl-1-propylpyrrolidinium bis(trifluoromethylsulfonyl)imide         | 285.1 | 12.3  | 43.1   |
| 1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide          | 265.73 | 21.9 | 82.4   |
| 1-Butyl-1-methylpyrrolidinium tetracyanoborate                            | 295.3 | 35.6  | 120.6  |
| 1-Butyl-1-methylpyrrolidinium tricyanomethanide                          | 264.4 | 9.43  | 35.67  |
| 1-Butyl-1-methylpyrrolidinium trifluoromethanesulfonate                  | 272.9 | 12.07 | 44.23  |
| 1-Butyl-1-methylpyrrolidinium 1,1,2,2-tetrafluoroethanesulfonate          | 318.5 | 10.9  | 34.2   |
| 1-Butyl-1-methylpyrrolidinium perfluorobutanesulfonate                   | 364  | 8.78  | 24.12  |
| 1-Pentyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide         | 281.1 | 22.5  | 80.0   |
| 1-Decyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide          | 283  | 8     | 28     |
| 1-Methyl-1-octadecylpyrrolidinium bis(trifluoromethylsulfonyl)imide      | 345  | 32.3  | 94     |
| 1-Isobutyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide       | 272.9 | 13.1  | 48     |
| 1-(2-Methoxyethyl)-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate | 273.3 | 14.3  | 52.3   |
| **Piperidinium**                                                         |     |       |        |
| 1-Ethyl-1-methylpiperidinium bis(trifluoromethylsulfonyl)imide            | 358.04 | 16.61 | 46.39  |
| 1-Methyl-1-propylpiperidinium bis(trifluoromethylsulfonyl)imide          | 285.7 | 25.6  | 89.6   |
| 1-Butyl-1-methylpiperidinium trifluoromethanesulfonate                   | 309  | 23    | 75     |
| Ammonium                                      | Mol Wt | Log D  | octanol     |
|-----------------------------------------------|--------|--------|-------------|
| Methanammonium formate<sup>93</sup>           | 286.1  | 6.629  | 23.170      |
| Trimethylammonium bis(trifluoromethylsulfonyl)imide<sup>94</sup> | 357.4  | 17.36  | 48.58       |
| Ethylammonium formate<sup>93</sup>            | 258.1  | 5.558  | 21.534      |
| Ethylammonium acetate<sup>93</sup>            | 360.1  | 21.343 | 59.270      |
| Ethylammonium nitrate<sup>95</sup>            | 285    | 13.2   | 46          |
| Ethylammonium hydrogensulfate<sup>93</sup>    | 313.1  | 12.598 | 40.236      |
| N,N-Diethyl-N-methylammonium methanesulfonate<sup>92</sup> | 312    | 14     | 47          |
| N,N-Diethyl-N-methylammonium trifluoromethanesulfonate<sup>92</sup> | 268    | 17     | 63          |
| Triethylammonium hydrogensulfate<sup>96</sup> | 355.57 | 8.22   | 23.12       |
| Propylammonium formate<sup>93</sup>           | 323.1  | 17.242 | 53.364      |
| N,N-Dimethyl-N-propylammonium trifluoromethanesulfonate<sup>97</sup> | 293.1  | 20     | 68          |
| N-Ethyl-N,N-dimethyl-N-propylammonium bis(trifluoromethylsulfonyl)imide<sup>80</sup> | 263.1  | 21.6   | 82.1        |
| N,N-Diethyl-N-propylammonium trifluoromethanesulfonate<sup>97</sup> | 259    | 21     | 81          |
| N,N-Diethyl-N-methyl-N-propylammonium trifluoro(perfluoroethyl)borate<sup>98</sup> | 327    | 9.58   | 29.3        |
| N,N-Diethyl-N-methyl-N-propylammonium trifluoro(perfluoropropyl)borate<sup>96</sup> | 330    | 5.18   | 15.7        |
| N,N-Diethyl-N-methyl-N-propylammonium trifluoro(perfluorobutyl)borate<sup>98</sup> | 327    | 5.85   | 17.9        |
| N,N-Diethyl-N-methyl-N-propylammonium bis(trifluoromethylsulfonyl)imide<sup>98</sup> | 287    | 4.53   | 15.8        |
| N-Methyl-N,N-dipropylammonium trifluoromethanesulfonate<sup>97</sup> | 290.1  | 14     | 48          |
| Butylammonium formate<sup>93</sup>            | 275.1  | 7.984  | 29.022      |
| N-Butyl-N-trimethylammonium bis(trifluoromethylsulfonyl)imide<sup>33</sup> | 290.23 | 11.4   | 39.3        |
| N-Butyl-N-ethyl-N,N-dimethylammonium ethylsulfate<sup>99</sup> | 307    | 11.7   | 38.1        |
| N-Butyl-N,N-diethyl-N-methylammonium trifluoro(perfluoroethyl)borate<sup>98</sup> | 288    | 9.42   | 32.7        |
| N-Butyl-N,N-diethyl-N-methylammonium trifluoro(perfluoropropyl)borate<sup>98</sup> | 323    | 13.3   | 41.1        |
| N-Butyl-N,N-diethyl-N-methylammonium trifluoro(perfluorobutyl)borate<sup>98</sup> | 333    | 9.86   | 29.6        |
| N-Butyl-N,N-diethyl-N-methylammonium bis(trifluoromethylsulfonyl)imide<sup>98</sup> | 282    | 24.7   | 87.6        |
