

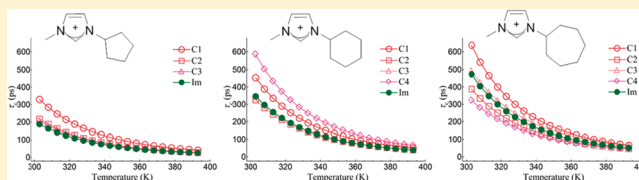
Comparison between Cycloalkyl- and *n*-Alkyl-Substituted Imidazolium-Based Ionic Liquids in Physicochemical Properties and Reorientational Dynamics

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S Supporting Information

ABSTRACT: We synthesized three series of imidazolium-based ionic liquids (ILs) containing cycloalkyl groups such as cyclopentyl, cyclohexyl, or cycloheptyl groups incorporating bis(trifluoromethanesulfonyl)amide anions and characterized them with respect to physicochemical properties and molecular reorientational dynamics. A comparison of the physicochemical properties revealed that cycloalkyl-substituted imidazolium ILs have higher densities, viscosities, and glass transition temperatures than the respective *n*-alkyl-substituted imidazolium ILs. Among three series, the cyclopentyl-substituted IL exhibits exceptionally lower viscosity. Observation of correlation times by ¹³C NMR spectroscopy revealed that a remarkably lower viscosity for the cyclopentyl-substituted IL and a considerably higher viscosity for the cyclohexyl- and cycloheptyl-substituted ones are closely related to the respective reorientational motion of the cations. The cause of these distinctions is suggested to be attributed to the difference of activation energy for the conformational interconversion of their substituents.



1. INTRODUCTION

Ionic liquids (ILs) have attracted significant attention in recent years owing to their diverse properties, such as negligible vapor pressure, nonflammability, high ionic conductivity, and high thermal, chemical, and electrochemical stabilities, which lead to their potential to serve as alternatives to traditional organic solvents.^{1–3} On the basis of these characteristic features of ILs, they can be applied in chemical,^{4–11} biological,^{12,13} and material science fields.^{14–25} Because ILs are typically composed of combinations of organic cations and the appropriate organic or inorganic anions, simple chemical modification of the ions offers an opportunity to control their physicochemical properties and to import desired functionality. Thus, a comprehensive understanding of the correlation between chemical structures and physicochemical properties is important from both a fundamental and application-based standpoint.

1,3-Dialkylimidazolium cations are one of the most typical constituent ions of ILs, and it is well-known that the flexibility and conformational diversity of the alkyl substituents strongly affect thermal properties, viscosity, and ionic conductivity.^{26–31} Among a variety of ILs designed and synthesized until now, *n*-alkyl-substituted imidazolium-based ILs have been studied extensively. In this study, we focused on cycloalkanes as flexible alicyclic substituent groups. Because some cycloalkanes possess conformational diversity owing to their flexible molecular frames, they have potential as substituents for ILs. In a previous report, we synthesized imidazolium ILs with a cyclohexyl group at the *N*-position of the imidazolium cation, and we observed a characteristic motion of the cyclohexyl group in the ILs by nuclear magnetic resonance (NMR) spectroscopy in solution.³²

However, a correlation between imidazolium ILs with other alicyclic groups and their physicochemical properties has not been sufficiently described.^{33,34}

In this report, we synthesized a series of imidazolium ILs substituted with 5-, 6-, or 7-membered cycloalkyl groups, hereafter abbreviated as *Cyn/X*, in which *Cy5*, *Cy6*, and *Cy7* denote the imidazolium cations with a cyclopentyl, a cyclohexyl, and a cycloheptyl group, respectively. To derive characteristic features of the cycloalkyl groups, we compared their physicochemical properties and ion dynamics to those of the respective *n*-alkyl-substituted imidazolium-based ILs (*Nn/X*, *n* = 5–7). We focus on the dynamics of ions because they closely relate to the flexibility and conformational diversity of ILs. In particular, it is considered that the reorientational dynamics is an important factor to dictate the physicochemical properties of the ILs in a molecular aggregated state such as a viscous liquid state.

