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## Ammonium·18-crown-6 bis(trifluoromethylsulfonyl)amide

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We report synthesis and characterization of an ammonium-based molten salt, ammonium bis(trifluoromethylsulfonyl)amide-18-crown-6 (1/1), i.e.  $[\text{NH}_4^+\cdot 18\text{C}6][\text{Tf}_2\text{N}^-]$  ( $\text{Tf} = \text{SO}_2\text{CF}_3$ ). Raman spectra shows  $[\text{NH}_4^+\cdot 18\text{C}6][\text{Tf}_2\text{N}^-]$  consists of  $\text{NH}_4^+$  ion encapsulated by 18C6 and  $\text{Tf}_2\text{N}^-$  anion. The melting point of  $[\text{NH}_4^+\cdot 18\text{C}6][\text{Tf}_2\text{N}^-]$  was around 100 °C. At 140 °C, the viscosity of  $[\text{NH}_4^+\cdot 18\text{C}6][\text{Tf}_2\text{N}^-]$  was 14.7 mPa s, the conductivity was 8.0 mS  $\text{cm}^{-1}$ , and the density was 1.23  $\text{g cm}^{-3}$ . These properties were comparable to those of common ionic liquids.

### Introduction

Ammonium ( $\text{NH}_4^+$ ) ion has some unique properties as a charge carrier, i.e., natural abundance and lightweight properties. Compared with metal cations (such as  $\text{Li}^+$ ,  $\text{Na}^+$ , and  $\text{K}^+$ ),  $\text{NH}_4^+$  ion shows the highest intercalation potential and comparable cycling performance for Prussian blue-type positive electrode materials,  $\text{KM}[\text{Fe}(\text{CN})_6]$  ( $M = \text{Ni}$  and  $\text{Cu}$ ) (1). More recently, the first rocking-chair-type  $\text{NH}_4^+$  ion battery has been proposed (2). The electrolytes for  $\text{NH}_4^+$  ion batteries, however, have rarely been investigated except for aqueous solutions and solid state electrolytes (2, 3). Therefore, electrolytes which enable fast  $\text{NH}_4^+$  ion transport at medium temperatures, i.e. 100–200 °C, have been of great interest.

Molten salts, especially ionic liquids (ILs), have received considerable attention as novel electrolyte materials for future electrochemical devices owing to their various characteristics such as negligible volatility, low flammability, high thermal/electrochemical stability, and high ionic conductivity (4–6). We have reported a hydronium ( $\text{H}_3\text{O}^+$ ) solvate IL, which is described as  $[\text{H}_3\text{O}^+\cdot 18\text{C}6][\text{Tf}_2\text{N}^-]$  (7–9). In  $[\text{H}_3\text{O}^+\cdot 18\text{C}6][\text{Tf}_2\text{N}^-]$ , protic  $\text{H}_3\text{O}^+$  ion (i.e., solute) is solvated by 18C6 ligand (i.e., solvent) to form a  $[\text{H}_3\text{O}^+\cdot 18\text{C}6]$  complex cation (i.e., solvate), and its physicochemical properties satisfy the criteria of solvate ILs (10).

It is well known that 18C6 features a six-oxygen cavity and matches well with  $\text{NH}_4^+$  as well as  $\text{H}_3\text{O}^+$  in a  $C_{3v}$  coordination, while the degree of off-center of  $[\text{NH}_4^+\cdot 18\text{C}6]$  is larger than that of  $[\text{H}_3\text{O}^+\cdot 18\text{C}6]$  (11). As far as we know, however,  $\text{NH}_4^+$ -based molten salts or ILs for electrolytes have never been reported, while alkyl ammonium-based ones have already been studied (12). Herein, we report synthesis and characterization of  $[\text{NH}_4^+\cdot 18\text{C}6][\text{Tf}_2\text{N}^-]$  (Figure 1).

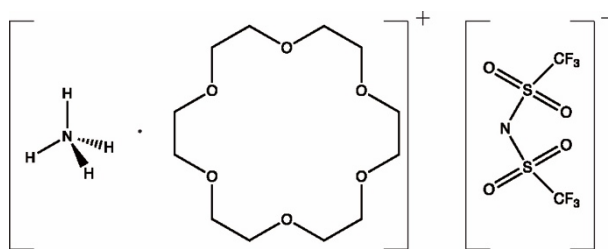


Figure 1. Schematic structure of 18C6,  $\text{NH}_4^+$ , and  $\text{Tf}_2\text{N}^-$ , of which  $[\text{NH}_4^+\cdot 18\text{C6}][\text{Tf}_2\text{N}^-]$  consists.