| N-Butyl-N,N-dimethyl-N-propylammonium bis(trifluoromethylsulfonyl)imide<sup>90</sup> | 293    | 16     | 53          |
| Tetrabutylammonium chloride<sup>100</sup>     | 314.1  | 20.502 | 65.272      |
| Pentylammonium formate<sup>93</sup>           | 285.1  | 7.858  | 27.562      |
| Tetrapentylammonium thiocyanate<sup>100</sup> | 322.65 | 19.665 | 60.948      |
| Tetrahexylammonium nitrate<sup>100</sup>      | 345.15 | 17.573 | 50.914      |
| Tetrahexylammonium tetrafluoroborate<sup>100</sup> | 367    | 19.246 | 52.420      |
| N-Heptyl-N,N-triheptylammonium nitrate<sup>100</sup> | 345    | 33.5   | 97.1        |
| N-Heptyl-N,N-triheptylammonium iodide<sup>100</sup> | 371    | 20.502 | 55.239      |
| N,N-Diheptyl-N,N-dihexylammonium iodide<sup>100</sup> | 373    | 26.778 | 71.762      |
| N,N,N-Triheptyl-N-heptanumammonium bromide<sup>100</sup> | 369    | 36     | 98          |
| Tricoctylpropylammonium bromide<sup>100</sup> | 351    | 44.4   | 126.4       |
| Tetraoctylammonium oleate<sup>40</sup>        | 252.4  | 19.4   | 76.9        |
| N-Decyl-N,N,N-triethylammonium bis(trifluoromethylsulfonyl)imide<sup>101</sup> | 264    | 19.21  | 72.76       |
| N,N-Didecyl-N,N-dimethylammonium nitrate<sup>102</sup> | 304.8  | 9.88   | 32.41       |
| N,Dodecyl-N,N,N-triethylammonium bis(trifluoromethylsulfonyl)imide<sup>101</sup> | 279.02 | 19.82  | 71.04       |
| N,N,N-Triethyl-N-tetradecylammonium bis(trifluoromethylsulfonyl)imide<sup>101</sup> | 295.6  | 33.58  | 119.29      |
| Ethanolammonium nitrate<sup>93</sup>          | 324.1  | 12.41  | 38.29       |
| Chemical Name                                                                 | Molecular Weight | % H₂O | % C | % N |
|------------------------------------------------------------------------------|------------------|-------|----|-----|
| Ethanolammonium methylsulfate                                               | 372.1            | 26.67 | 71.67 |
| Ethanolammonium tetrafluoroborate                                           | 306.76           | 8.61  | 28.08 |
| N-(2-Hydroxyethyl)-N,N,N-trimethylammonium butanesulfonate                  | 324              | 25    | 77   |
| Choline tosylate                                                            | 346              | 19.1  | 51   |
| N-Ethyl-N-(2-hydroxyethyl)-N,N-dimethylammonium dicyanamide                 | 282.7            | 8.6   | 30.4 |
| N-Ethyl-N-(2-hydroxyethyl)-N,N-dimethylammonium methanesulfonate            | 317              | 20.06 | 63.28 |
| N-Ethyl-N-(2-hydroxyethyl)-N,N-dimethylammonium hexafluorophosphate         | 272              | 10.6  | 39.0 |
| N-Ethyl-N-(2-hydroxyethyl)-N,N-dimethylammonium butanesulfonate             | 293              | 23.8  | 81.2 |
| N-Ethyl-N-(2-hydroxyethyl)-N,N-dimethylammonium octanesulfonate             | 320              | 29.9  | 93.4 |
| N-(2-Hydroxyethyl)-N,N-dimethyl-N-propylammonium bromide                    | 372.6            | 4.12  | 11.06 |
| N-(2-Hydroxyethyl)-N,N-dimethyl-N-undecyloxymethylammonium dicyanamide     | 283.5            | 7.15  | 25.22 |
| N-Hexyl-N-(2-hydroxyethyl)-N,N-dimethylammonium bromide                     | 355.3            | 3.78  | 10.64 |
| Diethanolammonium tetrafluoroborate                                         | 303.84           | 7.26  | 23.89 |
| Tris(2-hydroxyethyl)ammonium tetrafluoroborate                             | 345.26           | 15.449| 44.746|
| 2-Methylpropylammonium formate                                              | 299.1            | 6.196 | 20.715|
| 3-Methylbutylammonium formate                                               | 320.1            | 12.52 | 39.11 |
| 2-Methylbutylammonium formate                                               | 272.1            | 6.926 | 25.454|
| (2-Decanoyloxyethyl)dimethylpentyloxymethylammonium trifluoroacetate       | 279.8            | 7.83  | 27.98 |
| Choline bis(trifluoromethylsulfonyl)imid                                   | 295.2            | 4.68  | 15.85 |
| 2-Methoxyethyl-N,N,N-trimethylammonium tetrafluoroborate                    | 327              | 15.0  | 45.8 |
| 2-Methoxyethyl-N,N,N-trimethylammonium trifluoro(trifluoromethyl)borate     | 350              | 11.7  | 33.3 |
| 2-Methoxyethyl-N,N,N-trimethylammonium trifluoro(perfluoroethyl)borate      | 303              | 11.6  | 38.4 |
