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Tetra-Branched Tetra-Cationic Ionic Liquids: Effects of Spacer and Tail Structure on Physical Properties

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Abstract

Herein, the synthesis of ten tetra-branched tetra-cationic ionic liquids, which consist of a pentaerythritol-based core, alkylene or ethylenedioxy spacers, imidazolium cationic units, and short alkyl tails, is described. The physical properties of the tetra-cations, including their glass transition and thermal decomposition temperatures, densities, viscosities, and ionic conductivities, were investigated. The tetra-cations were analyzed to determine the effects of the spacer and tail structure on the above-mentioned physical properties. The spacer unit located between the pentaerythrityl core and cationic unit was confirmed to be the key for improving ionic conductivity. A maximum ionic conductivity of $2.8 \times 10^{-4}\,\mathrm{S\,cm^{-1}}$ (25 °C under anhydrous conditions) and a minimum viscosity of 1.6 Pa s (25 °C) were observed. While the physical values of the tetra-cationic ionic liquids are close to those of di-cationic ionic liquids, their structure-property relationship is similar to that of poly-cations rather than di-cations.

Keywords: Ionic liquids | Branched structure | Ion conductivity

1. Introduction

Electrolytes are key materials that support information society because they are included in most electronic devices, *e.g.* batteries,[1–5] supercapacitors,[6–8] fuel cells,[9–11] and electrochromic devices,[12–14] *etc.* Ionic organic compounds, such as ionic liquids, have attracted increasing attention due to their designability and non-volatility.[15,16] Ionic organic compounds cover a large molecular-weight range, from 10^2 Da (mono-cationic ionic liquids) to 10^6 Da (polyelectrolytes). Mono-cationic ionic liquids have been extensively studied over the past two decades and the details of their physical properties have been revealed.[17,18] Studies on polymer electrolytes also have a long history, and many applications have been examined.[19–22] Meanwhile, the intermediate molecular-weight region, between that of mono-cationic ionic liquids and polyelectrolytes, has not yet been well explored. Despite the limited number of examples, multi-cationic ionic liquids have been confirmed to exhibit some superior properties compared to their mono-cationic counterparts, such as high thermal stabilities,[23–25] high capacities as supercapacitors,[6,26,27] and higher performance as stationary phases for gas chromatography, *etc.*[28,29] Among di-,[30–32] tri-,[33,34] and tetra-cationic ionic liquids,[35] the latter are the most unexplored because they are the most difficult to synthesize. Although some groups have reported a facile synthesis of multi-cationic ionic liquids utilizing oligosilsesquioxane frameworks, no physical properties such as viscosity and ionic conductivity have been reported so far.[36,37]

With the above background in mind, this study focused on tetra-cationic ionic liquids. Generally, multi-cationic ionic liquids are highly viscous and poorly ionically conductive because of their high molecular masses; these physical properties are unfavorable for electronic materials. In order to improve the ionic conductivity as much as possible, we focused on a branched structure, since branched molecules, such as dendrimers, have low viscosities.[38] In our previous study, we successfully prepared tetra-branched tetra-cationic ionic liquids (Figure 1a); however, these tetra-cations exhibited low ionic conductivities (the order of $10^{-6}\,\mathrm{S\,cm^{-1}}$).[39] Therefore, in this study, improving molecular design for achieving high ionic conductivity became the key challenge. Figure 1b shows the molecular design concept of new tetra-cations investigated in this study. Spacer unit (R_1) was introduced between the pentaerythrityl core and the cationic unit. It should be noted that the 1,2,3-triazolium cationic unit previously used was changed to

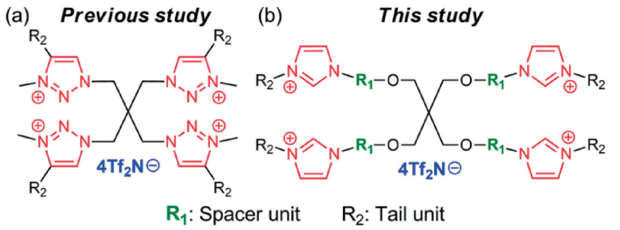


Figure 1. Molecular design of tetra-cationic ionic liquids in (a) previous study and (b) this study.

the imidazolium to avoid the risk of handling explosive azide compounds. Here, the effects of the spacer and tail structure on key physical properties (glass transition and thermal decomposition temperatures, density, viscosity, and ionic conductivity) are reported. It was confirmed that the introduction of spacer units could improve ionic conductivity by two orders of magnitude.

2. Experimental

Method. NMR spectra were recorded on a JEOL ECS-400 (400 MHz and 100 MHz for ^{1}H and ^{13}C nuclei, respectively) with residual solvent as the internal standard. The density was measured using 1 mL glass specific gravity pycnometer (Thomas Scientific). The viscosity was measured using a rolling-ball viscometer Lovis 2000 M/ME (Anton Paar). Differential scanning calorimetry (DSC) was performed on a Shimadzu DSC-60 Plus at a heating/cooling rate of 10 °C min^{-1} under N_2 flow. Thermogravimetric analysis (TGA) was performed with a Shimadzu DTG-60 at a heating rate of 10 °C min^{-1} under N_2 flow. Ionic conductivity was measured using two-terminal impedance spectroscopy on a Solartron SI 1260 with a 1296 Dielectric Interface. The sample was placed on a disk-type blocking electrode (diameter: 5 mm) of a Solartron 12962A dielectric sample holder. The spacing between two electrodes was set to 300 µm. The frequency was swept from 1 MHz to 1 Hz by applying a sinusoidal voltage of 10 mV. The sample holder was placed inside a programmable thermostat chamber ESPEC SH-221 filled with dry N_2 gas. The sample was completely dried at 100 °C for 1 h before starting the measurement. The impedance data were collected from 100 to 10 °C at a cooling rate of 20 °C h^{-1} (0.33 °C min^{-1}). The data were processed using ZView® Ver. 3.3c software.

