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A Hydronium Solvate Ionic Liquid: Facile Synthesis of Air-Stable Ionic Liquid with Strong Brønsted Acidity

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A new kind of ionic liquid (IL) with strong Brønsted acidity, i.e., a hydronium (H$_3$O$^+$) solvate ionic liquid, is reported. The IL can be described as [H$_3$O$^+$ · 18C$_6$]Tf$_2$N, where water exists as the H$_3$O$^+$ ion solvated by 18-crown-6-ether (18C$_6$), of which the counter anion is bis(trifluoromethylsulfonyl)amide (Tf$_2$N$^-$; Tf = CF$_3$SO$_2$). The hydrophobic Tf$_2$N$^-$ anion makes [H$_3$O$^+$ · 18C$_6$]Tf$_2$N stable in air. The Hammett acidity function ($H_0 = -4.4$) of molten [H$_3$O$^+$ · 18C$_6$]Tf$_2$N, evaluated using the indicator method, is a new record for ILs and indicates strong acidity. The findings regarding this proton-condensed solvate IL are of fundamental interest, and will help in the design of media for new acid-base reactions.

When two or more kinds of substances are mixed, the properties of the mixture can differ from those of the pure substances. Depending on the interactions between the components, some components undergo ionization, e.g. dissociation, protonation, solvation and complexation, due to the neutralization of Brønsted or Lewis acids and bases. Sometimes, the acid-base mixtures can be categorized as ionic liquids (ILs) with melting points below 100 °C, which consist only of cations and anions. ILs are regarded as “the third liquid” and some ILs have fascinating physicochemical properties, such as low volatility, low flammability, high chemical, and thermal stability. Furthermore, ILs have received growing interest due to their various uses as media in chemical, biochemical, and/or electrochemical systems.

Common anions of ILs such as BF$_4^-$, PF$_6^-$, and AlCl$_4^-$ are produced by neutralization, i.e. the adducts of a Lewis acid (BF$_3$, PF$_5$, or AlCl$_3$) and a Lewis base (F$^-$ or Cl$^-$). Examples of ILs prepared through neutralization include solvate ILs. Solvate ILs often consist of equimolar molten mixtures of polyethers (linear or cyclic ones, i.e. glymes or crown ethers) and certain metal salts, where the Lewis acidic metal cations are solvated by equimolar amounts of Lewis basic glymes to give complex cations. Besides, neutralization of Brønsted acids and bases produces so-called proctic ILs, which are preferred as acid-catalyzed reaction media due to the presence of an acidic proton.

Although protons are often written as H$^+$, H$^+$ cannot exist as a bare ion in liquids. In aqueous solutions, “H$^+$” exists as H$^+$ (H$_2$O)$_n$, with $n = 1, 2, 3, \ldots$ i.e. H$_2$O$^+$, H$_3$O$^+$, H$_4$O$^+$, etc. The simplest form is H$_3$O$^+$, commonly called a hydronium ion. In a monohydrate acid (HA · H$_2$O), the protons are not bonded to the anion atoms. Protons generally exist as hydronium ions to form H$_2$O$^+$ · A$^-$, where HA = HNO$_3$, H$_2$SO$_4$, HClO$_4$, HTTO (TT = CF$_3$SO$_2$), etc. However, there is an exception. In solid, anhydrous HTf$_2$N, the proton is bonded to the anion nitrogen and two oxygens of a neighboring HTf$_2$N molecule. Likewise, in the case of monohydrate, the imide superacid HTf$_2$N remains associated and does not protonate water, as suggested experimentally and theoretically. In the infrared measurements for an H$_2$O and HTf$_2$N mixture in CCl$_4$, strong Fermi vibrations for N-H vibrations serves as evidence that HTf$_2$N remains intact, and from the ab initio calculations, spontaneous proton dissociation was not observed for the HTf$_2$N molecule with the addition of one H$_2$O molecule. Notably, in a non-fluorinated analogue i.e. (CH$_3$SO$_2$)$_2$NH · H$_2$O imide monohydrate, the proton remains bonded to the anion nitrogen, although the network may change at elevated temperatures to form H$_2$O$^+$ trapped in an anionic cage, as reported for HClO$_4$ · H$_2$O. Protonation of water using equimolar HTf$_2$N could occur only if H$_2$O$^+$ were solvated by ligands, thereby synthesizing a new series of ionic materials, i.e. hydronium solvate ILs, the active protons of which would show strong acidicities in the form of (solvate) IL.

