Short communication

Ionic liquids based on aliphatic tetraalkylammonium dications and TFSI anion as potential electrolytes

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Abstract

A new series of ionic liquids containing aliphatic tetraalkylammonium dications with alkyl linkage chains and TFSI anion as potential electrolytes were prepared and characterized. Some of the important physicochemical and electrochemical properties of these prepared ionic liquids, including melting point, density, solubility in common solvents, ionic conductivity, thermal and electrochemical stability, were investigated. These ammonium dicationic ionic liquids exhibited five types of phase transition behavior on heating and one stage decomposition behavior. The spacer length and the head group overall length were responsible for the solid/liquid transformation temperature, and the spacer length was more effective in lowering the solid/liquid transformation temperature than the head group overall length. The interesting findings for such dicationic ionic liquids was that they showed the lowest solid–liquid transformation temperatures among analogues with alkyl links, and belonged to the greatest thermal stable ionic liquids. The Arrhenius equation approximately described the relationship between conductivity and temperature for several prepared dicationic ionic liquids in the low temperature region studied. The electrochemical windows were about 4.3 V for $C_9(N_{222})_2$-$TFSI_2$ and $C_{12}(N_{222})_2$-$TFSI_2$, and 4.7 V for $C_6(N_{118})_2$-$TFSI_2$ at room temperature.
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1. Introduction

Ionic liquids (ILs) are organic molten salts that have melting points below 100 °C. They have received much attention due to their excellent characteristics such as negligible volatility, non-flammability and high thermal stability [1,2].

To date, most studies have primarily involved the organic monocationic-type ILs [3–9]. Among these ILs, imidazolium, pyrrolidinium and some other monocations have been extensively investigated. On the anionic side, tetrafluoroborate (BF_4), hexafluorophosphate (PF_6) and bis(trifluoromethanesulfonyl) imide (TFSI) have been popular. Especially for TFSI anion, as this fluoroanion could provide ILs with very useful properties, monocationic ILs containing TFSI anion have appeared as elec-

trolytes in various electrochemical devices, such as lithium-ion batteries, dye-sensitized solar cells and super capacitors [10–25]. Relative to them, physical or electrochemical researches regarding dicationic ILs are quite rare [26–29], especially aliphatic tetraalkylammonium-based dicationic ILs with TFSI anion.

In order to gain further understanding and extend the applications of dicationic ILs electrolytes, investigation on aliphatic tetraalkylammonium-based dicationic ILs is necessary and important. As part of our interest to find this type of dicationic ILs, in the present paper, we report the preparation and characterization of an extensive new family of ILs comprised of aliphatic tetraalkylammonium dications with alkyl links and TFSI anion used as potential electrolytes, as shown in Scheme 1. Some of these prepared dicationic compounds are liquids at room temperature (25 °C). At the same time, we investigated the thermal properties, solubility in some common solvents, as well as electrochemical characteristics of the newly synthesized dicationic ILs.

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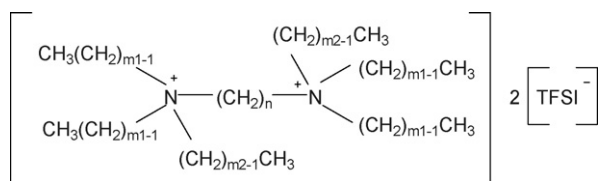
Scheme 1. Structure and abbreviations for prepared dicationic ionic liquids. $n = 2, 3, 6$; $m1 = 1$, $m2 = 2–8$, $C_n(N_{11m2})_2$-TFSI$_2$ (compounds **1–15**) and $n = 9$, 12; $m1 = m2 = 2$, $C_n(N_{222})_2$-TFSI$_2$ (compounds **16** and **17**); n, spacer length; $m = 2(2m1 + m2)$, head group overall length.