General Procedure of t-R$_1$-O-THP Synthesis. Tetrahydropyranyl (THP) derivative of **OH-R$_1$-O-THP** (65 mmol) was dissolved in DMF (50 mL). NaH (60 wt% dispersion in oil, 3.0 g) was added portion-wise. The reaction mixture was stirred for 30 min at room temperature. After adding pentaerythrityl tetrabromide (13 mmol), the reaction mixture was stirred for 24 h at 100 °C under N_2 atmosphere. The solvent was removed by evaporation. The residue was dissolved in diethyl ether (150 mL) and washed with water (50 mL) using a separation funnel. The organic layer was recovered, dried with $MgSO_4$, filtrated and concentrated with an evaporator. The crude product was purified by column chromatography (SiO_2, Hex/AcOEt = 1/1).

t-C2-O-THP: Yield: 85%. ^{1}H NMR (400 MHz, CD_3CN): $\delta = 1.40$–1.82 (m, 24H), 3.30–3.56 (m, 24H), 3.66–3.86 (m, 8H), 4.58 (t, $J = 3.4$ Hz, 4H); ^{13}C NMR (100 MHz, CD_3CN): $\delta = 20.3$, 26.3, 31.5, 46.6, 62.6, 67.2, 70.5, 71.8, 99.6.

t-C3-O-THP: Yield: 76%. ^{1}H NMR (400 MHz, CD_3CN): $\delta = 1.40$–1.82 (m, 32H), 3.34 (s, 8H), 3.40–3.50 (m, 16H), 3.70–3.85 (m, 8H), 4.55 (t, $J = 3.4$ Hz, 4H); ^{13}C NMR (100 MHz, CD_3CN): $\delta = 21.4$, 27.2, 31.8, 32.5, 47.2, 63.7, 65.9, 69.9, 71.2, 100.6.

t-C4-O-THP: Yield: 80%. ^{1}H NMR (400 MHz, CD_3CN): $\delta = 1.40$–1.82 (m, 40H), 3.26–3.46 (m, 24H), 3.65 (m, 4H), 3.78 (m, 4H), 4.52 (t, $J = 3.4$ Hz, 4H); ^{13}C NMR (100 MHz, CD_3CN): $\delta = 20.5$, 26.3, 27.3, 27.4, 31.6, 46.3, 62.8, 67.9, 70.3, 71.9, 99.6.

t-C5-O-THP: Yield: 72%. ^{1}H NMR (400 MHz, CD_3CN): $\delta = 1.35$–1.84 (m, 48H), 3.28–3.48 (m, 24H), 3.68 (m, 4H), 3.81 (m, 4H), 4.55 (t, $J = 3.4$ Hz, 4H); ^{13}C NMR (100 MHz, CD_3CN): $\delta = 20.5$, 23.9, 26.3, 30.3, 30.3, 31.6, 46.3, 62.7, 68.0, 70.2, 72.0, 99.5.

t-C6-THP: Yield: 76%. ^{1}H NMR (400 MHz, CD_3CN): $\delta = 1.35$ (m, 16H), 1.40–1.82 (m, 40H), 3.25–3.46 (m, 24H), 3.64 (m, 4H), 3.78 (m, 4H), 4.51 (t, $J = 3.4$ Hz, 4H); ^{13}C NMR (100 MHz, CD_3CN): $\delta = 20.5$, 26.4, 26.9, 30.4, 30.6, 31.6, 46.3, 62.7, 68.0, 70.3, 72.0, 99.6.

t-EG2-O-THP: Yield: 82%. ^{1}H NMR (400 MHz, CD_3CN): $\delta = 1.40$–1.82 (m, 24H), 3.36 (s, 8H), 3.40–3.60 (m, 32H), 3.70–3.84 (m, 8H), 4.57 (t, $J = 3.4$ Hz, 4H); ^{13}C NMR (100 MHz, CD_3CN): $\delta = 20.4$, 26.3, 31.5, 46.4, 62.7, 67.5, 70.5, 71.0, 71.2, 72.0, 99.7.

t-EG3-O-THP: Yield: 85%. ^{1}H NMR (400 MHz, CD_3CN): $\delta = 1.42$–1.84 (m, 24H), 3.38 (s, 8H), 3.42–3.66 (m, 48H), 3.75–3.88 (m, 8H), 4.59 (t, $J = 3.4$ Hz, 4H); ^{13}C NMR (100 MHz, CD_3CN): $\delta = 20.4$, 26.3, 31.5, 46.4, 62.8, 67.5, 70.5, 71.0, 71.2, 71.3, 71.3, 72.0, 99.8.

General Procedure of t-R$_1$-OH Synthesis. **t-R$_1$-O-THP** (7.7 mmol) and pyridinium *p*-toluenesulfonate (PPTS, 3.2 mmol) were dissolved in MeOH (300 mL). The reaction mixture was stirred for 16 h at 70 °C under N_2 atmosphere. The solvent was removed by evaporation. The residue was directly subjected to column chromatography (SiO_2, CH_2Cl_2/Acetone = 1/1; Acetone/MeOH = 9/1).

t-C2-OH: Yield: 83%. ^{1}H NMR (400 MHz, CD_3CN): $\delta = 3.06$ (br, 4H), 3.38–3.48 (m, 16H), 3.56 (br, 8H); ^{13}C NMR (100 MHz, CD_3CN): $\delta = 46.3$, 61.8 70.7, 73.7.

t-C3-OH: Yield: 88%. ^{1}H NMR (400 MHz, CD_3CN): $\delta = 1.72$ (m, 8H), 3.03 (t, $J = 5.4$ Hz, 4H), 3.34 (s, 8H), 3.48 (t, $J = 6.2$ Hz, 8H), 3.59 (q, $J = 6.0$ Hz, 8H); ^{13}C NMR (100 MHz, CD_3CN): $\delta = 34.2$, 46.9, 61.3, 70.6, 71.8.

t-C4-OH: Yield: 74%. ^{1}H NMR (400 MHz, CD_3CN): $\delta = 1.46$–1.58 (m, 16H), 2.79 (t, $J = 5.2$ Hz, 4H), 3.30 (s, 8H), 3.37 (t, $J = 6.0$ Hz, 8H), 3.48 (q, $J = 5.6$ Hz, 8H); ^{13}C NMR (100 MHz, CD_3CN): $\delta = 27.0$, 30.5, 46.2, 62.5, 70.3, 72.0.

t-C5-OH: Yield: 78%. ^{1}H NMR (400 MHz, CD_3CN): $\delta = 1.37$ (m, 8H), 1.46–1.58 (m, 16H), 2.74 (t, $J = 5.4$ Hz, 4H), 3.31 (s, 8H), 3.37 (t, $J = 6.4$ Hz, 8H), 3.49 (q, $J = 6.0$ Hz, 8H); ^{13}C NMR (100 MHz, CD_3CN): $\delta = 23.4$, 30.2, 33.4, 46.3, 62.6, 70.2, 72.1.

t-C6-OH: Yield: 75%. ^{1}H NMR (400 MHz, CD_3CN): $\delta = 1.27$–1.38 (m, 16H), 1.42–1.56 (m, 16H), 2.67 (t, $J = 5.2$ Hz, 4H), 3.28 (s, 8H), 3.34 (t, $J = 6.2$ Hz, 8H), 3.46 (q, $J = 6.2$ Hz, 8H); ^{13}C NMR (100 MHz, CD_3CN): $\delta = 26.5$, 26.9, 30.4, 33.6, 46.3, 62.6, 70.2, 72.0.

t-EG2-OH: Yield: 73%. ^{1}H NMR (400 MHz, CD_3CN): $\delta =$ 3.16 (t, $J = 5.2$ Hz, 4H), 3.38 (s, 8H), 3.47–3.62 (m, 32H); ^{13}C NMR (100 MHz, CD_3CN): $\delta =$ 46.3, 62.0, 70.8, 70.9, 71.9, 73.3.

t-EG3-OH: Yield: 83%. ^{1}H NMR (400 MHz, CD_3CN): $\delta =$ 3.24 (t, $J = 5.8$ Hz, 4H), 3.40 (s, 8H), 3.47–3.64 (m, 48H); ^{13}C NMR (100 MHz, CD_3CN): $\delta =$ 46.2, 61.9, 70.9, 70.9, 71.0, 71.1, 71.8, 73.3.