| 2-Methoxyethyl-N,N,N-trimethylammonium trifluoro(perfluoropropyl)borate     | 296              | 13.6  | 45.9 |
| 2-Methoxyethyl-N,N,N-trimethylammonium trifluoro(perfluorobutyl)borate      | 323              | 17.6  | 54.4 |
| 2-Methoxyethyl-N,N,N-trimethylammonium bis(trifluoromethylsulfonyl)imid     | 310              | 26.5  | 85.6 |
| N-Ethyl-2-methoxyethyl-N,N-dimethylammonium trifluoro(trifluoromethyl)borate| 281              | 8.1   | 28.8 |
| N-Ethyl-2-methoxyethyl-N,N-dimethylammonium trifluoro(perfluoroethyl)borate | 277              | 15.2  | 55.0 |
| N-Ethyl-2-methoxyethyl-N,N-dimethylammonium trifluoro(perfluoropropyl)borate| 240              | 13.9  | 57.9 |
| N-Ethyl-2-methoxyethyl-N,N-dimethylammonium trifluoro(perfluorobutyl)borate | 245              | 14.7  | 60.2 |
| N,N-Diethyl-2-methoxy-N-methylmethan-1-amine trifluoroacetoborate           | 281              | 17.1  | 61.0 |
| N,N-Diethyl-2-methoxyethyl-N-methylammonium trifluoro(trifluoromethyl)borate| 251              | 7.5   | 29.9 |
| N,N,N-Triethyl-2-methoxyethylammonium trifluoro(trifluoromethyl)borate      | 283              | 17.2  | 60.7 |
| N,N,N-Triethyl-2-methoxyethylammonium trifluoro(perfluoroethyl)borate       | 276              | 24.4  | 88.4 |
| N,N,N-Triethyl-2-methoxyethylammonium trifluoro(perfluoropropyl)borate      | 279              | 8.6   | 30.7 |
| N,N,N-Triethyl-2-methoxyethylammonium trifluoro(perfluorobutyl)borate       | 284              | 7.4   | 26.1 |
| N,N,N-Triethyl-2-methoxyethylammonium tetrafluoroborate                    | 329              | 18.8  | 57.0 |
| N,N,N-Triethyl-2-methoxyethylammonium                                      | 293              | 23.8  | 81.3 |
| Compound                                                                 | Molecular Weight | pKa | log D  |
|-------------------------------------------------------------------------|------------------|-----|--------|
| bis(trifluoromethylsulfonyl)imide                                       | 98               |     |        |
| N,N-Diallyl-N-methylammonium trifluoromethanesulfonate                   | 254              | 11  | 43     |
| N-Allyl-N,N-dimethylammonium trifluoromethanesulfonate                   | 289              | 21  | 73     |
| N-Allyl-N,N-diethylammonium trifluoromethanesulfonate                    | 259              | 21  | 81     |
| N-Butyronitrile-N,N,N-trimethylammonium tetafluoroborate                 | 334.1            | 12.3| 36.8   |
| N-Butyronitrile-N,N,N-trimethylammonium bis(trifluoromethylsulfonyl)imide | 331.3            | 20.2| 61.0   |
| N,N-Dimethyl-N-isopropyl-N-propylammonium bis(trifluoromethylsulfonyl)imide | 290              | 14  | 48     |
| N-Butyl-N,N-dimethyl-N-isopropylammonium bis(trifluoromethylsulfonyl)imide   | 283              | 10  | 35     |
| N-Decyl-N-isopropyl-N,N-dimethylammonium bis(trifluoromethylsulfonyl)imide | 270              | 26  | 96     |
| Phosphonium                                                             | 94               |     |        |
| Tetrabutylphosphonium methanesulfonate                                   | 107              | 335.35| 11.105| 33.115 |
| Tetrabutylphosphonium tris(pentafluoroethyl)trifluorophosphate          | 52               | 347  | 7.8   | 22.5   |
| Tetraoctylphosphonium bis(trifluoromethylsulfonyl)imide                  | 108              | 284.3| 45.43 | 159.80 |
| Other                                                                   | 109              | 334.22| 15     | 45     |
| N-Octylbenzothiazolium hexafluorophosphate                               | 109              | 359.3| 20.1  | 55.9   |
| 3-Heptylbenzothiazolium hexafluorophosphate                              | 109              | 358.79| 23.5  | 65.5   |
| N-Hexylbenzothiazolium hexafluorophosphate                               | 110              | 358  | 26.1  | 72.9   |
| 1,5-Diamino-4-methyltetrazolium dinitramide                              | 111              | 329.62| 44.4  | 133.91 |
| 1-Butylquinolinium bis(trifluoromethylsulfonyl)imide                     | 112              | 321  | 46.13 | 143.71 |
| 2-Butylisoquinolinium bis(trifluoromethylsulfonyl)imide                  | 113              | 327.2| 58.64 | 179.22 |
