Partially Naked Fluoride in Solvate Ionic Liquids

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ABSTRACT. Truly naked fluoride only exists in the gas phase. Fluoride can be stabilized by a complexing agent and an organic cation, resulting in anhydrous or dehydrated fluoride which is "partially naked." This partially naked fluoride enables fluorination reactions at much lower temperatures than hydrated fluorides. Here we show a simple method for preparing fluoride based solvate ionic liquids (SILs) by mixing 1-alkyl-3-methylimidazolium (1-ethyl-3-methylimidazolium or 1-butyl-3-methylimidazolium) bromide, silver fluoride (AgF), and EG (1:1:1 in molar ratio) in dry methanol. Removal of the methanol produced anhydrous SILs, $[C_2C_1im]F \cdot EG$ and $[C_4C_1im]F \cdot EG$. This is the first SIL reported that comprises fluoride. ^{1}H-NMR and IR spectroscopy reveals fluoride hydrogens bonds with EG OH groups and cation aromatic H atoms, but not cation tail group protons. Fluorination reactions on benzyl bromide show that $[C_2C_1im]F \cdot EG$ has high reactivity with reasonable yield under mild conditions, confirming the fluoride ion is partially naked.

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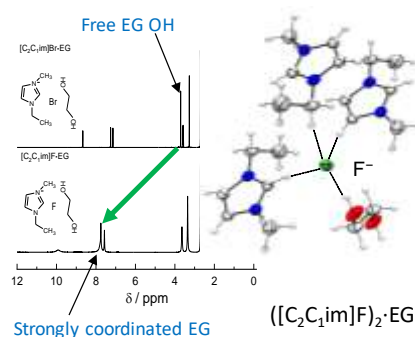
KEYWORDS. Fluorides • Ionic liquids • Hydrogen bonds • Solvation structure • Fluorination

Fluorination is critical for a wide range of chemical applications in the pharmaceutical, medicinal, and materials sciences, etc.[1-2] "Naked fluoride" refers to dehydrated (or desolvated) fluoride ions. While gaseous naked fluoride is known,[3] naked fluoride does not exist in water (or other solvents), as analogous to H^+ in water, fluoride is always hydrated, or otherwise closely associated with its cation;[4] if it could be prepared, liquid phase naked fluoride would be extremely basic and have immense catalytic activity. [3-6] The relative "nakedness" of fluoride is strongly affected by the cation size; the larger size of the cation, the more weakly it associates with the fluoride, and the more naked the fluoride becomes.[7] This implies that naked fluoride could be obtained from salts of large elemental ions like cesium in aprotic solvents, but in actuality reactions only occur on the solid surface of CsF because of its low solubility.[4]

An alternative method to hinder fluoride – cation interactions to produce naked fluoride would be to use large organic cations. However, fluoride ions are unstable with most organic cations due to reaction with hydrocarbon β-hydrogens.[6, 8-10] Fluoride is only stable with organic cations that lack β-hydrogens, such as tetramethylammonium fluoride (TMAF),[9] or cations like azabicyclo[2.2.2]octane, where the β-hydrogen is sterically hindered towards elimination.[3] However, to produce naked fluoride requires dissolution of these salts in dry aprotic solvents, in which their solubility is very low. Conceivably, these salts could be employed in molten form, but they most likely have high melting point or decompose without forming a liquid phase (decomposition temperature: 170 °C for TMAF and 140 °C for azabicyclo[2.2.2]octane fluoride).