General Procedure of t-R_1-Ts Synthesis. **t-R_1-OH** (6.4 mmol), triethylamine (TEA, 43 mmol), and 4-dimethylamino-pyridine (DMAP, 4.1 mmol) were dissolved in CH_2Cl_2/THF mixed solvent (50 mL/50 mL). *p*-Toluenesulfonyl chloride (TsCl, 42 mmol) was added to the solution. The reaction mixture was stirred for 16 h at room temperature under N_2 atmosphere. The solution was washed with 1 M HCl aqueous solution. The solution was dried with $MgSO_4$, filtered and concentrated by evaporation. The crude product was purified by column chromatography (SiO_2, CH_2Cl_2/AcOEt = 4/1).

t-C2-Ts: Yield: 92%. ^{1}H NMR (400 MHz, CD_3CN): $\delta =$ 2.41 (s, 12H), 3.03 (s, 8H), 3.43 (t, $J = 4.2$ Hz, 8H), 4.04 (t, $J = 4.2$ Hz, 8H), 7.40 (d, $J = 8.4$ Hz, 8H), 7.75 (d, $J = 8.4$ Hz, 8H); ^{13}C NMR (100 MHz, CD_3CN): $\delta =$ 21.6, 46.2, 69.6, 69.9, 70.9, 128.7, 131.0, 133.9, 146.3.

t-C3-Ts: Yield: 92%. ^{1}H NMR (400 MHz, CD_3CN): $\delta =$ 1.78 (m, 8H), 2.43 (s, 12H), 3.03 (s, 8H), 3.27 (t, $J = 5.6$ Hz, 8H), 4.05 (t, $J = 6.4$ Hz, 8H), 7.43 (d, $J = 8.4$ Hz, 8H), 7.78 (d, $J = 8.4$ Hz, 8H); ^{13}C NMR (100 MHz, CD_3CN): $\delta =$ 22.6, 30.6, 46.9, 68.2, 70.1, 70.8, 129.6, 131.9, 134.8, 147.2.

t-C4-Ts: Yield: 90%. ^{1}H NMR (400 MHz, CD_3CN): $\delta =$ 1.44 (m, 8H), 1.62 (m, 8H), 2.41 (s, 12H), 3.10 (s, 8H), 3.21 (t, $J = 6.2$ Hz, 8H), 4.01 (t, $J = 6.2$ Hz, 8H), 7.40 (d, $J = 8.4$ Hz, 8H), 7.75 (d, $J = 8.4$ Hz, 8H); ^{13}C NMR (100 MHz, CD_3CN): $\delta =$ 21.7, 26.2, 26.7, 46.0, 70.1, 71.2, 72.0, 128.7, 131.0, 134.0, 146.2.

t-C5-Ts: Yield: 94%. ^{1}H NMR (400 MHz, CD_3CN): $\delta =$ 1.31 (m, 8H), 1.42 (m, 8H), 1.61 (m, 8H), 2.44 (s, 12H), 3.21 (s, 8H), 3.26 (t, $J = 6.2$ Hz, 8H), 4.01 (t, $J = 6.2$ Hz, 8H), 7.43 (d, $J = 7.6$ Hz, 8H), 7.78 (d, $J = 7.6$ Hz, 8H); ^{13}C NMR (100 MHz, CD_3CN): $\delta =$ 21.7, 22.9, 29.2, 29.6, 46.2, 70.1, 71.6, 72.0, 128.7, 131.0, 134.0, 146.2.

t-C6-Ts: Yield: 91%. ^{1}H NMR (400 MHz, CD_3CN): $\delta =$ 1.17–1.28 (m, 16H), 1.40 (q, $J = 7.0$ Hz, 8H), 1.57 (q, $J = 7.0$ Hz, 8H), 2.41 (s, 12H), 3.20–3.28 (m, 16H), 3.98 (t, $J = 6.4$ Hz, 8H), 7.40 (d, $J = 8.4$ Hz, 8H), 7.75 (d, $J = 8.4$ Hz, 8H); ^{13}C NMR (100 MHz, CD_3CN): $\delta =$ 21.7, 25.8, 26.3, 29.4, 30.1, 46.2, 70.2, 71.8, 72.0, 128.7, 131.0, 134.1, 146.2.

t-EG2-Ts: Yield: 92%. ^{1}H NMR (400 MHz, CD_3CN): $\delta =$ 2.41 (s, 12H), 3.27 (s, 8H), 3.40 (t, $J = 4.4$ Hz, 8H), 3.44 (t, $J = 4.4$ Hz, 8H), 3.58 (t, $J = 4.4$ Hz, 8H), 4.08 (t, $J = 4.4$ Hz, 8H), 7.40 (d, $J = 8.4$ Hz, 8H), 7.75 (d, $J = 8.4$ Hz, 8H); ^{13}C NMR (100 MHz, CD_3CN): $\delta =$ 21.7, 46.3, 69.2, 70.3, 70.9, 71.0, 71.7, 128.7, 131.0, 133.9, 146.3.

t-EG3-Ts: Yield: 90%. ^{1}H NMR (400 MHz, CD_3CN): $\delta =$ 2.45 (s, 12H), 3.34 (s, 8H), 3.44–3.54 (m, 32H), 3.61 (t, $J = 4.6$ Hz, 8H), 4.12 (t, $J = 4.6$ Hz, 8H), 7.44 (d, $J = 8.4$ Hz, 8H), 7.79 (d, $J = 8.4$ Hz, 8H); ^{13}C NMR (100 MHz, CD_3CN): $\delta =$ 21.7, 46.4, 69.2, 70.5, 71.0, 71.0, 71.1, 71.2, 71.9, 128.8, 131.0, 133.8, 146.3.