| 1-Hexylisoquinolinium bis(trifluoromethylsulfonyl)imide                  | 114              | 317.2| 63.54 | 200.32 |
| 1-Octylquinolinium bis(trifluoromethylsulfonyl)imide                     | 115              | 321.3| 62.91 | 195.80 |
| Trimethylsulfonium bis(trifluoromethylsulfonyl)imide                     | 116              | 357.4| 53    | 148    |
| Diethylmethysulfonium bis(trifluoromethylsulfonyl)imide                  | 117              | 256.5| 12.5  | 48.7   |
| Hexyltrimethylferrocenium tetracyanoethylene                              | 118              | 262.8| 6.98  | 26.56  |
| Butyloctamethylferrocenium bis(trifluoromethylsulfonyl)imide             | 119              | 354.1| 39    | 110    |
| Hexyloctamethylferrocenium bis(trifluoromethylsulfonyl)imide             | 120              | 307.6| 26.54 | 86.3   |
| 1-Hexyl-1,4-diaza[2.2.2]bicyclooctanion bis(trifluoromethylsulfonyl)imide | 121              | 300.9| 25.45 | 84.6   |
| 4-(3-Cyanopropyl)-4-methylmorpholinium tricyanomethanide                  | 122              | 309  | 5.3   | 17.0   |
| Tetramethylguanidinium nitrate                                           | 123              | 368.6| 19.84 | 53.83  |
| Pyrimethanil laurate                                                     | 124              | 321.52| 67.245| 209.28 |
| N-Benzyl-N-dimethyl-Ntetradecylammonium vannilliate                      | 125              | 320.5| 35.59 | 111.05 |
| Lead dibutanoate                                                        | 126              | 346.5| 14.7  | 42.4   |
Table S2. $T_m$, $\Delta_{\text{fus}}H$, and $\Delta_{\text{fus}}S$ data for alkali halide.\textsuperscript{123}

| Alkali halide | $T_m$ / K | $\Delta_{\text{fus}}H$ / kJ mol\textsuperscript{-1} | $\Delta_{\text{fus}}S$ / J K\textsuperscript{-1} mol\textsuperscript{-1} |
|--------------|-----------|---------------------------------|---------------------|
| LiF          | 1121      | 27.1                            | 24.1                |
| LiCl         | 883       | 19.9                            | 22.6                |
| LiBr         | 823       | 17.7                            | 21.5                |
| LiI          | 742       | 14.6                            | 19.7                |
| NaF          | 1268      | 33.6                            | 25.9                |
| NaCl         | 1073      | 28.0                            | 26.1                |
| NaBr         | 1020      | 26.1                            | 25.6                |
| NaI          | 933       | 23.6                            | 25.3                |
| KF           | 1131      | 28.2                            | 25.0                |
| KCl          | 1043      | 26.5                            | 25.4                |
| KBr          | 1007      | 25.5                            | 25.4                |
| KI           | 954       | 24.0                            | 25.2                |
| RbF          | 1068      | 25.7                            | 24.1                |
| RbCl         | 995       | 23.7                            | 23.8                |
| RbBr         | 965       | 23.3                            | 24.1                |
| RbI          | 920       | 22.0                            | 24.0                |
| CsF          | 986       | 21.7                            | 22.3                |
| CsCl         | 918       | 20.3                            | 22.0                |
| CsBr         | 909       | 23.6                            | 25.9                |
| CsI          | 899       | 23.6                            | 26.2                |
Table S3. $T_m$, $\Delta_{fus}H$, and $\Delta_{fus}S$ data for [C$_1$mim]X.$^a$

| IL            | $T_m$ / K | $\Delta_{fus}H$ / kJ mol$^{-1}$ | $\Delta_{fus}S$ / J K$^{-1}$ mol$^{-1}$ |
|---------------|-----------|---------------------------------|------------------------------------------|
| [C$_1$mim]I   | 361.4     | 12.3                            | 34.1                                     |
| [C$_1$mim]NO$_3$ | 337.2     | 19.8                            | 58.8                                     |
| [C$_1$mim]CH$_3$CO$_2$ | 308.7     | 14.2                            | 46.0                                     |
| [C$_1$mim]CF$_3$CO$_2$ | 326.7     | 19.0                            | 58.1                                     |