2. Experimental

2.1. Reagents and materials

The following reagents and materials were used as received: N,N,N',N'-tetramethyl-1,3-propanediamine (TMPDA) 99+%, Lithium bis (trifluoromethylsulfonyl)imide (LiTFSI) (Aldrich); N,N,N',N'-tetramethyl-1,6-hexanediamine (TMHDA) 99%, 1-bromohexane (99+%), 1-bromooctane (99%), 1,9-dibromononane (97%), 1,12-dibromododecane (96%) (Acros); triethylamine (AR, Shanghai Chemical Reagent Company). N,N,N',N'-Tetramethyl-ethylenediamine (TMEDA) (98%, Fluka) was purified by redistillation under dry nitrogen atmosphere before use. 1-bromoethane, 1-bromopropane, 1-bromobutane, 1-bromopentane, 1-bromoheptane (C.P., Shanghai Chemical Reagent Company) were purified by redistillation before use. All the other chemicals used in this work were of A.R. grade.

2.2. Synthesis and characterization of ammonium dicationic ionic liquids

The synthesis procedure was divided into two steps. The desired aliphatic tetraalkylammonium dications were formed, and converted into the corresponding bis (trifluoromethylsulfonyl)imide (TFSI) by anion exchange. The detailed procedure can be seen in the following. Compared to reported dicationic ILs, the starting materials of these dicationic ILs were cheaper.

2.2.1. General procedure for the preparation of compounds 1–15

1-Alkylbromide (0.12 mol) was added dropwise to a solution of TMEDA, TMPDA or TMHDA (0.04 mol) in acetone (100 mL) with stirring in an ice bath under dry nitrogen atmosphere in a round bottle. For TMEDA, aluminium foil was needed to cover bottle, since TMEDA used is light-sensitive. The mixture was stirred under reflux for 24 h. The white precipitate was separated, and washed with acetone for three times (3× 50 mL). The solid was collected by filtration, and dried in vacuo at 60 °C for 3 days. The resultant white solid (4 mmol) was dissolved in deionized water (40 mL) and LiTFSI (8 mmol) was added. After the mixture was stirred at room temperature for 24 h, the dication bis(trifluoromethylsulfonyl)imide compound was precipitated as a solid or phase separated as a liquid, depending on the compound species. For solid dication bis(trifluoromethylsulfonyl)imide compound, the white precipitate was separated, and washed with deionized water

(3× 80 mL) until no residual by-product (LiBr) was detected with the use of AgNO$_3$. The solid was collected by filtration, and dried in vacuo at 70 °C for 3 days. For liquid dication bis(trifluoromethylsulfonyl)imide compound, the top aqueous layer was decanted. The residual ionic liquid layer was dissolved in dichloromethane (50 mL) and washed with deionized water (3× 50 mL) until no residual by-product (LiBr) was detected with the use of AgNO$_3$. The dichloromethane was removed by rotary evaporation. The ionic liquid was dried under vacuum for 3 days at 70 °C and dried over activated 4A molecular sieves for 24 h.

2.2.2. General procedure for the preparation of compounds 16 and 17

Triethylamine (0.08 mol) was added dropwise to a solution of 1,9-dibromononane or 1,12-dibromododecane (0.02 mol) in 2-propanol (100 mL) with stirring in a round bottle under dry nitrogen atmosphere. The mixture was stirred under reflux for 24 h, then condensed by rotovap under a vacuum to remove solvent and unreacted reagent. The residual solid was washed with anhydrous diethyl ether for three times (3× 50 mL), collected by filtration, and dried in vacuo at 70 °C for 2 days. The resultant white solid (8 mmol) was dissolved in deionized water (60 mL) and LiTFSI (16 mmol) was added. After the mixture was stirred at room temperature for 24 h, the top aqueous layer was decanted. The residual ionic liquid layer was dissolved in dichloromethane (120 mL) and washed with deionized water (3× 50 mL) until no residual by-product (LiBr) was detected with the use of AgNO$_3$. The dichloromethane was removed by rotary evaporation. The ionic liquid was dried under vacuum for 2 days at 90 °C and dried over activated 4A molecular sieves for 24 h.

The structures of synthesized compounds were identified by ^{1}H NMR and ^{13}C NMR (Mercury Yplus 400), and [D$_6$]acetone for all prepared compounds. The characterization data are as follows.