NMR spectroscopy is one of the most suitable methods to study the reorientational dynamics of ILs.^{35–39} This is because the relaxation times in an NMR experiment provide valuable information on the relative dynamics of molecules. To examine the reorientational dynamics of ILs in the liquid state, we selected the bis(trifluoromethanesulfonyl)amide (NTf₂) anion as the counteranion, which led to the generation of ILs that were in the liquid state at ambient temperature. By comparing the longitudinal relaxation times of ¹³C nuclei (¹³C-*T*₁) and the

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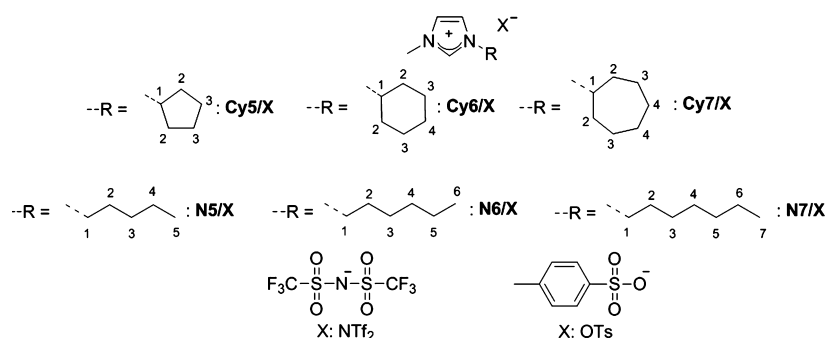


Figure 1. Chemical structures of Cyn/X and Nn/X. Each number in the cation structures correlates to atomic labels mentioned in the discussion.

Table 1. Physicochemical Properties of Cyn/NTf₂, Nn/NTf₂, and the Respective Hydrocarbons

| samples | MW (g/mol) | T_g (K) | T_m (K) | density ^a (g/cm ³) | V_{vdw} ^b (Å ³) | viscosity (cP) |
|----------------------|------------|-----------|-----------|---|--|----------------|
| Cy5/NTf ₂ | 431.4 | 194.3 | n.o. | 1.483 | 306.5 | 81.18 |
| Cy6/NTf ₂ | 445.4 | 211.8 | n.o. | 1.451 | 323.5 | 273.5 |
| Cy7/NTf ₂ | 459.5 | 209.6 | n.o. | 1.432 | 340.5 | 284.6 |
| N5/NTf ₂ | 433.1 | 189.6 | 267.1 | 1.408 | 317.9 | 78.74 |
| N6/NTf ₂ | 447.4 | 189.8 | 265.4 | 1.376 | 334.9 | 86.04 |
| N7/NTf ₂ | 461.5 | 190.3 | n.o. | 1.349 | 351.9 | 99.89 |
| cyclopentane | 70.13 | | 179.2 | 0.746 | 85.0 | 0.439 |
| cyclohexane | 84.16 | | 267.0 | 0.774 | 102.0 | 0.977 |
| cycloheptane | 98.19 | | 261.2 | 0.812 | 119.0 | 1.469 |
| n-pentane | 72.15 | | 142.2 | 0.626 | 96.4 | 0.229 |
| n-hexane | 86.18 | | 178.0 | 0.656 | 113.4 | 0.320 |
| n-heptane | 100.2 | | 182.2 | 0.679 | 130.4 | 0.417 |

^aViscosity and density of ILs were measured at 293 K. ^b V_{vdw} denotes van der Waals volume.

correlation times (τ_c) of Cyn/NTf₂ and Nn/NTf₂, we elucidated differences in the reorientational dynamics of their segmental carbons and the entire ions.

2. EXPERIMENTAL SECTION

2.1. Syntheses and Characterization. Figure 1 displays the chemical structures of Cyn/X and Nn/X synthesized in this study. Abbreviations for each imidazolium IL are also shown in the figure. Complete synthetic procedures for each imidazolium IL and analytical data are provided in the Supporting Information. Cyn ILs with tosylate (OTs) anions, as the precursors of Cyn/NTf₂, were synthesized by reacting methyl *p*-toluenesulfonate with the respective imidazole derivatives having the desired cycloalkyl groups at the *N*-position. N5/OTs and N6/OTs were prepared according to the standard synthetic procedures.^{3,26} Only for the preparation of N7/NTf₂, N7/Br was synthesized as the precursor.³² These reactions were performed under an argon atmosphere. Anion metathesis reactions involving LiNTf₂ were performed by previously published procedures.³² Imidazolium ILs paired with OTs anions were obtained as white crystals at ambient temperature. On the other hand, all ILs having NTf₂ anions prepared in this study are in the liquid state under similar conditions. All imidazolium ILs were characterized using ¹H and ¹³C NMR spectroscopy and elemental analyses. These results demonstrate that the synthesized ILs are in high purity.