Attempts to produce ionic liquids (pure salts with low melting points[11]) comprising naked fluoride ions have failed; common ionic liquid cations have β-hydrogens, which the fluoride attacks.[12] A recent attempt to synthesize an anhydrous dialkylimidazolium fluoride ionic liquids produced a hydrated fluoride anion rather than naked fluoride.[5] Fluorohydrogenate ionic liquids

where the anion is a fluoride ion solvated by HF, such as $[C_2C_1im][(FH)_nF]$ ($C_2C_1im^+$ = 1-ethyl-3-methylimidazolium) have low melting point and high ionic conductivity. Unfortunately, the strong F···H bond suppresses the activity (nakedness) of the fluoride ion in $(FH)_nF^-$,[13-15] but nonetheless this suggests the possibility of producing an ionic liquid with naked (or near naked) fluoride by incorporating a hydrogen bond donor (HBD) / ligand weaker than HF. Such an approach shares conceptual similarities of deep eutectic solvents (DESs),[16-18] where mixing a salt and HBD at an appropriate ratio (often 1:2) produces a low melting point liquid, and solvate ionic liquids (SILs),[19-21] where mixing a salt and ligand (often a glyme in a 1:1 ratio) also results in a low melting point liquid. For DESs, while a liquid has been prepared by mixing choline fluoride and urea system, the fluoride solvation state (nakedness) and synthetic properties are unclear.[16] To the authors' knowledge, SILs incorporating fluoride have not been reported.

Here we report a simple method to produce fluoride based SILs comprising 1-alkyl-3-methylimidazolium cations, fluoride and ethylene glycol (EG) in a 1:1:1 ratio. Hydrogen bonding between the fluoride and the alcohol groups of ethylene glycol and cation ring hydrogens prevent the fluoride from attacking cation alkyl chain β-hydrogens, but the fluoride retains sufficient activity to act as a fluorinating agent, demonstrated via the fluorination of benzyl bromide under mild conditions with good yield. The physicochemical properties and solvation structures of the SIL are reported. Combined, these results show the fluoride in these SILs is "partially naked".

The fluoride based SILs were prepared via in one-step by mixing 1-alkyl-3-methylimidazolium (either $C_2C_1im^+$ or $C_4C_1im^+$ (1-butyl-3-methylimidazolium)) bromide and silver fluoride (AgF), and EG (1:1:1 in molar ratio) in dry methanol. Anhydrous light yellow liquids, $[C_2C_1im]F·EG$ and $[C_4C_1im]F·EG$, were obtained by filtration and removal of the dry methanol at a yield of ~100%. Quantitative X-ray fluorescence analysis identified trace amounts of Ag (<0.01 mol%) and Br

(<0.9 mol%) impurities. Differential scanning calorimetry revealed glass transition temperatures of −71 °C and −65 °C for $[C_2C_1im]F·EG$ and $[C_4C_1im]F·EG$, respectively, (Fig.S1a, Supporting Information). This glassy behavior is similar to many conventional ionic liquids[11, 22-23] and SILs.[24] $[C_2C_1im]F·EG$ and $[C_4C_1im]F·EG$ were stable under high vacuum for more than 12 hours. By contrast, over the same period pure EG evaporated, and the mass loss of the corresponding bromide based liquids (~0.5 g) was about 40%. Thermogravimetric analysis (TGA) (Fig. S1b, Supporting Information) shows 5% mass loss for $[C_2C_1im]F·EG$ and $[C_4C_1im]F·EG$ is not reached until 110 °C and 143 °C, respectively. Potentially, HF could form in these liquids if fluoride abstracted a proton from an alcohol group of ethylene glycol. However, it is highly unlikely significant HF is present in either $[C_2C_1im]F·EG$ or $[C_4C_1im]F·EG$ because the boiling point of HF is just 19.5 °C meaning mass loss would occur at much lower temperatures, and HF would be rapidly removed under vacuum leading to a reduction in the sample mass. Combined, these results show $[C_2C_1im]F·EG$ and $[C_4C_1im]F·EG$ have negligible room temperature vapour pressure, are liquids at less than 100°C, and that physical properties associated with the pure components are not observed, meaning they satisfy 3 key criteria for SILs.[25]