Compound **1**—^{1}H NMR: δ (ppm) 4.35 (s, 4H), 3.85–3.80 (m, 4H), 3.49 (s, 12H), 1.58–1.55 (t, 6H); ^{13}C NMR: δ (ppm) 121.92–118.75, 62.06, 55.76, 50.84, 7.85. Compound **2**—^{1}H NMR: δ (ppm) 4.37 (s, 4H), 3.72–3.68 (m, 4H), 3.49 (s, 12H), 2.02–1.94 (m, 4H), 1.52–1.39 (m, 4H), 0.99–0.96 (t, 6H); ^{13}C NMR: δ (ppm) 125.11–115.44, 66.30, 56.34, 51.16, 24.34, 19.38, 12.96. Compound **3**—^{1}H NMR: δ (ppm) 4.38 (s, 4H), 3.73–3.69 (m, 4H), 3.50 (s, 12H), 1.99 (m, 4H), 1.42–1.31 (m, 12H), 0.89–0.85 (t, 6H); ^{13}C NMR: δ (ppm) 121.90–118.68, 66.47, 56.49, 51.32, 31.20, 25.79, 22.53, 22.35, 13.38. Compound **4**—^{1}H NMR: δ (ppm) 4.39 (s, 4H), 3.74–3.69 (m, 4H), 3.50 (s, 12H), 2.01 (broad, 4H), 1.38–1.27 (m, 20H), 0.88–0.84 (t, 6H); ^{13}C NMR: δ (ppm) 121.97–118.76, 66.45, 56.54, 51.26, 31.69, 26.16, 22.61, 22.54, 13.56 (three C peaks were overlapped). Compound **5**—^{1}H NMR: δ (ppm) 3.72–3.66 (m, 8H), 3.34 (s, 12H), 2.76–2.70 (m, 2H), 1.50–1.47 (t, 6H); ^{13}C NMR: δ (ppm) 121.92–118.70, 60.76, 60.06, 50.33, 17.16, 7.71. Compound **6**—^{1}H NMR: δ (ppm) 3.71–3.67 (t, 4H), 3.57–3.52 (m, 4H), 3.35 (s, 12H), 2.78–2.71 (m, 2H), 1.98–1.92 (m, 4H), 1.01–0.98 (t, 6H); ^{13}C NMR: δ (ppm) 121.92–118.78, 66.40, 60.81, 50.91, 17.33, 15.95, 9.98. Compound **7**—^{1}H NMR: δ