| [C$_1$mim]CH$_3$SO$_3$ | 367.4     | 23.1                            | 62.9                                     |
| [C$_1$mim]CF$_3$SO$_3$ | 310.5     | 18.5                            | 59.7                                     |
| [C$_1$mim][OTs] | 365.2     | 24.6                            | 67.4                                     |
| [C$_1$mim]SCN  | 295.2     | 15.7                            | 53.2                                     |
| [C$_1$mim]N(CN)$_2$ | 306.4     | 15.4                            | 50.3                                     |
| [C$_1$mim]C(CN)$_3$ | 322.6     | 21.7                            | 67.4                                     |
| [C$_1$mim]PF$_6$ | 364.3     | 17.3                            | 47.6                                     |
| [C$_1$mim]CH$_3$SO$_4$ | 308.9     | 16.58                           | 53.67                                    |

$^a$Melting point ($T_m$) was taken from the onset temperature from the DSC traces. Standard uncertainties are $u(T_m) = 0.8$ K; $u(\Delta_{fus}H) = 0.4$ kJ mol$^{-1}$; $u(\Delta_{fus}S) = 1.2$ J K$^{-1}$ mol$^{-1}$. $^b$The data is not contained in ILThermo. $^c$The data is contained in ILThermo as listed in Table S1.
**Table S4.** Solid-solid phase transition temperature ($T_{s-s}$), enthalpy change (Δ$_{s-s}$H), and entropy change (Δ$_{s-s}$S) during heating for [C$_{1}$mim]X. A slight exothermic peak in [C$_{1}$mim]SCN (Figure S1H) is omitted because phase transitions do not occur exothermically during heating.

| IL          | $T_{s-s}$ / K | Δ$_{s-s}$H / kJ mol$^{-1}$ | Δ$_{s-s}$S / J K$^{-1}$ mol$^{-1}$ |
|-------------|---------------|----------------------------|-----------------------------------|
| [C$_{1}$mim]NO$_{3}$ | 274.1         | 0.5                        | 1.9                               |
| [C$_{1}$mim][OTs] | 325.3         | 2.0                        | 6.2                               |
| [C$_{1}$mim]N(CN)$_{2}$ | 252.3         | 1.0                        | 4.0                               |
| [C$_{1}$mim]N(CN)$_{2}$ | 265.2         | 2.3                        | 8.7                               |
Table S5. Calculated gas-phase entropies (J K\(^{-1}\) mol\(^{-1}\)) at 1 bar for NaCl and the ILs.

| Ion/ion pair | \(S_{\text{tra}}\) | \(S_{\text{rot}}\) | \(S_{\text{vib}}\) | Total |
|--------------|-----------------|-----------------|-----------------|------|
| Single ion   |                 |                 |                 |      |
| Na\(^+\)     | 147.8           | 0.0             | 0.0             | 147.8|
| Cl\(^-\)     | 153.1           | 0.0             | 0.0             | 153.1|
| [C\(_2\)mim]\(^+\) | 167.5          | 117.8           | 93.8            | 379.1|
| [C\(_4\)mim]\(^+\) | 170.3          | 126.2           | 148.0           | 444.4|
| PF\(_6\)\(^-\) | 170.8           | 88.6            | 45.3            | 304.7|
| Ion pair     |                 |                 |                 |      |
| NaCl         | 159.4           | 65.5            | 4.9             | 229.7|
| [C\(_2\)mim]PF\(_6\) | 177.9         | 134.9           | 234.2           | 547.0|
| [C\(_4\)mim]PF\(_6\) | 179.2          | 139.0           | 286.2           | 604.4|
| Melting point\(^a\) |                 |                 |                 |      |
| Single ion   |                 |                 |                 |      |
| Na\(^+\)     | 174.8           | 0.0             | 0.0             | 174.8|
| Cl\(^-\)     | 180.0           | 0.0             | 0.0             | 180.0|
| [C\(_2\)mim]\(^+\) | 170.1          | 119.4           | 107.1           | 396.6|
| PF\(_6\)\(^-\) | 173.4           | 90.1            | 55.2            | 318.7|
| [C\(_4\)mim]\(^+\) | 168.6          | 125.1           | 135.2           | 428.9|
|PF\(_6\)\(^-\) | 169.1           | 87.5            | 39.5            | 296.1|
| Ion pair     |                 |                 |                 |      |
| NaCl         | 186.3           | 76.3            | 14.8            | 277.4|
| [C\(_2\)mim]PF\(_6\) | 180.5          | 136.5           | 263.8           | 580.8|
| [C\(_4\)mim]PF\(_6\) | 177.5          | 138.0           | 265.6           | 581.1|

\(^a\)Estimated from the MD simulations in this work (NaCl: 1089K, [C\(_2\)mim]PF\(_6\): 338 K, and [C\(_4\)mim]PF\(_6\): 275 K).
