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Physicochemical Properties of Nitrile-Functionalized Ionic Liquids

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A series of ionic liquids (ILs) based on nitrile-functionalized imidazolium, pyridinium, and quaternary ammonium as cations and chlorides and tetrafluoroborate, hexafluorophosphate, dicyanamide, and bis(trifluoromethanesulfonyl)imide as anions have been prepared and characterized. The physicochemical properties such as spectroscopic, thermal, solubility, surface, electrochemical, tribological, and toxic properties were comparatively studied. The results showed that the incorporation of a CN group to cations could result in remarkable changes in these properties. The reason resulting in such remarkable differences in the properties may be attributed to the conformational changes in the imidazolium groups caused by the interaction between the CN group with other neighboring cations or anions and the enhancement in hydrogen-bonding interactions due to the incorporation of a CN group.

Introduction

Currently, functionalized ionic liquids (ILs) with peculiar physicochemical characteristics have been one of the hot topics in the field of IL research.[1−3] To achieve this goal, incorporation of different functional groups such as $-NH_2$,[4] $-SH$,[5] $-NHCONH_2$,[6] $-OH$,[7] $-SO_3H$,[8] etc. into the alkyl side chains on the imidazolium, pyridinium, etc. cations has been implemented to prepare so-called “task specific” ionic liquids (TSILs) named first by Davis and Rogers,[9] and their potential applications in synthesis,[10] catalysis,[11] separation analysis,[12] electrochemistry,[13] clean energy, and function material[14] have been preliminarily demonstrated. The emergence of functionalized ILs has endowed the ILs with huge diversity both in quantity and properties and with more space for further development. Among these functionalized ILs, nitrile-functionalized pyridinium, imidazolium, and trimethyl ammonium salts, which were first reported by Dyson et al.,[15] have been paid much attention because such ILs have been shown to be suitable reaction media and ligands for catalytic reactions such as carbon−carbon coupling and Stille reactions and could be promising electrolytes for lithium battery and dye-sensitized solar cells.[15] In comparison with those with $-NH_2$, $-SH$, $-OH$, $-COOH$, and $-NHCONH_2$ as functional groups attached, ILs with a CN group are expected to possess simultaneously peculiar properties and relatively higher stabilities, which make these kinds of TSILs more attractive for versatile practical applications.

Although several nitrile-functionalized ILs have been prepared and preliminarily characterized (crystal structures or water effect on the structure by Dyson, Zakeeruddin, and Hamaguchi),[14a,15,16] most of them are solids at room temperatures, i.e., ca. 25 °C or even lower, which would decrease the possibility of their potential applications. However, there is still some room to develop new nitrile-functionalized ILs that may be liquids at lower temperatures, and also it should be noted that detailed characterization of physicochemical properties of these nitrile-functionalized ILs has not been investigated yet. In this work, an attempt was made to systematically characterize nitrile-functionalized ILs on the basis of four kinds of cations and five kinds of anions as shown in Scheme 1, and the detailed comparison of the differences in physicochemical characteristics such as density, viscosity, phase behavior, thermal stability, heat capacity, refractive index, surface tension, solubility property, electrochemical property, tribological performance, and toxicity before and after incorporation of a CN group were particularly emphasized.

Experimental Section

Materials. Most of the chemicals used in this work were of analytical grade and were used as received. 1,2-Dimethylimidazole (98.0%) was obtained from Merck. Lithium trifluoromethanesulfonimide (≥99.95%) and sodium dicyanamide (96%) were purchased from Aldrich. [BMIm]NTf_2 and [BMIm]$N(CN)_2$ were prepared according to the methods reported in the literature[17] and, for the purpose of comparison, [BMIm]BF_4 and [BMIm]PF_6 with high purity were also purchased from Merck.

Synthesis and Characterization. All the nitrile-functionalized ILs were prepared according to the similar approach reported previously.[15,16] 1-Butyronitrile-3-methylimidazolium chloride ([C_3CNMIm]Cl) was prepared with high yield from the reaction of 1-methylimidazole and 4-chlorobutyronitrile of appropriate amount to afford 1-alkyl-3-methylimidazolium chlorides[18] with slight modification, and 1-butyronitrile-2,3-dimethylimidazolium chloride ([C_3CNMMIm]Cl) and *N*-butyronitrile pyridinium chloride ([C_3CNPy]Cl) were prepared similarly via the quaternization reactions of 1,2-dimethylimidazolium or pyridinium with 4-chlorobutyronitrile in

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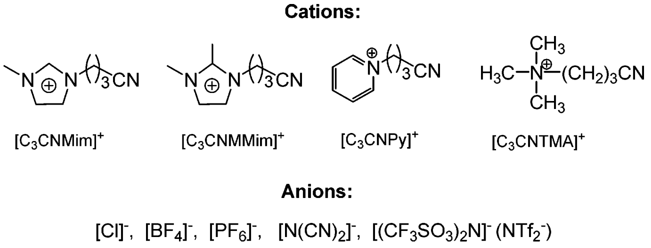
SCHEME 1: Structure and Abbreviations of the Cations and Anions Employed in This Work



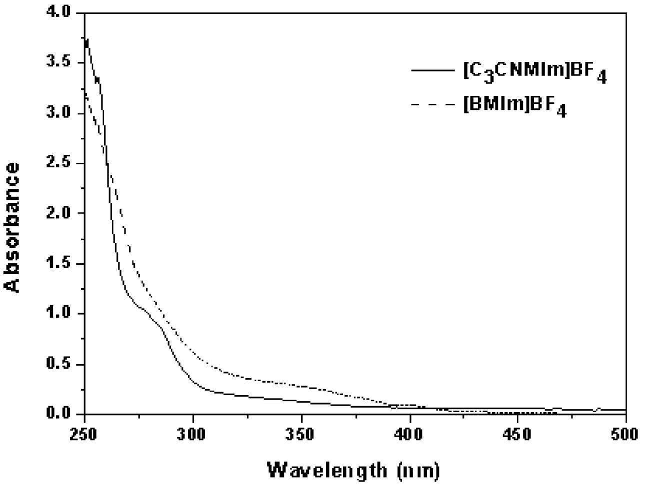


Figure 2. UV−vis spectra of [BMIm]BF_4 (neat) and [C_3CNMIm] BF_4 (neat).