A plausible ligand for complexation of H$_2$O$^+$ is a crown ether, 18-crown-6-ether (18C$_6$). 18C$_6$ is a good hydrogen-bonding acceptor that binds H$_2$O$^+$ cation selectively due to its cavity size resulting in the formation of an [H$_3$O$^+$ · 18C$_6$] complex cation. In this paper, we report for the first time that H$_2$O$^+$ can be stabilized by the addition of 18C$_6$ to HTf$_2$N · H$_2$O, forming [H$_3$O$^+$ · 18C$_6$]Tf$_2$N (see Fig. 1a). The successful synthesis of [H$_3$O$^+$ · 18C$_6$]Tf$_2$N clarified
its unusually low melting point of 68–70 °C, compared with the known [H₃O⁺ · 18C6] complexes with common anions of ILs, such as ClO₄⁻, SbF₆⁻, PF₆⁻, TFO⁻, BF₄⁻, FeCl₄⁻ (110–170 °C). Moreover, the Tf₂N⁻ anion is known for its strong hydrophobicity and high chemical stability.34,35 These characteristic features allowed the facile synthesis of air-stable or non-hygroscopic [H₃O⁺ · 18C6]Tf₂N just by vacuum drying of an equimolar 18C6-HTf₂N aqueous solution. We confirm that the hydronium complex [H₃O⁺ · 18C6]Tf₂N satisfies the criteria of a solvate IL, containing a negligible amount of neutral molecules. We also reveal that the hydronium solvate IL is highly acidic (Hammett acidity function H₀ = −4.4), marking a new record of H₀ among acidic ILs.

**Experimental**

**Materials for [H₃O⁺ · 18C6]Tf₂N.**—18-crown-6 (18C6; Kanto Chemical, 99% purity) and bis(trifluoromethylsulfonylimidide (HTf₂N; Aldrich, ≥95% purity) were used without further purification. Deionized water was prepared using a Merck Milli-Q Reference A system. Note: Wilson et al. have discussed the naming of H₂Tf₂N and Tf₂N⁺ anion.36 HTf₂N was originally named as bis(trifluoromethylsulfonylimidide.37 According to IUPAC nomenclature, HTf₂N is a “sulfonamide”, named as 1,1,1-trifluoro-N-[(trifluoromethyl)sulfonyl]-methanesulfonamide.38 Besides, HTf₂N can be viewed as bis(trifluoromethanesulfonylimidide or bis(trifluoromethanesulfonamide). However, its conjugate base anion i.e. Tf₂N⁻ anion is clearly an amide, bis(trifluoromethylsulfonylimidide or bis(trifluoromethanesulfonylimidide, commonly abbreviated to TFSA. In some literature, the anion is referred to as an “imide” with the abbreviation TFSI; however, the now-accepted naming is “amide”.

**Synthesis of [H₃O⁺ · 18C6]Tf₂N.**—18C6 (5 mmol) and HTf₂N (5 mmol) in 5 mL of water were stirred at 500 rpm and heated at 50°C for 1 day in air, followed by vacuum-drying at 50°C for 3 days. A white, non-hygroscopic (air-stable) solid was obtained at room temperature (RT), which melts at ~70°C, forming a colorless liquid (see Fig. 1b).