(ppm) 3.71–3.67 (t, 4H), 3.61–3.56 (t, 4H), 3.35 (s, 12H), 2.76–2.70 (m, 2H), 1.92–1.86 (m, 4H), 1.46–1.37 (m, 4H), 0.97–0.95 (t, 6H); ^{13}C NMR: δ (ppm) 121.86–118.66, 65.06, 60.59, 50.88, 24.37, 19.40, 17.17, 12.94. Compound **8**—^{1}H NMR: δ (ppm) 3.74–3.69 (t, 4H), 3.62–3.58 (t, 4H), 3.37 (s, 12H), 2.79–2.74 (m, 2H), 1.94 (s, 4H), 1.40–1.34 (m, 8H), 0.92–0.88 (t, 6H); ^{13}C NMR: δ (ppm) 121.88–118.69, 65.29, 60.63, 50.83, 28.28, 22.18, 21.90, 17.39, 13.20. Compound **9**—^{1}H NMR: δ (ppm) 3.73–3.69 (t, 4H), 3.62–3.58 (t, 4H), 3.37 (s, 12H), 2.78–2.74 (m, 2H), 1.97–1.85 (m, 4H), 1.39–1.27 (m, 12H), 0.89–0.85 (t, 6H); ^{13}C NMR: δ (ppm) 121.90–118.68, 65.35, 60.60, 50.89, 50.40, 31.31, 25.89, 22.46, 22.36, 13.43. Compound **10**—^{1}H NMR: δ (ppm) 3.71–3.67 (t, 4H), 3.61–3.58 (m, 4H), 3.35 (s, 12H), 2.76–2.70 (m, 2H), 1.91 (s, 4H), 1.38–1.28 (m, 16H), 0.88–0.85 (t, 6H); ^{13}C NMR: δ (ppm) 125.12–115.44, 65.39, 60.67, 50.81, 31.57, 26.16, 22.50, 22.47, 17.36, 13.59 (two C peaks were overlapped). Compound **11**—^{1}H NMR: δ (ppm) 3.72–3.68 (t, 4H), 3.62–3.58 (m, 4H), 3.36 (s, 12H), 2.79–2.73 (m, 2H), 1.92 (s, 4H), 1.37–1.27 (m, 20H), 0.88–0.85 (t, 6H); ^{13}C NMR: δ (ppm) 121.92–118.68, 65.38, 60.64, 50.65, 31.67, 28.84, 26.24, 22.56, 22.53, 17.39, 13.64 (two C peaks were overlapped). Compound **12**—^{1}H NMR: δ (ppm) 3.61–3.57 (m, 4H), 3.51–3.47 (m, 4H), 3.24 (s, 12 H), 1.96 (s, 4H), 1.57–1.53 (m, 4H), 1.46–1.42 (t, 6H); ^{13}C NMR: δ (ppm) 125.12–116.46, 63.57, 59.84, 50.16, 25.59, 22.10, 7.74. Compound **13**—^{1}H NMR: δ (ppm) 3.53–3.47 (m, 8H), 3.26 (s, 12H), 1.96–1.82 (m, 8H), 1.56–1.52 (m, 4H), 1.46–1.39 (m, 4H), 0.99–0.96 (t, 6H); ^{13}C NMR: δ (ppm) 121.98–118.72, 64.35, 50.58, 25.88, 24.40, 22.35, 19.60, 12.97 (two C peaks were overlapped). Compound **14**—^{1}H NMR: δ (ppm) 3.52–3.46 (m, 8H), 3.25 (s, 12H), 1.96–1.88 (m, 8H), 1.55–1.51 (m, 4H), 1.39–1.32 (m, 12H), 0.89–0.86 (t, 6H); ^{13}C NMR: δ (ppm) 125.58–115.95, 64.99, 64.70, 51.01, 31.64, 26.36, 26.29, 22.86, 22.82, 22.78, 13.90. Compound **15**—^{1}H NMR: δ (ppm) 3.46–3.41 (m, 8H), 3.19 (s, 12H), 1.88 (broad, 8H), 1.50 (s, 4H), 1.37–1.27 (m, 20H), 0.88–0.85 (t, 6H); ^{13}C NMR: δ (ppm) 125.13–115.48, 64.52, 64.20, 50.48, 31.71, 29.86, 28.71, 26.20, 25.63, 22.54, 22.43, 22.23, 13.67. Compound **16**—^{1}H NMR: δ (ppm) 3.45–3.40 (m, 12H), 3.31–3.27 (m. 4H), 1.77 (s, 4H), 1.40 (s, 8H), 1.37–1.32 (m, 18H), 1.08–1.06 (d, 2H); ^{13}C NMR: δ (ppm) 125.09–115.51, 57.13–57.08, 52.95–52.88, 26.27–26.19, 21.87, 21.54, 7.00. Compound **17**—^{1}H NMR: δ (ppm) 3.52–3.48 (m, 12H), 3.37–3.33 (d, 4H), 1.82 (s, 4H), 1.40–1.36 (m, 18H), 1.30 (s, 16H); ^{13}C NMR: δ (ppm) 121.97–118.77, 61.79, 57.13–57.07, 52.94–52.88, 34.19, 32.92, 26.37–26.00, 21.61–21.59, 7.03.

2.3. Measurement

The water content in the prepared ILs, which were liquids at and below 25 °C, were detected by a moisture titrator (Metrohm 73KF Coulometer) according to Karl–Fischer method, and the values was less than 100 ppm. The density was approximately determined by measuring the weight of prepared compounds (2.0 mL) at 25 °C. The solubility was estimated by gradual addition of solvents in compounds. The thermal measurements were performed with a differential scanning calorimeter (DSC,

