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Supramolecular gelators comprising 1,3,5-benzenetricarboxylic acids and amino acid methyl esters (glycine, L-alanine, L-valine, L-leuicine, L-methionine, and L-phenylalanine) for ionic liquids were developed. Ten types of ionic liquids were gelated using the above-mentioned gelators at relatively low concentrations. Field emission–scanning electron microscopy and confocal laser scanning microscopy analyses revealed that these gelators self-assembled into an entangled fibrous structure in ionic liquids, leading to the gelation of the ionic liquids. Comparison studies, involving compounds analogous to the gelators, and Fourier transform infrared spectroscopy measurements suggested that hydrogen bonding played a key role in the self-assembly of the gelator molecule. The ionogels displayed reversible thermal transition characteristics and viscoelastic properties typical of a gel. The gelation of the ionic liquids studied under a wide range of gelator concentrations did not affect the intrinsic conductivity of the ionic liquids.

Introduction

Highly ion-conductive polymer electrolytes have attracted much interest because of their potential application in a variety of electrochemical devices. In particular, there has been a strong demand for the fabrication of highly conductive, flexible, and transparent solid polyelectrolytes with diverse configurations. Ionic liquids are an attractive electrolyte because of their high ionic conductivity, low vapor pressure, good thermal stability, wide electrochemical stability window, and tunable properties.[1,2] Chemical or physical solidification of ionic liquids are potential approaches for preparing highly ion-conductive solid polyelectrolytes. The solidification of ionic liquids is classified into two categories, namely covalent polymerization of ionic liquid monomers, and gelation (quasi-solidification) of ionic liquids using additives. The latter technique appears to be preferable as it leads to ionogels with good ionic conductivities.[3–5] The three currently employed methods to gelate ionic liquids proceed *via* (i) an organic polymer-based gelation,[5–7] (ii) an inorganic polymer-based gelation,[8,9] and (iii) a low-molecular-weight-gelator-induced gelation (supramolecular gelator).[4, 10–16] Kimizuka and Nakashima first reported the gelation of ionic liquids, using supramolecular gelators, whereby the gelation was induced by the molecular self-assembly of the synthesized glycolipids.[10] Hanabusa *et al.* also succeeded in the gelation of ionic liquids, using cyclic peptide amphiphiles as supramolecular gelators at relatively low concentrations. They reported that the ionic conductivity of the ionic liquids was maintained even after the gelation, and was minimally influenced by the gelator concentration.[4] We also demonstrated that the ionic conductivity of ionic liquids was unaffected by gelation, using a amphiphile-type gelator.[16] In many cases of these reports, amino acids or amide bonds in peptides played important roles in the molecular self-assembly.

Molecular self-assembly is essential for the supramolecular gelation of ionic liquids. Molecular self-assembly processes in aqueous and organic solvents have been widely reported.[17–19] Recently, molecular self-assembly processes in ionic liquids have become an emerging area of broad interest among scientists. The self-assembly of traditional amphiphiles (micelles, emulsions, microemulsions, and liquid crystals) has been studied since the 1990s.[20,21] However, only a limited number of studies relating to the supramolecular gelation of ionic liquids have been reported.[4,10-16,22,23] This is because of our lack of understanding of the specific molecular interactions involved between the solute molecules in ionic liquids as well as between the solute molecule and the solvent (ionic liquid). The successful reports regarding supramolecular gelators suggested that hydrogen bonding and solvophobic interactions could be useful for instigating molecular self-assembly processes in ionic liquids. [4,10-16,22,23]

In the present study, benzenetricarboxamides were examined as a core unit to prepare effective supramolecular gelators for ionic liquids. 1,3,5-Benzenetricarboxamide has a C_3-symmetrical structure and benzenetricarboxamide with amino acids can provide intermolecular hydrogen bonding and π–π interactions that can induce molecular self-assembly processes in both conventional organic solvents and in the solid state.[24–26] A variety of 1,3,5-benzenetricarboxamides, substituted with amino acids and amino acid methyl esters, were synthesized and investigated for the gelation of ionic liquids.

Experimental

Materials.