**Characterization as a solvate IL.**—For Raman measurements at RT an integrated Raman system (B&W Tek, innoRam 785), consisting of a semiconductor laser light source (785 nm), an axial transmissive spectrograph, a holographic probe head, and a CCD detector, was used. To lessen the interference by fluorescence, the sample was mixed with active carbon in acetone overnight, then filtered and finally vacuum-dried to obtain a purified sample. The purity was evaluated by chemical analysis. The spectral acquisition time, i.e., exposure time of CCD and the number of exposures was varied for each sample to improve the signal-to-noise ratio of each spectrum. Infrared (IR) measurements were conducted using a JASCO FT/IR-460 plus system. For the IR measurement, Nujol and hexachlorobutadiene mulls painted on a barium fluoride window were used at RT. Nuclear magnetic resonance (NMR) spectra were obtained using a JNMR–ECA600 FT NMR spectrometer (JEOL Ltd.). ¹H NMR, ¹³C NMR, and ³¹P NMR spectra were obtained at 75°C. The use of a double NMR tube, purchased from Shimemi Corp. (catalog No. SC-002), prevented mixing of the sample and an external standard: traces of dimethyl sulfoxide-d₆ (Aldrich, 99.9 atom %D) were placed in the outer tube (5.2 mmφ), and [H₃O⁺ · 18C6]Tf₂N in the internal tube (5.0 mmφ). The melting point of the complex was evaluated by means of a differential scanning calorimeter (DSC; Shimadzu, DSC–60) with a sweeping rate of 5°C min⁻¹ by heating from room temperature up to 80°C and then cooling down to 40°C. Thermal gravimetric analysis (TGA) measurements were performed using a Netzsch STA 2500 instrument in a helium atmosphere at 5 K min⁻¹. The 4.9-mg sample was placed on an Al pan and Al₂O₃ was used as a standard.

**Viscosity and conductivity.**—Conductivity measurements were performed between 75°C and 95°C by the AC impedance method using a Radiometer Analytical CDM230. Viscosity measurements were conducted using Sekonic VM-10A and VM-1G calibrated using a standard solution (Nippon Grease Co., Ltd.). The density of the sample was calculated to be 1.32 g cm⁻³ at 70°C using the measured values of weight and volume.

**Electrochemical measurements.**—Linear sweep voltammetry (LSV) was conducted in air for [H₃O⁺ · 18C6]Tf₂N at 90°C without agitation using a potentiostat (HSV-110, Hokuto Denko). A Pt disk electrode (3 mmφ, PT-6355, EC Frontier) and a glassy carbon electrode (Toyo Tanso) were used as the working electrode (WE) and counter electrode (CE), respectively. It is reported that a Sn electrode shows stable potential and can be used as the reference electrode (RE).39 Thus, as the RE a Sn rod was immersed in 50 mmol dm⁻³ Sn(Tf₂N)Cl in 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonimide)amide (EMITf₂N; Kanto Chemical, 99.9% purity), separated from the main electrolyte by porous Vycor glass. Before the measurements, the WE and CE were washed with acetone and the RE was washed with 1 mol dm⁻³ HCl aqueous solution.

**Determination of hammett acidity function.**—The Brønsted acidity was evaluated from the determination of the Hammett acidity function, by an indicator method via UV-visible spectrosopy.40,41 The Hammett acidity function (H₀) is defined as

\[ H₀ = pK(\text{I}_\text{aq}) + \log [\text{I}]/[\text{I}^+] \]  

where pK(\text{I}_\text{aq}) is the pKᵢ value of the spectroscopic indicator referred to in aqueous solution. [I]ᵢ indicates the molar concentration of the unprotonated (I) form of the indicator in the solvent; [I⁺]ᵢ represents the molar concentration of the protonated (I⁺) forms. 2,4-dinitroaniline (2.74×10⁻⁴ mol dm⁻³) was used as an indicator. H₀ of [H₃O⁺ · 18C6]Tf₂N at 75°C was measured by a UV-visible spectrometer (U-3500, Hitachi). 2,4-dinitroaniline (2.74×10⁻⁴ mol dm⁻³) was added and stirred into [H₃O⁺ · 18C6]Tf₂N at 75°C to form a solution. The reference absorbance was obtained using 2.74×10⁻⁴ mol dm⁻³ of 2,4-dinitroaniline in anhydrous ethanol (Wako Chemical).