Perkin-Elmer Pyris 1) in the temperature range −60 °C to a predetermined temperature. The samples were sealed in aluminium pans, and then heated and cooled at scan rate of 10 °C min^{-1} under a flow of nitrogen. The thermal data were collected during heating in the second heating–cooling scan. The thermal stabilities were measured with TGA (Perkin-Elmer, 7 series thermal analysis system). The samples were placed in the aluminium pans, and heated at 10 °C min^{-1} from room temperature to 600 °C under nitrogen. Ionic conductivities were measured by using a DDS-11A conductivity meter with a DJS-1C conductivity cell having a nominal cell constant of 0.999/25 °C. The electrochemical measurement was carried out by cyclic voltammetry (scan rate 10 mV s^{-1}) using an HSV-100 electrochemical working station (Hokuto Denko) with three-electrode cell in an argon-filled UNILAB glove box ([O_2] < 1 ppm, [H_2O] < 1 ppm). Platinum disk (geometric area = 3.14 × 10^{-2} cm^2) was used as working electrode, and lithium metal was used as both counter electrode and reference electrode.

3. Results and discussion

3.1. Thermal properties of ammonium dicationic ionic liquids prepared

The solid–liquid phase transition behaviors for these compounds were examined using DSC, and the thermal data are summarized in Table 1. Compound **17** did not exhibit transition behavior in experimental condition. The other compounds fall into one of five categories. The typical DSC curves for these five types of phase transition behavior are exemplified in Fig. 1. The first class had only a melting transition (compounds **2**, **3**, **5**, **12** and **13** in Table 1). The second class only showed glass transitions at a low temperature without melting (compounds **15** and **16**). The third class (compounds **7**, **8**–**10** and **14**) exhibited
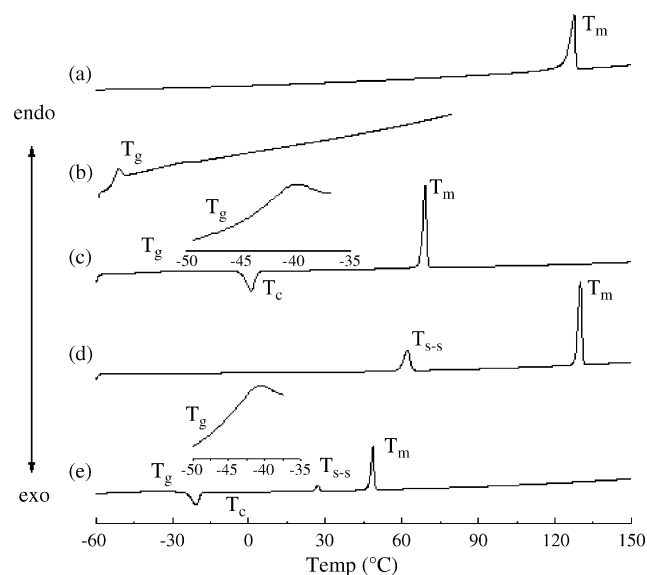

Fig. 1. DSC curves of (a) C$_2$(N$_{114}$)$_2$-TFSI$_2$ (compound **2**), (b) C$_9$(N$_{222}$)$_2$-TFSI$_2$ (compound **16**), (c) C$_3$(N$_{116}$)$_2$-TFSI$_2$ (compound **9**), (d) C$_3$(N$_{113}$)$_2$-TFSI$_2$ (compound **6**), and (e) C$_3$(N$_{118}$)$_2$-TFSI$_2$ (compound **11**).

Table 1
Physical properties of prepared dicationic ILs (25 °C)