1,3,5-Benzenetricarbonyl trichloride, 1,3,5-tris(bromomethyl)benzene, methyl ester hydrochlorides of amino acids (glycine (Gly), L-alanine (L-Ala), L-valine (L-Val), L-leuicine (L-Leu), L-methionine (L-Met), and L-phenylalanine (L-Phe)), and 1,3,5-triethylbenzene were purchased from Tokyo Chemical Industry (Tokyo, Japan). All solvents used in the syntheses were purchased from Wako Pure Chemical Industries (Osaka, Japan). Ionic liquids [EtMeIm][TFSA], [BuMeIm][TFSA], [HeMeIm][TFSA], and [BuPy][TFSA] were synthesized from [EtMeIm][Cl], [BuMeIm][Cl], [HeMeIm][Cl], [BuPy][Br], and [Li][TFSA] as reported previously.[14] [EtMeIm][CF_3SO_3], [BuMeIm][CF_3SO_3], [BuMeIm][BF_4], [EtMeIm][PF_6], and [BuMeIm][PF_6] were purchased from Merck. [TMPA][TFSA] and [EtMeIm][BF_4] were purchased from Kanto Chemical Co., Inc. (Tokyo, Japan). 1-Ethyl-3-methylimidazolium hydroxide solution was purchased from Sigma–Aldrich and [EtMeIm][Phe] was synthesized previously as reported.[27] Full names of the ionic liquids were in the ESI.

Synthesis

Gelators 1–6. A solution of amino acid methyl ester hydrochloride (16.5 mmol) in dichloromethane (200 mL) was cooled to 0 °C, and triethylamine (4.5 mL) was added. 1,3,5-Benzenetricarbonyl trichloride (5.5 mmol) in dichloromethane (15 mL) was added dropwise to the solution, and stirred for 18 h at room temperature. After the reaction, the solution was filtered and the dichloromethane solution was successively washed with HCl (10 mM) and deionized water twice. The organic phase was collected and dried over anhydrous Mg_2SO_4. The solvent was evaporated and dried under vacuum. The gelators were obtained as a dry white powder. The yields of gelators **1–6** were 50, 91, 91, 97, 82, and 84%. ^1H NMR assignments, elemental analyses, FTIR, and MALDI-TOF/MS are provided in the ESI.

Compound A. 1,3,5-Tris(bromomethyl)benzene (5 mmol), L-Leu methyl ester hydrochloride (16.5 mmol), and K_2CO_3 (30 mmol) were dissolved in dimethyl formamide (30 mL), and refluxed for 24 h at 60 °C under N_2 atmosphere. After the reaction, the solution was filtered and evaporated. The residue was dissolved in dichloromethane and successively washed with HCl (10 mM) and deionized water twice. The organic phase was collected and dried over anhydrous Mg_2SO_4. The solvent was evaporated and dried under vacuum. Compound **A** was obtained as a yellow solution. The yield was 58%.

Instrumentation

^1H NMR spectra were obtained on a 500 MHz Bruker Avance-500. Fourier transform infrared spectroscopy (FTIR) measurements were carried out on a Bruker Alpha-E, equipped with an attenuated total reflectance (ATR) unit. Electrospray ionization mass spectroscopy (ESI–MS) measurements were performed on a JMS-T100LP AccuTOF LC-plus (JEOL, Tokyo, Japan). Matrix-assisted laser desorption and ionization time-of-flight mass spectroscopy (MALDI–TOF/MS) measurements were carried out using an UltrafleXtreme TM (Bruker, Germany).

To assess the gelation of different solvents, the gelators were first dissolved in the required solvent at a given concentration in a glass tube (inner diameter: 10 mm) by heating. The resulting solutions were then slowly cooled to room temperature. Formation of the gels (gelation) was confirmed by inverting the glass tube containing the solution.

Field emission–scanning electron microscopy (FE–SEM) measurements were carried out on a scanning electron microscope (JSM-7500F, JEOL, Japan), operating at an accelerating voltage of 7 kV. For sample analysis, the ionogels were converted to xerogels, as prepared using the procedure reported by Hanabusa *et al.*[4] Briefly, the ionogel underwent a solvent exchange from ionic liquid to water by immersing the ionogel in fresh solutions of water for 3 days. The gel, containing water only, was then freeze-dried under vacuum to produce the xerogel. The organogel was also converted to the xerogel by freeze-drying under vacuum. The xerogel was then mounted on an aluminum stub and coated with osmium by vapor deposition.