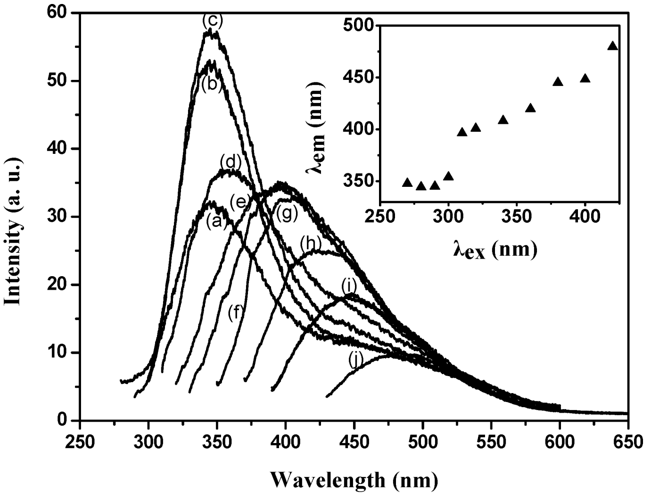


Figure 3. Excitation wavelength-dependent emission behavior of neat [BMIm]BF_4. λ_{exc} (nm) = 290 (a), 310 (b), 320 (c), 330 (d), 340 (e), 350 (f), 360 (g), 380 (h), 400 (i), and 420 (j).

appropriate solvents. Butyronitrile-trimmethylammonium chloride ([C_3CNTMA]Cl) was obtained from the reaction of trimethyl amine solution (≥33%) with equimolar 4-chlorobutyronitrile at room temperature. The functionalized ILs with BF_4^-, PF_6^-, NTf_2^-, and $N(CN)_2^-$ as anions were easily obtained with high quality via the anion exchange reaction among the above-mentioned four types of chlorides with the corresponding inorganic salts, i.e., $NaBF_4$, NH_4PF_6, $NaN(CN)_2$, and $LiNTf_2$, respectively. In order to ensure that these salts are free from colored impurities, further purification of the ILs was made before every test of physicochemical properties. All the ILs were diluted with acetone or acetonitrile and then treated with activated carbon for at least 6 h. After filtration, the liquids thus prepared were then transferred in clean and dry reagent bottles and kept in a vacuum (pressure $10^{-2}-10^{-3}$ mbar) at 95−100 °C for 12 h for the removal of any organic impurities or water. The purified ILs were stored in a desiccator under dry nitrogen wrapped by aluminum foils. ^{1}H NMR spectra were recorded on a Bruker AMX FT 400 MHz NMR spectrometer. Chemical shifts were reported downfield in parts per million (ppm, δ) from a tetramethylsilane reference. IR spectra were recorded on a Thermo Nicolet 5700 FTIR spectrophotometer. Ultra-Vis spectra were conducted on an Agilent 8453 UV−vis spectrophotometer. The fluorescence spectra were recorded at room temperature on a Hitachi model F-4500 FL spectrophotometer at a scan speed of 240 nm/min. Measurements of phase-transition temperatures, melting and freezing points, transitions of melting enthalpy (ΔH_m), and heat capacities were carried out on a Mettler-Toledo differential scanning calorimeter, model DSC822^e, and the data were evaluated using the Mettler-Toledo STARe software version 7.01. The thermal decomposition temperatures (T_d) with a 5% weight loss were assessed by employing a Beijing WCT-2C TG/DTA analyzer at a heating rate of 10 °C/min under nitrogen atmosphere. The viscosity and density of each IL were measured on a Stabinger Viscosimeter SVM 3000/GR. Measurements of refractive indices were conducted with a WAY-2s Abbe refractometer (Shanghai Precision & Scientific Instrument Co.), calibrated by the refractive indices of deionized water. Equilibrium measurements of the apparent surface tension were performed with use of a DUNuoy Tensiometer with a platinum ring. Solubility properties of the selected gases and organic compounds as solutes in these

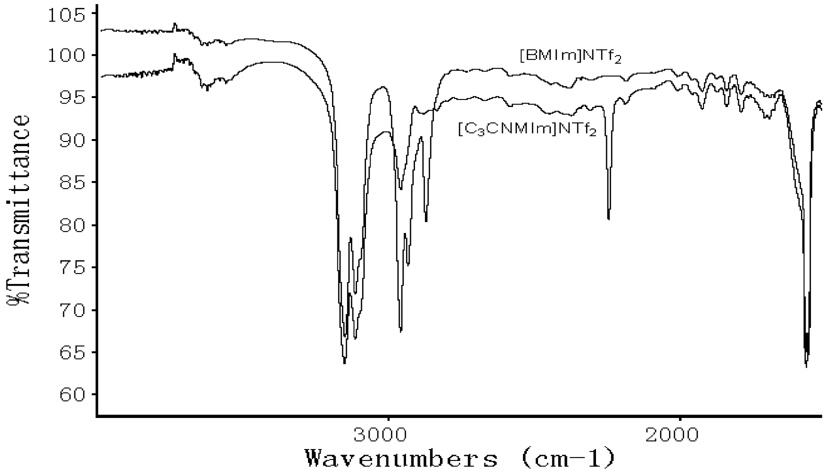


Figure 1. FTIR spectra of [BMIm]NTf_2 and [C_3CNMIm]NTf_2.

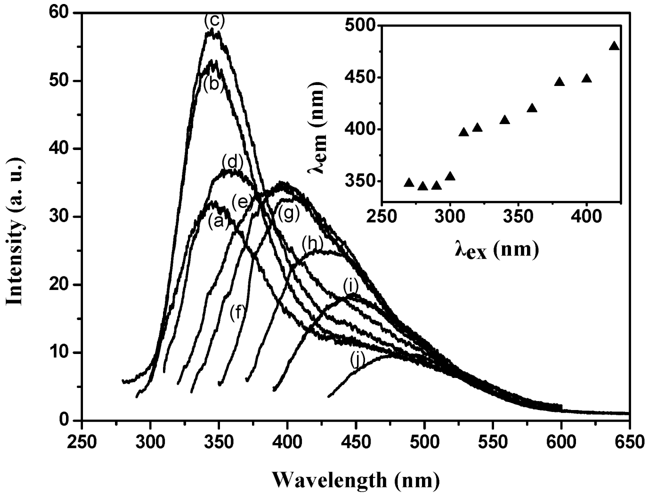


Figure 4. Excitation wavelength-dependent emission behavior of neat $[C_3CNMIm]BF_4$. λ_{exc} (nm) = 270 (a), 280 (b), 290 (c), 300 (d), 310 (e), 320 (f), 340 (g), 360 (h), 380 (i), 400 (j), and 420 (k).

ILs were investigated via the determination of the corresponding Herny coefficients or infinite dilution activity coefficients by a gas chromatographic method.[19] The tribological behaviors of the ILs were evaluated using an Optimol SRV oscillating friction and wear tester with a ball-on-disc configuration. The ion conductivity was measured using a Mettler-Toledo Seven Muliti meter. The cyclic voltammetry was conducted using a CHI 660A Electrochemical Work Station with a GC working electrode and an Ag wire pseudoreference electrode. The details of the sample preparation, characterization, and spectroscopy information were described in the Supporting Information.