Table S6. Results from the PSCP cycle. All units are in kJ mol\(^{-1}\). Reference temperatures of NaCl, \([\text{C}_2\text{mim}]\text{PF}_6\), and \([\text{C}_4\text{mim}]\text{PF}_6\) were 1100 K, 380 K, and 340 K, respectively.

|      | \(\Delta_1A\)  | \(\Delta_2A\)  | \(\Delta_3A\)  | \(\Delta_4A\)  | \(p\Delta V\) | \(\Delta_{\text{up}}G\)  |
|------|----------------|----------------|----------------|----------------|---------------|----------------|
| NaCl | 574.75 ± 0.02 | 109.45 ± 0.01 | -13.06 ± 0.00 | -671.42 ± 0.01 | 0.0009        | -0.29 ± 0.02   |
| \([\text{C}_2\text{mim}]\text{PF}_6\) | 134.55 ± 0.01 | 85.83 ± 0.02  | -5.93 ± 0.00  | -216.79 ± 0.02 | 0.0015        | -2.33 ± 0.04   |
| \([\text{C}_4\text{mim}]\text{PF}_6\) | 144.61 ± 0.03 | 117.83 ± 0.02 | -7.25 ± 0.00  | -259.59 ± 0.02 | 0.0018        | -4.40 ± 0.03   |
Table S7. Calculated $T_m$, $\Delta_{fus} H$, and $\Delta_{fus} S$ values of NaCl and the ILs. The reported experimental and MD values are also shown.

| Salt      | MD (This work) | Exp.       | MD (reported) |
|-----------|----------------|------------|---------------|
|           | $T_m$ / K      |            |               |
| NaCl      | 1088.8 ± 0.9   | 1073$^{123}$ | 1082$^{125}$  |
| $[C_2\text{mim}]PF_6$ | 337.7 ± 0.6    | 332.8$^{126}$, 334.1$^{127}$, 334.2$^{128}$ | 330$^{5,6}$, 330$^7$, 355$^4$ |
| $[C_4\text{mim}]PF_6$ | 275.4 ± 0.4    | 283.5$^{135}$, 280.03$^{129}$, 281.83$^{130}$, 282.3$^{43}$ | 284$^{4,6}$, 284$^7$ |
|           | $\Delta_{fus} H$ / kJ mol$^{-1}$ |            |               |
| NaCl      | 28.13 ± 0.01   | 28.0$^{123}$ | 28.1$^{125}$  |
| $[C_2\text{mim}]PF_6$ | 18.17 ± 0.05   | 17.86$^{126}$, 17.99$^{127}$, 17.7$^{128}$ | 17.7$^{5,6}$, 17.32$^7$, 19.3$^4$ |
| $[C_4\text{mim}]PF_6$ | 17.95 ± 0.13   | 19.60$^{135}$, 19.91$^{129}$, 20.67$^{130}$, 20.9$^{43}$ | 18.83$^{5,6}$, 17.95$^7$ |
|           | $\Delta_{fus} S$ / J K$^{-1}$ mol$^{-1}$ |            |               |
| NaCl      | 25.83 ± 0.02   | 26.1$^{123}$ | 25.9$^{125}$  |
| $[C_2\text{mim}]PF_6$ | 53.81 ± 0.17   | 53.67$^{126}$, 53.85$^{127}$, 53.2$^{128}$ | 53.64$^{5,6}$, 52.51$^7$, 51.6$^4$ |
| $[C_4\text{mim}]PF_6$ | 65.16 ± 0.37   | 69.14$^{135}$, 71.10$^{129}$, 73.34$^{130}$, 73.5$^{43}$ | 66.32$^{5,6}$, 63.22$^7$ |
Table S8. Populations of conformations and $S_{\text{confor}}$ for $[\text{C}_2\text{mim}]\text{PF}_6$ at 338 K.