Confocal laser scanning microscopy (CLSM) analyses were performed on an Olympus FV1000-D at room temperature. Prior to analysis, the ionogel was stained with rhodamine B (30 μM).

Rheological measurements were carried out using a rheometer (Anton Paar Physica MCR301, Germany) with a cone plate (diameter = 2.5 cm), at a strain of 0.1% and a gap of 1.0 mm. For sample measurements, the gelator-containing ionic liquid solution (1 wt%) was loaded on a sample plate whose temperature was set at 90 °C. The sample plate was then cooled to 30 °C, and the measurement was started.

The gel–sol transition temperature, T_{gel}, was measured by differential scanning calorimetry (PerkinElmer 8500, Perkin Elmer), using aluminum pans with a heating rate of 1 °C/min.

The conductivity of the ionogels was measured at 25 °C using a Hioki Chemical Impedance Meter (3532-80). The isotropic hot ionic liquid solution, containing the gelator, was injected

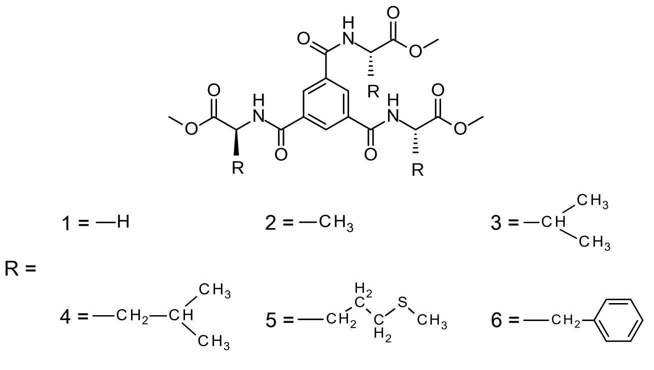

Chart 1. Molecular structures of gelators **1–6**.

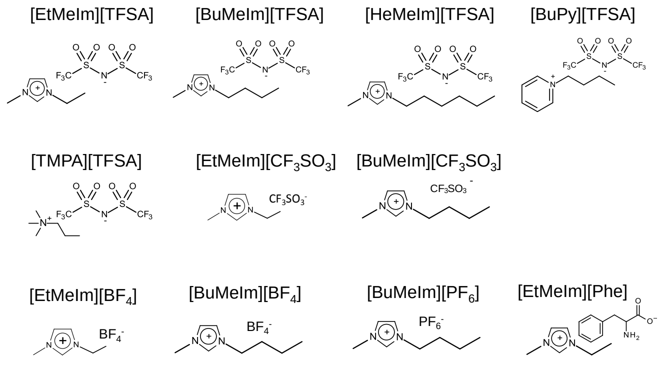

Chart 2. Molecular structures of the studied ionic liquids.

into a U-tube, followed by gelation. The cell constant was determined by measuring the conductivity of a KCl solution (7.44 g/L).

Results and discussion

Gelation of ionic liquids and other solvents

The herein developed gelators with simple molecular structures are shown in Chart 1. All gelators comprised 1,3,5-benzenetricarboxylic acid and amino acid methyl ester groups. The methyl esters, as derived from the six amino acids (Gly, L-Ala, L-Val, L-Leu, L-Met, and L-Phe), were used for the conjugation of 1,3,5-benzenetricarbonyl trichloride. Intermolecular hydrogen bonding between the amide groups and π–π interactions are expected to play important roles for the fibrous self-assembly of the gelator molecule in ionic liquids, as indicated by the numerous reports relating to the assembly of benzenetricarboxamide derivatives in common organic solvents.[24–26, 28] The gels were prepared by heating the solutions, containing the gelators, up to ~160 °C, and subsequent cooling to room temperature. It should be noted that the preparation of the gels was carried out at a temperature below the melting points of gelators 1–6, which were above 180 °C.