Results and Discussion

All nitrile-functionalized ILs were obtained with yields of 72−93%. They are moisture stable. Among them, $[C_3CNMIm]BF_4$, $[C_3CNMIm]NTf_2$, $[C_3CNMIm]N(CN)_2$, $[C_3CNMMIm]NTf_2$, $[C_3CNMMIm]N(CN)_2$′$[C_3CNPy]BF_4$, $[C_3CNPy]NTf_2$′, and $[C_3CNPy]N(CN)_2$ are colorless liquids at room temperature (ca. 25 °C) and can be miscible with water except for those with the NTf_2^- anion; the others are white solids at room temperature.

Spectroscopic Properties. First, NMR and FTIR spectroscopy were used to characterize the structures of the ILs prepared, and the information obtained showed that they are all the compounds as expected. For all nitrile-functionalized ILs, the main feature in the FTIR spectra was that the characteristic absorption of a CN group ranging from 2237 to 2254 cm^{-1} was observed. In comparison with $[BMIm]NTf_2$, some other changes in the FTIR spectra could also be observed over $[C_3CNMIm]NTf_2$. The replacement of a terminal methyl group with the CN group resulted in the disappearance of the aliphatic C−H vibrations at 2880 and 2940 cm^{-1}. The reason is that these two absorptions of $[BMIm]NTf_2$ are derived from the C−H vibration modes of the terminal methyl group of the butyl chain, and this assignment has also been confirmed by isotopically labeling the butyl chain with deuterium where the two peaks are then absent.[20,21]

The UV−vis absorption spectra of ILs with or without a CN group have also been compared. Generally, they possess similar absorption characteristics, and the main feature is that all of them have strong absorption below 300 nm, and the absorption tail extends beyond 400 nm. However, differences in absorption, particularly in the UV region, were still remarkable. From the typical UV−vis absorption spectra of $[BMIm]BF_4$ and $[C_3CNMIm]BF_4$ (Figure 2), the absorption characteristics can be seen in the UV region: the absorption intensity of $[C_3CNMIm]BF_4$ at 250−260 nm was larger than that of $[BMIm]BF_4$, and a new but weak absorption band at 275−285 nm was observed for $[C_3CNMIm]BF_4$. Because the absorption in the UV region is related to the excitation of π-electrons on the imidazolium ring, this means that a CN group may influence the fine structure of the imidazolium ring through the interaction with other neighboring cations or anions.

The fluorescence behaviors of pure $[BMIm]BF_4$ and $[C_3CNMIm]BF_4$ are strongly dependent on the excitation wavelength (Figure 3 and Figure 4). For $[BMIm]BF_4$, no fluorescence could be observed when excited wavelengths were below 290 or over 420 nm. The fluorescence appeared with longer wavelength and became stronger in intensity with an emission band centered on 410 nm, and then, the intensity decreased quickly with the maximum emission shifted from 410 to 480 nm as excited wavelengths increased from 290 to 420 nm. As for $[C_3CNMIm]BF_4$, relatively strong fluorescence

TABLE 1: Thermal Properties of Twenty Nitrile-Functionalized ILs

ionic liquids	T_m (°C)	T_f (°C)	T_{cc} (°C)	T_g (°C)	ΔC_p[a] ($J\ g^{-1}\ K^{-1}$)	ΔH_m ($kJ\ mol^{-1}$)	ΔS_m[b] ($J\ K^{-1}\ mol^{-1}$)	C_p (J/g/ K)	T_d (°C)
$[C_3CNMIm]Cl$	90.3		26.0	−34.1	0.50	−19.1	52.6	1.56	254.9
$[C_3CNMIm]BF_4$				−63.2	0.33			1.82	264.9
$[C_3CNMIm]PF_6$	72.0	28.0	26.4			−17.5	58.1	1.20	275.2
$[C_3CNMIm]NTf_2$				−70.7	0.30			1.40	384.3
$[C_3CNMIm]\ N(CN)_2$				−71.8	0.47			2.01	278.1
$[C_3CNMMIm]Cl$				−18.9	0.45			1.41	248.7
$[C_3CNMMIm]\ BF_4$				−46.5	0.32			1.35	352.3
$[C_3CNMMIm]\ PF_6$	90.5		37.9	−35.5	0.24	−35.1	96.6	1.56	369.6
$[C_3CNMMIm]\ NTf_2$				−61.5	0.28			1.61	424.7
$[C_3CNMMIm]\ N(CN)_2$				−61.0	0.44			1.93	289.2
$[C_3CNPy]Cl$	69.2	10.9				−13.9	40.7	1.22	223.6
$[C_3CNPy]BF_4$	60.8		23.5	−56.0	0.35	−12.4	37.10	1.77	321.4
$[C_3CNPy]PF_6$	101.0	44.8				−14.5	38.9	1.44	330.5
$[C_3CNPy]NTf_2$				−62.3	0.32			1.48	273.9
$[C_3CNPy]N(CN)_2$				−64.3	0.45			1.98	226.4
$[C_3CNTMA]Cl$	78.8	63.5				−13.8	38.1	1.54	216.8
$[C_3CNTMA]BF_4$	60.9		26.5	−47.2	0.37	−12.3	36.8	1.35	249.2
$[C_3CNTMA]PF_6$	162.5	61.1				−20.5	47.1	1.20	347.3
$[C_3CNTMA]NTf_2$	58.1	17.6	22.4			−20.2	60.9	1.12	362.6
$[C_3CNTMA]\ N(CN)_2$	43.2	−8.7	22.4			−16.1	51.0	1.73	240.9

[a] ΔC_p is the heat capacity change during the glass transition. [b] ΔS_m calculated from $\Delta H_m/T_m$ is the entropy change during the melting.