Fluoride solvation by EG and the cation in $[C_2C_1im]F·EG$ and $[C_4C_1im]F·EG$ was first probed using ^{19}F-NMR. The spectra have one signal, at −113 ppm for $[C_2C_1im]F·EG$ and −112 ppm for $[C_4C_1im]F·EG$ (Fig. S2, Supporting Information). Although this might show there is only one form of fluoride in the liquids, fluoride ions might coordinate with different H atoms in the SILs as it is not possible to distinguish them by the NMR technique. The similarity of the ^{19}F-NMR chemical shifts for $[C_2C_1im]F·EG$ and $[C_4C_1im]F·EG$ shows the fluorine solvation environments are essentially the same. This means, as may be expected on polarity grounds, interactions between fluoride and the (different length) cation alkyl chains are minimal. The chemical shifts of −113

ppm and −112 ppm are close to those for fluoride solvated by water (−119 ppm) but significantly downfield of fluoride in methanol (−149 ppm).[26-27] That is, the groups solvating fluorine in $[C_2C_1im]F \cdot EG$ and $[C_4C_1im]F \cdot EG$ deshield fluoride electrons to a similar extent as water, and much less than methanol.

Fig. 1 shows infrared (IR) spectra for $[C_2C_1im]F \cdot EG]$ and $[C_4C_1im]F \cdot EG$ between 500−4000 cm^{-1}, along with $[C_2C_1im]Br \cdot EG$, $[C_4C_1im]Br \cdot EG$, $[C_2C_1im]Br$, and EG for comparison. The characteristic pure EG OH stretching at 3300 cm^{-1} is observed in the same region for $[C_2C_1im]Br \cdot EG$ and $[C_4C_1im]Br \cdot EG$, but absent for $[C_2C_1im]F \cdot EG$ and $[C_4C_1im]F \cdot EG$. For O−H, C−H, and N−H stretching modes, strong hydrogen bonding leads to band broadening accompanied by a shift to lower frequency.[28-30] Therefore, red shift of the EG peaks to between 2300 and 2700 cm^{-1} for $[C_2C_1im]F \cdot EG$ and $[C_4C_1im]F \cdot EG$ reveals strong hydrogen bonding between EG alcohol groups and fluoride.

Increasing the amount of EG in $[C_2C_1im]$:F:EG from 1:1:1 to 1:1:1.5 leads to the re-appearance of the EG OH stretching band at around 3350 cm^{-1} (Fig. S3, Supporting Information), and further increasing $[C_2C_1im]$:F:EG from 1:1:2 increases the bands intensity. This indicates the presence of free EG in the $[C_2C_1im]$:F:EG 1:1:1.5 and 1:1:2 $[C_2C_1im]$:F:EG liquids. Therefore, the absence of the EG OH stretching band at around 3350 cm^{-1} in 1:1:1 for $[C_2C_1im]$:F:EG shows all the EG in this liquid is complexed with fluoride, which satisfies another criteria for SILs.[25]
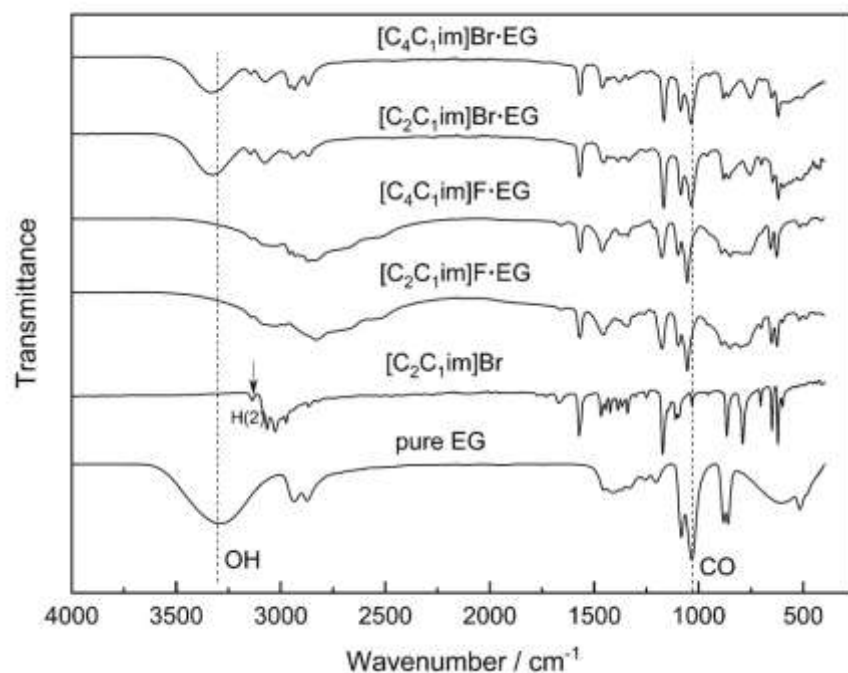
Figure 1. Infrared spectra of [C$_2$C$_1$im]F·EG], [C$_2$C$_1$im]Br·EG, [C$_4$C$_1$im]F·EG, [C$_4$C$_1$im]Br·EG, [C$_2$C$_1$im]Br, and pure EG at 20 °C .