Table 1 presents the results of the gelation tests, performed in varying ionic liquid, aqueous, and organic solutions, using gelators 1–6. Eleven different types of ionic liquids were examined (Chart 2). As shown in Table 1, gelators 2–5 gelated 10 kinds of ionic liquids that were composed of varying cations and anions, at relatively low concentrations. Widely studied imidazolium- and pyridinium-based ionic liquids were gelated. Gelators 3 and 4, which had L-Val and L-Leu residues, displayed higher gelation abilities towards ionic liquids that featured trifluoromethanesulfonate anions, $[CF_3SO_3]^-$, in comparison to those having BF_4^-, PF_6^- or tri(fluoromethylsulfonyl)amide ions, $[TFSA]^-$. The ionogels, containing $[CF_3SO_3]^-$, were translucent whereas the other ionogels were opaque. Several ionic liquids were gelated at 1 wt% or below 1 wt% (for gelators 3 and 4). Gelators 2 and 5, which had L-Ala and L-Met residues, exhibited higher gelation abilities towards ionic liquids, possessing BF_4^- ions. The amino acid-based ionic liquid, [EtMeIm][Phe], was not gelated regardless of the gelators herein studied. Hence, the nature of the anion of the ionic liquid appears to significantly influence the gelation properties.

Table 1. Gelation properties of gelators **1**–**6** for ionic liquids, aqueous solutions, and organic solvents

	Gelator					
Solvent	**1** Gly	**2** L-Ala	**3** L-Val	**4** L-Leu	**5** L-Met	**6** L-Phe
[EtMeIm][TFSA]	P	G(1.7)	G(1.0)	G(1.0)	G(0.9)	S
[BuMeIm][TFSA]	P	G(0.9)	G(0.9)	G(0.5)	G(1.0)	G(1.8)
[HeMeIm][TFSA]	I	G(1.0)	G(0.9)	G(0.9)	G(1.0)	S
[BuPy][TFSA]	P	G(1.3)	G(1.0)	G(0.8)	G(0.6)	S
[TMPA][TFSA]	P	G(1.0)	vS	G(1.4)	G(0.8)	G(0.9)
[EtMeIm][CF_3SO_3]	S	G(1.1)	G(0.6)	G(0.1)	G(1.3)	G(2.0)
[BuMeIm][CF_3SO_3]	I	G(1.0)	G(0.7)	G(0.4)	G(1.3)	vS
[EtMeIm][BF_4]	P	G(0.5)	I	I	G(0.5)	vS
[BuMeIm][BF_4]	S	G(0.5)	G(0.9)	G(1.3)	G(0.7)	S
[BuMeIm][PF_6]	S	G(1.1)	G(0.9)	vS	G(0.9)	G(2.0)
[EtMeIm][Phe]	S	S	S	S	S	S
Deionized water	I	I	I	I	I	I
HCl (aq., 0.1 M)	P	I	I	I	I	I
Phosphate buffer (0.1 M, pH 7)	PG	I	I	I	I	I
NaCl (aq., 0.1 M)	P	I	I	I	I	I
Ethanol	P	G(2.0)	G(2.0)	P	G(2.0)	P
1-Propanol	I	P	P	PG	I	P
Toluene	I	I	I	G(2.0)	PG	PG
Ethyl acetate	I	I	I	G(2.0)	G(2.0)	S
Acetonitrile	P	G(2.0)	G(2.0)	PG	P	P

G, PG, vS, P, S, and I denote gel, partial gel, viscous solution, precipitation, soluble, and insoluble, respectively; the critical gelation concentration [wt%] is given by the number in parentheses.

Gelator 1, which had L-Gly residues, was soluble in all ionic liquids, except for [HeMeIm][TFSA] and [BuMeIm][CF_3SO_3], at elevated temperatures. However, at room temperature, gelator 1 precipitated in several ionic liquids (no gelation). Gelator 6, which had L-Phe residues, was expected to possess good gelation abilities because of the intermolecular π–π interactions between the aromatic rings of the L-Phe residues. However, gelator 6 only showed gelation abilities for a limited number of ionic liquids, and was highly soluble in the other ionic liquids. This was attributed to the steric hindrance effect, as exerted by the L-Phe residues, and also the resulting helical assembly configuration that altogether impeded on the efficiency of intermolecular interactions.[24,28] Benzenetricarboxamides are known to self-assemble into helical structures, which are non-favorable for the intermolecular π–π interactions because of the long distance between the relevant functional groups.[29] These results indicated that amino acid residues play a key role in directing the molecular self-assembly of the benzenetricarboxamides.

