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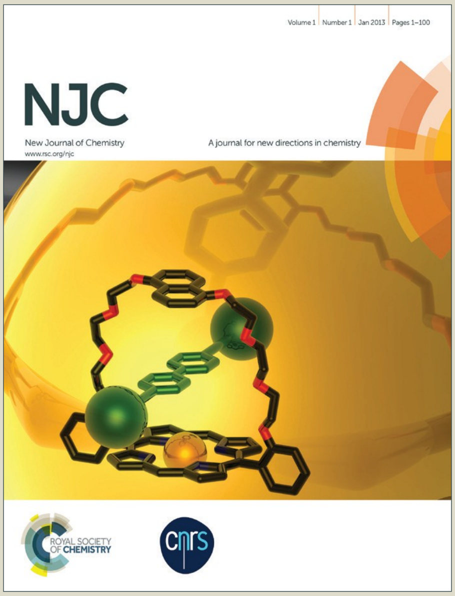

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ARTICLE

Facile Preparation of Supramolecular Ionogels Exhibiting High Temperature Durability as Solid Electrolytes

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Ionogels, solid-like materials maintaining much of the physicochemical properties of ionic liquids, have aroused much interest as excellent functional materials. Here, a facile strategy of preparation of supramolecular ionogels is reported. Benzenetricarboxylic acid (H_3BTC) and $Fe(NO_3)_3$•$9H_2O$ are selected as gelators, which form stable supramolecular ionogels within several seconds *via* metal-coordination interactions in ionic liquids *1*-butyl-*3*-methylimidazolium chloride (bmimCl) and *1*-butyl-*3*-methylimidazolium benzenesulfonate (bmimBsa). The time for preparing ionogels is reduced dramatically. The ionogel Fe-H_3BTC-bmimCl is broken down at 100 °C, but the ionogel Fe-H_3BTC-bmimBsa can remain stable at 150 °C, exhibiting high temperature durability. These ionogels are characterized further by Fourier transform infrared spectroscopy (FT-IR), scanning electron microscope (SEM), differential scanning calorimetry (DSC) and thermogravimetry (TG) in detail. In addition, oscillatory rheological measurement and electrochemical measurement show that these ionogels display superior mechanical property and high conductivity due to the high ionic liquid content.

Introduction

Ionic liquids are liquids that are composed of organic cations and anions at room temperature.[1] Due to their unique and advantageous properties,[2-5] such as low volatility, non-flammability, high thermal stability, wide electric windows and excellent conductivity, ionic liquids have been widely used in various fields, especially in electrochemistry.[6,7] However, leakage problems caused by ionic liquids may limit their applications in practical use.[8,9] As an immobilized solid or solid-like form, ionogel, ionic liquids swollen in solid scaffold, can overcome the key problems of ionic liquids, while retain the sought-after physicochemical properties of ionic liquids.[10] Kinds of ionogels have been developed for a variety of energy devices (thin film transistors,[11,12] solid-state supercapacitors,[13] solar cells,[14] fuel cells,[15,16] electrochemical sensors,[17,18] biosensors,[19] actuators[20,21] and ultracapacitors[22,23]). For example, Masayoshi Watanabe et al. have managed to apply ionogels stemming from protic ionic liquids supported by polymer scaffolds to fabricate a fuel cell system, which displays high thermal stability and outstanding electrochemical property.[24] Silicon based ionogels were synthesised by Andreas group, which also exhibited high thermal stability and superior electrochemical property with additional excellent mechanical characteristics.[25-27] Until now, researchers mainly used polymer or silica as the solid scaffold materials for the fabrication of conducting ionogels.[10,28] Unfortunately, the synthesis of these silicon scaffolds often need long time at high temperture.[29] In addition, both polymer and silica solid scaffolds show poor miscibility in ionic liquids, especially for polymers with high degrees of polymerization. Co-solvents[30,31] and *in-situ* polymerization in ionic liquids[32] have been employed to overcome the immiscibility, which need time- and energy-intensive drying processes or have limited degree of polymerization and harsh reaction conditions.[33,34] In addition, most of the process to prepare ionogels will take several minutes or even hours.[35-40]