	Compound	M_W[a] (g mol^{-1})	d[b] (g cm^{-3})	T_g[c] (°C)	T_c[d] (°C)	T_{s-s}[e] (°C)	T_m[f] (°C)	T_d[g] (°C)	ΔS_m[h] (J mol^{-1} K^{-1})
1	C$_2$(N$_{112}$)$_2$-TFSI$_2$	734.62				157	187	355	104.8
2	C$_2$(N$_{114}$)$_2$-TFSI$_2$	790.73					125	342	101.9
3	C$_2$(N$_{116}$)$_2$-TFSI$_2$	846.84					84	373	94.9
4	C$_2$(N$_{118}$)$_2$-TFSI$_2$	902.94				−23	80	382	58.9
5	C$_3$(N$_{112}$)$_2$-TFSI$_2$	748.65					178	377	70.6
6	C$_3$(N$_{113}$)$_2$-TFSI$_2$	776.70				56	124	362	85.7
7	C$_3$(N$_{114}$)$_2$-TFSI$_2$	804.76		−46	23		61	364	117.5
8	C$_3$(N$_{115}$)$_2$-TFSI$_2$	832.81		−45	13		51	363	82.2
9	C$_3$(N$_{116}$)$_2$-TFSI$_2$	860.86		−46	−10		64	378	67.1
10	C$_3$(N$_{117}$)$_2$-TFSI$_2$	888.92		−49	−27		47	389	51.0
11	C$_3$(N$_{118}$)$_2$-TFSI$_2$	916.97		−47	−24	26	47	357	41.3
12	C$_6$(N$_{112}$)$_2$-TFSI$_2$	790.73					45	413	78.6
13	C$_6$(N$_{114}$)$_2$-TFSI$_2$	846.84					86	401	99.4
14	C$_6$(N$_{116}$)$_2$-TFSI$_2$	902.94		−54	22		51	409	179.5
15	C$_6$(N$_{118}$)$_2$-TFSI$_2$	959.05	1.17	−56				409	
16	C$_9$(N$_{222}$)$_2$-TFSI$_2$	889.92	1.25	−53				410	
17	C$_{12}$(N$_{222}$)$_2$-TFSI$_2$	930.99	1.31			<−60		414	

[a] Molecular weight.

[b] Density.

[c] Glass transition temperature (onset of the heat capacity change).

[d] Crystallization temperature (onset of the crystallization peak).

[e] Solid–solid transition temperature (onset of the solid–solid peak).

[f] Melting point (onset of the endothermic peak).

[g] Decomposition temperature (onset of decomposition peak).

[h] Entropy of melting ($\Delta S_m = \Delta H_m/T_m$, where ΔH_m is melting enthalpy at T_m).

glass transitions at a low temperature in the range of −45 to −60 °C, subsequent crystallization at a relatively high temperature, and a final melting transition as the temperature increased further. The fourth class (compounds **1**, **4** and **6**) showed one solid–solid transition (T_{s-s}) before melting. The five class (compound **11**) exhibited similar phase transition to the third class, and it also showed a solid–solid transition. Moreover, compound **11** may show ionic plastic crystal behavior because its final melting entropy (41.3 J K^{-1} mol^{-1}) was close to the melting entropy of the salt exhibiting plastic phases based on TFSI$^-$, a relative large and flexible anion ($\Delta S_m \approx 40$ J K^{-1} mol^{-1}) [30,31].

Fig. 2 shows the solid/liquid transformation temperature (T_{s-l}) of these ammonium-based dicationic compounds. Most of
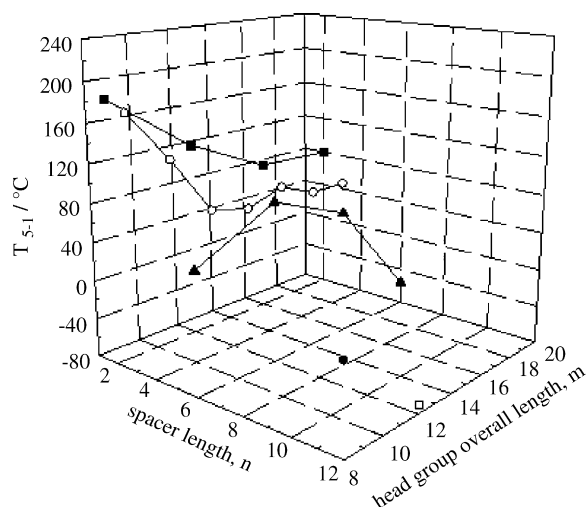

Fig. 2. Solid/liquid transformation temperature (T_{s-l}) of prepared dicationic ILs.