^{1}H-NMR measurements were also performed on neat [C$_2$C$_1$im]F·EG and [C$_4$C$_1$im]F·EG to further probe fluoride solvation and exclude other solvent effects. The ^{1}H-NMR spectra of neat [C$_2$C$_1$im]F·EG and [C$_4$C$_1$im]F·EG are shown in Fig. 2(A) and (C) with atom numbering schemes, along with data for [C$_2$C$_1$im]Br·EG and [C$_4$C$_1$im]Br·EG in Fig. 2 (B) and (D) for comparison. The ^{1}H-NMR signals are much broader for [C$_2$C$_1$im]F·EG and [C$_4$C$_1$im]F·EG than [C$_2$C$_1$im]Br·EG and [C$_2$C$_1$im]Br·EG due to the higher liquid viscosities.

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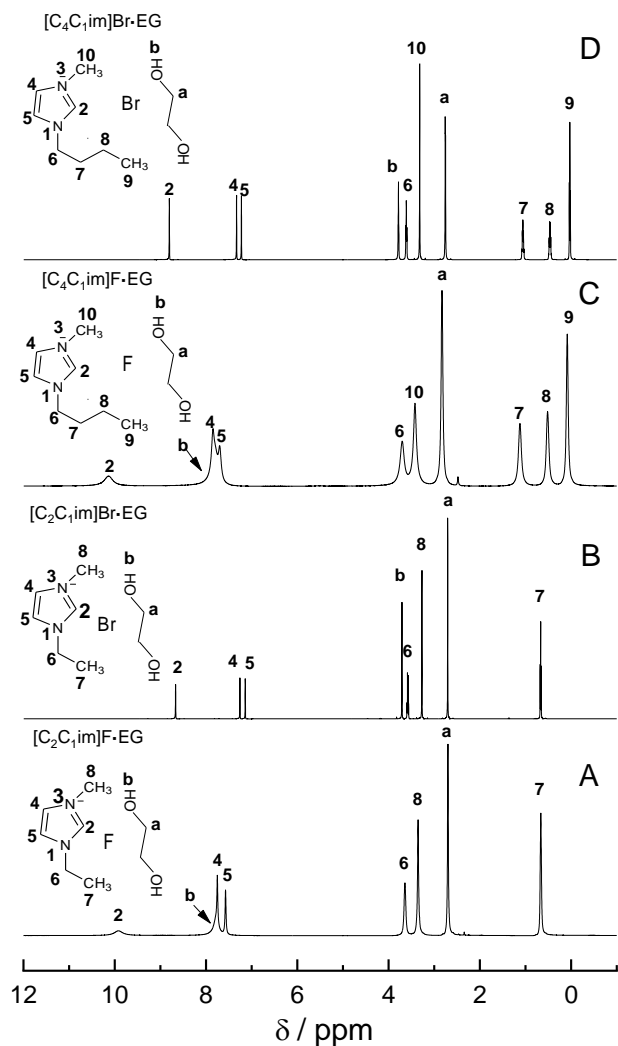
Figure 2. ^{1}H-NMR spectra of (A) [C$_2$C$_1$im]F·EG, (B) [C$_2$C$_1$im]Br·EG, (C) [C$_4$C$_1$im]F·EG, and (D) [C$_4$C$_1$im]Br-EG at 20 °C.