2.2. Measurements. The water contents of ILs was estimated by Karl Fischer titration using a Mettler Toledo Karl Fischer coulometer. The water contents of all imidazolium ILs was less than 150 ppm. Thermal properties such as glass transition temperatures (T_g) and melting points (T_m) were measured by differential scanning calorimetry (Rigaku, Thermo

plus EVO). The typical method involved a scanning rate of 10 K/min and a measured temperature range 173–423 K. A secondary scanning run was adopted to determine T_m and T_g . The T_m values were taken at the top of the corresponding endothermic peaks. The onset of the change in heat capacity was taken as T_g . The liquid density values were measured at 293 K by an oscillating U-tube densitometer (Anton Paar, DMA 4500). Viscosities were determined using a falling ball viscometer (Anton Paar, AMVn) at 293 K.

To evaluate the reorientational dynamics of various imidazolium ILs paired with NTf₂ anions, which are in the liquid state at ambient temperature, ¹³C- T_1 were measured using a JEOL LA-400 spectrometer with a ¹³C resonance frequency of 100 MHz. To measure ¹³C- T_1 , samples were prepared by placing each IL in a sample tube with an outer diameter of 4 mm, drying under a vacuum of 1 Torr at 313 K for 24 h, and then flame-sealing. The 4 mm sample tube was inserted into a 5 mm standard NMR sample tube. A deuterated solvent for field/frequency lock was infused in the narrow space between the 4 and 5 mm tubes. The ¹³C- T_1 values for each carbon were obtained as a function of temperature in the range from 303 to 393 K under the ¹H broadband decoupling condition by the inversion recovery method.³⁵ The measurements were conducted three times, and all deviations in the experimental values from the average were within $\pm 3\%$. τ_c for each carbon was obtained from the fitting of temperature-dependent ¹³C- T_1 curves.

Crystals of Cy5/OTs and N6/OTs that were suitable for single-crystal X-ray analysis were obtained from an acetonitrile/diethyl ether solution. Although conformational structures of cations would change by exchange of paired anion species, crystal structures of these imidazolium ILs provide some

important structural aspects. Thus, we performed single-crystal X-ray analyses. X-ray diffraction data were collected on a Bruker APEX II CCD area detector using Mo $K\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation. Because of the high hygroscopicity of the crystals, each single crystal was mounted on a glass pin coated with a minimal amount of manicure to avoid adsorbing moisture and cooled to 173 K by a stream of nitrogen gas. The crystal structures were determined by direct method SHELXS-97 and refined by full-matrix least-squares SHELXL-97.⁴⁰ Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included in their calculated positions.

3. RESULTS AND DISCUSSION

3.1. Physicochemical Properties. Table 1 summarizes the physicochemical properties of the cycloalkyl- and *n*-alkyl-substituted imidazolium ILs paired with NTf₂ anion prepared in this study. The properties of the neat hydrocarbons that correspond to the substituents on the ILs are also given in the table.

3.1.1. Density and Volume. It is clear from Table 1 that Cyn/NTf₂ has a higher density compared with the respective Nn/NTf₂, irrespective of the carbon number. With respect to the hydrocarbons, the densities of the cycloalkanes are higher than those of the respective *n*-alkanes; that result is consistent with the findings for the imidazolium ILs. This trend is explained in terms of the van der Waals volume (V_{vdw}) and excluded volume (V_{ex}). V_{vdw} values were calculated using the van der Waals increment, van der Waals radii, and bond lengths.^{41–43} The V_{vdw} values of the cycloalkanes are smaller than those of their acyclic counterparts. In addition, it is well-known that a cycloalkane has a smaller V_{ex} value than the respective *n*-alkane.^{44–46} Because smaller V_{vdw} and V_{ex} values leads to higher filling fractions in a liquid, the densities of cycloalkanes are higher than those of the respective *n*-alkanes. The density results for the ILs can also be explained in terms of similar V_{vdw} and V_{ex} effects.

