doi:10.1246/cl.2010.1006

Trialkyl(pentafluorocyclotriphosphazenyl)ammonium Bis(trifluoromethylsulfonyl)imide Acting as Nonflammable Room-temperature Ionic Liquids

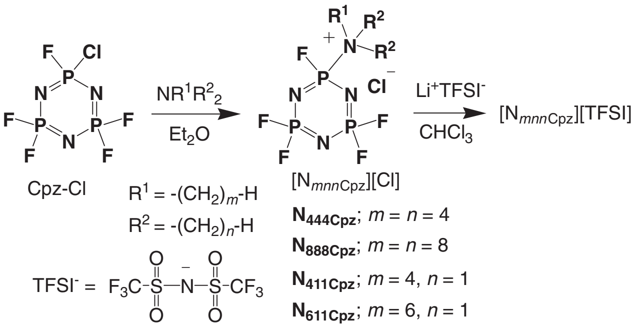
Tsutomu Shiragami,*[1] Yoko Nakamura,[1] Jin Matsumoto,[1] Masashi Otsuki,[2] and Masahide Yasuda[1]
[1]*Department of Applied Chemistry, Faculty of Engineering, University of Miyazaki, Gakuen-Kibanadai, Miyazaki 889-2192*
[2]*Central Research, Bridgestone Corporation, Ogawahigashi-Cho, Kodaira, Tokyo 187-8531*

(Received June 21, 2010; CL-100573; E-mail: t0g109u@cc.miyazaki-u.ac.jp)

Trialkyl(pentafluorocyclotriphosphazenyl)ammonium bis(trifluoromethylsulfonyl)imide were synthesized. They were nonflammable room-temperature ionic liquid which showed low ionic conductivity (0.29–2.32 mS cm^{-1}) and viscosity (33.3–56.2 mPa s). They displayed extremely low viscosity in spite of the high molecular weight.

Room-temperature ionic liquids (RTILs) are well known to have unique properties such as a very small vapor pressure, high thermal stability, and ionic conductivity. Therefore, much attention has been extensively paid to the application of RTILs to reaction solvents,[1] extraction solvents,[2] and electrolyte materials.[3] Recently the use of nonflammable RTILs have been applied to the electrolyte in batteries to reduce the fire and burn hazard. However, nonflammability of typical RTILs such as ammonium ($R_4N^+X^-$) and imidazolium (Im^+X^-) are insufficient, because they contain H and C atoms to some extent. On the other hand, pentafluorocyclotriphosphazenyl (Cpz) group is stable and nonflammable owing to the non-carbon aromatic ring.[4] Therefore, Cpz-Cl and its derivatives have been used in lithium ion batteries as an additive to resist to flame.[5] However, Cpz-Cl shows no conductivity at all, resulting in the decrease of current efficiency in batteries. Therefore, our strategy is to develop Cpz RTILs that can be used as nonflammable electrolyte. Here, we report the properties of RTILs consisting of trialkyl(Cpz)ammonium ([$N_{mnn\mathrm{Cpz}}$]) and bis(trifluoromethylsulfonyl)imide ([TFSI]), although there is an only report on RTILs with plural ammonium cations around cyclotriphosphazen moiety.[6]

The [$N_{mnn\mathrm{Cpz}}$][X] (X = Cl and TFSI) were prepared according to Scheme 1. The corresponding tertiary amines (1.0 mmol) were added to Et_2O solution (30 cm^3) of Cpz-Cl (1.0 mmol, Bridgestone Corp.), and the mixtures were stirred for 1 h at 20 °C. After evaporating the solvent, [$N_{mnn\mathrm{Cpz}}$][Cl] was subjected to an anion-exchange reaction performed by mixing a $CHCl_3$ solution (30 cm^3) of [$N_{mnn\mathrm{Cpz}}$][Cl] (2.2 mmol) and Li^+TFSI^- (2.2 mmol, Aldrich), to obtain a light yellow liquid after filtering the precipitate of LiCl. The [$N_{mnn\mathrm{Cpz}}$][TFSI] was purified by centrifugal separation and active charcoal treatment. In the ^{1}H NMR spectra of [$N_{444\mathrm{Cpz}}$][TFSI], for example, the chemical shift (δ) of α-proton of the butylamino group was shifted to a lower magnetic field ($\Delta\delta$ 0.67) than that of the free butylamine, and the spin–spin coupling between the α-proton and P atom (P_N) bonded with an N atom was also observed ($J_{\mathrm{P-H}} = 5.2$ Hz). Furthermore, δ of P_N was shifted 23.5 ppm to higher magnetic field than that of the P–Cl bond in Cpz-Cl, showing the transformation of the P–Cl bond to a P–N bond. Similar spectral data were obtained in another [$N_{mnn\mathrm{Cpz}}$][X].[7] IR spectra of [$N_{mnn\mathrm{Cpz}}$][X] revealed the characteristic absorption bands (957 and 1279 cm^{-1}) for the Cpz ring.[8] IR spectra of [$N_{mnn\mathrm{Cpz}}$][TFSI] gave two additional characteristic absorption bands; 1040 (S=O) and 1200 cm^{-1} (C–F). ^{13}C NMR showed CF_3 of $TFSI^-$ at 119.56 ppm. From the ratio of signal intensity between CF_3 and the carbon atom of the alkyl group, the quantitative ion-exchange reaction from Cl^- to $TFSI^-$ was confirmed.