Supramolecular gelators for ionic liquids can generally harden different types of solvents, as previously reported.[4,12,15,16,23] Thus, we also examined the gelation of aqueous and organic solvents using gelators 1–6. Gelators 2–6 were insoluble in the aqueous solutions, likely because of their high hydrophobicity. For the self-assembly of gelator molecules to proceed, the gelators need to be soluble in the selected solvent under the preparation conditions. On the other hand, gelator 1 (2.0 wt%), which was relatively hydrophilic, featured some hydrogel characteristics in a phosphate buffer solution. Gelators 1–6 were completely soluble in aqueous NaOH solution. However, the gelators did not gelate the NaOH solution, probably because of the hydrolysis of the ester bonds in the gelator molecules by the NaOH solution.

Gelators 2–5 only gelated some organic solvents such as ethanol, 1-propanol, toluene, ethyl acetate, and acetonitrile, thereby suggesting that the present gelators are unlikely to gelate conventional organic solvents. Furthermore, these results indicate that there might be a supramolecular gelator specifically suited for ionic liquids only, although many of the supramolecular gelators, previously reported,[4,12,15,16,23] for ionic liquids were comparable with or derived from organogelators or hydrogelators.

Benzenetricarboxamides, substituted with amino acids (gelators 1’ and 3’–6’), were prepared by the hydrolysis of gelators 1 and 3–6 (Chart S1), and tested for the gelation of ionic liquids, aqueous solutions, and organic solvents. As presented in Table S1, most of the solvents tested were not gelated by the gelators 1’ and 3’–6’. Only ethanol and 1-propanol were gelated by gelators 1’ and 5’. In many cases, gelators 1’ and 3’–6’ were insoluble in these organic solvents, even upon heating. Although, in the beginning, we anticipated that benzenetricarboxamides with amino acids would be good gelators for ionic liquids, it was difficult to dissolve them in ionic liquids and impossible to gelate ionic liquids. The carboxyl groups of the gelators seem to inhibit the solubilization of the gelators in these solvents.

Microscopic observation of gels

In general, supramolecular gels are composed of micro- or nanofibers, formed by the self-assembly of the gelator molecules. The morphology of the gels was assessed by FE–SEM (Fig. 1a–d) and CLSM (Fig. 1e). Both the ionogels and organogels featured a three-dimensional entangled fibrous network structure (Fig. 1a–d), as formed by the self-assembly of the gelator in the respective four solvents. The diameters of the corresponding fibers were ~0.5–1 µm, ~100–200 nm, ~1–2 µm, and ~1–1.5 µm (Fig. 1a–d). FE–SEM analysis was performed on the xerogels (dried gels). In contrast, CLSM was employed to analyze the ionogel in its natural form. To our knowledge, *in situ* observations of ionogels have not been reported. The ionogel ([BuMeIm][CF_3SO_3], containing 2.0 wt% gelator 3), was stained with 30 µM rhodamine B. As observed in Fig. 1e, rhodamine B was only detected between the fibers; staining of the fibers did not take place. Rhodamine B displays good solubility in [BuMeIm][CF_3SO_3] (>1 g/L). 1,3,5-Benzenetricarboxamides exhibit strong intermolecular interactions that are capable of excluding other compounds from their molecular assembly, thus explaining why the fibers were not stained.

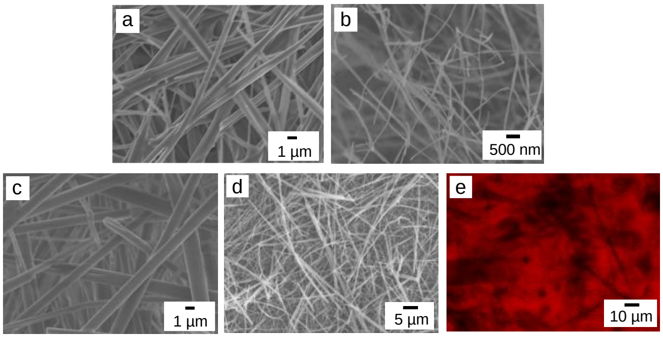

Fig. 1 FE–SEM images of (a, b) ionogels and (c, d) organogels, formed in the respective solvents: [BuMeIm][TFSA], [BuMeIm][CF_3SO_3], ethanol, and acetonitrile. (e) CLSM image of the ionogel stained by 30 µM rhodamine B (solvent: [BuMeIm][CF_3SO_3]). Gelator **3** was used at concentrations of (a, b, and e) 1.0 wt% and (c and d) 2.0 wt%. For the FE–SEM analysis, the ionic liquid in the ionogel was first replaced with water followed by freeze-drying; the organogels were also dried under vacuum.