General Procedure of t-R_1-I Synthesis. **t-R_1-Ts** (5.9 mmol) and NaI (0.12 mol) were dissolved in acetone (100 mL). The reaction mixture was stirred at 60 °C for 60 h under N_2 atmosphere. After removing the solvent by evaporation, the residue was partitioned between CH_2Cl_2 (150 mL) and water (150 mL). The organic layer was recovered, dried with $MgSO_4$, filtered and concentrated by evaporation. The crude product was purified by column chromatography (SiO_2, CH_2Cl_2/AcOEt = 9/1).

t-C2-I: Yield: 94%. ^{1}H NMR (400 MHz, CD_3CN): $\delta =$ 3.30 (t, $J = 6.0$ Hz, 8H), 3.45 (s, 8H), 3.67 (t, $J = 6.0$ Hz, 8H); ^{13}C NMR (100 MHz, CD_3CN): $\delta =$ 5.5, 46.8, 69.6, 72.5.

t-C3-I: Yield: 98%. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta =$ 2.04 (m, 8H), 3.27 (t, $J = 6.8$ Hz, 8H), 3.37 (s, 8H), 3.44 (t, $J = 6.8$ Hz, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 3.9, 33.6, 45.6, 69.6, 70.6.

t-C4-I: Yield: 94%. ^{1}H NMR (400 MHz, DMSO-d_6): $\delta =$ 1.56 (m, 8H), 1.82 (m, 8H), 3.22–3.31 (m, 16H), 3.35 (t, $J = 6.2$ Hz, 8H); ^{13}C NMR (100 MHz, DMSO-d_6): $\delta =$ 8.7, 29.9, 30.2, 44.8, 69.0, 69.6.

t-C5-I: Yield: 98%. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta =$ 1.46 (m, 8H), 1.56 (m, 8H), 1.84 (m, 8H), 3.19 (t, $J = 7.0$ Hz, 8H), 3.34–3.40 (m, 16H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 7.3, 27.5, 28.7, 33.4, 45.5, 69.9, 71.2.

t-C6-I: Yield: 95%. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta =$ 1.28–1.44 (m, 16H), 1.52 (q, $J = 7.0$ Hz, 8H), 1.81 (q, $J = 7.0$ Hz, 8H), 3.17 (t, $J = 7.2$ Hz, 8H), 3.30–3.38 (m, 16H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 7.1, 25.2, 29.4, 30.3, 33.5, 45.4, 69.8, 71.2.

t-EG2-I: Yield: 93%. ^{1}H NMR (400 MHz, CD_3CN): $\delta =$ 3.29 (t, $J = 6.4$ Hz, 8H), 3.39 (s, 8H), 3.53 (t, $J = 4.8$ Hz, 8H), 3.58 (t, $J = 4.8$ Hz, 8H), 3.70 (t, $J = 6.4$ Hz, 8H); ^{13}C NMR (100 MHz, CD_3CN): $\delta =$ 5.2, 46.4, 70.6, 70.6, 71.9, 72.4.

t-EG3-I: Yield: 98%. ^{1}H NMR (400 MHz, CD_3CN): $\delta =$ 3.32 (t, $J = 6.4$ Hz, 8H), 3.39 (s, 8H), 3.52–3.64 (m, 32H), 3.73 (t, $J = 6.4$ Hz, 8H); ^{13}C NMR (100 MHz, CD_3CN): $\delta =$ 5.0, 46.4, 70.5, 70.9, 71.1, 71.2, 71.9, 72.4.

General Procedure of t-R_1-R_2Im•Tf_2N Synthesis. **t-R_1-I** (2.0 mmol) and **R_2Im** (42 mmol) were mixed. The reaction mixture was stirred at 100 °C for 72 h under N_2 atmosphere. The reaction mixture was diluted with distilled water (150 mL). The aqueous solution was washed with CH_2Cl_2 (100 mL × 4) and diethyl ether (100 mL × 3). Lithium bis(trifluoromethanesulfonyl)imide (Li•Tf_2N) aqueous solution (10 g in 10 mL water) was added to the aqueous solution. The solution was stirred for 1 h at room temperature. The aqueous solution was concentrated to 100 mL by evaporation. The turbid aqueous solution was subjected to centrifugation (6000 rpm × 10 min). The supernatant was removed by decantation. The precipitate was dissolved in acetone and dried with $MgSO_4$, filtrated and concentrated by evaporation.

t-C2-EtIm•Tf_2N: Yield: 89%. ^{1}H NMR (400 MHz, CD_3CN): $\delta =$ 1.45 (t, $J = 7.4$ Hz, 12H), 3.23 (s, 8H), 3.56 (t, $J = 5.0$ Hz, 8H), 4.12–4.26 (m, 16H), 7.34 (t, $J = 1.8$ Hz, 4H), 7.41 (t, $J = 1.8$ Hz, 4H), 8.43 (s, 4H); ^{13}C NMR (100 MHz, CD_3CN): $\delta =$ 15.6, 46.0, 46.2, 50.5, 69.8, 70.3, 120.9 (q, $J =$ 318.4 Hz), 123.0, 124.0, 136.3.

t-C3-EtIm•Tf_2N: Yield: 84%. ^{1}H NMR (400 MHz, CD_3CN): $\delta =$ 1.49 (t, $J = 7.2$ Hz, 12H), 2.07 (m, 8H), 3.38

(s, 8H), 3.43 (t, $J = 6.0$ Hz, 8H), 4.16–4.23 (m, 16H), 7.39 (t, $J = 1.8$ Hz, 4H), 7.44 (t, $J = 1.8$ Hz, 4H), 8.47 (s, 4H); ^{13}C NMR (100 MHz, CD$_3$CN): $\delta = 15.4$, 30.7, 46.0, 46.2, 48.0, 68.2, 70.4, 120.9 (q, $J = 318.4$ Hz), 123.1, 123.7, 136.0.

t-C4-EtIm·Tf$_2$N: Yield: 93%. ^{1}H NMR (400 MHz, CD$_3$CN): $\delta = 1.43$–1.54 (m, 20H), 1.86 (m, 8H), 3.32 (s, 8H), 3.36 (t, $J = 6.2$ Hz, 8H), 4.09–4.20 (m, 16H), 7.37 (t, $J = 1.8$ Hz, 4H), 7.40 (t, $J = 1.8$ Hz, 4H), 8.45 (s, 4H); ^{13}C NMR (100 MHz, CD$_3$CN): $\delta = 15.4$, 27.0, 27.8, 45.9, 46.3, 50.5, 70.7, 71.4, 120.9 (q, $J = 318.5$ Hz), 123.2, 123.4, 135.9.

t-C5-EtIm·Tf$_2$N: Yield: 83%. ^{1}H NMR (400 MHz, CD$_3$CN): $\delta = 1.35$ (m, 8H), 1.48 (m, 12H), 1.55 (m, 8H), 1.86 (m, 8H), 3.30 (s, 8H), 3.35 (t, $J = 6.4$ Hz, 8H), 4.12 (t, $J = 7.2$ Hz, 8H), 4.18 (q, $J = 7.2$ Hz, 8H), 7.39 (t, $J = 1.8$ Hz, 4H), 7.42 (t, $J = 1.8$ Hz, 4H), 8.47 (s, 4H); ^{13}C NMR (100 MHz, CD$_3$CN): $\delta = 15.4$, 23.6, 29.7, 30.4, 45.9, 46.3, 50.5, 70.4, 71.8, 120.9 (q, $J = 318.5$ Hz), 123.1, 123.4, 135.8.