To compare the acidity between [H₃O⁺ · 18C6]Tf₂N and HTf₂N, [H₃O⁺ · 18C6]Tf₂N or HTf₂N was dissolved in a common IL, and H₀ was measured at RT. Note that since the use of an IL as a solvent will certainly affect the results, the acidity depends on the selected solvent. In this work, a common IL, EMITf₂N, was chosen as the solvent. 2.0×10⁻⁴ mol dm⁻³ of 2,4-dinitroaniline in EMITf₂N was stirred for 1 day at 110°C in an Ar-filled glove box to remove water. Then [H₃O⁺ · 18C6]Tf₂N or HTf₂N was added and stirred in the indicator solution for 10 min at RT in the glove box. These EMITf₂N solutions were placed into screw-capped cells in the glove box, and transferred into a UV-visible spectrometer (U-3500, Hitachi) for measurements at RT. Concentrations of [H₃O⁺ · 18C6]Tf₂N ranged from 50 to 2000 mmol dm⁻³, and those of HTf₂N from 50 to 1000 mmol dm⁻³.

**Results and Discussion**

**Facile synthesis of [H₃O⁺ · 18C6]Tf₂N.**—The strong hydrophobicity and high chemical stability of the Tf₂N⁻ anion allowed the facile synthesis of [H₃O⁺ · 18C6]Tf₂N. Here, water acts bifunctionally, i.e. both as a reactant and as the reaction solvent, from which a solid sample of [H₃O⁺ · 18C6]Tf₂N was obtained successfully via vacuum drying at 50°C. In contrast, the known [H₃O⁺ · 18C6] complexes have been synthesized using an organic solvent (e.g. tetrahydrofuran, benzene, CH₃Cl₂), into which only a stoichiometric amount of H₂O was added as a reactant with 18C6 and an acid.42,43 We believe that the reason why an organic solvent was used is that some of the anions (e.g. BF₄⁻ and FeCl₄⁻) are hydrophilic and it is difficult to obtain the pure [H₃O⁺ · 18C6] complexes. Another reason is that an excess amount of water can cause hydrolysis or decomposition of anions (SbF₆⁻, PF₆⁻, BF₄⁻, FeCl₄⁻), which creates impurities such as H⁺ or HCl. For
Table I. Result of chemical analysis for [H$_3$O$^+ \cdot 18$C$_6$]Tf$_2$N.

<table>
<thead>
<tr>
<th>element</th>
<th>H [wt%]</th>
<th>C [wt%]</th>
<th>N [wt%]</th>
<th>F [wt%]</th>
<th>S [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>experimental</td>
<td>4.90</td>
<td>29.97</td>
<td>2.40</td>
<td>20.07</td>
<td>11.35</td>
</tr>
<tr>
<td>calculated</td>
<td>4.83</td>
<td>29.84</td>
<td>2.49</td>
<td>20.23</td>
<td>11.38</td>
</tr>
</tbody>
</table>

example, it is reported that the PF$_6^-$ anion can be decomposed by moisture and result in HF, POF$_3$, etc. In contrast, Tf$_2$N$^-$ salts are known to be dehydrated without significant decomposition.

**Classification of [H$_3$O$^+ \cdot 18$C$_6$]Tf$_2$N into a solvate IL.**—According to Mandai et al., solvate ILs should satisfy all the following criteria (1)–(5):

1. Form a solvate compound between an ion and a ligand(s) in a certain stoichiometric ratio.
2. Consist entirely of complex ions (solvates) and their counter ions in the molten state.
3. Show no physicochemical properties based on both pure ligands and precursor salts under usage conditions.
4. Have a melting point below 100 $^\circ$C, which satisfies the criterion for typical ILs.
5. Have a negligible vapor pressure under typical application conditions.

Firstly, chemical analysis data for H, C, N, F, and S were consistent with the suggested formulation [H$_3$O$^+ \cdot 18$C$_6$]Tf$_2$N (within ±0.2 wt% of the calculated value; see Table I). The H$_2$O content of the complex was 3.29 wt% analyzed by Karl-Fischer coulometric titration, in good agreement with the calculated value (3.20 wt%). In addition, the H$_2$O content of the sample, kept in a screw-capped vial (not a septum) in air at RT for 2 weeks, did not vary within the experimental limit. This proved the air-stable nature of [H$_3$O$^+ \cdot 18$C$_6$]Tf$_2$N, i.e. water absorption is very slow. Consequently, these quantitative analysis results strongly support that the complex was 18C$_6$:H$_2$O:HTf$_2$N = 1:1:1 by mole, satisfying criterion (1).