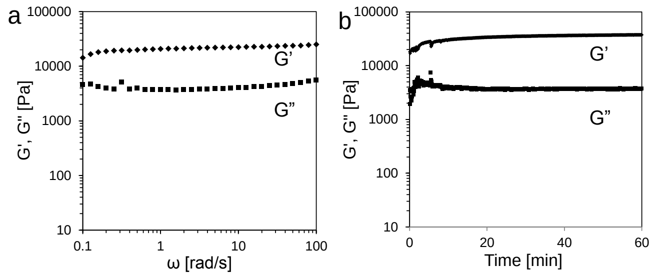

Fig. 2. Viscoelastic properties of the ionogel, prepared with [EtMeIm][CF_3SO_3] and gelator **4** (1.0 wt%). (a) Dynamic frequency sweep at 30 °C, (b) dynamic time sweep at a frequency of 1 rad/s at 30 °C.

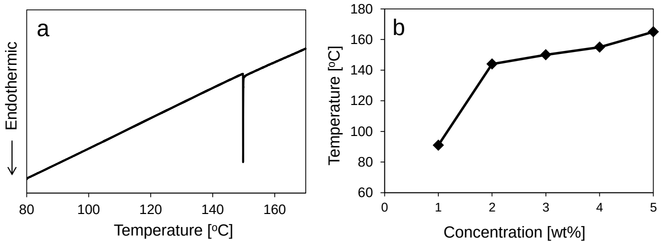

Fig. 3. (a) DSC thermograph of the ionogel of [EtMeIm][CF_3SO_3] using gelator **4** (3.0 wt%). (b) Gel–sol transition temperature (T_{gel}) profile of the ionogel prepared with [EtMeIm][CF_3SO_3] and varying concentrations of gelator **4**.

Rheological and calorimetry measurements of the ionogel

To evaluate the viscoelastic properties of the ionogels, dynamic frequency and time sweep rheological measurements of the ionogels were carried out. The rheological measurements with dynamic frequency of the ionogel ([EtMeIm][CF_3SO_3], containing 1.0 wt% gelator 4), were performed 1 h after sample cooling (Fig. 2a). In the range of 0.1–100 rad/s, the value of G’ (storage elastic modulus) remained higher than that of G” (loss elastic modulus). This confirms that [BuMeIm][CF_3SO_3], containing 1.0 wt% gelator 4, exhibited gel-like characteristics. Figure 2b shows that both G’ and G” rapidly increased within a few minutes following sample cooling to 30 °C, prior to reaching a steady state value. The steady state value of G’ was about 20 times larger than that of G”, thus indicating that nearly complete formation of the ionogel occurred within a few minutes after sample cooling to 30 °C.

Facile thermoreversible gel–sol transition is a notable feature of supramolecular gels. The gel–sol transition temperature, T_{gel}, of the ionogel, [EtMeIm][CF_3SO_3], containing gelator 4 was measured by DSC (Fig. 3). An endothermic peak was observed at 150 °C for the ionogel, containing 3.0 wt% gelator 4 (Fig. 3a). By visual inspection, the sample was liquid above this temperature and was a gel below this temperature. The T_{gel} for the different gelator concentrations (1–5 wt%) ranged from 90 to 160 °C. Higher gelator concentrations produced higher T_{gel} values. A rapid increase in T_{gel} was observed as the concentration increased from 1 to 2 wt% (Fig. 3b). Hanabusa *et al.* also reported a steep increase in T_{gel} for ionogels as the concentration of the gelator changes from a very low value to a higher value.[4] At the higher concentrations, the fibers are more intricately and densely entangled, thereby requiring high temperatures to break the fiber structure.