t-C6-EtIm·Tf$_2$N: Yield: 90%. ^{1}H NMR (400 MHz, CD$_3$CN): $\delta = 1.25$–1.40 (m, 16H), 1.42–1.54 (m, 20H), 1.81 (q, $J = 7.4$ Hz, 8H), 3.28 (s, 8H), 3.32 (t, $J = 6.6$ Hz, 8H), 4.10 (t, $J = 7.2$ Hz, 8H), 4.16 (q, $J = 7.3$ Hz, 8H), 7.37 (t, $J = 1.8$ Hz, 4H), 7.40 (t, $J = 1.8$ Hz, 4H), 8.46 (s, 4H); ^{13}C NMR (100 MHz, CD$_3$CN): $\delta = 15.4$, 26.3, 26.6, 30.2, 30.5, 45.9, 46.3, 50.6, 70.4, 72.0, 120.9 (q, $J = 318.5$ Hz), 123.1, 123.4, 135.9.

t-EG2-MeIm·Tf$_2$N: Yield: 83%. ^{1}H NMR (400 MHz, CD$_3$CN): $\delta = 3.34$ (s, 8H), 3.51 (m, 8H), 3.57 (m, 8H), 3.79 (t, $J = 4.8$ Hz, 8H), 3.85 (s, 12H), 4.27 (t, $J = 4.8$ Hz, 8H), 7.35 (t, $J = 1.8$ Hz, 4H), 7.41 (t, $J = 1.8$ Hz, 4H), 8.45 (s, 4H); ^{13}C NMR (100 MHz, CD$_3$CN): $\delta = 36.9$, 46.4, 50.5, 69.4, 70.5, 70.9, 71.7, 120.9 (q, $J = 318.5$ Hz), 123.9, 124.3, 137.2.

t-EG2-EtIm·Tf$_2$N: Yield: 91%. ^{1}H NMR (400 MHz, CD$_3$CN): $\delta = 1.46$ (t, $J = 7.2$ Hz, 12H), 3.32 (s, 8H), 3.48 (m, 8H), 3.56 (m, 8H), 3.78 (t, $J = 5.2$ Hz, 8H), 4.17 (q, $J = 7.2$ Hz, 8H), 4.25 (t, $J = 5.2$ Hz, 8H), 7.40 (t, $J = 1.8$ Hz, 4H), 7.41 (t, $J = 1.8$ Hz, 4H), 8.48 (s, 4H); ^{13}C NMR (100 MHz, CD$_3$CN): $\delta = 15.5$, 45.9, 46.4, 50.5, 69.4, 70.6, 71.0, 71.8, 120.9 (q, $J = 318.5$ Hz), 122.8, 124.1, 136.3.

t-EG2-BuIm·Tf$_2$N: Yield: 90%. ^{1}H NMR (400 MHz, CD$_3$CN): $\delta = 0.93$ (t, $J = 7.4$ Hz, 12H), 1.31 (m, 8H), 1.81 (m, 8H), 3.32 (s, 8H), 3.47 (m, 8H), 3.55 (m, 8H), 3.77 (t, $J = 5.0$ Hz, 8H), 4.13 (t, $J = 7.4$ Hz, 8H), 4.25 (t, $J = 5.0$ Hz, 8H), 7.38 (t, $J = 1.8$ Hz, 4H), 7.41 (t, $J = 1.8$ Hz, 4H), 8.46 (s, 4H); ^{13}C NMR (100 MHz, CD$_3$CN): $\delta = 13.6$, 20.0, 32.6, 46.4, 50.4, 50.5, 69.4, 70.6, 70.9, 71.8, 120.9 (q, $J = 318.5$ Hz), 123.1, 124.0, 136.6.

t-EG3-MeIm·Tf$_2$N: Yield: 86%. ^{1}H NMR (400 MHz, CD$_3$CN): $\delta = 3.35$ (s, 8H), 3.48–3.62 (m, 32H), 3.79 (t, $J = 5.2$ Hz, 8H), 3.85 (s, 8H), 4.28 (t, $J = 5.2$ Hz, 8H), 7.36 (t, $J = 1.8$ Hz, 4H), 7.44 (t, $J = 1.8$ Hz, 4H), 8.51 (s, 4H); ^{13}C NMR (100 MHz, CD$_3$CN): $\delta = 36.9$, 46.4, 50.5, 69.3, 70.5, 70.9, 70.0, 71.1, 71.9, 120.9 (q, $J = 318.5$ Hz), 124.0, 124.3, 137.4.

t-EG3-EtIm·Tf$_2$N: Yield: 81%. ^{1}H NMR (400 MHz, CD$_3$CN): $\delta = 1.49$ (t, $J = 7.4$ Hz, 12H), 3.35 (s, 8H), 3.47–3.62 (m, 32H), 3.79 (t, $J = 4.8$ Hz, 8H), 4.19 (q, $J = 7.4$ Hz, 8H), 4.28 (t, $J = 4.8$ Hz, 8H), 7.42 (t, $J = 1.8$ Hz, 4H), 7.45 (t, $J = 1.8$ Hz, 4H), 8.54 (s, 4H); ^{13}C NMR (100 MHz, CD$_3$CN): $\delta = 15.5$, 45.9, 46.4, 50.5, 69.2, 70.5, 70.9, 71.1, 71.9, 120.9 (q, $J = 318.5$ Hz), 122.7, 124.1, 136.4.

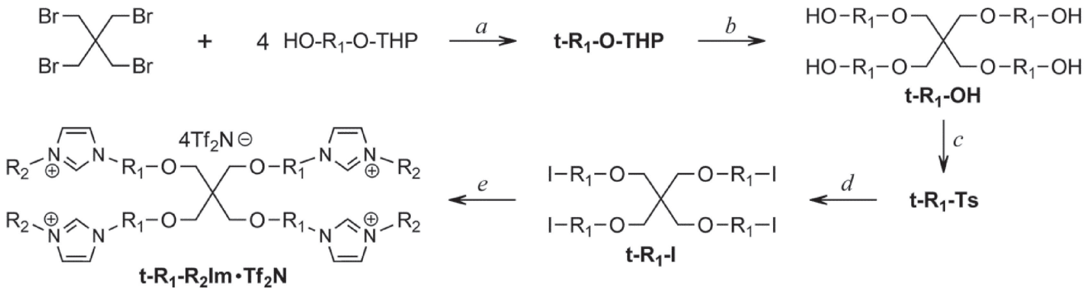
3. Results and Discussion

3.1 Synthesis of Tetra-Cationic Ionic Liquids. Scheme 1 shows the synthetic route used to prepare the tetra-cationic ionic liquids. The Williamson ether synthesis was used to graft HO-R$_1$-O-THP to the pentaerythrityl core. R$_1$ with 2–6 alkylene carbons or 2–3 ethylenedioxy units were selected as spacers. After removing the THP groups, each compound was transformed into the corresponding tetra-iodide through tosylation followed by a Finkelstein reaction. The tetra-iodide was then reacted with excess 1-alkylimidazole in the absence of solvent. Methyl, ethyl, and *n*-butyl groups were selected as tail units (R$_2$). After ion-metathesis, tetra-cations with Tf$_2$N counter ions were successfully obtained as pale yellow liquids. The chemical structures of the tetra-cations were confirmed by ^{1}H and ^{13}C NMR spectroscopy (see the Supporting Information), which revealed perfect imidazolium functionalization. In our previous study, we attempted to introduce the imidazolium unit directly onto the pentaerythrityl core without a spacer, but this strategy failed, presumably due to steric hindrance.[39] The spacer units contribute to relieving steric crowding around the core. The names of ten tetra-cations are summarized in Scheme 1, along with their chemical structures of the R$_1$ and R$_2$ units.