|                  | Crystal   | Liquid    |
|------------------|-----------|-----------|
| $p$              | 0.010 ± 0.000 | 0.109 ± 0.000 |
| $n$              | 0.973 ± 0.001 | 0.445 ± 0.002 |
| $n'$             | 0.017 ± 0.001 | 0.446 ± 0.002 |
| $S_{\text{confor}} / \text{J K}^{-1} \text{ mol}^{-1}$ | 1.17 ± 0.02 | 8.00 ± 0.00 |
Table S9. Populations of conformations and $S_{\text{confor}}$ for [C$_4$ mim]PF$_6$ at 275 K

|       | Crystal | Liquid   |
|-------|---------|----------|
| ptt   | 0       | 0.022 ± 0.001 |
| ptg   | 0       | 0.008 ± 0.000 |
| ptg'  | 0       | 0.007 ± 0.000 |
| ptg   | 0       | 0.003 ± 0.001 |
| pgg   | 0       | 0.001 ± 0.000 |
| pgg'  | 0       | 0.000 ± 0.000 |
| pg't  | 0       | 0.003 ± 0.000 |
| pg'g  | 0       | 0.000 ± 0.000 |
| pg'g' | 0       | 0.001 ± 0.000 |
| ntt   | 0.015 ± 0.001 | 0.188 ± 0.006 |
| ntt   | 0.000 ± 0.000 | 0.069 ± 0.003 |
| ntt   | 0.000 ± 0.000 | 0.056 ± 0.002 |
| ntt   | 0.094 ± 0.009 | 0.054 ± 0.004 |
| ntt   | 0.001 ± 0.001 | 0.019 ± 0.001 |
| ntt   | 0.000 ± 0.000 | 0.002 ± 0.000 |
| ntt   | 0.888 ± 0.010 | 0.061 ± 0.004 |
| ntt   | 0.000 ± 0.000 | 0.002 ± 0.000 |
| ntt   | 0.001 ± 0.000 | 0.026 ± 0.002 |
| ntt   | 0.000 ± 0.000 | 0.186 ± 0.005 |
| ntt   | 0.000 ± 0.000 | 0.061 ± 0.003 |
| ntt   | 0.000 ± 0.000 | 0.072 ± 0.004 |
| ntt   | 0.000 ± 0.000 | 0.056 ± 0.001 |
| ntt   | 0.000 ± 0.000 | 0.021 ± 0.004 |
| ntt   | 0.000 ± 0.000 | 0.002 ± 0.001 |
| ntt   | 0.000 ± 0.000 | 0.057 ± 0.004 |
| ntt   | 0.000 ± 0.000 | 0.002 ± 0.000 |
| ntt   | 0.000 ± 0.000 | 0.021 ± 0.001 |
| $S_{\text{confor}}$ / J K$^{-1}$ mol$^{-1}$ | 3.43 ± 0.19 | 21.40 ± 0.11 |
Table S10. Absolute entropies (J K$^{-1}$ mol$^{-1}$) of the salts in the crystal state calculated by the MD simulations (this work) and reported experimentally. Configurational entropies ($S_{\text{config}}$) in the crystal state are assumed to be zero, which would be reasonable because the positional and orientational disorders of the ILs were negligible, judging from the MD trajectories.

|                | MD (This work) | Exp.  |
|----------------|----------------|-------|
|                | $S_{\text{tr}}$ | $S_{\text{rot}}$ | $S_{\text{vib}}$ | $S_{\text{confor}}$ | Total |       |
| NaCl at 1089 K | Na$^+$         | 67.5 ± 0.0 | 0 | 0 | 0 | 140.3 ± 0.0 | 145.0 |
|                | Cl$^-$         | 72.8 ± 0.0 | 0 | 0 | 0 |        |       |
| $[\text{C}_2\text{mim}]\text{PF}_6$ at 338 K | $[\text{C}_2\text{mim}]^+$ | 61.7 ± 0.1 | 55.8 ± 0.1 | 111.6 ± 0.3 | 1.17 ± 0.02 | 440.9 ± 0.7 | n/a |
|                | $\text{PF}_6^-$ | 69.1 ± 0.1 | 73.5 ± 0.1 | 68.0 ± 0.2 | 0 |        |       |
| $[\text{C}_4\text{mim}]\text{PF}_6$ at 275 K | $[\text{C}_4\text{mim}]^+$ | 56.3 ± 0.1 | 46.7 ± 0.2 | 126.2 ± 0.2 | 3.43 ± 0.19 | 411.1 ± 0.8 | 392.9 |
|                | $\text{PF}_6^-$ | 62.8 ± 0.2 | 63.7 ± 0.1 | 51.9 ± 0.1 | 0 |        |       |
Table S11. Decompositions of calculated $\Delta_{\text{fus}}$S of NaCl, [C$_2$mim]PF$_6$, and [C$_4$mim]PF$_6$. Unit is in J K$^{-1}$ mol$^{-1}$.