Moreover, liquid densities of typical hydrocarbons (*n*-alkanes and cycloalkanes) increase with the increasing carbon number. The reason for this phenomenon is attributed to the fact that van der Waals interactions between hydrocarbon molecules become stronger as the number of carbons increases. However, the densities of both Cyn/NTf₂ and Nn/NTf₂ showed a trend that was opposite to that observed for the hydrocarbons. It is well-known that the density values for typical 1,3-dialkylimidazolium salts decrease as the length of the alkyl chain increases.^{26,29} Because an increase in the number of carbons per substituent on the imidazolium cations causes a decrease in charge density on the cations and an increase of the free volume, the densities of the liquid imidazolium ILs decrease.

3.1.2. Viscosity. The viscosities of Cyn/NTf₂ and Nn/NTf₂ at 293 K are shown in Table 1. These results indicated that cycloalkyl substituents have different effects on the viscosity. The viscosity values of Cy6/NTf₂ and Cy7/NTf₂ have more than tripled as those of N6/NTf₂ and N7/NTf₂, respectively. It is known that the mobility of the substituent strongly contribute to the viscosity of ILs.^{26,27,30} In the cases of the respective hydrocarbons, their relative viscosities conformed well to those of the corresponding ILs. This result implies that the cyclohexyl and cycloheptyl substituents have similar effects on the mobility as the respective cyclic hydrocarbons. In contrast, Cy5/NTf₂ had a viscosity value similar to N5/NTf₂, whereas the viscosity of cyclopentane is ~ 2 times as high as that of *n*-pentane. The reason for this discrepancy between the

substitution effects of cycloalkyl groups on the viscosity is discussed in section 3.2.

3.1.3. Thermal Properties. As listed in Table 1, Cyn/NTf₂ showed only a glass transition without crystallization under this scanning condition. In addition, the T_g values of Cyn/NTf₂ were higher than those of the respective Nn/NTf₂. As for Cy6/NTf₂ and Cy7/NTf₂, their T_g values are ~ 20 K higher than those of the corresponding Nn/NTf₂. On the other hand, the T_g value of Cy5/NTf₂ was substantially lower than those of the other Cyn/NTf₂ and a little higher than that of N5/NTf₂. This trend of T_g values of Cyn/NTf₂ is analogous to the results which were observed in the viscosities of them, as described above. Because the glass transition temperature is closely related to the molecular mobility,³⁰ these results are considered to be reasonable.

The thermal properties and crystal structures of the imidazolium ILs paired with OTs anions, which were the precursors for the ILs with NTf₂ anions, were also studied because they may provide some useful information. The thermal and crystallographic data of them are summarized in the Supporting Information. The T_m values of Cyn/OTs ILs are higher than those of the respective Nn/OTs ILs. The cause of this phenomenon can be explained in terms of crystal structures and substituent flexibility.

3.2. Reorientational Dynamics. To estimate the reorientational dynamics, which is a dominant factor of the molecular mobility in viscous liquids, the temperature dependence of ^{13}C - T_1 for the liquid imidazolium ILs was measured using a high-resolution NMR spectrometer. In general, the T_1 value is composed of multiple components derived from various relaxation mechanisms and is described as follows:

$$\frac{1}{T_1} = \frac{1}{T_1^{\text{DD}}} + \frac{1}{T_1^{\text{CSA}}} + \frac{1}{T_1^{\text{SR}}} + \frac{1}{T_1^{\text{SC}}} + \frac{1}{T_1^{\text{Q}}} \quad (1)$$