Intermolecular interactions of benzenetricarboxamide gelators in ionic liquids

As mentioned earlier, the amide bonds present in the gelator molecules can participate in hydrogen bonding that plays an important role for the self-assembly of supramolecular gelators. The influence of hydrogen bonding in the studied gelators was assessed by comparing the gelation abilities of gelator 4 and a synthesized compound A (Fig. 4a). The concentrations of both compounds were 2 wt%. Compound A is structurally similar to gelator 4 aside from the amide groups. Gelator 4 gelated both [BuMeIm][TFSA] and [BuMeIm][CF_3SO_3] (Fig. 4b and d); however, compound A was soluble in the ionic liquids and remained in a solution state at 25 °C. Thus, these ionic liquids were not gelated by compound A (Fig. 4c and e). This indicates that hydrogen bonding derived from the amide bonds is important for the self-assembly of the gelator molecules. It should be also noted that the removal of amide bonds caused the conformational flexibility of the molecule, which might also prevent the self-assembly of the compound A. The rigid planar structure of the benzenetricarboxamide would help the intermolecular interaction and the molecular self-assembly.

To confirm the presence of hydrogen bonding in the benzenetricarboxamide, FTIR analysis of the ionogel prepared with [EtMeIm][CF_3SO_3] and gelator 4 was performed (Fig. 5a). The position of the amide II peak (1510–1580 cm^{-1}) can be used to evaluate the presence of hydrogen bonding between the supramolecular gelators during the sol–gel transition.[30] For the sample measurements, the gel sample with 0.5 wt% gelator 4 (solvent: [EtMeIm][CF_3SO_3]) was sandwiched between two silicon wafers. The sol sample, obtained at 150 °C, displayed an absorbance peak at 1570 cm^{-1}, which mainly corresponds to N–H bending and C–N stretching vibrations (Fig. 5b). As the sample was cooled to 110, 70, and 30 °C, the peak position shifted to 1573, 1574, and 1575 cm^{-1}, respectively. The shift was attributed to the change in the vibration states of the amide bonds in gelator 4, as instigated by the development of hydrogen bonding.[30] This analysis further confirmed that hydrogen bonding is important for the self- assembly of gelator molecules.

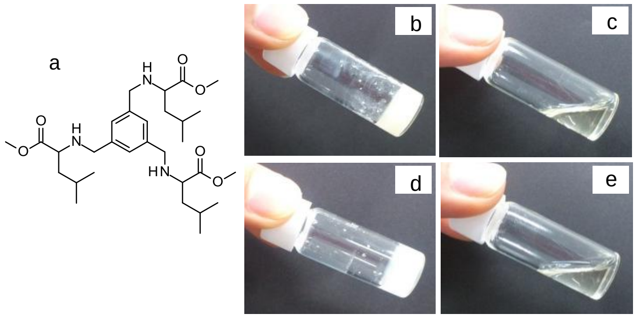

Fig. 4. (a) Molecular structure of compound **A. (b-e)** Photographs of ionic liquids, containing (b and d) gelator **4** and (b and d) compound **A**. Solvents were (b and c) [BuMeIm][TFSA] and (d and e) [BuMeIm][CF_3SO_3]. The concentrations of gelator **4** and compound **A** were 2.0 wt%.

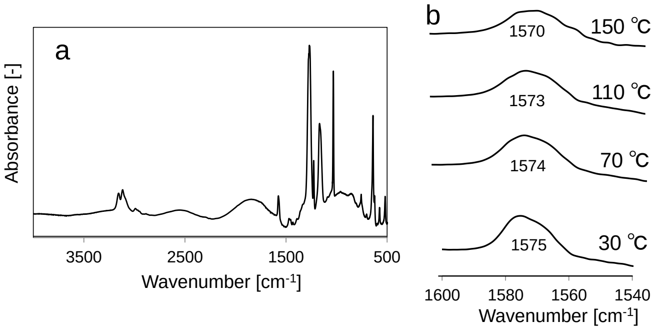

Fig. 5. (a) FTIR spectra of the ionogel prepared with [EtMeIm][CF_3SO_3] and gelator **4** (0.5 wt%) at 30 °C. (b) Peak shift of the amide II band at varying temperatures from 150 to 30 °C. The associated wavelength of the peak is indicated.