Scheme 1.

The [$N_{444\mathrm{Cpz}}$][Cl] and [$N_{mnn\mathrm{Cpz}}$][TFSI] were liquid at room temperature (20 °C) while [$N_{888\mathrm{Cpz}}$][Cl], [$N_{411\mathrm{Cpz}}$][Cl], and [$N_{611\mathrm{Cpz}}$][Cl] were obtained as a solid state. The presence of a long alkyl chain was requisite to being liquid at room temperature. The [$N_{mnn\mathrm{Cpz}}$][TFSI] were miscible with EtOAc, $CHCl_3$, CH_2Cl_2, acetone, MeCN, and MeOH. The polarity of [$N_{mnn\mathrm{Cpz}}$][X] was determined to be $E_T(30)$ obtained by use of Reichardt's dye. The values were found to be 55–57 kcal mol^{-1}, comparable to MeOH, showing that [$N_{mnn\mathrm{Cpz}}$][X] had high polarity. The decomposition temperature of [$N_{mnn\mathrm{Cpz}}$][X] was found by TGA to be 182–204 °C, lower than that of Im^+TFSI^- (ca. 400 °C).[9] Furthermore, it was shown that all [$N_{mnn\mathrm{Cpz}}$][TFSI] were nonflammable by UL94HB, a standard method for determination of flammability.[10] The physical properties are summarized in Table 1.

The viscosity (η) was determined to be 33.3 to 65.4 mPa sec for oily [$N_{mnn\mathrm{Cpz}}$][X]. In general, it is known that the η values of ILs strongly depend on their molecular weight. Figure 1 shows the relationship between η and molecular weight of [$N_{mnn\mathrm{Cpz}}$][X] in comparison with $(R)Et_3N^+TFSI^-$ (R = $-CH_2OCH_3$, $-C_2H_4OCH_3$, $-(CH_2)_n-H$, $n = 5$, 8, and 12) systems.[11] As a characteristic of [$N_{mnn\mathrm{Cpz}}$][X], it was noted that they had much lower η values independently of molecular weight, while those of $(R)Et_3N^+TFSI^-$ increased proportionally to molecular weight. As a reason why η was extremely small, we considered two speculations. One is the existence of fluorine in molecule, because fluorine induces a decreasing of intermolecular interaction. In fact, it was reported the decreasing of η by partially fluorination of ILs.[12] Second is the formation of aggregation due to high electrostatic interaction of [$N_{mnn\mathrm{Cpz}}$][X].

Table 1. Physical properties of $1^{+}X^{-}$

RTILs	Yield[b] /%	M_r[c]	d[d] /g cm^{-3}	$E_T(30)$ /kcal mol^{-1}	T_{dec}[e] /°C	η[f] /mPa s	σ[g] /mS cm^{-1}	Λ[h] /S cm^2 mol^{-1}
$[N_{444Cpz}][Cl]$	16	450.74	1.11	55	182	65.4	0.19	0.08
$[N_{444Cpz}][TFSI]$[a]	12	695.43	1.12	57	204	43.8	1.01	0.63
$[N_{888Cpz}][TFSI]$[a]	13	863.75	1.13	57	196	56.2	0.29	0.22
$[N_{411Cpz}][TFSI]$	4	611.27	1.12	56	195	33.3	2.32	1.27
$[N_{611Cpz}][TFSI]$	5	639.32	1.12	56	194	55.8	0.50	0.29

[a]Water content was below 5 ppm. [b]Based on **2** used. [c]Molecular weight. [d]Density at 25 °C. [e]Thermal decomposition temperature of 10% weight loss. [f]Viscosity at 25 °C. [g]Ionic conductivity at 25 °C. [h]Molar conductivity at 25 °C.

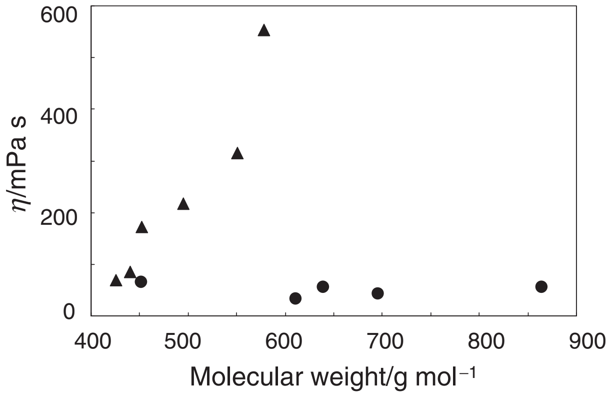


Figure 1. Plots of η versus molecular weight in $[N_{mnnCpz}][X]$ (●) and $R_4N^{+}TFSI^{-}$ (▲) (ref. 11).

