ABSTRACT: A facile synthetic route for tetra-branched tetraimidazolium and tetrapyrrolidinium ionic liquids was developed. In contrast to the previous synthetic scheme, the new synthetic route requires only three reaction steps instead of seven. The total yield of tetracation was also improved from 17−21 to 39−41%. Using the new synthetic scheme, four kinds of tetracations were synthesized from the combination of two cationic units (imidazolium and pyrrolidinium) and two counteranions [bis-(fluorosulfonyl)imide (FSI) and bis(trifluoromethanesulfonyl)-imide (TFSI)]. Basic physical properties including glass transition temperature, thermal decomposition temperature, density, viscosity, and ionic conductivity were determined. The counterion exchange from TFSI to FSI resulted in lower glass transition temperature and higher ionic conductivity. Tetrapyrrolidinium exhibited higher viscosity and lower ionic conductivity than tetraimidazolium. The counterion exchange from TFSI to FSI resulted in lower viscosity in the case of tetraimidazolium, while the opposite result was obtained in the case of tetrapyrrolidinium. Tetracations composed of ethyl imidazolium units, diethylene glycol spacers, and FSI counterions exhibited the highest ionic conductivity of 3.5 × 10⁻⁴ S cm⁻¹ at 25 °C under anhydrous conditions.

1. INTRODUCTION

Ionic liquids, which are defined as molten salts around room temperature, are promising materials in many fields, e.g., electrolytes for batteries,¹⁻³ cellulose processing,¹⁴ green solvents or catalysts for chemical reactions,¹⁵,¹⁶ etc. Since the middle of the 2000s, multicationic ionic liquids have been developed and characterized as emerging functional liquids.⁸⁻¹⁸ Multicationic ionic liquids are recognizable as the mesomaterials between the conventional monocationic ionic liquids and poly(ionic liquid)s. Compared with monocationic ionic liquids, multicationic ionic liquids have higher viscosity and lower ionic conductivity because of higher molecular weight. However, the multicationic ionic liquids have some superior properties to their monocationic counterparts, such as higher thermal stabilities,⁸⁻¹⁰,¹⁷,¹⁸ better antimicrobial property,¹¹ higher capacities as supercapacitors,¹²,¹³ higher performance as stationary phases for gas chromatography,¹⁶,¹⁷,¹⁸ etc. Meanwhile, the multicationic ionic liquids have lower viscosity and higher ionic conductivity than poly(ionic liquid)s because of their lower molecular weight. Since poly(ionic liquid)s have polydispersity, it is difficult to prepare exactly the same sample again. Therefore, the physical property data of poly(ionic liquid)s vary depending on the samples. On the other hand, the physical property data of multicationic ionic liquids are reliable because they have well-defined molecular structures. This is another advantage of multicationic ionic liquids over poly(ionic liquid)s.

Recently, tetra-branched tetracationic ionic liquids, in which four cationic units were grafted onto a pentaerythritol core through spacer units, have been developed as new multicationic ionic liquids.²⁴,²⁵ In our previous study, tetracations were synthesized through seven reaction steps (Scheme S1).²⁵ This time-consuming and painstaking synthetic route motivated us to explore a new synthetic route. The objective of this study is to develop a facile synthetic route for tetra-branched tetracationic ionic liquids. Using the new synthetic route, one can reach the product in three steps. Here, four kinds of tetracations were synthesized from the combination of two cationic units [1-ethyl imidazolium (EtIm) and 1-methylpyrrolidinium (MePy)] and two counteranions [bis-(fluorosulfonyl)-imide (FSI) and bis-(trifluoromethanesulfonyl)-imide (TFSI)] (Figure 1). Three tetracations are new compounds. In our previous study, only tetraimidazolium derivatives were synthesized as representative of aromatic cations. In this study, tetrapyrrolidinium derivatives were also synthesized as representative of aliphatic cations. Diethylene glycol was selected as a spacer because it...
afforded the best ionic conductivity in our previous study. The physical properties of these tetracations including glass transition temperature, thermal decomposition temperature, density, viscosity, and ionic conductivity were determined.