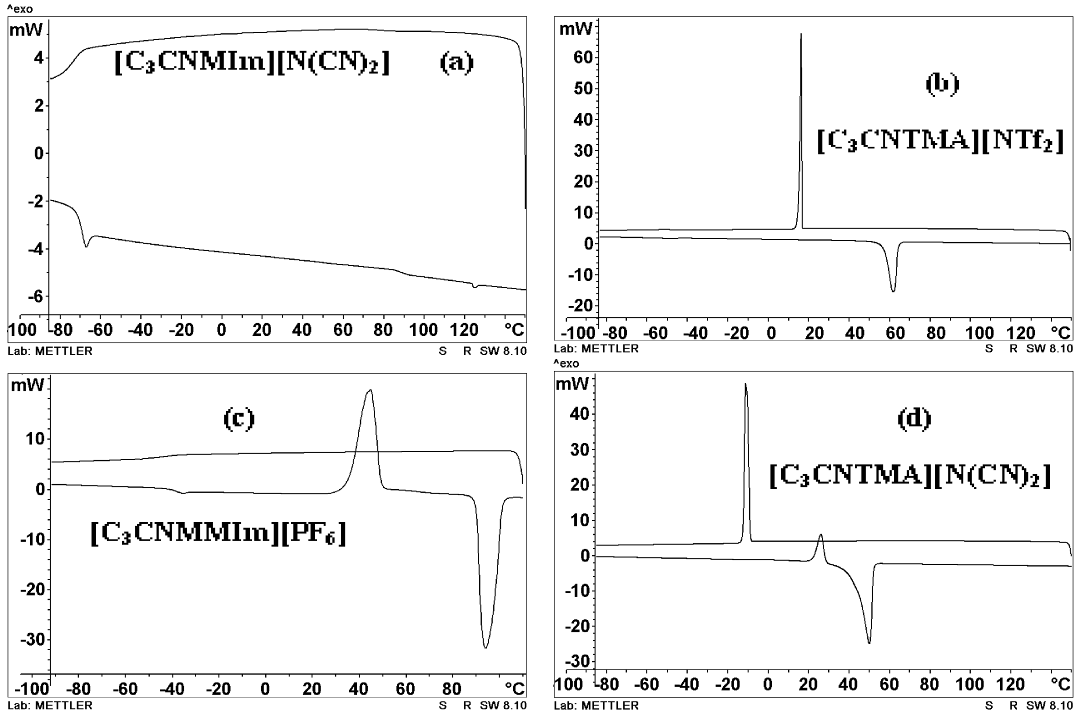


Figure 5. Different phase behaviors of the ILs in a heating and cooling cycle.

TABLE 2: Density, Viscosity, Refractive Index, and Surface Tension of the Selected ILs at 25 °C

	density: $\rho = a - bT$ [g/cm^3] (T in K)					
ionic liquids	ρ	a	b	viscosity (cP)	refractive index (n)	surface tension (mJ/m^2)
[BMIm]BF$_4$	1.260			219	1.4188	38.1
[BMIm]PF$_6$	1.368			173	1.4083	42.7
[BMIm]NTf$_2$	1.436			44	1.4264	46.3
[C$_3$CNMIm]BF$_4$	1.319			352	1.4349	48.3
[C$_3$CNMIm]NTf$_2$	1.519	1.78	8.97×10^{-4}	286	1.4398	52.2
[C$_3$CNMIm]N(CN)$_2$	1.165	1.35	6.19×10^{-4}	206	1.5258	51.4
[C$_3$CNMMIm]NTf$_2$	1.483	1.74	8.80×10^{-4}	506	1.4435	45.2
[C$_3$CNMMIm]N(CN)$_2$	1.168			370	1.5255	40.5
[C$_3$CNPy]NTf$_2$	1.534			409	1.4561	44.8
[C$_3$CNPy]N(CN)$_2$	1.168			152	1.5453	39.1

could be observed as the excited wavelengths were as low as 270 nm. When the excited wavelengths were further increased from 270 to 420 nm, the intensity of fluorescence increased quickly and then had two maximum emissions around 345 and 400 nm. Also, it is worth noting that much higher quantum yield could be achieved when the excitation wavelength is shifted to >380 nm in comparison with that of [BMIm]BF$_4$, which implies that [C$_3$CNMIm]BF$_4$ might be a kind of photoluminescence material. These results showed that the incorporation of a CN group could greatly affect the fluorescence characteristic of [BMIm]BF$_4$ through changing the related structures with both short- and long-range spatial correlations of the cation−anion and cation−cation pairs.

Thermal Properties. The phase behaviors of ILs with a CN group such as melting and freezing points (T_m, T_f), crystal−crystal transition (T_{cc}), glass phase transition (T_g), melting enthalpy change (ΔH_m), and the corresponding entropy change (ΔS_m) as well as thermal decomposition temperatures (T_d) were investigated by DSC and thermogravimetric analysis (Table 1).

Relatively complicated phase behaviors were exhibited during decreasing and then increasing temperatures over these ILs with a CN group, and four types of DSC thermograms phase could be observed (Figure 5): (a) Only a glass transition but with varied temperatures from −18.9 to −71.8 °C appeared in a heating and cooling cycle over the nitrile-functionalized imidazolium or pyridinium ILs with BF$_4^-$, NTf$_2^-$, or N(CN)$_2^-$ as anions, which were similar to that of [BMIm]BF$_4$ (T_g = −85.0 °C). The corresponding enthalpy relaxations during the glass transition indicated that these ILs were not under the thermodynamic equilibrium below T_g and therefore showed endothermal phenomenon during the glass transition in order to relax to equilibrium. The reason may be attributed to a relaxation (with concurrent disordering) of the interdigitated arrangement of the alkyl chains in the imidazolium ring, and this phenomenon can be tracked by the heat capacity change (ΔC_p) during the glass transition. (b) Distinct freezing and melting points were observed only over the [C$_3$CNPy]Cl, [C$_3$CNPy]PF$_6$, [C$_3$CNTMA]Cl, [C$_3$CNTMA]PF$_6$, and [C$_3$CNTMA]NTf$_2$, and this kind of phase behavior is similar to [BMIm]Cl. (c) Subcooling phenomena were exhibited over [C$_3$CNMIm]Cl, [C$_3$CNPy]BF$_4$, [C$_3$CNMMIm]PF$_6$, and [C$_3$CNTMA]BF$_4$; i.e., no crystals formed during cooling and only a glass transition occurred. However, upon heating, the IL first passed from the glass state to a subcooled phase, and then a cold crystallization occurs, followed by a melting transition. (d) A cold crystallization, i.e., a crystal−crystal transition, occurred over [C$_3$CNMIm]PF$_6$ and [C$_3$CNTMA]N(CN)$_2$ before the melting process, which might be attributed to the structural rearrangements driven by a thermally activated increase of the molecular mobility. Generally, after incorporation of a CN group, the T_m, T_f, and T_g all increased; e.g., the T_m values of [BMIm]Cl and [C_3CNMIm]Cl are 65.4 and 90.3 °C, and the T_g values of [BMIm]NTf_2 and [C_3CNMIm]NTf_2 are −86.2 and −70.7 °C, increased by 24.9 and 15.5 °C, respectively. This may be attributed to the increased hydrogen-bonding interactions caused by the incorporation of a CN group. Like the melting points of all ILs, the phase behaviors are dependent upon so many factors and therefore are less predictable. For example, [BMIm]NTf_2 not only has a glass transition at −87 °C but also has a melting point at −2 °C. After incorporation of a CN group, [C_3CNMIm]NTf_2 only has a glass transition at −70.7 °C. However, not all the phase behavior of the ILs with a CN group changed appropriately in comparison with those without a CN group; e.g., both [BMIm]BF_4 and [C_3CNMIm]BF_4 showed only a glass transition in a heating and cooling cycle, and no other phase behaviors were observed. The transitions of melting enthalpy (ΔH_m) and entropy (ΔS_m) have been calculated over those ILs that exhibited distinct melting points (Table 1). After incorporation of a CN group, the ΔH_m and ΔS_m for most ILs decreased. For example, the ΔH_m and ΔS_m of [BMIm]Cl and [C_3CNMIm]Cl are 25.86 and 19.1 kJ mol^{-1} and 77.1 and 19.1 J K^{-1} mol^{-1}, respectively. This may be attributed to the conformational changes in the nitrile-functionalized imidazolium groups and the enhancement in hydrogen-bonding interactions due to the incorporation of a CN group.