## Experimental

18-crown-6 (18C6; Kanto Chemical, 99% purity), ammonia aqueous solution (Nakalai, 28%,  $0.9 \text{ g cm}^{-1}$ ), and bis(trifluoromethylsulfonyl)imide ( $\text{HTf}_2\text{N}$ ; Kanto Chemical, 99% purity) were used without further purification. Ultrapure water was prepared using a Merck Milli-Q Reference A system. First,  $\text{NH}_4\text{Tf}_2\text{N}$  was synthesized by neutralization of  $\text{HTf}_2\text{N}$  and  $\text{NH}_3$  in water, followed by heating the precipitates at  $100 \text{ }^\circ\text{C}$  for 24 h under Ar atmosphere, and the subsequent vacuum-drying at  $80 \text{ }^\circ\text{C}$  for 24 h. Then, we added equimolar amount of  $\text{NH}_4\text{Tf}_2\text{N}$  to 18C6 and stirred at 500 rpm at  $150 \text{ }^\circ\text{C}$  for 2.5 h to obtain  $[\text{NH}_4^+\cdot 18\text{C6}][\text{Tf}_2\text{N}^-]$ .

The melting point of  $[\text{NH}_4^+\cdot 18\text{C6}][\text{Tf}_2\text{N}^-]$  was determined using a differential scanning calorimeter (DSC; Rigaku, DSC8231) with the heating rate of  $5 \text{ }^\circ\text{C min}^{-1}$ . Raman spectra were obtained using 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. We conducted the thermogravimetric analysis (TGA) for  $[\text{NH}_4^+\cdot 18\text{C6}][\text{Tf}_2\text{N}^-]$ , 18C6, and  $\text{NH}_4\text{Tf}_2\text{N}$  with the heating rate of  $5 \text{ }^\circ\text{C min}^{-1}$ , using TG-DTA8122 (Rigaku) instrument in dry air. The conductivity at molten state was determined by electrochemical impedance spectroscopy (Bio-Logic Science Instruments SAS, VSP-300) using stainless steel electrodes. The cell constant was calibrated with 0.1 and  $1 \text{ mol dm}^{-3}$  KCl aqueous solutions. The measurement was carried out in a thermostatic chamber (Espec Co., SU-222) at  $140 \text{ }^\circ\text{C}$ . Viscosity measurements were performed at the same temperature as conductivity measurements using a viscometer (Kyoto Electronics Manufacturing Co., Ltd., EMS-1000). The density was calculated using the measured values of weight and volume.

## Results and discussion

A differential scanning calorimetry revealed that  $[\text{NH}_4^+\cdot 18\text{C6}][\text{Tf}_2\text{N}^-]$  melts at around  $100 \text{ }^\circ\text{C}$  (Figure 2). Since no additional peaks were seen around the melting points of pure 18C6 ( $39\text{--}40 \text{ }^\circ\text{C}$ ) and pure  $\text{NH}_4\text{Tf}_2\text{N}$  ( $165\text{--}168 \text{ }^\circ\text{C}$ ), neither free ligands nor precursor  $\text{NH}_4\text{Tf}_2\text{N}$  were included.

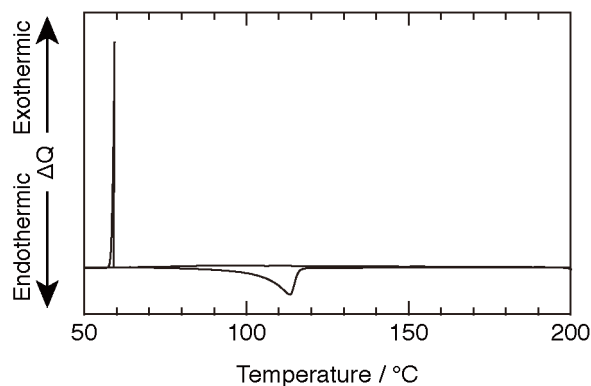


Figure 2. DSC curves for  $[\text{NH}_4^+\cdot 18\text{C}6][\text{Tf}_2\text{N}^-]$  with the heating rate of  $5\text{ }^\circ\text{C min}^{-1}$ .

Figure 3 shows a set of Raman spectra for  $[\text{NH}_4^+\cdot 18\text{C}6][\text{Tf}_2\text{N}^-]$  and 18C6.  $[\text{NH}_4^+\cdot 18\text{C}6][\text{Tf}_2\text{N}^-]$  displayed two sharp peaks at  $870$  and  $830\text{ cm}^{-1}$  instead of the broad Raman bands assignable to pure 18C6, just like potassium–glyme complex in solid state (13). This indicates a change in the COC stretching and  $\text{CH}_2$  rocking modes of 18C6 as a result of complexation. The Raman bands for  $\text{Tf}_2\text{N}^-$  anions emerged at around  $745\text{ cm}^{-1}$ . Consequently, the mixture of  $\text{NH}_4\text{Tf}_2\text{N}$  and 18C6 consists of  $\text{NH}_4^+$  ion (i.e., solute) solvated by 18C6 ligand (i.e., solvent) to form a  $[\text{NH}_4^+\cdot 18\text{C}6]$  complex cation (i.e., solvate), and  $\text{Tf}_2\text{N}^-$  anion.