2. RESULTS AND DISCUSSION

2.1. Synthesis of Tetracations. Scheme 1 shows the new synthetic route for the tetracations. In the first step, Williamson ether synthesis was carried out on pentaerythritol in a mixture of 50 wt % NaOH aqueous solution and excess bis(2-chloroethyl)-ether in the presence of the phase transfer catalyst tetrabutylammonium hydrogensulfate (TBA·HSO4). In the work-up process, the product and bis(2-chloroethyl)ether were extracted with diethyl ether. It was confirmed that TBA·HSO4 remained in an aqueous layer. Although this reaction requires a lot of bis(2-chloroethyl)ether, most of the unreacted dichloride could be recovered by distillation under reduced pressure and it was reusable next time. After the purification with SiO2 column chromatography, the tetrachloride compound (t-EG2-Cl) was obtained as a pale yellow liquid in 45% yield, which was comparable to the reported yield for a similar compound. In the second step, t-EG2-Cl was reacted with excess amine compound at 80 °C for 24 h. No solvent was required for the synthesis of imidazolium derivative. In the case of the pyrrolidinium derivative synthesis, however, N,N-dimethylformamide (DMF) was added to ensure mixing by the magnetic stir bar. Without DMF, the stirring stopped due to viscosity increase during the reaction. As a consequence, the reaction did not proceed efficiently. Although these quaternization reactions were conducted with a microwave reactor, no significant difference was recognized between conventional thermal heating and microwave heating. Tetracations with chloride counterions were recovered in yields of 96–98%. In the last step, the counterion metathesis was conducted in an aqueous media with the lithium salt of TFSI or FSI. The products were obtained as pale yellow oils in yields of 90–93%. Compared to the previous synthetic route, the total yield of tetracationic ionic liquids improved from 17–21 to 39–41%. It was confirmed that the physical properties of t-EG2-EtIm·TFSI synthesized in this study were almost identical to those reported previously.

Chemical structures were confirmed by 1H, 13C NMR spectra (Figures S1–S7), and high-resolution mass spectra (HRMS; Figures S15–S21). Figure 2 shows the 13C NMR spectra of t-EG2-EtIm·FSI and t-EG2-MePy·TFSI. The peaks were assigned with the help of 1H-1H COSY, 1H-13C HMQC, and 1H-13C HMBC spectra (Figures S8–S14). The carbons of the pentaerythritol core, diethylene glycol spacer, cationic unit, and counteranion are colored in green, black, red, and blue, respectively. It should be noted that no peak of the impurities was observed. In the cases of the tetracations with TFSI counterions, typical quartets of the CF3 group were observed at 120.9 ppm (coupling constant J = 319 Hz; Figure 2b). Those peaks were not detectable for the tetracations with FSI counterions.

The densities of the tetracations were determined by pycnometry (Table 1). The densities ranged between 1.40 and 1.50, which are comparable to the reported values of conventional ionic liquids.

2.2. Thermal Properties and Viscosities of Tetracations. Thermal properties were characterized using differential scanning calorimetry (DSC). The DSC charts of the tetracations are shown in Figure 3. In all cases including the tetracations with the chloride counterions, the thermograms showed glass transition alone without melting and crystallization peaks in the range from −90 to 200 °C. Table 1 and Figure 4 summarize the glass transition temperatures (Tg) of the tetracations. The tetracations with FSI counterions have lower Tg than those with TFSI counterions.

The thermal decomposition behaviors of the tetracations were characterized using thermogravimetric analysis (TGA).
The TGA charts are shown in Figure S22. All tetracations showed weight losses less than 0.2% at 150 °C, indicating a small water content. From the 5% weight loss temperature ($T_{ds5}$), it was confirmed that the thermal stabilities of tetracations with FSI counterions were inferior to those with TFSI counterions (Table 1), which is consistent with the results reported for other electrolytes with FSI and TFSI counteranions.29,30

The viscosities were measured using a rolling-ball viscometer and are summarized in Table 1 and Figure 4. The viscosities of the tetracations with the chloride counterions were too high to analyze using a rolling-ball viscometer. The viscosities of the tetrapyrrolidinium ionic liquids were higher than those of the tetraimidazolium analogues. This result is consistent with the general trend for the monocationic ionic liquids.31,32 This result is attributable to the charge delocalization effect of the imidazolium cation, which weakens the electrostatic interaction.32,33 In the case of the tetraimidazolium, the counterion exchange from FSI to TFSI increased the viscosity. This is also consistent with a general trend of monocationic ionic liquids.28

The tetrapyrrolidinium with FSI counterions gave higher viscosity than that with TFSI counterions. Presumably, in the case of the tetrapyrrolidinium, van der Waals interactions would induce attractive force between the hydrocarbon chains in the pyrrolidinium units, although delocalized charge over the imidazolium ring would induce an electrostatic repulsive force. The smaller counterion makes the neighboring pyrrolidinium units closer. It is considered that multivalent interactions between the tetrapyrrolidinium molecules would result in high viscosity.