The heat capacities (C_p) of the ILs with a CN group at 25 °C have been measured (Table 1) and ranged from 1.12−2.01 J/g/K. Generally, after incorporation of a CN group, the heat capacities of ILs increased. For example, [C_3CNMIm]BF_4 possessed a heat capacity of 1.82 J/g/K (25 °C), and the C_p of [BMIm]BF_4 from Merck is 1.51 J/g/K (25 °C). Although the heat capacity was affected by both cations and anions, anions have a more apparent effect than cations. Among the anion employed in this work, ILs with a $N(CN)_2^-$ anion have higher heat capacities than those with other anions, and [C_3CNMIm]$N(CN)_2$ gave the highest heat capacity (2.01 J/g/K), which is even higher than thermal oil (1.907 J/g/K).[22]

Thermal stabilities of the ILs before and after incorporation of a CN group were also investigated, and the temperatures of thermal decomposition (T_d, i.e., the temperatures at which the weight loss of the ILs in an aluminum pan under N_2 atmosphere reached 5%) of the ILs employed in this work were ranged 216.8−424.7 °C (Table 1). The T_d of ILs with incorporation of a CN group decreased remarkably. For example, the T_d of [BMIm]BF_4 is 403 °C, and the T_d of [C_3CNMIm]BF_4 is only 265 °C under the same conditions, which means that the incorporation of a CN group would activate the ILs. From the results in Table 1, general tendencies can be summarized: (1) imidazolium cations tend to be more stable in thermal stability than tetraalkyl animonium and pyridinium cations; (2) the relative thermal stabilities of cations studied in this work are [C_3CNMMIm] > [C_3CNMIm] > [C_3CNPy] > [C_3CNTMA]; (3) the relative thermal stabilities of anions are [NTf_2] > [PF_6] > [BF_4] > [$N(CN)_2$] > [Cl]. Among these studied salts, [C_3CNMMIm]NTf_2 showed the highest thermal stability (T_d = 424.7 °C); [C_3CNTMA]Cl gave the lowest thermal stability (T_d was only 216.8 °C).

Density, Viscosity, Refractive Index, and Surface Tension. The densities (ρ), viscosities (η), refractive indices (n), and surface tensions (γ) have been measured over those ILs with and without a CN group, which are liquids at 25 °C (Table 2). The densities and viscosities of [BMIm]BF_4 and [BMIm]NTf_2 were measured, and the data obtained were in agreement with the values in previously reported literature,[23] which indicates that our measurements were reliable. In comparison with the ILs without incorporation of a CN group, the densities of corresponding ILs increased after incorporation of a CN group, and as expected, the densities decreased linearly with increasing temperature (Figure 6). The strong dipole moment of the nitrile group may be responsible for the formation of a more ordered structure of cation and anion in the IL molecule and thus results in the increase of densities of ILs. The experimental data of densities were fitted using the linear equations, and the values of the fit parameters are presented in Table 2. It can also be seen that the density of [C_3CNMIm]NTf_2 (1.519 g/cm^3) is much higher than that of [C_3CNMIm]$N(CN)_2$ (1.165 g/cm^3); the densities of [C_3CNMIm]$N(CN)_2$, [C_3CNMMIm]$N(CN)_2$, and [C_3CNPy]$N(CN)_2$ ranged from 1.165 to 1.168 g/cm^{-3}, indicating that variation of anions has a stronger impact than that of cations on the density.

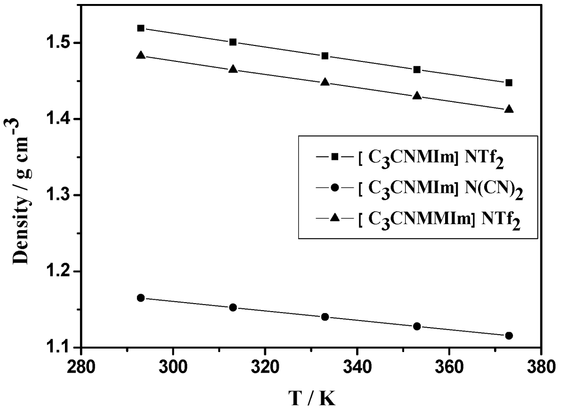


Figure 6. Densities as a function of temperature.

The viscosities (η) of the ILs after incorporation of a CN group increased obviously. For example, the η values of [BMIm]NTf_2 and [C_3CNMIm]NTf_2 are 44 and 286 cP, respectively. Among the studied ILs with a CN group, [C_3CNPy]$N(CN)_2$ gave the lowest viscosity (152 cP), which is lower than that of [BMIm]BF_4 (219cP) but is still much higher than that of [EMIm]$N(CN)_2$ (21cP). The increased hydrogen-bonding interactions derived from a CN group may be responsible for the increases in the viscosity of the ILs because the CN group is an electron donor and liable to form hydrogen bonging. The effect of temperature on viscosities for three studied ILs showed that viscosities decreased with increasing temperatures (Figure 7), and the viscosity was more affected particularly at lower temperatures.

The refractive indices (n) of the ILs with a CN group, which are liquids at 25 °C, ranged from 1.4349 to 1.5453, which are higher than those of the corresponding ILs without a CN group. The high refractive indices of the ILs with a CN group reflect particularly high electron mobility around the CN group. Therefore, it is expected that [C_3CNMIm]$N(CN)_2$, [C_3CNMMIm]$N(CN)_2$, and [C_3CNPy]$N(CN)_2$ containing three CN groups have higher n values than other ILs containing one or two CN groups. Among the studied ILs, [C_3CNPy]$N(CN)_2$ gave the highest refractive index (1.5453). Furthermore, the effect of temperature on the refractive index was also studied (Figure 8), and the n values decreased linearly with the increased temperatures. Although the n values of the ILs after incorporation of a CN group increased, the effect of the temperatures on the n values was almost unchanged in comparison with the corresponding ILs without a CN group.

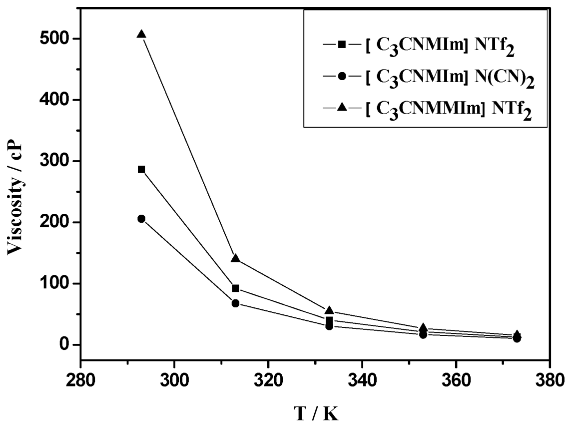


Figure 7. Viscosities as a function of temperature.