^{1}H-NMR signals for EG CH protons (labelled **a** in Fig. 2) appear at ~2.8 ppm for the four liquids. The EG OH protons (labelled **b**) are at 3.7 ppm for [C$_2$C$_1$im]Br·EG and [C$_4$C$_1$im]Br·EG, slightly downfield of H6 signals, whereas the chemical shift of the OH protons in pure EG is 4.8 ppm. The 1.1 ppm downfield shift in [C$_2$C$_1$im]Br·EG and [C$_4$C$_1$im]Br·EG is attributed to weak hydrogen bonding between EG OH groups and bromide. There is no obvious signal for the EG OH protons in the spectra for the fluoride based liquids, near the H6 signal or otherwise. However, careful

analysis of the [C_2C_1im]F·EG and [C_4C_1im]F·EG spectra reveals the H4 at 7.7 ppm is broad, and integration of the peak intensities shows three protons contribute to the H4 signals, not one as expected. This reveals the EG OH proton signal shifts downfield by approximately 4.0 ppm (from 3.7 ppm to 7.7 ppm, c.f. the "b" label in Fig. 2 A and C) and overlaps with H4 due to strong F^-···HO hydrogen bonds in [C_2C_1im]F·EG and [C_4C_1im]F·EG. This is consistent with reports that strongly hydrogen bonded protons experience a strong ^{1}H-NMR downfield shift due to deshielding,[31] and with the IR data presented above.

The [C_2C_1im]:F:EG 1:1:1.5 and 1:1:2 [C_2C_1im]:F:EG samples were also probed using ^{1}H-NMR (Fig.S4, Supporting Information). The EG OH signal shifts upfield with EG content, from 7.7 ppm for 1EG, to 6.8 ppm for 1.5EG, and 6.2 ppm for 2EG, and peak integration reveals stoichiometric amounts of OH protons. ^{1}H-NMR is sensitive to the average state of EG OH protons in the liquids. As the EG content increases and there is more free EG, the EG OH proton signal shifts upfield. This is consistent with the IR spectra, which also revealed increased free EG for higher EG ratios in the liquid.

The chemical shift of cation H2 ring proton for [C_2C_1im]F·EG and [C_4C_1im]F·EG shifts downfield (~10 ppm) by ~1.3 ppm for [C_2C_1im]F·EG with significant broadening compared to the analogue bromide liquids. The H4 and H5 ring protons also shift downfield, but by just 0.59 ppm and 0.42 ppm, respectively, and the signals remain sharp. This data shows fairly strong F^-···H2 hydrogen bonds form in these liquids consistent with the H2 proton being the most acidic in these cations.[32-33] Weaker hydrogen bonds form between fluorine and H4 and H5, but not appreciably with other cation protons.

Increasing the temperature increases the kinetic energy of molecules and ions in a liquid, which weakens hydrogen bonds and increases proton exchange, which deshields protons, resulting in an

upfield shift. To confirm the presence of $F^-\cdots H2$, $F^-\cdots H4$, $F^-\cdots H5$ and $F^-\cdots HO$ hydrogen bonds in [C_2C_1im]F·EG and [C_4C_1im]F·EG, the effect of temperature on the ^{1}H-NMR signals associated with these interactions was probed between 5 to 60 °C (Fig. S5, Supporting Information). The EG OH and cation ring (H2, H4, and H5) protons signals become sharper with decreasing temperature, consistent with hydrogen bonds between these groups and fluoride. All other signals (methyl and methylene protons in the cation and EG) become broader with decreasing temperature owing to increased viscosity.

The picture that emerges for [C_2C_1im]F·EG and [C_4C_1im]F·EG is of fluoride complexed by relatively strong hydrogen bonds with the two EG OH protons and cation C2 proton, and weaker hydrogen bonds with cation H4 and H5 protons. Corresponding bonds in the bromide analogue liquids are weak or absent, consistent with the reduced electronegativity of bromide.

