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Adamantane Ionic Liquids

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We report synthesis and characteristic thermal properties of the adamantane-based ionic salts. The ion salts with adamantane carboxylates and imidazolium cations were prepared via neutralization. It was found that the assembly of the ion pairs on the adamantane core can improve the thermal stability and lower melting temperatures even though the molecular weight increases. Finally, the thermally-stable room temperature-ionic liquids, which are defined as a salt with the melting temperature below 25 °C, can be obtained based on adamantane. The tetrahedral-like distribution of ion pairs could be responsible for simultaneously improving thermal stability and lowering melting temperatures of ion pairs.

Ionic liquids (ILs) which are defined as the salt with melting temperatures below 100 °C attract attention for the application in various fields because of their wide versatility. For example, some of ILs have high ion conductivity and flame resistance.^[1,2] Based on these characteristics, ILs have been attempted to be applied as an electrolyte in a lithium battery.^[3] In addition, the material properties of ILs can be readily tuned by changing component ions. Recently, we reported the modulation of dispersibility of the IL-modified metal nanoparticles.^[4,5] By the anion exchange of ILs at the surface of the particles, the compatibility with solvent molecules was greatly changed. As a result, the dispersion/aggregation of the nanoparticles can be controlled under mild conditions. Moreover, by altering the affinity to DNA, the catch and release system for DNA can be accomplished by anion exchange.^[6] Thus, the development of new component molecules has large potential to produce new series of ILs. In particular, since the anion species significantly influence on the properties of ILs, the synthesis of new anions with bulky structures is of great significance for obtaining advanced functionalized ILs as well as desired materials.^[7]

In general, the increase of molecular weight of components tends to increase melting temperatures of ion pairs. Therefore, there is fewer ILs with multiple ion pairs in the single molecule comparing to those with a single ion pair. We have recently found that the thermal properties of ion pairs were crucially changed by tethering to the vertices of polyhedral oligomeric silsesquioxane (POSS, Figure 1)^[8,9]. Melting temperatures of the POSS-tethered ion pairs can be reduced by inhibiting molecular interaction because of the isolation effect by the cubic core. Moreover, thermal

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Fig. 1 Chemical structures and abbreviations of the ion salts used in this study. The number of ion pairs around the adamantane core and the length of the alkyl chain in methyl imidazolium are represented as *m* and *n*, respectively.

stability can be improved by suppressing molecular motions by the rigid silica cube and highly-symmetrical structure of POSS. Finally, despite there are eight ion pairs in the single molecule, we obtained the room temperature-ILs which have the melting temperature below 25 °C.^[8,9] More recently, the molecular filler for enhancing thermal stability and lowering melting temperature of conventional ILs was presented.^[10] According to these results, we suggested that the introduction of the rigid and symmetrical core could be essential to reduce melting temperatures and enhance thermal stability of ion pairs for obtaining ILs based on polymers or macromolecules. To show the generality of this suggestion, the other example should be offered as the ILs having multiple ion pairs tethered to the rigid steric core.

We focused on adamantane as a core for assembling ion pairs. Adamantane possesses the minimum unit structure of a diamond crystal and therefore has been used as a building block for constructing thermally-stable or robust materials.^[11] Furthermore, each ion pair should be located as tetrahedral-like distribution around the adamantane core by tethering to the vertices of adamantane. Thereby, adamantane should be a good example as a scaffold to evaluate the steric core effect on the thermal properties of ion pairs. Herein, we report the characteristic thermal properties of the adamantane-tethered ion salts (Figure 1). The series of ion salts with adamantane carboxylates and imidazolium cations were prepared. The influence of chemical structures of adamantane-based salts on melting temperatures and thermal stability was investigated with various numbers of ion pairs around the

Table 1 Melting and decomposition temperatures of the tetra-substituted ion salts

C_n	T_m (°C) ^a			T_d (°C) ^b		
	Ada	Arm	Δ	Ada	Arm	Δ
4	31	n.d. ^c	–	224	217	+7
6	27	n.d. ^c	–	223	214	+9
8	n.d. ^c	n.d. ^c	–	225	220	+5
10	n.d. ^c	26	–	219	218	+1
12	21	40	–19	220	218	+2
14	n.d. ^c	56	–	232	217	+15
16	31	65	–34	249	217	+32
18	41	73	–32	253	221	+32

^aObtained from the first heating curves in the DSC profiles.

^bDetermined from the onsets in the TGA curves.

^cn.d. = not determined.