3.2 Thermal Properties of Tetra-Cationic Ionic Liquids. The thermal properties of the tetra-cationic ionic liquids were examined by differential scanning calorimetry (Table 1). The thermograms of the tetra-cations did not show melting peaks, but heat-capacity changes due to glass transitions (Figure S18 in the Supporting Information). Figure 2 summarizes the glass transition temperatures (T_gs) of the tetra-cations, which reveals that all samples have T_gs that are below −43 °C, which is much lower than those reported for tetra-cations without spacer units (ca. −35 °C, Figure 1a).[39] In cases of the tetra-cations with alkylene spacers (**t-C*n*-EtIm·Tf$_2$N**), the T_g values decreased drastically with increasing the spacer length from C2 to C4, while the T_g values of the tetra-cations with C4, C5, and C6 spacers were almost the same. Although a longer spacer decreases the T_g value due to higher degree of conformational freedom, it can cause larger molecular interactions between alkylene chains to increase the T_g value. Therefore, there is an optimum chain length to give the lowest T_g.[23,25,33] The T_g values of the tetra-cations with EG3 spacer were lower than those with EG2 spacer. As for the effect of the tail structure, the ethyl group provided lower T_gs than the methyl group, but the T_gs of **t-EG2-BuIm·Tf$_2$N** and **t-EG2-EtIm·Tf$_2$N** were the same.

The thermal-decomposition behavior of the tetra-cations was characterized by thermogravimetric analysis (Figure S19 in the Supporting Information). The 5% weight-loss temperatures (T_{d5}) ranged between 346 °C and 403 °C (Table 1). It must be emphasized that the spacer could improve thermal stability, since the T_{d5} values of tetra-cations without spacer units in our previous study (Figure 1a) were all below 310 °C.[39] The spacer unit relieves mechanical stresses around the pentaerythrityl core, concurrently increasing the distance between the imidazole units. These effects suppress thermal reactions between the imidazoles.

3.3 Density and Viscosity of Tetra-Cationic Ionic Liquids. The densities of the tetra-cations were measured by pycnometry. The results are summarized in Table 1. Densities were



R$_1$	R$_2$	Tetra-cation
-C$_2$H$_4$-	-C$_2$H$_5$	**t-C2-EtIm•Tf$_2$N**
-C$_3$H$_6$-	-C$_2$H$_5$	**t-C3-EtIm•Tf$_2$N**
-C$_4$H$_8$-	-C$_2$H$_5$	**t-C4-EtIm•Tf$_2$N**
-C$_5$H$_{10}$-	-C$_2$H$_5$	**t-C5-EtIm•Tf$_2$N**
-C$_6$H$_{12}$-	-C$_2$H$_5$	**t-C6-EtIm•Tf$_2$N**

R$_1$	R$_2$	Tetra-cation
-C$_2$H$_4$OC$_2$H$_4$-	-CH$_3$	**t-EG2-MeIm•Tf$_2$N**
-C$_2$H$_4$OC$_2$H$_4$-	-C$_2$H$_5$	**t-EG2-EtIm•Tf$_2$N**
-C$_2$H$_4$OC$_2$H$_4$-	-C$_4$H$_9$	**t-EG2-BuIm•Tf$_2$N**
-C$_2$H$_4$OC$_2$H$_4$OC$_2$H$_4$-	-CH$_3$	**t-EG3-MeIm•Tf$_2$N**
-C$_2$H$_4$OC$_2$H$_4$OC$_2$H$_4$-	-C$_2$H$_5$	**t-EG3-EtIm•Tf$_2$N**

Scheme 1. Synthesis of tetra-branched tetra-cationic ionic liquids. Reaction conditions: a) NaH, DMF, 100 °C, 24 h; b) PPTS, MeOH, 70 °C, 16 h; c) TEA, DMAP, TsCl, THF, r.t., 16 h; d) NaI, acetone, 60 °C, 60 h; e) R$_2$-imidazole, 100 °C, 72 h then Li•Tf$_2$N, water, r.t., 1 h. Chemical structures and sample names are summarized at bottom.

Table 1. Physical properties of tetra-cationic ionic liquids

Tetra-cation	M_w[a] g mol^{-1}	T_g[b] °C	T_{d5}[c] °C	Density[d] g cm^{-3}	Viscosity[e] Pa s
t-C$_2$-EtIm•Tf$_2$N	1749.4	−43	403	1.52	4.4
t-C$_3$-EtIm•Tf$_2$N	1805.5	−45	393	1.50	3.4
t-C$_4$-EtIm•Tf$_2$N	1861.7	−51	346	1.46	2.5
t-C$_5$-EtIm•Tf$_2$N	1917.8	−51	361	1.43	2.8
t-C$_6$-EtIm•Tf$_2$N	1973.9	−52	375	1.40	3.0
t-EG2-MeIm•Tf$_2$N	1869.5	−47	382	1.52	2.9
t-EG2-EtIm•Tf$_2$N	1925.7	−52	387	1.47	1.8
t-EG2-BuIm•Tf$_2$N	2037.9	−52	382	1.39	2.2
t-EG3-MeIm•Tf$_2$N	2045.8	−50	370	1.48	2.1
t-EG3-EtIm•Tf$_2$N	2101.9	−53	364	1.45	1.6

[a] Molecular weight. [b] Glass transition temperature. [c] 5 wt% loss temperature. [d] Measured using pycnometer at 25 °C. [e] Measured using a rolling-ball viscometer at 25 °C.

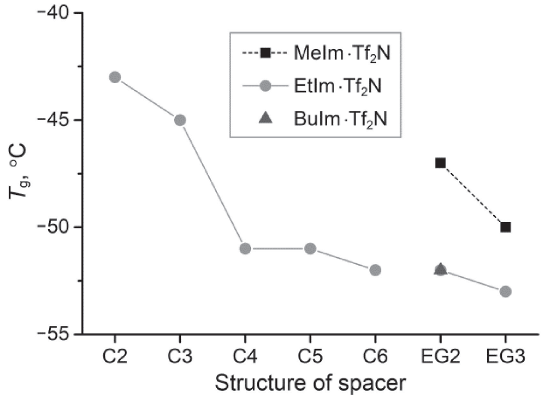


Figure 2. Effects of spacer and tail structure on glass transition temperature.

found to range between 1.39 and 1.52 g cm^{-3}. These values are comparable to those of conventional ionic liquids.[17] The relationship between molecular weight and density was plotted (Figure 3). Tetra-cation with longer spacer generally gives lower density than that with shorter spacer, and the densities of the tetra-cations with ethylenedioxy spacers are somewhat higher than those with alkylene spacers.