|                  | $\Delta_{\text{kin}}$S | $\Delta_{\text{str}}$S | $\Delta_{\text{tra}}$S | $\Delta_{\text{rot}}$S | $\Delta_{\text{vib}}$S | $\Delta_{\text{confor}}$S | $\Delta_{\text{config}}$S | Total   |  $\Delta_{\text{fus}}$S |
|------------------|------------------------|------------------------|------------------------|------------------------|------------------------|---------------------------|---------------------------|---------|------------------------|
| **NaCl at 1089 K** |                        |                        |                        |                        |                        |                           |                           |         |                       |
| Na$^+$           | 11.7 ± 0.0             | 0.0                    | 0.0                    | 0.0                    | 25.2 ± 0.1             | 0                         | 0.7 ± 0.1                  | 0.7 ± 0.1 | 25.8 ± 0.0             |
| Cl$^-$           | 13.4 ± 0.0             | 0.0                    | 0.0                    | 0.0                    | 0                      |                           |                           |         |                       |
| **[C$_2$mim]PF$_6$ at 338 K** |                   |                        |                        |                        |                        |                           |                           |         |                       |
| [C$_2$mim]$^+$   | 4.1 ± 0.2              | 7.0 ± 0.1              | −0.2 ± 0.3             | 6.8 ± 0.1              | 16.9 ± 0.9             | 6.8 ± 0.0                 | 30.0 ± 0.9                | 36.9 ± 0.9 | 53.8 ± 0.2             |
| PF$_6^-$         | 4.3 ± 0.2              | 2.1 ± 0.2              | −0.4 ± 0.2             | 0                      |                        |                           |                           |         |                       |
| **[C$_4$mim]PF$_6$ at 275 K** |                   |                        |                        |                        |                        |                           |                           |         |                       |
| [C$_4$mim]$^+$   | 3.8 ± 0.2              | 9.3 ± 0.2              | −1.2 ± 0.2             | 19.1 ± 1.2             | 18.0 ± 0.2             | 28.1 ± 1.3                | 46.1 ± 1.3                | 65.2 ± 0.4 |                       |
| PF$_6^-$         | 3.4 ± 0.3              | 5.6 ± 0.4              | −1.9 ± 0.1             | 0                      |                        |                           |                           |         |                       |
Table S12. Diffusion coefficients of ions in NaCl (1089 K), [C\textsubscript{2}mim\textsubscript{+}]PF\textsubscript{6} (338 K), and [C\textsubscript{4}mim\textsubscript{+}]PF\textsubscript{6} (275K) in addition to their experimental viscosity data.

| Salt        | Ion        | Simulated $D$ (this work) / m\textsuperscript{2} s\textsuperscript{-1} | Experimental $D$ / m\textsuperscript{2} s\textsuperscript{-1} | Experimental viscosity / mPa s |
|-------------|------------|--------------------------------------------------------------------------------|---------------------------------------------------------------|--------------------------------|
| NaCl        | Na\textsuperscript{+} | $8.44 \pm 0.24 \times 10^{-9}$ | $7.75 \times 10^{-9}$ \textsuperscript{132} | 1\textsuperscript{133} |
|             | Cl\textsuperscript{-} | $7.75 \pm 0.26 \times 10^{-9}$ | $6.13 \times 10^{-9}$ \textsuperscript{132} | 132 |
| [C\textsubscript{2}mim\textsubscript{+}]PF\textsubscript{6} | [C\textsubscript{2}mim\textsubscript{+}] | $6.13 \pm 0.27 \times 10^{-11}$ | n/a | 28\textsuperscript{134} |
|             | PF\textsubscript{6}\textsuperscript{-} | $4.00 \pm 0.17 \times 10^{-11}$ | n/a | 28\textsuperscript{134} |
| [C\textsubscript{4}mim\textsubscript{+}]PF\textsubscript{6} | [C\textsubscript{4}mim\textsubscript{+}] | $1.19 \pm 0.16 \times 10^{-12}$ | $1.18 \times 10^{-12}$ \textsuperscript{135} | 1459\textsuperscript{136} |
|             | PF\textsubscript{6}\textsuperscript{-} | $0.50 \pm 0.07 \times 10^{-12}$ | $0.82 \times 10^{-12}$ \textsuperscript{135} | 1459\textsuperscript{136} |
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