where T_1^{DD} is the dipolar–dipolar relaxation, T_1^{CSA} is the chemical shift anisotropy, T_1^{SR} is the spin rotation relaxation, T_1^{SC} is the scalar relaxation, and T_1^{Q} is the electric quadrupole interaction. Because the T_1^{Q} mechanism is significant only when the nuclei contain spins over 1/2, a contribution from T_1^{Q} can be neglected. T_1^{SC} has practically no effect on T_1 relaxation, except for the case of occurring chemical exchange. The magnetic fields fluctuate in response to the magnetic moment originating from the rotational motion of a small rigid molecule with charge distribution. Thus, the T_1^{SR} mechanism becomes important when considering the relaxation of gas molecules. We need to examine the contribution from T_1^{CSA} when the samples have double bonds, aromatic groups, and carbonyl carbons. Our samples in this study contain cations involving aromatic imidazolium moieties. However, the T_1^{CSA} term for the imidazolium carbons is small enough that its contribution to the ^{13}C - T_1 values can be neglected, as shown in previously published reports.^{38,47} In addition, the cross-relaxation effect on the dipolar–dipolar relaxation mechanism of ^{13}C - T_1 under the proton-decoupling condition is also considerably small.⁴⁷ Therefore, we assume that the observed ^{13}C - T_1 values depend primary on T_1^{DD} . Thus, for a dipolar–

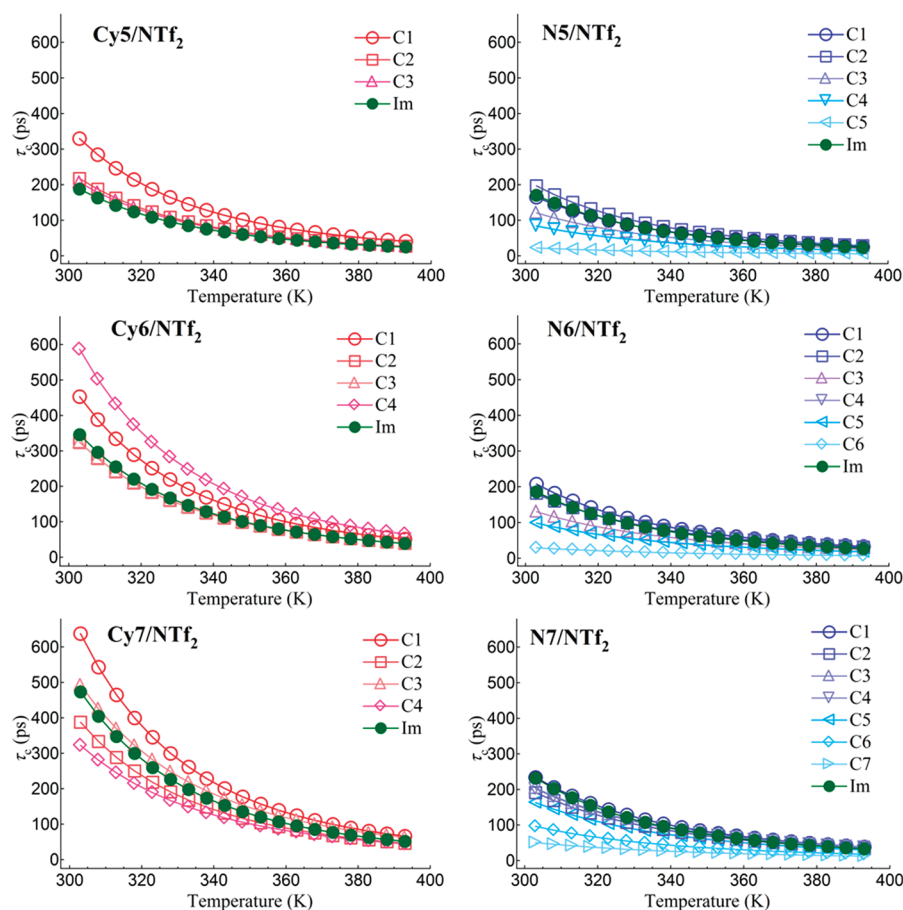


Figure 2. Temperature dependences of correlation times in ^{13}C NMR spectroscopy for **Cyn/NTf₂** and **Nn/NTf₂**. Atomic labels in each figure are consistent with those in Figure 1. “Im” represents an average correlation time among carbons at the 2-, 4-, and 5-positions of the imidazolium ring.