The viscosities of the tetra-cations were measured using a rolling-ball viscometer (Table 1). The results are summarized in Figure 4. Among the tetra-cations with alkylene spacer (**t-C*n*-EtIm•Tf$_2$N**), **t-C4-EtIm•Tf$_2$N** exhibited the lowest viscosity of 2.5 Pa s. The relatively short spacers (C2, C3, and C4) are effective to lower the molecular interaction between the pentaerythrityl cores to decrease the viscosity. On the other hand, the alkylene spacer longer than C4 causes larger molecular interaction between alkylene chains to increase the viscosity.[23,25,33] In cases of the tetra-cations with ethylenedioxy spacer (**t-EG*n*-R$_2$Im•Tf$_2$N**), longer spacers gave lower viscosities. The flexibility of the ethylenedioxy spacer is considered to contribute to lowering the viscosity. As for the tail unit, the ethyl-substituted imidazoles were found to be less viscous than the methyl- and *n*-butyl-substituted imidazoles.

The lowest viscosity of 1.6 Pa s was observed for **t-EG3-EtIm•Tf$_2$N**. The viscosity of the representative mono-cationic

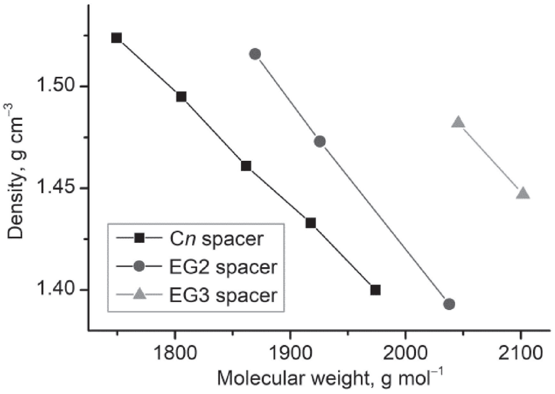


Figure 3. Relationship between molecular weight and density. Temperature: 25 °C.

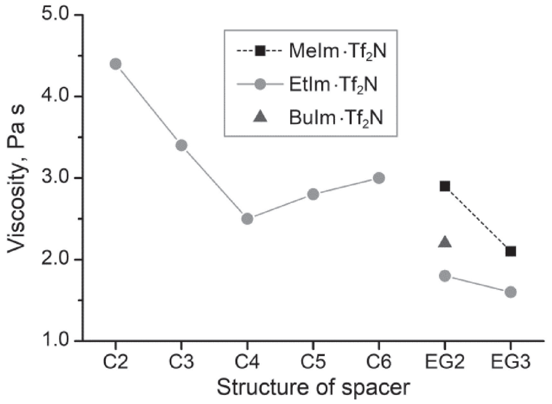


Figure 4. Effects of spacer and tail structure on viscosity. Temperature: 25 °C.

ionic liquid (1-Ethyl-3-methylimidazolium Tf_2N, **EMIm·Tf_2N**) was reported to be 28 mPa s (26 °C).[17] Much higher viscosity of the tetra-cation is attributable to larger molecular weight of the tetra-cation.

3.4 Ionic Conductivity of Tetra-Cationic Ionic Liquids. The ionic conductivity of each tetra-cation was determined by impedance spectroscopy under anhydrous conditions.[40] The direct current conductivity (σ_{DC}) was obtained from the plateau region of the real component of the conductivity vs. frequency plot (Figure S20 in the Supporting Information),[41,42] and the relationships between ionic conductivity and reciprocal temperature are shown in Figure 5. Ionic conductivities were observed to follow a Vogel-Fulcher-Tammann-type (VFT-type) temperature dependence, which reflects ion diffusion in viscous media.[41] The data were fitted using the following equation:

$$\sigma_{DC} = \sigma_{\infty} \times \exp(-B/(T - T_0)) \qquad (1)$$

where σ_{∞}, B, and T_0 are constants,[43] the values of which were obtained by data fitting and are summarized in Table 2.

Figure 6 summarizes the ionic conductivities of the tetra-cations at 25 °C. All of the tetra-cations showed 10^{-4} S cm^{-1} order ionic conductivity, which is two orders of magnitude higher than those reported for the tetra-cations without spacer units (ca. 4.7–7.6 × 10^{-6} S cm^{-1}).[39] These results indicate that the introduction of the spacer unit effectively improves ionic conductivity. Compared to the large differences in the ionic conductivities of the tetra-cations with and without spacers, the changes in the chemical structures of the spacer and tail units make little difference in ionic conductivity. Among the tetra-cations with alkylene spacer (**t-C*n*-EtIm·Tf_2N**), **t-C4-EtIm·Tf_2N** exhibited the highest ionic conductivity (1.9 × 10^{-4} S cm^{-1}). The tetra-cations with ethylenedioxy spacer afforded better ionic conductivities than those with alkylene spacers. As for the tail units, the ethyl-substituted imidazole exhibited higher ionic conductivity than the methyl- and *n*-butyl-imidazoles.

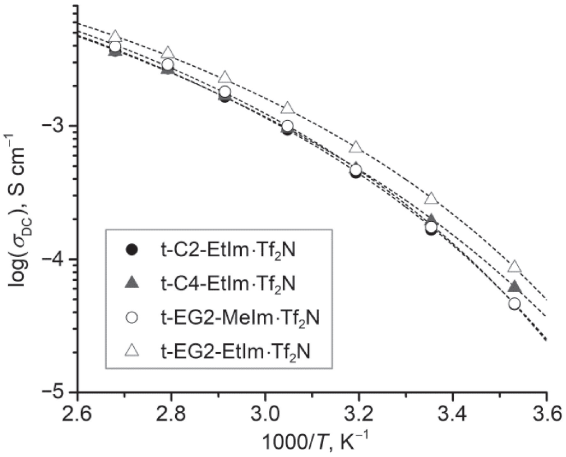


Figure 5. Ionic conductivities as functions of reciprocal temperature. Dashed curves are fitting using eq (1).