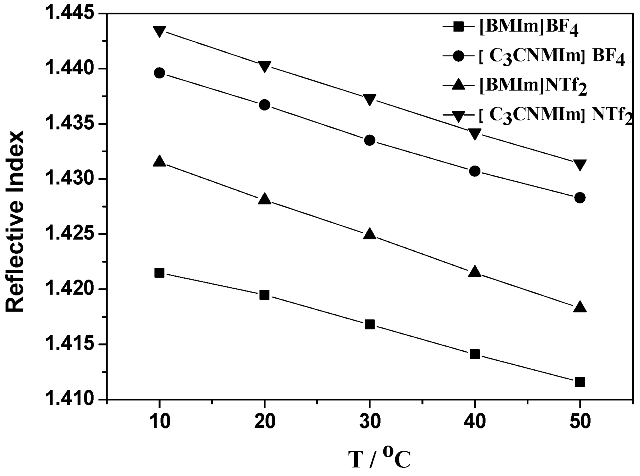


Figure 8. Refractive indices of four ILs as a function of temperature.

The surface tensions (γ) of several ILs were also measured, and the influence on surface tension after the incorporation of the CN group was investigated. As the results showed, the surface tension increased after the incorporation of the CN group. For example, the surface tension values of [BMIm]BF_4 and [C_3CNMIm]BF_4 are 38.1 and 48.3 mJ/m^2, respectively. For the same cation, [C_3CNMIm]$^+$, the IL having the larger anion exhibited a relatively higher surface tension. For example, the surface tension of [C_3CNMIm]NTf_2 (52.2 mJ/m^2) is higher than that of [C_3CNMIm]BF_4 (48.3 mJ/m^2). In addition, the incorporation of a methyl group at the two position of the imidazolium cation leads to the slight decrease in the surface tensions of ILs, suggesting that the substitution of the hydrogen at the two position with a methyl group may result in some changes of molecular orientation occurring in the IL surface.

Solubility Properties for Some Selected Gases and Organic Compounds. Selective solubility and solubility tunable are important properties of the functionalized ILs. Because Henry coefficients (*H*) or the infinite dilution activity coefficients (γ^∞) in a given solvent can be used to estimate the value of the solvent solubility, the solubility properties of selected gases and organic compounds as solutes in the selected ILs with and without incorporation of a CN group, which are liquids at 25 °C, were indirectly estimated through determination of Henry coefficients or the infinite dilution activity coefficients with a gas chromatographic method at 30 °C (Table 3). Generally, lower values of Henry coefficients and infinite dilution activity coefficients denote the presence of an attractive force between solute and solvent, i.e., relative higher solubility. Though not shown here, H_2, O_2, CO, CH_4, and N_2 are almost not soluble in these ILs with and without incorporation of a CN group because the Henry coefficients were so large that they could not be obtained. CO_2 gave smaller Henry coefficients than C_2H_4 in all the studied ILs. That is, CO_2 has a larger solubility than that of C_2H_4 in these ILs. After incorporation of a CN group, Henry coefficients of CO_2 and C_2H_4 in [BMIm]NTf_2 and [C_3CNMIm]NTf_2 increased from 33.44 to 42.10 and from 87.34 to 195.33, respectively, suggesting that the solubilities of both CO_2 and C_2H_4 decreased. This may be attributed to the increase of the ILs' polarity induced by the CN group and also suggested that the polarity of the side chain on the imidizolium cation could have much more effect on the solubility of C_2H_4 in ILs than that of CO_2. In addition, the incorporation of a methyl group at the two position of the imidazolium cation leads to the slight decrease in the solubilities of CO_2 and C_2H_4, suggesting that the substitution of the weak Lewis acidic hydrogen at the two position with a methyl group may result in a decrease in the interaction between CO_2 and the cation of ILs.

The γ^∞ values of hexane, cyclohexane, 1-hexene, benzene, and methanol in [BMIm]NTf_2 without a CN group showed the following order: hexane > cycloalkane >1-hexene > benzene ≈ methanol, and the corresponding order of the solubilities could be methanol ≈ benzene >1-hexene > cycloalkane > hexane, which is consistent what has been reported previously.[26] After incorporation of a CN group, the solubilities of methanol, benzene, 1-hexene, cyclohexane, and hexane in the ILs decreased from a slight to a large extent. This may be attributed to the higher polarity of cations due to the incorporation of a CN group. The substitution of H with a methyl group at the two position leads to the decrease of solubility of polar solutes such as methanol; in contrast, the solubilities of nonpolar solutes such as benzene, 1-hexene, cyclohexane, and hexane were increased greatly, which may be explained as the decreasing possibility of hydrogen-bonding interactions of solutes with the IL solvent if the active H at the two position was substituted by a methyl group. It is worth noting that [C_3CNMIm]$N(CN)_2$ possesses highly selective solubility for the hexane and benzene in comparison with [BMIm]NTf_2 because the γ^∞ values of hexane and benzene are 12.2 and 0.8 for [BMIm]NTf_2 and 546.28 and 2.3 for [C_3CNMIm]$N(CN)_2$, which may be promising for potential applications in the separation of hexane and benzene.

The hydrophilic or hydrophobic properties of the ILs with and without a CN group were also estimated. After incorporation of a CN group, the γ^∞ value of water in [C_3CNMIm]NTf_2, where the NTf_2^- anion was hydrophobic, decreased, indicating ILs with a CN group tended to be more hydrophilic because of the increased polarity of the cation. For [C_3CNMIm]$N(CN)_2$ and [C_3CNMMIm]$N(CN)_2$, γ^∞ values were too small to be measured, indicating that the interactions between H_2O and the ILs were very strong.