compounds had T_{s-l} below 100 °C, which could be considered as ILs. Particularly, compounds **15** and **16** had T_{s-l} at −56 and −53 °C, respectively, and compound **17** had T_{s-l} below −60 °C, indicating that they had the lowest solid/liquid transformation temperature of all the dicationic ILs with alkyl links as reported so far. For ammonium-based dicationic ILs with same head group overall length, increasing the spacer length had a trend of decrease in the T_{s-l}. The overall length of head group was also responsible for the T_{s-l}. In the cases involving the ethane linkage chain, the T_{s-l} was lowered as the head group overall length increased. A nearly similar trend was observed for the ILs containing the propane linkage chain. However, for ILs with a hexane linkage chain, their T_{s-l} initially increased as head group overall length increased, and reached a maximum values, then tended to decrease with further increasing the head group length. In addition, when comparing the T_{s-l} for these ILs having the same formular weight, i.e. compounds **2** and **12**, it was seen that the T_{s-l} for compound **2** is nearly 80 °C higher than that for compound **12**, which appeared that for ammonium-based dicationic ILs, the spacer length played a more important role in lowering the T_{s-l} than the head group overall length.

Fig. 3 shows decomposition temperature of ammonium dicationic ionic liquids. The decomposition temperature (T_d) values for prepared dicationic ILs were in the range of 340–420 °C. These dicationic ILs all exhibited one stage decomposition behavior. In addition, all prepared dicationic ILs undergo exothermic decomposition, which were different from those obtained for ammonium monocationic ILs by Ngo et al., it was reported that tetraalkyl ammonium salts, such as TEATFSI, undergo endothermic decomposition [32].
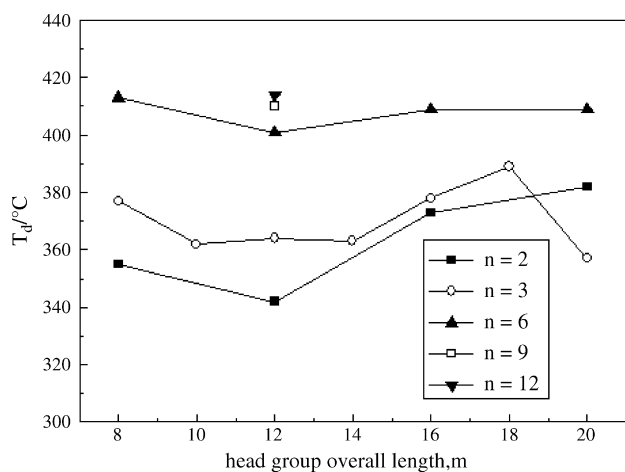
Fig. 3. Decomposition temperature of prepared dicationic ILs.

Fig. 5. Cyclic voltammograms of $C_6(N_{118})_2$-TFSI$_2$, $C_9(N_{222})_2$-TFSI$_2$ and $C_{12}(N_{222})_2$-TFSI$_2$ at 25 °C. Scan rate: 10 mV s^{-1}; working electrode: Pt; counter electrode and reference electrode: Li.

3.2. Solubility of ammonium dicationic ionic liquids in organic solvents

All the prepared ammonium dicationic ionic liquids were immiscible in diethyl ether and water, however, miscible in dichloromethane and in 99.7% ethanol (w/w) and in acetone, which was also observed for monocationic ionic liquids and imidazolium dicationic ionic liquids with TFSI anion [3–5,28].

3.3. Electrochemical properties of prepared ammonium dicationic ionic liquids

The Arrhenius plots of conductivity for $C_6(N_{118})_2$-TFSI$_2$, $C_9(N_{222})_2$-TFSI$_2$ and $C_{12}(N_{222})_2$-TFSI$_2$, which were liquids at and below 25 °C, are shown in Fig. 4. Monocationic ILs with TFSI anion used in electrochemical studies have reported room temperature conductivities ranging from 0.1 to 10 ms cm^{-1}, depending on the cation used [33]. The conductivities of $C_9(N_{222})_2$-TFSI$_2$, $C_{12}(N_{222})_2$-TFSI$_2$ and $C_6(N_{118})_2$-TFSI$_2$ were about 0.14, 0.13, 0.05 ms cm^{-1} at 25 °C, respectively. It could be seen that the conductivity values of $C_9(N_{222})_2$-TFSI$_2$ and $C_{12}(N_{222})_2$-TFSI$_2$ falled within the same