### 2.3. Ionic Conductivity of Tetracations.

The ionic conductivities of the tetracations were analyzed by impedance measurements under anhydrous conditions.34 The direct current conductivity ($\sigma_{DC}$) was determined from the plateau region in the frequency-dependent conductivity plot. The relationships between the $\sigma_{DC}$ value and reciprocal temperature are shown in Figure 5. Ionic conductivity followed a Vogel–Fulcher–Tammann (VFT-type) temperature dependence, which reflects ion diffusion in viscous media. The data were fitted using the following equation

$$\sigma_{DC} = \sigma_{\infty} \times \exp\left(-\frac{B}{(T - T_0)}\right)$$  \hspace{1cm} (1)

Table 1. Physical Properties of Tetra-Branched Tetracationic Ionic Liquids

| sample                  | $T_g^a$ (°C) | $T_{ds5}^b$ (°C) | $\rho$ (g cm$^{-3}$) | $\eta$ (Pa s) | $\sigma_{DC}^e$ (mS cm$^{-1}$) | $\sigma_{\infty}^e$ (S cm$^{-1}$) | $B^f$ (K) | $T_0^f$ (K) |
|-------------------------|---------------|-------------------|-----------------------|---------------|-------------------------------|---------------------------------|-----------|------------|
| t-EG2-EtIm-Cl           | −48           | 384               | 1.35                  | 1.6           | 0.26                          | 0.1361 ± 0.040                 | 538.0     | 211.7      |
| t-EG2-EtIm-Cl           | −52           | 425               | 1.42                  | 1.9           | 0.35                          | 0.1361 ± 0.040                 | 538.0     | 211.7      |
| t-EG2-MePy-Cl           | −57           | 376               | 1.38                  | 1.5           | 0.21                          | 0.1361 ± 0.040                 | 538.0     | 211.7      |
| t-EG2-MePy-Cl           | −51           | 452               | 1.43                  | 1.8           | 0.31                          | 0.1361 ± 0.040                 | 538.0     | 211.7      |

$^a$Glass transition temperature (onset value in DSC heating process). $^b$5% weight loss temperature. $^c$Density at 25 °C. $^d$Viscosity at 25 °C. $^e$DC conductivity at 25 °C. $^f$Vogel–Fulcher–Tammann (VFT) parameters in eq 1 (value ± standard error).
where $T_0$ and $B$ are constants. These VFT parameters obtained from data fitting are summarized in Table 1. All of the tetracations showed $10^{-4}$ S cm$^{-1}$ order ionic conductivity at 25 °C (Table 1). The ionic conductivities of the di-imidazolium and di-pyrrolidinium derivatives linked by oligo(ethylene glycol) spacers were 6.5–7.9 $\times$ 10$^{-4}$ and 0.97–1.4 $\times$ 10$^{-3}$ S cm$^{-1}$, respectively (25 °C). Taking the molecular weight difference into account, the ionic conductivities of the tetracations are reasonable. The ionic conductivities of tetracations are higher than those of the tetraimidazolium ionic liquids ever reported.

**4. EXPERIMENTAL SECTION**

**4.1. Materials and Methods.** Pentairythritol, bis(2-chloroethyl)ether, TBA-HSO$_4$, 1-ethylimidazole, and 1-methylpyrrolidine were purchased from Tokyo Chemical Industry (TCI). Lithium FSI, lithium TFSI, and DMF were purchased from Kanto Chemical. Sodium hydroxide (NaOH), activated carbon, and pure water was purchased from Nacalai tesque. Some reactions were conducted with a microwave reactor (Discover SP, CEM). High-resolution electrospray ionization mass spectra (HR ESI MS) were recorded on a timsTOF (Bruker). The samples with chloride counternions and the others were dissolved in distilled water and acetonitrile, respectively (concentration: 5 μg mL$^{-1}$). The MS data were analyzed using the software Compass DataAnalysis Ver. 5.2 (Bruker). The other instrumental analyses are the same as those in our previous report.$^{25}$