Tribological Properties. Because 1-methyl-3-hexylimidazolium hexafluorophosphate ([HMIm]BF_4) was found to possess excellent tribological properties),[14c] the synthesis of novel ILs with good tribological performance has received considerable attention. Tribological performance of ILs with a CN group as the lubricant for various sliding contacts was also evaluated in this work. For the purpose of comparison, popular fluorine-containing lubricant perfluoropolyether (PFPE) and [HMIm]BF_4 were also employed. From the test results of friction and wear of various ball-on-disc systems lubricated with four studied ILs as lubricants (Table 4), the ILs with a CN group showed much lower friction coefficients in comparison with PFPE; i.e., these nitrile-functionalized ILs have more

TABLE 3: Henry and Infinite Dilution Activity Coefficients of Selected Gases and Organic Solutes in Different ILs at 30 °C

	ILs				
solutes	[BMIm] NTf_2	[C_3CNMIm] NTf_2	[C_3CNMMIm] NTf_2	[C_3CNMIm] $N(CN)_2$	[C_3CNMMIm] $N(CN)_2$
	Henry Coefficients (H, bar)				
CO_2	33.44	42.10	46.20	110.56	136.26
C_2H_4	87.34	195.33	182.05	546.28	266.56
	Infinite Dilution Activity Coefficients (γ^∞)				
hexane	12.2	165.9	66.3	212.9	163.0
cyclohexane	7.4	55.4	48.4	81.7	97.5
1-hexene	6.2	54.2	32.0	71.7	103.6
benzene	0.8	1.8	1.9	2.3	3.0
methanol	0.8	1.1	1.9	0.3	0.4
H_2O	2.6	1.8	2.2	too small	too small

TABLE 4: Friction Coefficients for Several Frictional Pairs Lubricated with Different ILs[a]

	friction coefficient				
frictional pair (ball/disk)	[C_3CNMIm] BF_4	[C_3CNMIm] NTf_2	[C_3CNMIm] $N(CN)_2$	[BMIm]BF_4	PFPE
steel/steel	0.065	0.082	0.110	0.065	0.145
steel/Al	0.070	0.102	0.132	0.075	−
steel/Cu	0.055	0.090	0.065	0.040	0.145
steel/Si(100)	0.072	0.095	0.097	0.050	0.132
Si_3N_4/steel	0.075	0.091	−	0.069	*
Si_3N_4/Cu	0.067	0.083	0.085	0.040	*

[a] − means lubrication failure, and * means not detected.

TABLE 5: Tribological Properties of Different ILs for Steel/Steel Contact[a]

	friction coefficient					
load (N)	[C_3CNMIm] BF_4	[C_3CNMIm] NTf_2	[C_3CNMIm] $N(CN)_2$	[C_3CNMMIm] NTf_2	[BMIm]BF_4	PFPE
200	0.060	0.075	0.125	0.076	0.060	0.120
300	0.058	0.073	0.120	0.074	0.055	0.110
400	0.054	0.070	0.100	0.075	0.050	0.105
500	0.052	0.070	0.092	0.075	0.045	−
600	0.050	0.067	0.090	0.072	0.045	−

[a] − means lubrication failure

excellent tribological properties than PFPE. Among them, [C_3CNMIm]BF_4 gave the comparative tribological performance with [HMIm]BF_4, and even slightly better results could be obtained over [C_3CNMIm]BF_4 for steel/steel and steel/Al contacts. However, the other two ILs with NTf_2^- and $N(CN)_2^-$ as anions showed slightly lower wearing performance than [C_3CNMIm]BF_4, which showed that the anion had strong impact on the tribological properties, although the detailed mechanism is still not clear at this stage. In addition, other ball-on-disc wear tests such as steel/Cu, steel/Si(100), Si_3N_4/steel, and Si_3N_4/Cu have also been conducted, and three ILs with a CN group all showed inferior results in comparison with [HMIm]BF_4; that is, the incorporation of a CN group could not improve further the tribological properties for these sliding contacts. Tribological performance was further tested under relative high loads (≥200 N, Table 5). The corresponding friction coefficient from [HMIm]BF_4 and [C_3CNMIm]BF_4 remained at a comparative level with increasing loads. Although the other three ILs with NTf_2^- and $N(CN)_2^-$ as anions showed inferior tribological performance than [C_3CNMIm]BF_4, the tribological performance (friction coefficient = 0.082, 200 N) of the IL with a NTf_2^- anion was still much better than that of the popular lubricant PFPE.

TABLE 6: Electrochemical Potential Windows of ILs with and without a −CN Group

ionic liquid	temperature (°C)	reductive voltage (V)	oxidative voltage (V)	electrochemical window (V)
[BMIm]BF_4	25	−2.2	2.5	4.7
[BMIm]PF_6	25	−2.2	2.6	4.8
[BMIm]NTf_2	25	−2.2	2.6	4.8
[C_3CNMIm]BF_4	25	−2.2	3.1	5.3
[C_3CNMIm]NTf_2	25	−2.2	3.1	5.3
[C_3CNMMIm]NTf_2	35	−2.2	3.1	5.3
[C_3CNPy]NTf_2	40	−1.0	3.0	4.0
[C_3CNTMA]NTf_2	60	−2.6	3.2	5.8

Electrochemical Properties. The data of the reduction and oxidation potentials for [BMIm]BF_4 and [BMIm]PF_6 from Merck (Table 6) were consistent with the data reported previously,[24] which indicated that the electrochemical measurement system used in this work is accurate and reliable. It can be seen that the electrochemical stabilities of ILs after the incorporation of a CN group became much higher than that without a CN group. For example, the electrochemical windows are 5.3 V for [C_3CNMIm]NTf_2 and [C_3CNMMIm]NTf_2 and 5.8 V for [C_3CNTMA]NTf_2, which are all wider than that of [BMIm]NTf_2 (4.8V). It is worth noting that the increase in the electrochemical windows were derived from the increasing of oxidative voltage of the NTf_2^- anions other than from reductive potentials of the dialkyl imidazolium cation with a CN group; that is to say, for ILs with the same anion, such as NTf_2^- and BF_4^-, the electrochemical stability of the anion was remarkably extended by ca. 0.5 V resulting from the presence of the dialkyl imidazolium cation with a CN group, and at the same time, the reductive potential of the dialkyl imidazolium cation with a CN group was not changed in comparison with the corresponding dialkyl imidazolium cation without a CN group. This may be attributed either to the passivation of the anodic electrode induced by the cation with a CN group or to stronger interactions between the cation with a CN group and the anion via hydrogen bonding, which enhanced the electrochemical stability

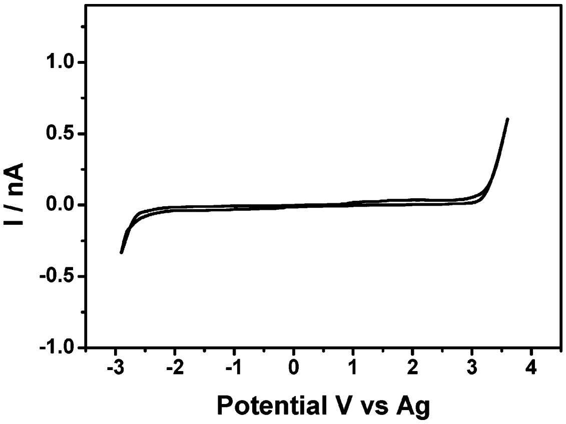


Figure 9. Cycle voltammogram of [C_3CNTMA][NTf_2], working electrode: GC electrode.