Secondly, the Raman results shown in Fig. 2 satisfy criteria (2) and (3). This point is also supported by the IR results shown in Fig. 3. The Raman spectrum for molten [H$_3$O$^+ \cdot 18$C$_6$]Tf$_2$N clearly illustrates that any bands attributable to free 18C$_6$ ligand molecules are absent. The appearance of the Raman peak centered at 873 cm$^{-1}$, the so-called breathing mode, means a change in the COC stretching and CH$_2$ rocking modes of 18C$_6$ due to the complex formation, as in the case of alkali metal ether complexes. In the IR spectra, the COC stretching absorption for pure 18C$_6$ is seen as a broad band at 1125 cm$^{-1}$, which disappeared and split into sharp bands at 1138 cm$^{-1}$ and 1091 cm$^{-1}$ because of [H$_3$O$^+ \cdot 18$C$_6$] formation (see Fig. 3a). The presence of H$_3$O$^+$ with 18C$_6$ is readily established from the characteristic bands in the IR spectra i.e. $\nu_1$–$\nu_4$ (see Fig. 3b). The $\nu_1$ and $\nu_2$ stretching modes give a very broad band centered at 2920 cm$^{-1}$, which overlaps the sharper maximum at 2880 cm$^{-1}$ arising from the C–H stretching motions of 18C$_6$. The $\nu_3$ band at 1100 cm$^{-1}$ is not clearly observed, where a strong band from 18C$_6$ overlaps. Consequently, the IR spectra clearly display the presence of H$_3$O$^+$. Therefore, it is proved that all 18C$_6$ ligands coordinate to hydronium cations to form [H$_3$O$^+ \cdot 18$C$_6$]. The anionic band appears at 739 cm$^{-1}$ without shoulder peaks. Although the resolution is low, its full width at half maximum (FWHM) is comparable to that of the anionic band for “free” Tf$_2$N$^-$ in our previous report. This indicates that the Tf$_2$N$^-$ anions are “free” and not forming complex anions such as [H(Tf$_2$N)$_2$]$^-$.45

Thirdly, DSC measurements revealed a single endothermic peak and a corresponding exothermic peak (see Fig. 4). The ratio of integrated peak areas for the melting and those for subsequent crystallization was close to unity. The melting point was 68–70 $^\circ$C, satisfying criterion (4). Since no additional peaks were seen around the melting points of pure 18C$_6$ (39–40 $^\circ$C) and pure HTf$_2$N (52–56 $^\circ$C), neither
free ligands nor precursor HTf$_2$N were included in the sample. This satisfies criterion (3).

Fourthly, the $^1$H NMR spectra for the molten state (75°C, Fig. 5a) show only two singlets at 10.85 ppm and 3.23 ppm. The former is for H$_3$O$^+$ and the latter is for CH$_2$ of 18C6. These chemical shifts agree with those for [H$_3$O$^+$ · 18C6] salts dissolved in an organic solvent. $^{13}$C NMR (shown in Fig. 5b) also revealed the presence of 18C6 ligands and Tf$_2$N$^-$ anions with an equimolar ratio: a singlet for 18C6 at 69.37 ppm and a quartet for CF$_3$ of Tf$_2$N$^-$ (122.89 ppm, 120.76 ppm, 118.62 ppm, 116.50 ppm) with a peak area ratio of 6:1, which agrees the theoretical $^{13}$C ratio 18C6:Tf$_2$N$^- = C$_{12}$H$_{24}$O$_6$:N(SO$_2$CF$_3$)$_2 = 12:2$. In comparison, the NMR results for pure 18C6 at molten state (60°C) showed a distinguishable change in chemical shift (3.26 ppm for H, 70.43 ppm for C; not shown). Fig. 5c displays $^{19}$F NMR which exhibits a singlet at −79.79 ppm, the region characteristic of ionic CF$_3$SO$_2$ derivatives: they fall between −71 ppm and −80 ppm (CFCl$_3$), shifting to a higher field as the charge on the CF$_3$SO$_2$ group increases.$^{37}$ Consequently, the [H$_3$O$^+$ · 18C6] complex is the only component cation and Tf$_2$N$^-$ is the only component anion in molten [H$_3$O$^+$ · 18C6]Tf$_2$N. These NMR results satisfy criteria (1)–(4).