Evidence for stronger hydrogen bonding in the fluoride based liquids is also obtained from macroscopic physical properties. The temperature dependent viscosity, ionic conductivity, and density for [C_2C_1im]F·EG and [C_4C_1im]F·EG, and the corresponding bromide salts, are shown in Fig. S6 and S7, Supporting Information. Viscosity and ionic conductivity are fitted by the Vogel-Tammann-Fulcher equation[34-35] with the fitting parameters shown in Table S1 (Supporting Information).[36-37] The viscosities of [C_2C_1im]F·EG and [C_4C_1im]F·EG at 25 °C are 575 and 1044 mPa s, respectively. This is an order of magnitude higher than for the bromide analogues, which have viscosities of 35 and 74 mPa s for [C_2C_1im]Br·EG and [C_4C_1im]Br·EG, respectively. This difference is consistent with much stronger interactions in the fluoride-based liquids. This is also reflected in the low diffusion coefficients measured by pulsed-gradient field spin-echo (PGSE)-NMR for C_2C_1im$^+$ and EG (3.4×10^{-7} and 2.6×10^{-7} cm^2 s^{-1} at 40 °C, respectively) (*cf.* 8.0×10^{-7} and 6.8×10^{-7} cm^2 s^{-1} for C_2C_1im$^+$ and BF$_4^-$ in [C_2C_1im][BF$_4$] at 40 °C).[38] These values increase upon

by heating to 7.8×10^{-7} and 7.2×10^{-7} cm^2 s^{-1} at 60 °C. As expected, ionic conductivity is inversely related to viscosity,[37] and increases in the order of [C$_4$C$_1$im]F·EG < [C$_2$C$_1$im]F·EG < [C$_4$C$_1$im]Br·EG < [C$_2$C$_1$im]Br·EG. The ionic conductivities of [C$_2$C$_1$im]F·EG and [C$_4$C$_1$im]F·EG at 25 °C are 1.03 and 0.35 mS cm^{-1}, respectively, which is similar to ionic liquids[39-40] and deep eutectic solvents[41] with similar viscosities.

About 1 month after synthesis, a few crystals precipitated from [C$_2$C$_1$im]F·EG, indicating this liquid is meta-stable at room temperature. Some well-known traditional ionic liquids are also meta stable at room temperature, for example, ethanolammonium nitrate.[42] The crystals formed were found to have a composition in [C$_2$C$_1$im]:F:EG as 1:1:0.5 (([C$_2$C$_1$im]F)$_2$·EG) which had a melting point of 85 °C, but decomposition occurred almost simultaneously, c.f. Fig. S8, Supporting Information. No crystals were present in [C$_4$C$_1$im]F·EG several months after synthesis.

Although the [C$_2$C$_1$im]F·EG liquid structure is dynamic, the structure of the crystals recovered provide an indication of the favoured interactions. Fig. 3 shows the X-ray crystal structure of ([C$_2$C$_1$im]F)$_2$·EG (see Tables S2 and S3 for crystallographic data and selected geometrical parameters). The coordination environment of fluoride ion is best described as distorted tetrahedron (82.5° < H···F$^-$···H angle < 137.0°), with the fluoride surrounded by two aromatic hydrogen atoms, one methylene hydrogen atom, and one OH hydrogen (Fig. 3(b)). The F$^-$···HO distance is 1.66 Å, which is similar to the value of 1.598 Å of F$^-$·HO reported for KF·CH$_2$(CO$_2$H)$_2$,[43] and significantly shorter than the sum of the van der Waals distances of hydrogen and fluorine atoms (2.7 Å).[44] The F1···H2 distance (1.88 Å) is shorter than the F1···H4 distance (2.08 Å), and the fluoride to methylene hydrogen atom (H6a) distance is long (2.23 Å), revealing a weak interaction. Interactions between atoms are inversely correlated with bond

strength, so these differences reflect the strength of F···H interactions, and agree well with the proton acidities.[32-33]