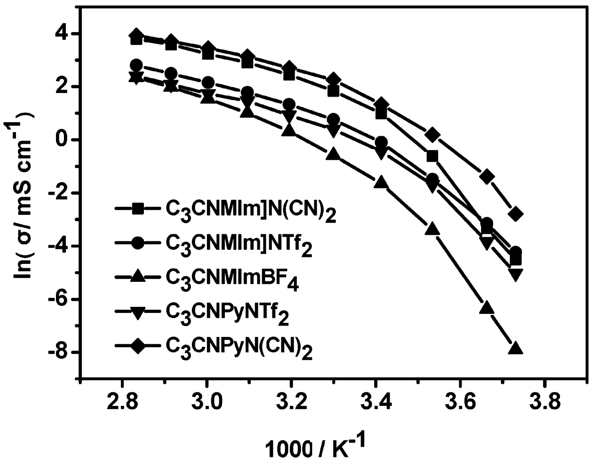


Figure 10. Arrhenius plots of ion conductivity for different ILs with a CN group.

of the anion. A typical curve of cyclic voltammetry for [C_3CNTMA]NTf_2 showed that the ILs prepared in this work are highly pure because no unexpected reduction or oxidation peaks were observed (Figure 9).

The ionic conductivities (κ) of five ILs with a CN group were measured at varied temperatures ranging from −5 to 80 °C. Generally, after incorporation of a CN group, the conductivities of ILs decreased at lower temperature. The results showed that, for the same cation, the conductivity values of anions had the following order: $N(CN)_2^- > NTf_2^- > BF_4^-$, which is the same as the viscosity order of the anions. It suggested that the conductivities of these salts at lower temperatures are remarkably affected by their viscosities. Among the studied salts, ILs with a CN group on the cation and with a $[N(CN)_2]^-$ anion have higher conductivities than other ILs, and at 25 °C, [C_3CNPy]$N(CN)_2$ gives the highest conductivity (5.07 mS/cm^{-1}). This may be explained by its lower viscosity, which may improve the rate of ion mobility. However, such ionic conductivity was still lower in comparison with that of the corresponding ILs without a CN group such as [BMIm]$N(CN)_2$ (14.38 mS/cm^{-1} at 25 °C). The temperature dependency of ionic conductivities of [C_3CNMIm]BF_4, [C_3CNMIm]NTf_2, [C_3CNMIm]$N(CN)_2$, [C_3CNPy]NTf_2, and [C_3CNPy]$N(CN)_2$ at the temperatures ranging from 20 to 80 °C were investigated, and their Arrhenius plots (Figure 10) showed that temperatures a have strong impact on the conductivities, particularly at lower temperatures, A typical example is [C_3CNMIm]BF_4: at low temperatures, the κ value is strongly affected by its viscosity, and at higher temperatures, the intrinsic structure and characteristics of the ILs may determine κ value.

TABLE 7: Death Number (*N*) and the Living Time (*T*) of the Rats with Varied ILs[a]

	[BMIm]BF_4				[C_3CNMIm]BF_4				[C_3CNMIm]$N(CN)_2$			
	male (5)		female (5)		male (5)		female (5)		male (5)		female (5)	
conc mg/mL	*N*	*T*	*N*	*T*	*N*	*T*	*N*	*T*	*N*	*T*	*N*	*T*
500	5	20 m	5	10 m	3	2 h	5	2 h	5	2 h	5	1 h
100	5	2 h	5	1 h	0	−	1	2 d	1	1 d	3	1 d
50	5	5 h	5	2 h	0	−	0	−	0	−	1	2 d
10	3	2 d	4	2 d	0	−	0	-	0	−	0	−
1	0	−	0	−	0	−	0	−	0	−	0	−

[a] − means no death occurs within 7 days.

Toxicity. Because the toxicity of ILs and their impact on the environment have received more and more attention, related investigations about this issue are emerging.[25,26] In order to compare the possible differences in toxicity of the ILs with and without a CN group, a preliminary comparison experiment about the toxicity of five ILs with and without a CN group and acetonitrile for the purpose of comparison have been conducted through a test of acute toxicity toward the Kunming albino rats. In each experiment, a dose of 0.4 mL of aqueous solution containing 0.1 mg/mL to 500 mg/mL of each IL was simultaneously fed to five male and five female rats through a feeding trough, and the relative toxicity of the ILs could be estimated through the comparison with the living time and death number of the rats (Table 7). All the rats died in 10 min to 5 h after 0.4 mL of aqueous solution containing ≥50 mg/mL of the [BMIm]BF_4 was fed to them. Only one female in ten rats, however, died in 2 days after being fed 0.4 mL of the aqueous solution containing 100 mg/mL of [C_3CNMIm]BF_4, and no rat deaths were observed when the content of [C_3CNMIm]BF_4 in solution was lower than 100 mg/mL. These results suggested that the incorporation of a CN group would remarkably decrease the toxicity of the IL. As for [C_3CNMIm]$N(CN)_2$, [C_3CNMIm]Cl, and [C_3CNTMA]Cl, it can be seen that the toxicity of [C_3CNMIm]$N(CN)_2$ is slightly higher than that of [C_3CNMIm]BF_4 but still lower than that of [BMIm]BF_4. [C_3CNMIm]Cl possessed a similar toxicity to [C_3CNMIm]BF_4, but all the rats died in 2 h after the solution containing 100 mg/mL of the [C_3CNTMA]Cl was fed, which indicated that the [C_3CNTMA] cation has higher toxicity than that of [C_3CNMIm] cation. It is worth noting that no rat death occurred when 1 mg/mL sample from any one of the five ILs was fed. Because [BMIm]BF_4 has been proved to be not acutely toxic by Rogers et al.,[26] these nitrile-functionalized ILs can be thought to be a kind of environment-friendly ILs. For the purpose of comparison, the toxicity of acetonitrile (100 mg/mL) was also tested, and the result showed that six in ten rats died in 2 h, which indicated that the toxicity of [BMIm]BF_4 is even slightly lower than that of acetonitrile.

Conclusions

A series of ILs based on nitrile-functionalized imidazolium, pyridinium, and quaternary ammonium as cations and chloride and tetrafluoroborate, hexafluorophosphate, dicyanamide, and bis(trifluoromethanesulfonyl)imide as anions have been prepared and characterized. The physicochemical properties such as spectroscopic, thermal, solubility, electrochemical, tribological, and toxic properties were comparatively studied. The results showed that the incorporation of a CN group to a cation could result in remarkable changes in these properties such as enhanced electrochemical stabilities, remarkably decreased in toxicity, and relatively complicated behaviors in thermal, spectroscopic, and solubility properties. The reason resulting in such remarkable differences in the properties may be attributed to the conformational changes in the imidazolium groups causing the interaction between the CN group with other neighboring cations or anions and the enhancement in hydrogen-bonding interactions due to the incorporation of a CN group.

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Supporting Information Available: Experimental details with ^{1}H NMR, FTIR, as well as characterizations of physicochemical properties with DSC, TG, EW, etc. are available free of charge via the Internet at http://pubs.acs.org.

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