dipolar relaxation mechanism, eq 1 can be rewritten as follows:^{36,48}

$$\frac{1}{T_1} = \frac{1}{T_1^{\text{DD}}} = \frac{1}{20} N_{\text{H}} \left(\frac{\mu_0}{4\pi} \right)^2 \frac{\gamma_{\text{C}}^2 \gamma_{\text{H}}^2 \hbar^2}{r^6} \left[\frac{2\tau_{\text{c}}}{1 + (\omega_{\text{C}} - \omega_{\text{H}})^2 \tau_{\text{c}}^2} + \frac{6\tau_{\text{c}}}{1 + \omega_{\text{C}}^2 \tau_{\text{c}}^2} + \frac{12\tau_{\text{c}}}{1 + (\omega_{\text{C}} + \omega_{\text{H}})^2 \tau_{\text{c}}^2} \right] \quad (2)$$

where μ_0 is the permittivity of vacuum, γ_{C} and γ_{H} are the gyromagnetic ratios of the ^{13}C and ^1H nuclei, respectively, \hbar is $h/2\pi$ where h is Planck's constant, r is the distance between a carbon and a directly bonded proton, τ_{c} is the rotational correlation time, and ω_{C} and ω_{H} are the resonance frequencies of the ^{13}C and ^1H nuclei, respectively. It can be considered that the temperature-dependent ^{13}C - T_1 values are a function of the correlation time. The correlation times obey the Arrhenius equation:^{35,39}

$$\tau_{\text{c}} = \tau_0 \exp\left(\frac{E_{\text{a}}}{RT}\right) \quad (3)$$

where τ_0 is the correlation time at an extremely high temperature, E_{a} is the activation energy, and R is the gas constant.

The τ_{c} values obtained by fitting the temperature dependence of ^{13}C - T_1 using eqs 2 and 3 for **Cyn/NTf₂** and **Nn/NTf₂** are shown in Figure 2. Atomic labels correspond to those in Figure 1. Generally, the dipolar–dipolar relaxation mechanism for viscous liquids is dominated by a molecular reorientation involving anisotropic molecular motion and intramolecular segmental motion.³⁷ Thus, τ_{c} represents the reorientational dynamics. Average values of τ_{c} for the ^{13}C of each alkyl substituent at 323 K are 89.5, 218, 246, 71.6, 85.5, and 103 ps for **Cy5/NTf₂**, **Cy6/NTf₂**, **Cy7/NTf₂**, **N5/NTf₂**, **N6/NTf₂**, and **N7/NTf₂**, respectively. The average τ_{c} values for the cyclohexyl and cycloheptyl group carbons are substantially longer than those for the others. Moreover, the average values of τ_{c} for the carbons of each imidazolium ring at 323 K are 108, 191, 260, 99.9, 110, and 137 ps for **Cy5/NTf₂**, **Cy6/NTf₂**, **Cy7/NTf₂**, **N5/NTf₂**, **N6/NTf₂**, and **N7/NTf₂**, respectively. Although τ_{c} for **Cy5/NTf₂**, **N5/NTf₂**, **N6/NTf₂**, and **N7/NTf₂** are nearly comparable, those for **Cy6/NTf₂** and **Cy7/NTf₂** are substantially longer as are the case of the substituent carbons. These results indicate that both the segmental motion of the substituent carbons and the full molecular reorientational motion for **Cy6/NTf₂** and **Cy7/NTf₂** are slow compared to those for the other imidazolium ILs. This is consistent with the fact that **Cy6/NTf₂** and **Cy7/NTf₂** showed considerably higher viscosities than the other ILs. The reason for the relatively slow motion for **Cy6/NTf₂** and **Cy7/NTf₂** might be attributed to the activation free energy for the interconversion of the substituents. The energies of cyclohexane (10.1 kcal/mol) and