In the crystal, the EG molecule adopts a *trans* conformation (see Fig. S9a, Supporting Information), with the O−C−C−O angle being crystallographically restricted to be 180°, as observed in pure EG crystal.[45] The EG bridges two $C_2C_1im^+$ cations through the F^-···HO interactions (see Fig. S9b, Supporting Information for the packing diagram). The oxygen atom in the OH group has a short contact with H5 aromatic hydrogen atom (O···H distance of 2.30 Å), which may also contribute to the stabilization of this system in the liquid state. The crystallographic model suggests the order of hydrogen bonding strength: OH proton > H2 > H4 ≈ H5 > H6, which agrees with the NMR results. Although the *gauche* conformer of EG molecule with the O−C−C−O angle ≈ 60° may be possible, stereochemical repulsion does not allow the bidentate coordination to fluoride ion. If this persists in the liquid state, this will create three dimensional hydrogen bond networks in $[C_2C_1im]F·EG$ and $[C_4C_1im]F·EG$.
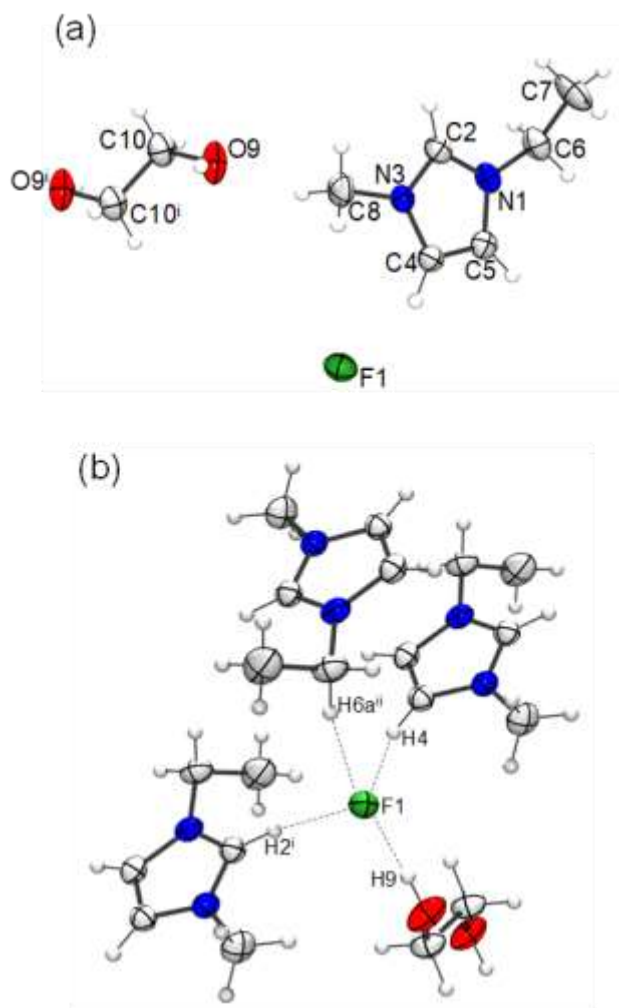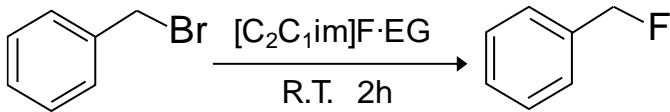
Figure 3. X-ray crystal structures of ([C$_2$C$_1$im]F)$_2$·EG. (a) asymmetric unit [symmetric code: (i) −x, 1−y, 2−z] and (b) coordination environment of F$^-$ [symmetric code: (i) 1+x, y, z; (ii) 1−x, 1−y, 1−z]. Selected contact distances and angles (Å, deg): F1···H2 1.88, F1···H4 2.09, F1···H6a 2.3, F1···H9 1.66, H9···F1···H2 106.4, H9···F1···H4 123.5, H2···F1···H4 107.8, H9···F1···H6a 137.0, H2···F1···H6a 94.6, H4···F1···H6a, 82.5. Green: fluorine, blue: nitrogen red: oxygen, gray: carbon and hydrogen.