π–π interactions between the aromatic rings are also expected to be important for molecular self-assembly processes; as reported, there have been studies describing the contribution of π–π interactions in the assembly of 1,3,5-benzenetricarboxamide derivatives.[26,28,29] To evaluate the effect of π–π interactions on the self-assembly of the present benzenetricarboxamides, an excess amount of 1,3,5-triethylbenzene (more than 10 equimolar amounts of gelator 4) was added to [BuMeIm][CF_3SO_3], containing gelator 4 (1.0 wt%), at an elevated temperature, and the resulting solution was then cooled to room temperature. The ionic liquid, containing both gelator 4 and 1,3,5-triethylbenzene (more than 10 equimolar to gelator 4), was gelated. The molecular structure of 1,3,5-triethylbenzene is similar to that of gelator 4. 1,3,5-Triethylbenzene featured a relatively electron-rich aromatic ring as opposed to that of gelator 4 that was relatively electron-poor because of the presence of the three amide groups. Although π–π and electron donor–acceptor interactions in gelator 4 and 1,3,5-triethylbenzene (excess amount) are expected to induce the solubilization of the gelator molecules,[31,32] the gelation results indicate that the presence of π–π interactions is not as significant towards the self-assembly of gelator molecules in ionic liquids. Moreover, Srinivasulu *et al.* suggested that the molecular assembly of 1,3,5-benzenetricarbonyl phenylalanine (gelator 6') was mainly based on hydrogen bonding rather than π–π interactions, as deduced from the crystal structure.[25]

Conductivity of ionic liquids

Ionic liquids display distinct electrochemical properties. The ionic conductivities of the ionic liquids and the ionogels, prepared by gelator 3 (solvent: [EtMeIm][TFSA], [BuMeIm][TFSA], [BuMeIm][CF_3SO_3], and [HeMeIm][TFSA]), are shown in Fig. 6. All the ionogels retained the high intrinsic conductivity as featured by the corresponding ionic liquids, even at the high gelator concentration (*i.e.*, 4.0 wt%). It should be noted that the concentration of gelator 3 required for the formation of the ionogels was above 1.0 wt%. Polymer-based gelation of ionic liquids is reported to result in a marked decline in the conductivity of the resulting ionogels, probably because of the high polymer concentrations required for gelation.[5] In contrast, in the present study, we believe that the high conductivity was maintained by the presence of relatively large voids between the fibers (Fig. 1), owing to the low gelator concentration required, that facilitate the movement of the ions in both the solution and gel states.[4,16]

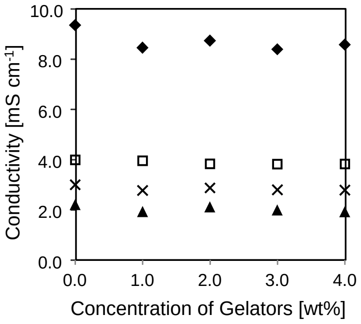

Fig. 6. Ionic conductivity of the ionic liquids and ionogels at 25 °C. Gelator **3** was used at varying concentrations from 0 to 4.0 wt%. (♦) [EtMeIm][TFSA], (☐) [BuMeIm][TFSA], (×) [BuMeIm][CF_3SO_3], and (▲) [HeMeIm][TFSA].

Conclusions

Supramolecular gelators consisting of 1,3,5-benzenetricarboxylic acid and amino acid methyl esters (Gly, L-Ala, L-Val, L-Leu, L-Met, and L-Phe) were developed. These gelators self-assembled into a fiber structure in ionic liquids and in a few of the organic solvents studied, leading to the gelation of these solutions. Hydrogen bonding played a key role in the self-assembly of the gelator molecules in ionic liquids, as deduced from the comparison studies, employing analogous compounds, and FTIR measurements. The developed gelators featured a relatively low critical gelation concentration for ionic liquids. The resulting ionogels possessed reversible thermal transition properties and viscoelastic properties typical of a gel. The ionogels retained the high intrinsic conductivity of the ionic liquids even at high gelator concentrations, thus demonstrating that the characteristics of the ionic liquids were maintained following gelation. The herein developed supramolecular gelators have potential application in new types of electrochemical materials.

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