Finally, in the TGA data obtained at 5 K min$^{-1}$ no mass loss was detected below 100°C (see Fig. 6). This indicates that neither free 18C6, H$_2$O nor precursor HTf$_2$N were included in the sample, satisfying criterion (3). Moreover, a 5 wt% loss was detected at 132°C, a temperature 60°C higher than its melting point. The TGA results suggest a low vapor pressure of [H$_3$O$^+$ · 18C6]Tf$_2$N at around its melting point, that is, [H$_3$O$^+$ · 18C6]Tf$_2$N has a limited window of usage, e.g. between 50–75°C. At such a temperature range, however, the vapor pressure can be negligible, satisfying criterion (5).

In all, criteria (1)–(5) were satisfied to classify [H$_3$O$^+$ · 18C6]Tf$_2$N as a solvate IL. The solvate ILs reported so far are binary mixtures of alkali-metal salts and polyethers.$^{7–13}$ In contrast, the hydronium solvate IL, the first example of a nonmetal-cation-solvate IL, is a ternary mixture of water, crown ether, and fluorinated imide superacid. Surveying the analogous compounds would give hydronium solvate ILs that have wide temperature windows of usage.

**Conductivity and viscosity of the hydronium solvate IL [H$_3$O$^+$ · 18C6]Tf$_2$N.**—It is interesting to study the bath properties of molten [H$_3$O$^+$ · 18C6]Tf$_2$N, since the observed strong acidity implies high proton conduction. Table II lists the conductivities and viscosities at several temperatures. Although the temperature range is narrow, we estimated the activation energy from Arrhenius plots.
Table II. Viscosities and conductivities of molten [H$_3$O$^+$ - 18C6]Tf$_2$N.

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>Viscosity [mPa s]</th>
<th>Conductivity [mS cm$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>75</td>
<td>42.9</td>
<td>2.36</td>
</tr>
<tr>
<td>80</td>
<td>37.0</td>
<td>2.72</td>
</tr>
<tr>
<td>85</td>
<td>32.3</td>
<td>3.05</td>
</tr>
<tr>
<td>89</td>
<td>29.1</td>
<td>3.43</td>
</tr>
<tr>
<td>94</td>
<td>25.5</td>
<td>3.91</td>
</tr>
</tbody>
</table>

giving comparable values: 28.0 kJ mol$^{-1}$ for ionic conduction and 28.9 kJ mol$^{-1}$ for viscous flow with the correlation coefficients $R^2 = 0.999$ in both cases. Figure 7 shows a plot of molar conductivity ($\Lambda$$_{imp}$; measured by AC impedance method) vs. fluidity ($\eta$$^{-1}$), i.e. the Walden plot of [H$_3$O$^+$ - 18C6]Tf$_2$N. Here $\Lambda$$_{ideal}$ is assumed to be the ideal molar conductivity at a given fluidity of an ideal KCl aqueous solution, where the K$^+$ and Cl$^-$ ions are completely dissociated and act in an independent fashion. In other words, the absolute value of $\Lambda$$_{ideal}$ (S cm$^{-1}$ mol$^{-1}$) is equal to that of fluidity, $\eta$$^{-1}$ (Poise$^{-1}$ or 10 Pa s$^{-1}$), giving the ideal KCl line (solid line in Fig. 7). The ionicity, i.e. the degree of cation-anion dissociation, is estimated as a conductivity ratio $\Lambda$$_{imp}$/\Lambda$$_{ideal}$: in the Walden plot the measure of ionicity is the vertical deviation from the ideal line $\Delta W = \log(\Lambda$$_{imp}$/\Lambda$$_{ideal}$). The value of $\Delta W$ for [H$_3$O$^+$ - 18C6]Tf$_2$N is $-0.36$, resulting in $\Lambda$$_{imp}$/\Lambda$$_{ideal}$ = 0.44 (10$^{-0.36}$ = 0.44); this represents the situation where the IL is exhibiting as high as 44% of the conductivity that might be expected on the basis of its viscosity. Using ionicity, solvate ILs have been categorized as good ILs ($0 > \Delta W > -1$) and poor ILs ($-1 > \Delta W$):$^{7,8,13}$ thus, the hydronium solvate IL is a good IL, and is comparable to common ILs.