**4.2. Synthesis of t-EG2-Cl.** Pentairythritol (2.0 g, 15 mmol), TBA-HSO$_4$ (6.0 g, 18 mmol), and bis(2-chloroethyl)ether (50 mL) were mixed in a 1000 mL round-bottom flask, then 50 wt% NaOH aqueous solution (50 mL) was added. The reaction mixture was vigorously stirred at 30 °C for 24 h. After adding water (150 mL), the product was extracted with diethyl ether (150 mL × 2). The organic solution was dried with MgSO$_4$, and concentrated with an evaporator. Bis(2-chloroethyl)ether was recovered by distillation (75 °C, 1.5 kPa). The product was purified by SiO$_2$ column chromatography (solvent: CH$_3$Cl/acetone = 19/1). Pale yellow liquid. Yield: 3.7 g (45%).$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 3.46 (s, 8H), 3.58 (m, 8H), 3.60–3.66 (m, 16H), 3.76 (t, $J$ = 6.4 Hz, 8H);$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 43.0, 45.6, 70.1, 70.6, 71.2, 71.4; HRMS (ESI): $m/z$: found: 583.1367 [M + Na]$^+$; C$_2$H$_5$ClO$_4$Na requires: 583.1369.

**4.3. Synthesis of t-EG2-EtIm-Cl.** t-EG2-Cl (2.8 g, 5.0 mmol) and 1-ethylimidazole (6.0 mL, 62 mmol) were mixed and stirred at 80 °C for 24 h under a N$_2$ atmosphere. After cooling to room temperature, the reaction mixture was diluted with 5 mL of MeOH. The solution was added dropwise to diethyl ether (100 mL). After centrifugation (4000 rpm, 3 min), the supernatant was removed by decantation. This purification procedure using diethyl ether was done again. The solvent was removed under a vacuum for 48 h at 120 °C. Orange transparent solid. Yield: 4.6 g (98%).$^1$H NMR (400 MHz, D$_2$O): $\delta$ = 1.46 (t, $J$ = 7.4 Hz, 12H), 3.36 (s, 8H), 3.55 (m, 8H), 3.64 (m, 8H), 3.87 (t, $J$ = 5.0 Hz, 8H), 4.21 (q, $J$ = 7.4 Hz, 8H), 4.36 (t, $J$ = 5.0 Hz, 8H), 7.51 (m, 8H), 8.80 (t, 4H);$^{13}$C NMR (100 MHz, D$_2$O): $\delta$ = 15.2, 45.6, 45.8, 49.7, 69.2, 70.1, 70.3, 71.2, 122.7, 123.4, 136.1; HRMS (ESI): $m/z$: found: 437.2512 [M–2Cl]$^{25}$; C$_9$H$_{11}$Cl$_2$N$_2$O$_8$ requires: 437.2420; $T_r$ = 10 °C.

**4.4. Synthesis of t-EG2-MePy-Cl.** t-EG2-Cl (2.8 g, 5.0 mmol), 1-methylpyrrolidine (8.0 mL, 75 mmol), and DMF (5.0 mL) were mixed and stirred at 80 °C for 24 h under a N$_2$ atmosphere. During the reaction, phase separation took place. After cooling to room temperature, the supernatant was removed by decantation. The orange residue was dissolved in MeOH (5 mL). The solution was added dropwise to diethyl ether (100 mL). The work-up procedure was the same as that for t-EG2-EtIm-Cl. Orange transparent solid. Yield: 4.3 g (96%).$^1$H NMR (400 MHz, D$_2$O): $\delta$ = 2.19 (br, 16H), 3.08 (s, 12H), 3.44 (s, 8H), 3.52–3.69 (m, 40H), 3.94 (br, 8H);$^{13}$C NMR (100 MHz, D$_2$O): $\delta$ = 21.7, 45.8, 49.1, 63.4, 65.5, 65.9, 70.3, 70.4, 71.2; HRMS (ESI): $m/z$: found: 415.2909 [M–2Cl]$^{25}$; C$_{48}$H$_{48}$Cl$_2$N$_2$O$_8$ requires: 415.2828; $T_r$ = 23 °C.

Figure 5. Ionic conductivities as a function of reciprocal temperature. Dashed curves are fitted using eq 1.
4.5. General Procedure for Counterion Metathesis.

The tetracation with chloride counterion (2 mmol) was dissolved in distilled water (100 mL). An aqueous solution (10 mL) containing lithium salt (LiTFSI or LiFSI, 20 mmol) was added. The reaction mixture was stirred at room temperature for 2 h. After centrifugation (4000 rpm, 3 min), the supernatant was removed by decantation. After rinsing with temperature for 2 h. After centrifugation (4000 rpm, 3 min), the product was dissolved in acetone and dried with the supernatant was removed by decantation. After rinsing with

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