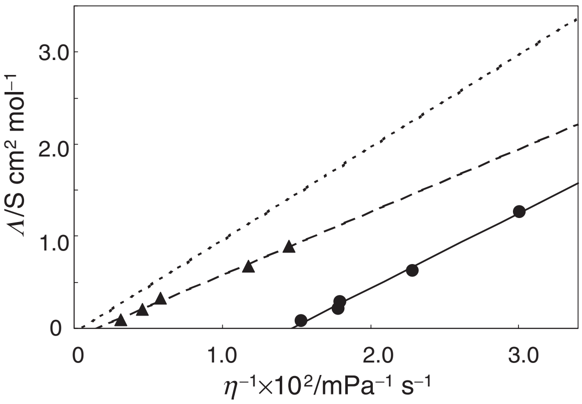


Figure 2. Plots of Λ versus η^{-1} in $[N_{mnnCpz}][X]$ (●) and $R_4N^{+}TFSI^{-}$ (▲) (ref. 11). The dotted line shows the ideal Walden line.

Moreover, the ionic conductivity (σ) was measured and was converted to molar conductivity (Λ). The Λ of $[N_{mnnCpz}][X]$ were too low to use as the electrolyte in batteries, lower than $Im^{+}TFSI^{-}$, a typical RTIL.[13] However, a plot of Λ versus the reciprocal of η in $[N_{mnnCpz}][X]$, a Walden plot,[14] gave a good linear correlation, strongly indicating that the $[N_{mnnCpz}][X]$ should be RTILs (Figure 2). In general, the large deviation from the Walden line showed that the electrostatic interaction between cations and anions is stronger.[14] Therefore, the large deviations indicated that the electrostatic interactions between $[N_{mnnCpz}]$ and [TFSI] are much larger than those of the tertiary amine RTILs.

In conclusion, $[N_{mnnCpz}][X]$ are a nonflammable RTIL with the low η and Λ. Although the Λ values were not sufficient for use as battery electrolytes, they can be used as a flame-retardant additive without decreasing current efficiency. Extended studies are still in progress in our group.

References

1 a) P. Wasserscheid, T. Welton, *Ion Liquids in Synthesis*, Wiley-VCH, Weinheim Germany, **2003**. b) T. Itoh, E. Akasaki, K. Kudo, S. Shirakami, *Chem. Lett.* **2001**, 262.

2 J. G. Huddleston, R. D. Rogers, *Chem. Commun.* **1998**, 1765.

3 M. Yoshizawa, A. Narita, H. Ohno, *Aust. J. Chem.* **2004**, *57*, 139.

4 a) H. R. Allcock, *Chem. Rev.* **1972**, *72*, 315. b) B. S. Nader, K. K. Kar, T. A. Morgan, C. E. Pawloski, W. L. Dilling, *Tribol. Trans.* **1992**, *35*, 37.

5 a) Q. Zhang, H. Noguchi, H. Wang, M. Yoshio, M. Otsuki, T. Ogino, *Chem. Lett.* **2005**, *34*, 1012. b) M. Otsuki, T. Ogino, K. Amine, *ECS Trans.* **2006**, *24*, 13.

6 B. A. Omotowa, B. S. Phillips, J. S. Zabinski, J. M. Shreeve, *Inorg. Chem.* **2004**, *43*, 5466.

7 Supporting Information is available at http://www.csj.jp/journals/chem-lett/index.html.

8 L. G. Lund, N. L. Paddock, J. E. Proctor, H. T. Searle, *J. Chem. Soc.* **1960**, 2542.

9 H. L. Ngo, K. LeCompte, L. Hargens, A. B. McEwen, *Thermochim. Acta* **2000**, *357–358*, 97.

10 Standard method of "Under Whiters Laboratories Inc" in U. S. A.

11 K. Tsunashima, M. Sugiya, *Electrochem. Commun.* **2007**, *9*, 2353.

12 a) Y. Tsukada, K. Iwamoto, H. Furutani, Y. Matsushita, Y. Abe, K. Matsumoto, K. Monda, S. Hayase, M. Kawatsura, T. Itoh, *Tetrahedron Lett.* **2006**, *47*, 1801. b) M. Yoshino, R. J. Brodd, A. Kozawa, *Li-ion Batteries: Science and Technologies*, Springer Science+Business Media, New York, **2009**, p. 275.

13 a) P. Bonhôte, A.-P. Dias, N. Papageorgiou, K. Kalyanasundaram, M. Grätzel, *Inorg. Chem.* **1996**, *35*, 1168. b) H. Matsumoto, M. Yanagida, K. Tanimoto, M. Nomura, Y. Kitagawa, Y. Miyazaki, *Chem. Lett.* **2000**, 922. c) H. Matsumoto, H. Sakaebe, K. Tatsumi, *J. Power Sources* **2005**, *146*, 45.

14 M. Yoshizawa, W. Xu, C. A. Angell, *J. Am. Chem. Soc.* **2003**, *125*, 15411.