We stress that the conductivity of the [H$_3$O$^+$ - 18C6]Tf$_2$N sample is not assisted by excess water, which would help proton conduction. The IR spectra clearly show the absence of unprotonated water in the sample. The broad band due to unprotonated water was observed at 3480 cm$^{-1}$ for pure (as received) 18C6 (see Fig. 3);$^{47}$ the water content was 0.14 wt% analyzed by Karl–Fischer titration. For the “pure” complex, however, the broad band at 3480 cm$^{-1}$ due to unprotonated water disappeared, while a sharp band appeared at 3570 cm$^{-1}$, which may be due to the presence of H$_2$O$^+$. Notably, when excess water was added to [H$_3$O$^+$ - 18C6]Tf$_2$N, a broad band appeared at 3200–3600 cm$^{-1}$ (not shown). Therefore, unprotonated water, which would help proton conduction, is excluded in the [H$_3$O$^+$ - 18C6]Tf$_2$N sample, proving that intrinsic conductivity data are obtained.

Acidity of the hydronium solvate IL [H$_3$O$^+$ - 18C6]Tf$_2$N.—Figure 8 shows the LSV result for [H$_3$O$^+$ - 18C6]Tf$_2$N obtained at 90°C. An increase in reduction current was observed below approximately +0.026 V vs. Sn where the current reached 20 µA cm$^{-2}$. Since the redox potential of Sn/Sn$^{2+}$ in aqueous solution is $\sim$0.1375 V vs. SHE, the observed reduction potential was not far below 0 V vs. SHE. This strongly suggests high proton activity or high acidic strength of [H$_3$O$^+$ - 18C6]Tf$_2$N.

The pH acidity scale cannot be used for ILs because they are non-aqueous. Instead, the Hammett acidity function $H_0$ of an IL is evaluated from UV-visible measurements of the IL specimen mixed with an indicator.$^{40,42}$ By this evaluation method, the ILs with the strongest acidities were reported in 2007 and 2009: $H_0 = -3.6$, both being SO$_3$H-functionalized ILs.$^{18,19}$ Using the indicator 2,4-dinitroaniline with $pK_a = -4.53$, the Hammett acidity function $H_0$ was determined for [H$_3$O$^+$ - 18C6]Tf$_2$N. In Fig. 9, the UV-vis results showed a decrease in the intensity of the peak centered at $\sim$337.6 nm, indicating that 43% of the indicator was protonated. The value of $H_0$ was $-4.4$ for [H$_3$O$^+$ - 18C6]Tf$_2$N at 75°C, stronger than the previous record for acidic ILs ($H_0 = -3.6$).$^{18,19}$ The strong acidity in [H$_3$O$^+$ - 18C6]Tf$_2$N results from a combination of the weak bases 18C6 and H$_2$O and the superacid HTf$_2$N. In addition, since the amount of free water is negligible, the leveling effect of water is absent in [H$_3$O$^+$ - 18C6]Tf$_2$N.

Although [H$_3$O$^+$ - 18C6]Tf$_2$N is a solid at RT, it also showed strong acidity when dissolved into a RT IL. Table III lists the value of $H_0$ at several concentrations of [H$_3$O$^+$ - 18C6]Tf$_2$N in EMITf$_2$N solution. The strongest $H_0$ was $-4.6$, obtained at 2 mol dm$^{-3}$. For comparison, $H_0$ of HTf$_2$N in EMITf$_2$N solution was also investigated. Table IV lists...
of ILs via facile synthesis is of special interest for many bio- and electro-chemical applications.

Acknowledgments

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