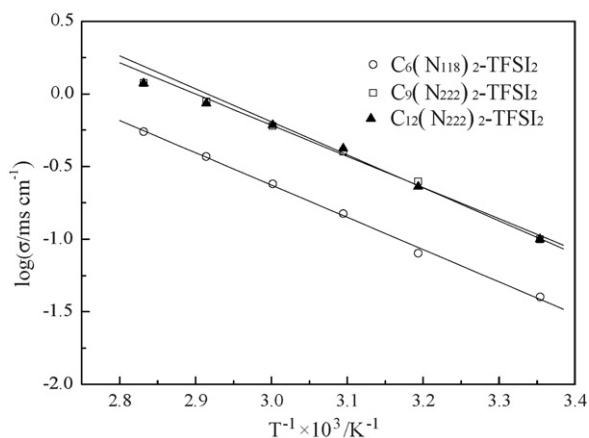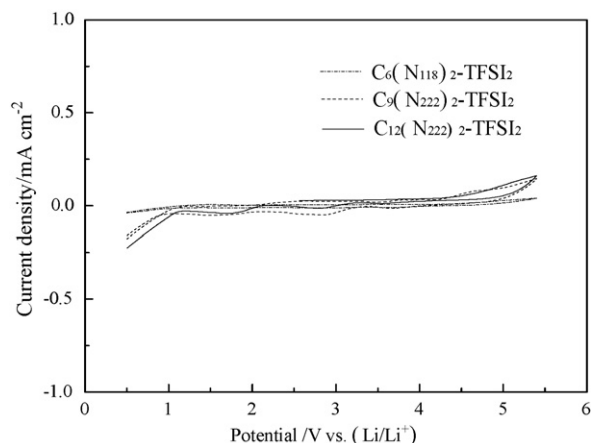Fig. 4. Temperature dependences of the conductivity of the prepared dicationic ILs.

range as monocationic ILs. The temperature dependences of the conductivity of above three dicationic ILs followed the Arrhenius relation in the low temperature region, like those of some monocationic ionic liquids [34,35], and the respective room temperature activation energies from the linear Arrhenius region around 25 °C were 42.5, 41.1 and 43.5 kJ mol^{-1}.

Cyclic voltammograms for $C_6(N_{118})_2$-TFSI$_2$, $C_9(N_{222})_2$-TFSI$_2$ and $C_{12}(N_{222})_2$-TFSI$_2$ are shown in Fig. 5. It was reported that the room temperature electrochemical windows of monocationic ILs were observed to range from 4.0 to 5.2 V when using Li/Li$^+$ as reference electrode [33,36]. $C_9(N_{222})_2$-TFSI$_2$ and $C_{12}(N_{222})_2$-TFSI$_2$ were all electrochemically stable in the range of 1–5.3 V versus Li/Li$^+$, which indicated that their electrochemical window values were about 4.3 V at 25 °C. Comparing with them, $C_6(N_{118})_2$-TFSI$_2$ was more stable by an additional 0.4 V toward reduction, showing an electrochemical window of ~4.7 V at 25 °C. Above results indicated that these three dicationic ILs had electrochemical windows falling in the same range as monocationic ILs.

4. Conclusions

A new class of ionic liquids electrolytes based on aliphatic tetraalkylammonium dications containing alkyl linkage chains with alkyl substituents and TFSI anion were synthesized and characterized, and some physical and electrochemical properties of these ionic liquids were determined. These prepared ammonium dicationic ionic liquids showed five types of phase transition behavior on heating, and exhibited one stage decomposition behavior. The spacer length and the head group overall length affected the solid/liquid transformation temperatures for these ionic liquids, and the spacer length played a more important role in lowering the solid/liquid transformation temperature than the head group overall length. In fact, several ammonium dicationic ionic liquids, having the lowest solid–liquid transformation temperatures among analogues with alkyl links, were found, moreover, they belonged to the greatest thermal stable ionic liquids. Additionally, two dicationic ionic liquids, $C_9(N_{222})_2$-TFSI$_2$ and $C_{12}(N_{222})_2$-TFSI$_2$ had an order of con-

ductivity of 10^{-1} ms cm^{-1}. The electrochemical windows were approximately 4.3 V for these two dicationic ionic liquids, and 4.7 V for $C_6(N_{118})_2$-TFSI$_2$ at room temperature.

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