Table 2. Ionic conductivity data and VFT parameters

Tetra-cation	σ_{DC}[a] mS cm^{-1}	σ_{∞}[b] S cm^{-1}	B[b] K	T_0[b] K
t-C2-EtIm·Tf_2N	0.17	0.1660	634.0	205.7
t-C3-EtIm·Tf_2N	0.15	0.1825	677.6	202.5
t-C4-EtIm·Tf_2N	0.19	0.1986	706.8	195.6
t-C5-EtIm·Tf_2N	0.15	0.2528	782.1	191.7
t-C6-EtIm·Tf_2N	0.14	0.1755	767.2	190.1
t-EG2-MeIm·Tf_2N	0.17	0.1653	609.3	208.8
t-EG2-EtIm·Tf_2N	0.28	0.1469	574.6	205.9
t-EG2-BuIm·Tf_2N	0.16	0.1863	713.3	196.1
t-EG3-MeIm·Tf_2N	0.15	0.1238	595.1	208.4
t-EG3-EtIm·Tf_2N	0.24	0.1967	639.4	201.6

[a] DC conductivity at 25 °C obtained from impedance measurement. [b] VFT parameters obtained from the fitting using eq (1).

The highest ionic conductivity of 2.8 × 10^{-4} S cm^{-1} was observed for **t-EG2-EtIm·Tf_2N**. It should be noted that **t-EG3-EtIm·Tf_2N** is less ionically conductive than **t-EG2-EtIm·Tf_2N** despite the former being less viscous than the latter. Since the ion concentration decreases with increasing the spacer length, it is considered that there is an optimal spacer length that provides the highest ionic conductivity. The ionic conductivity of the representative mono-cationic ionic liquid (**EMIm·Tf_2N**) was reported to be 8.4 mS cm^{-1} (26 °C).[17] Much lower ionic conductivity of the tetra-cation is attributable to higher viscosity of the tetra-cation.

3.5 Comparison with Other Multi-Cations. Tetra-cationic ionic liquids are considered to be *meso*-class electrolytes that lie between di-cationic ionic liquids (the simplest multi-

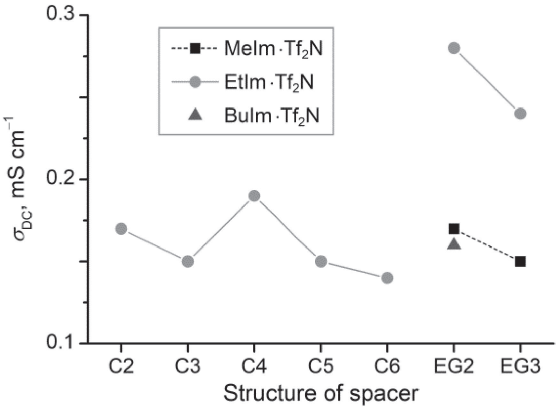


Figure 6. Effects of spacer and tail structure on ionic conductivity under anhydrous condition at 25 °C.

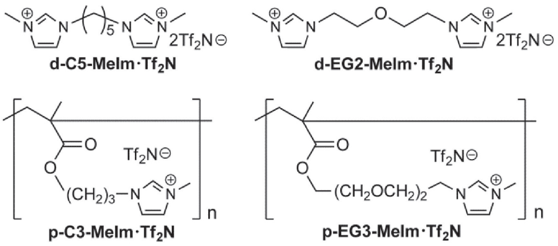


Figure 7. Chemical structures of di-cations and poly-cations.

Table 3. Physical properties of di-cations and poly-cations.

Multi-cation	Ref[a]	T_g[b] °C	Viscosity Pa s	σ_{DC}[c] mS cm^{-1}
d-C5-MeIm•Tf$_2$N	25, 31	−63	0.74	0.60
d-EG2-MeIm•Tf$_2$N	24, 32	−49	>1.5	0.52
p-C3-MeIm•Tf$_2$N	44	16	—	3.0×10^{-5}
p-EG3-MeIm•Tf$_2$N	45	−18	—	1.0×10^{-2}

[a] Reference. [b] Glass transition temperature. [c] DC conductivity at 25 °C.

cations) and poly-cations. It is interesting to compare the physical properties of the tetra-cations in this study with those of di- and poly-cations. The multi-cations shown in Figure 7 were selected as representative di-cationic ionic liquids[24,25,31,32] and poly-cations;[44,45] the physical properties of these multi-cations are summarized in Table 3.

The tetra-cations are more viscous and less ionically conductive than the di-cations, which is mainly attributable to the higher molecular weights of the tetra-cations than the di-cations. A larger molecular weight results in stronger molecular interactions and a lower ion concentration, which leads to higher viscosity and lower ionic conductivity. Despite unfavorable conditions for the tetra-cation, it should be noted that the viscosity of **t-EG3-EtIm•Tf$_2$N** is as low as that of **d-EG2-MeIm•Tf$_2$N**. In case of di-cations, changing the spacer from alkylene to ethylenedioxy chains resulted in increases in T_g and viscosity; consequently, decrease in ionic conductivity. This observation is attributable to increased molecular interactions due to ether oxygen atoms. On the other hand, poly-cation with ethylenedioxy spacer exhibited lower T_gs than that with alkylene spacer. The spacer structure-property relationship observed for the tetra-cations is similar to that of the poly-cations. In cases of poly-cations, the ethylenedioxy spacers reduce interactions between main chains, resulting in lower glass-transition temperatures. At the same time, the ethylenedioxy spacer increases the mobility of the cationic units.[19] In a similar way, the ethylenedioxy spacer is considered to reduce molecular interaction between the pentaerythritol-based cores and increase cation-unit mobility. Although the structure-property relationship of the tetra-cations is similar to that of the poly-cations, the physical parameters of the tetra-cations are closer in value to those of the di-cations rather than the poly-cations. These results highlight the unique physical properties of the tetra-branched tetra-cations, which are different from those of the di-cations and poly-cations. The cationic units of the tetra-cations without spacers (Figure 1a) are considered to become a part of the rigid core;[39] as a consequence, molecular interaction between the rigid cores increases and cation-unit mobility decreases, which is the reason why the introduction of the spacer units decreases viscosity and increases ionic conductivity.

4. Conclusion

Ten tetra-branched tetra-cationic ionic liquids with various spacers and tail units were successfully synthesized. The introduction of spacer units was confirmed to effectively decrease the glass transition temperature and increase the ionic conductivity compared to the tetra-cations without spacer units. As for the effect of the spacer structure on the physical properties of the tetra-cationic ionic liquids, the ethylenedioxy spacers were confirmed to afford lower viscosities and higher ionic conductivities than the alkylene spacers. While the tri-ethylenedioxy spacer was the best for lowering viscosity, the di-ethylenedioxy spacer was the best for improving ionic conductivity. As for the effect of the tail structure, the ethyl group was better for lowering viscosity and improving ionic conductivities than the methyl or *n*-butyl groups. The cationic units of tetra-cations without spacer units are considered to become a part of the rigid core, which leads to larger molecular interaction between the rigid cores. On the other hand, the spacer units are considered to reduce molecular interaction between pentaerythritol-based cores, which is the reason why the introduction of spacer units decreases viscosity and increases ionic conductivity.

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Supporting Information

Materials, NMR spectra, DSC and TGA charts, Impedance data. This material is available on https://doi.org/10.1246/bcsj.20200148.

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