cycloheptane (8.5 kcal/mol) are substantially higher than those of cyclopentane and acyclic hydrocarbons (~ 4 kcal/mol),^{49–51} leading to low flexibility for these cyclic hydrocarbons. It is known that the local flexibility, such as intramolecular rotational motion of alkyl groups, also affects the viscosity of imidazolium-based ILs.⁵² Thus, it can be concluded that the introduction of the cyclohexyl or cycloheptyl groups leads to lower mobility for not only the substituents but also the entire molecules and consequently higher viscosities of the ILs. As the discussion on Cy6/NTf₂ and Cy7/NTf₂, the remarkably lower viscosity of Cy5/NTf₂ is considered to be attributed to the lower conformational activation energy of cyclopentane. Moreover, the viscosity value of Cy7/NTf₂ is slightly higher than that of Cy6/NTf₂ despite the lower interconversion energy of cycloheptane compared to cyclohexane. This discrepancy would be attributed to the van der Waals interactions between substituted hydrocarbons.

As described above, τ_c in eq 2 involves the overall correlation time (τ_c^{all}) for the anisotropic molecular motion and the segmental correlation time (τ_c^{seg}) for the intramolecular segmental motion. Although we attempted to extract the τ_c^{seg} values of each substituent, we could not obtain them because it was difficult to estimate τ_c^{all} values from the observed τ_c for the cycloalkyl-substituted ILs.

Meanwhile, we examined τ_c of each carbon for each imidazolium IL. The anisotropic molecular motion involves various rotational motions. Although τ_c of the substituent carbons for Cy5/NTf₂ becomes shorter as the distance from the imidazolium moiety increases, τ_c of the C4 carbon, which is the farthest from the imidazolium moiety, is the longest for Cy6/NTf₂. In addition, for the case of Cy7/NTf₂, the order of the τ_c length of the cycloheptyl group is resemble to that of Cy5/NTf₂. This indicates that the position of the centroid of rotational motion in Cy6/NTf₂ differs from those in Cy5/NTf₂ and Cy7/NTf₂. In general, since angular momentum increases with the distance from the rotational centroid, τ_c would become shorter. Thus, it seems that there are rotational centroids around the imidazolium moiety for Cy5/NTf₂ and Cy7/NTf₂. In contrast, the rotational centroid might be near the C4 carbon for Cy6/NTf₂ because of the substantially longer τ_c of the C4 carbon compared to that of both the C2 and C3 carbons. This difference in the position of the rotational centroids might be caused by the structure and flexibility of substituent groups.

When we assumed that the centroid of molecular rotational motion is near the C4 carbon for Cy6/NTf₂, the order of the τ_c length should be C4 > C3 > C2 > C1. However, the observed order of was C4 > C1 > C3 = C2. This result can be explained in terms of the axial rotation component of the anisotropic molecular motion. τ_c becomes shorter as the distance from the rotational axes increases. For example, it is well-known that biphenyl has a rotational axis around the central C–C bond that links the two phenyl rings.⁵³ The Cyn/NTf₂ may have the rotational axis around the N–C bond that links the imidazolium cation and cycloalkyl groups, which is suggested by their structural analogy to biphenyl. In fact, the τ_c values of the C1 carbons for Cyn/NTf₂ are relatively long. Therefore, the reason for the difference in the order of the τ_c length among Cyn/NTf₂ can be explained in terms of the anisotropic molecular motion.

4. CONCLUSION

A series of imidazolium ILs having cycloalkyl substituents were synthesized and characterized in terms of physicochemical

properties and molecular reorientational dynamics. On comparison with the imidazolium ILs having *n*-alkyl substituents, it is found that the cycloalkyl substituents impart a higher melting point, glass transition temperature, density, and viscosity in their associated ILs. The temperature dependence of τ_c indicates that cyclohexyl and cycloheptyl groups have distinctly low mobility as substituents, which lead to low reorientational motion in the entire cations. This conclusion is consistent with the macroscopic observations, namely, the higher viscosities and glass transition temperatures of Cy6/NTf₂ and Cy7/NTf₂. On the other hand, the cyclopentyl group leads to substantially higher reorientational motion in the cation as is the case in the ILs-substituted *n*-alkyl groups and consequently results in the exceptionally lower viscosity in the corresponding IL, Cy5/NTf₂. The cause of these distinctions for the motion among them can be explained in terms of the activation energy for the conformational interconversion of the substituents.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details, Figures S1–S4, Tables S1, and CIF files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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