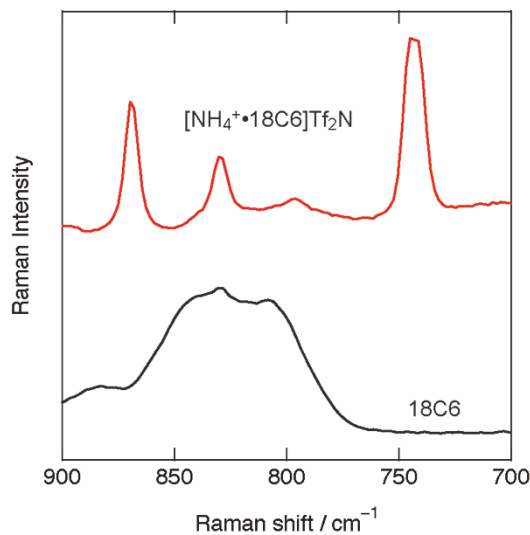


Figure 3. Raman spectra between  $900\text{--}700\text{ cm}^{-1}$  of  $[\text{NH}_4^+\cdot 18\text{C}6][\text{Tf}_2\text{N}^-]$  and 18C6 at room temperature i.e., solid state.

As shown in Fig. 4, in TGA data obtained at  $5\text{ }^\circ\text{C min}^{-1}$  no mass loss was detected below  $150\text{ }^\circ\text{C}$ . Moreover, a 5 wt.% loss was detected at  $212\text{ }^\circ\text{C}$ , a temperature  $100\text{ }^\circ\text{C}$  higher than its melting point, indicating that neither free 18C6 and precursor  $\text{NH}_4\text{Tf}_2\text{N}$  were included.

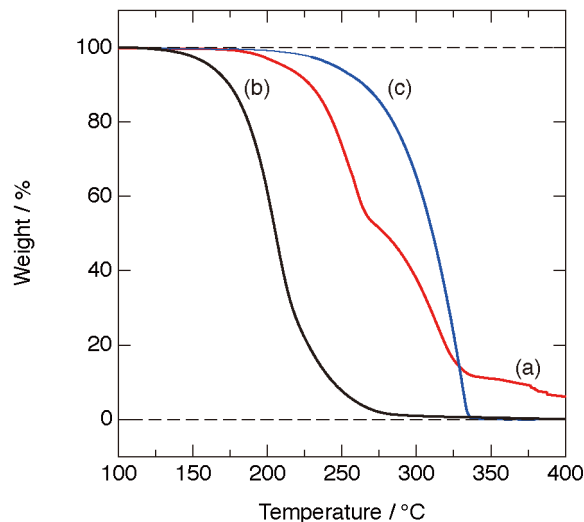


Figure 4. TGA data for (a)  $[\text{NH}_4^+\cdot 18\text{C}6][\text{Tf}_2\text{N}^-]$ , (b) 18C6, and  $\text{NH}_4\text{Tf}_2\text{N}$  at  $5\text{ }^\circ\text{C min}^{-1}$ .

At  $140\text{ }^\circ\text{C}$ , the viscosity of  $[\text{NH}_4^+\cdot 18\text{C}6][\text{Tf}_2\text{N}^-]$  was  $14.7\text{ mPa s}$ , the conductivity was  $8.0\text{ mS cm}^{-1}$ , and the density was  $1.23\text{ g cm}^{-3}$ . The bath properties of  $[\text{NH}_4^+\cdot 18\text{C}6][\text{Tf}_2\text{N}^-]$  were comparable to those of common ILs. Therefore,  $[\text{NH}_4^+\cdot 18\text{C}6][\text{Tf}_2\text{N}^-]$  has potential applications as electrolyte materials working at temperature higher than  $100\text{ }^\circ\text{C}$ .

## Conclusions

In conclusion, we synthesized ether-coordinated ammonium amide, i.e.  $[\text{NH}_4^+\cdot 18\text{C}6][\text{Tf}_2\text{N}^-]$ , of which melting point was around  $100\text{ }^\circ\text{C}$ . Raman spectroscopic measurement show that  $[\text{NH}_4^+\cdot 18\text{C}6][\text{Tf}_2\text{N}^-]$  consists  $\text{NH}_4^+$  cation encapsulated by 18C6 and an amide anion. The ether-coordinated ammonium amide has potential applications as electrolyte materials toward a new class of ammonium ion batteries.

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