Table 2 Melting and decomposition temperatures of [C(n)mim]_mAda(CH₂CH₂COO)_m

m	T_m (°C) ^a			T_d (°C) ^b		
	C4	C10	C18	C4	C10	C18
1	48	n.d. ^c	18	215	222	224
2	n.d. ^c	19	31	222	223	237
3	n.d. ^c	16	40	219	223	243
4	31	n.d. ^c	41	223	219	253

^aObtained from the first heating curves in the DSC profiles.

^bDetermined from the onsets in the TGA curves.

^cn.d. = not determined.

adamantane core and lengths of the alkyl chains in imidazolium cation. The roles of the structural feature of the adamantane core are evaluated from the experiments.

Synthesis of the series of adamantane-based salts was carried out according to the previous reports.^[12–14] The precursors of adamantane with various numbers of carboxylic groups, Ada(CH₂CH₂COOH)_m (m = 1, 2, 3 and 4), were obtained by modulating the feed ratio of bromine in bromination. After treating with acrylonitrile, hydrolysis provided Ada(CH₂CH₂COOH)_m with high purity. The series of the hydroxyl form of imidazolium salts with a methyl group and various lengths of alkyl chains (C4 to C18) were prepared via anion exchange from bromide salts which were synthesized under mild conditions to avoid the contamination of colored impurities. The neutralization was employed for receiving ion pairs by mixing the imidazolium salt with Ada(CH₂CH₂COOH)_m in methanol. After drying *in vacuo*, desired salts [C(n)mim]_mAda(CH₂CH₂COO)_m (m = 1–4, n = 4–18) were obtained as colorless and transparent products. We also prepared the ion pairs with propionic acid, [C(n)mim](ArmCOO) (n = 4–18), for the comparison to evaluate the effects of the connection to adamantane.

By comparing integration ratios of the peaks in the ¹H NMR spectra, the formation of a one-to-one pair between the carboxylate in adamantane and imidazolium cation was confirmed. The products were stored in a glove box under argon atmosphere, and water abundance can be kept below 1.5 wt% as determined by the Karl Fischer method. From previous reports, it was confirmed that the concentrations of residual bromide ion in imidazolium hydroxides were lower than the detectable level in the elemental analysis.^[8,9] Therefore, we summarized that all products were enough purity for evaluating thermal properties.

The T_{ms} of [C(n)mim]₄Ada(CH₂CH₂COO)₄ and [C(n)mim](ArmCOO) were initially compared from DSC measurements with a heating rate of 10 °C/min. The values of the obtained compounds are listed in Table 1. Interestingly, the series of [C(n)mim]₄Ada(CH₂CH₂COO)₄ showed the endothermic peaks

Fig. 2 XRD patterns of the [C(4)mim]_mAda(CH₂CH₂COO)_m.

Fig. 3 TGA thermograms of the [C(n)mim]₄Ada(CH₂CH₂COO)₄ under flowing nitrogen. The T_d values were determined from the onset of the curve.

assigned as the melting process below 100 °C. These data are the direct evidence that the adamantane-based salts are an IL. In particular, [C(12)mim]₄Ada(CH₂CH₂COO)₄ was melted at 21 °C. This result represents that the room temperature-IL can be obtained. Furthermore, [C(n)mim]₄Ada(CH₂CH₂COO)₄ showed lower T_{ms} than those of [C(n)mim](ArmCOO) with corresponded length of alkyl chains. These results suggest that the adamantane core should play a significant role in the decrease of the T_m of ion pairs. The decrease on the T_{ms} of ion pairs should be related with the increase of the rotational degree's of freedom of the –CH₂CH₂COO[–].

Next, we measured the T_{ms} of [C(n)mim]_mAda(CH₂CH₂COO)_m (m = 1–4, n = 4, 10, and 18) to evaluate the effect by changing the number of ion pairs around the adamantane core (Table 2). In the case of POSS-ILs, the number of ion pairs around the core greatly influenced on the thermal properties of ion pairs.^[8,9] In summary, when the larger number of ion pairs are accumulated on POSS, the T_{ms} decreased. Similar results with the POSS-ILs were obtained from the adamantane ILs. [C(4)mim]₄Ada(CH₂CH₂COO)₄ and [C(10)mim]₃Ada(CH₂CH₂COO)₃ possessed the lower T_m by 17 °C and 3 °C than that of [C(4)mim]Ada(CH₂CH₂COO) and [C(10)mim]₂Ada(CH₂CH₂COO)₂, respectively. The same explanation with the cubic core could be applicable on the decreases of T_{ms} by increasing the number of ion pairs around the adamantane core^[9]. By locating each ion pair at the vertices, the interaction should be suppressed. Moreover, sphere-like whole structures of the adamantane molecules could possess large exclusive volumes, leading to the reduction of intermolecular interaction. Hence, T_{ms} are reduced. The T_{ms} of adamantane ILs with C18 alkyl chain increase by adding the number of ion pairs. It is implied that the interaction among long alkyl chains might be generated, resulting in the enhancement of the T_{ms} . Similar tendencies were observed from the glass transition temperatures

(T_g s) as shown in Tables S1 and S2. These data support the effect of the adamantane core on the thermal properties.