Typical fluorination reactions require high temperatures and longer times using alkali metal fluorides, which are poorly soluble in organic solvents.[2] In order to assess how naked (available)

the fluoride ion is for reaction in these liquids, the reactivity of $[C_2C_1im]F \cdot EG$ was studied via

fluorination reactions with benzyl bromide with and without solvent (DMF) at two different molar

ratios of fluoride to bromide (1 or 1.5) at room temperature. $[C_2C_1im]F \cdot EG$ was stable in DMF as

confirmed by the ^1H and ^{19}F-NMR results (Fig.S10, Supporting Information). The reaction

mixtures were stirred at room temperature for 2 h, resulting in a colorless solution. The conversion

of benzyl bromide and the yield of product was determined by ^1H and ^{19}F NMR results,

respectively, (see Fig.S11 and S12, Supporting Information), are shown in Table 1. At equimolar

ratios of $[C_2C_1im]F \cdot EG$, fluorination of benzyl bromide was incomplete, resulting in a relatively

low yield (<50%), both with and without DMF. Increasing the equivalent molar benzyl

bromide:$[C_2C_1im]F \cdot EG$ to 1:1.5 increased conversion to 98% and the yield of benzyl fluoride to

~60%. This shows that the fluoride in $[C_2C_1im]F \cdot EG$ is, at least, partially naked.

Table 1. Fluorination reaction of benzyl bromide with $[C_2C_1im]F \cdot EG$.

entry	equiv of $[C_2C_1im]F \cdot EG$	Conversion (%)[a]	Yield (%)[b]
1	1	62	48
2	1.5	99	62
3	1 in DMF	81	41
4	1.5 in DMF	98	58

The ~60% yield of the benzyl fluoride obtained here is lower than the ~70% yield recently reported for a quaternary ammonium fluoride based on azabicyclo[2.2.2]octane,[3] but this fluorination agent requires the use of volatile, toxic, organic solvents (ACN, DMSO, etc). Fluorination achieved here in similar yield in the nonvolatile [C$_2$C$_1$im]F·EG liquid without added solvent in just 2 hours without the use of a quenching agent, which represent significant advantages. Further, the stability of [C$_2$C$_1$im]F·EG in DMF opens possibilities for many potential fluorination reactions with other organics.

In conclusion, new fluoride based solvate fluoride ionic liquids, [C$_2$C$_1$im]F·EG and [C$_4$C$_1$im]F·EG , synthesized by reaction of the respective bromide salts, silver fluoride and EG. The liquids have negligible room temperature vapour pressure, have melting points less than 100°C, all of the EG is associated with fluoride ions, and exhibit no physical properties associated with the pure components, thereby satisfying the criteria for SILs. NMR and IR reveal strong hydrogen bonding between fluoride ion and EG molecules, and with the imidazolium ring proton (H2), along with weaker interactions with the cation ring H4 and H5. No interactions are noted between fluorine and cation alkyl chain protons, raising the possibility that the SIL is nanostructured; this is the topic of further study. X-ray diffraction of crystal precipitated from the meta stable [C$_2$C$_1$im]F·EG show the fluoride binds to two EG molecules in the crystal. If this persists in the liquid state, this will create a three dimensional hydrogen bond network that may support surfactant self assembly. The reactivity of [C$_2$C$_1$im]F·EG was examined by fluorination of benzyl bromide with a reasonable yield both in neat form and in DMF, which opens high potential

application of $[C_nC_1im]F \cdot EG$ in organic reactions (currently underway). This reveals the fluoride in $[C_2C_1im]F \cdot EG$ and $[C_4C_1im]F \cdot EG$ is partially naked.

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.xxxxxxx. Experimental details and crystallographic, spectroscopic, and thermoanalytical data (PDF).

Accession Codes. CCDC 1870396 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENT

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