To investigate the packing of the adamantane derivatives in the solid states, XRD analyses were executed (Figure 2). [C(4)mim]₄Ada(CH₂CH₂COO)₄, [C(4)mim]₃Ada(CH₂CH₂COO)₃ and [C(4)mim]₂Ada(CH₂CH₂COO)₂, showed the typical spectra as amorphous compounds. On the other hand, the dispersed patterns were observed from [C(4)mim]Ada(CH₂CH₂COO) as well as Ada(CH₂CH₂COO)₄. The solid state of [C(4)mim]Ada(CH₂CH₂COO) should involve the regular structure similarly as Ada(CH₂CH₂COO)₄, while the increase of the number of ion pairs around the adamantane core should disturb the formation of the ordering structures. These data are corresponded to the results from the melting behaviors. The larger numbers of ion pairs around the adamantane core can disturb the crystalline formation and produce exclusive volumes. Thereby, the T_m s of [C(4)mim]₄Ada(CH₂CH₂COO)₄ and [C(4)mim]₃Ada(CH₂CH₂COO)₃ decreased. On the other hand, in the case of [C(4)mim]Ada(CH₂CH₂COO), aggregation could occur because of the strong hydrophobic interaction and the symmetric structure of the adamantane core. Thus, the crystal structures should be partially grown in the solid states similarly as that from Ada(CH₂CH₂COO)₄.

The influence on thermal stability of [C(n)mim]₄Ada(CH₂CH₂COO)₄ and [C(n)mim](ArmCOO) against pyrolysis was investigated. From the onsets of TGA curves, the T_d values were determined (Table 1). Two large weight losses were observed around 230 °C and 350 °C from both of adamantane and Arm salts (Figure 3). After the first weight loss, similar molecular weights were obtained. These data suggest that the pyrolysis should initially proceed at imidazolium cations. Two significant tendencies can be obtained from the series of T_d s: [C(n)mim]₄Ada(CH₂CH₂COO)₄ showed higher T_d s than those of [C(n)mim](ArmCOO) with corresponded length of alkyl chains. This fact clearly indicates that the connection of ion pairs to the adamantane core should be responsible for the enhancement of thermal stability of ion pairs. The rigid diamond-like structure of adamantane could efficiently suppress molecular motions of ion pairs. In addition, by elongating the alkyl chain in [C(n)mim]₄Ada(CH₂CH₂COO)₄, the T_d values significantly increased. This phenomenon was not observed from [C(n)mim](ArmCOO) and POSS-ILs.^[8,9] This is the characteristic feature obtained only from adamantane. The interaction between the alkyl chains of imidazolium cation and the adamantane core might occur via hydrophobic interaction. Thereby, the thermal stability could be reinforced.

The thermal stability with [C(n)mim]_mAda(CH₂CH₂COO)_m ($m = 1-4$, $n = 4, 10$, and 18) was evaluated (Table 2). The increase of T_d was observed from [C(18)mim]_mAda(CH₂CH₂COO)_m corresponded to the increase of the number of ion pairs. [C(18)mim]₃Ada(CH₂CH₂COO)₃ and [C(18)mim]₄Ada(CH₂CH₂COO)₄ showed higher T_d s by 24 °C and 30 °C than those of [C(4)mim]₃Ada(CH₂CH₂COO)₃ and [C(4)mim]₄Ada(CH₂CH₂COO)₄, respectively. The longer alkyl chains should be favorable to suppress molecular motions of ion pairs, leading to the inhibition of pyrolysis.

In conclusion, we demonstrate the characteristic thermal properties of adamantane-based salts. Assembly of ion pairs on the adamantane core improves the thermal stability and lower melting

temperatures even though the molecular weights of the components are large. Finally, the adamantane-based room temperature-ILs can be obtained. In addition, these ILs showed higher thermal stability. From the comparison study on thermal properties with the adamantane salts with various numbers of ion pairs around adamantane and lengths of alkyl chains in imidazolium cation, two significant issues were suggested: The tetrahedral-shaped distribution of ion pairs could be critical for simultaneously improving thermal stability and lowering melting temperatures. In addition, the adamantane core could have larger ability to interact with the alkyl chains in imidazolium cations than that of POSS. Therefore, the adamantane ILs with long alkyl chains showed high thermal stability. Our findings described here are feasible for establishing the strategy for preparing heat-resisting ILs based on polymers or macromolecules.

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