Supramolecular self-assembly *via* non-covalent interactions, such as hydrogen bonding, metal coordination, van der Waals interaction, π–π stacking interaction and solvophobic force, has shown great application potentials in various fields. Researchers have widely applied supramolecular self-assembly to fabricate various functional materials, such as vesicles, liquid crystals, hydrogels and organogels.[41-43] However, researches about ionogels prepared by self-assembly of small molecules (low molecular weight gelators, LMWG) are very rare, especially about conducting ionogels.[10,44] Compared with the polymer or silica, low molecular weight gelators show much excellent miscibility in ionic liquids. Thus preparing conducting ionogels *via* the self-assembly of LMWG can overcome the barrier of poor miscibility of solid scaffolds in ionic liquids. Yanagida and co-workers used *N*-benzyloxycarbonyl-*l*-isoleucyl aminooctadecane as a gelator to prepare ionogels in imidazolium ionic liquids, which were used as an electrolyte in a dye sensitized solar cell (DSSC) exhibiting excellent light-to-electricity conversion efficiency.[45] Dong et al. reported ionogels arising from imidazolium ionic liquids, bis(*4*-acylaminophenyl)methane and bis(*4*-acylaminophenyl)-ether with varied alkyl chains as geltors.[46] Besides that, Yan et al. discovered that β-cyclodextrin and ionic liquids can form ionogels *via* the host−guest interactions.[47] DSSCs based on the supramolecular ionogels electrolyte showed excellent long term stability and high light-to-electricity conversion efficiency. However, the gel-sol transition temperatures of all these supramolecular conducting ionogels are typically lower than 100 °C， which definitely restrict the applications of these conducting ionogels. The fabrication of supramolecular conducing ionogels with high temperature durability will be highly desirable and challengeable.

Based on the previous work, we report a facile synthetic strategy of supramolecular conducing ionogels *via* metal-coordination between iron(III) nitrate nonahydrate ($Fe(NO_3)_3$•$9H_2O$) and benzenetricarboxylic acid (H_3BTC) in ionic liquids *1*-butyl-*3*-methylimidazolium benzenesulfonate (bmimBsa) and *1*-butyl-*3*-methylimidazolium chloride (bmimCl). These ionogels are formed within several seconds at room temperature, which is much shorter than that required for preparing ionogels by other methods. The supramolecular ionogels formed by H_3BTC and $Fe(NO_3)_3$•$9H_2O$ in bmimBsa exhibit high temperature durability, which can remain gel state up to 150 °C. The high thermal stability is further characterized by thermogravimetric (TG) and differential scanning calorimetry (DSC). In addition, the superior mechanical properties and high conductivities of supramolecular conducting ionogels have been confirmed by oscillatory rheological and electrochemical measurements. These supramolecular conducting ionogels should have a wide range of applications in the fields of electrochemistry due to the high conductivities and high temperature durability.

Experimental

Materials

Gelators benzenetricarboxylic acid (H_3BTC) and iron(III) nitrate nonahydrate ($Fe(NO_3)_3$•$9H_2O$) were acquired from J&K Scientific Ltd. All the reagents were used without further purification. The ionic liquids bmimCl and bmimBsa were synthesized according to the previous literature.[48]

Preparation of supramolecular ionogel Fe-H_3BTC-80%bmimBsa

Supramolecular ionogel precursor solutions containing prescribed masses of bmimBsa (2.0g) and H3BTC (0.1288g, 0.6mmol) were prepared by heating. And then, the melting $Fe(NO_3)_3$•$9H_2O$ (0.3712g, 0.9mmol) was added to the precursor solutions and mixed rapidly, then left to stand. A yellow–brown ionogel can be obtained within several seconds. The other ionogels with various ionic liquid contents were prepared through the same procedure.

Preparation of xerogels for FT-IR and SEM

The ionogel samples were firstly put into acetone for five days (the acetone was changed every 12 hours). Then the acetone was changed to water and then the samples were dried *via* vacuum-freeze drying. After that, the xerogels have been prepared. Infrared spectra of the xerogels were taken in a KBr disc on a Nicolet/Nexus-670 FT-IR spectrometer in the range of 4000–450 cm^{-1}. A FEI Nova Nano SEM 600 scanning electron microscope was used to obtain surface morphology micrographs of the supramolecular ionogels at ambient temperature and low vacuum. The xerogel was mounted on an aluminum stub and coated to 100-150 Å thick with Au by sputtering.

Thermal properties

DSC and TGA were carried out on a PerkinElmer DSC 8500 and a Seiko Instruments TG DTA 6200C under a nitrogen atmosphere, respectively. The samples were tightly sealed in aluminum pans and heated under a nitrogen atmosphere at a flow rate of 20 mL/min. The scan rate of both DSC and TGA run is 10 °C/mim.

Rheology measurements

The rheological measurements were performed on a Haake Rheostress 6000 rheometer with a Rotor C35/1 system and a coaxial cylinder sensor system (Z41 Ti). The temperature was kept at 25.0 ± 0.1 °C. Dynamic frequency sweep measurements were conducted in the linear viscoelastic region of each sample. The region was determined from dynamic stress sweep measurement where the frequency was kept at 1.0 Hz.

Conductivity measurements

Conductivity of the conducting ionogels was determined by an electrochemical impedance spectroscopy technique that has been described elsewhere.[49] The ionic conductivities of the conducting ionogels were investigated by the alternating current impedance method in the frequency range of 100 mHz to 10 MHz with 0.01 mV oscillating voltage using an ITO cell consisting of a pair of ITO glass electrodes and a Teflon spacer. The electrical conductivity was calculated using the following equation.

$$\sigma = \frac{1}{R}\left(\frac{l}{A}\right) \qquad (1)$$

where σ is the conductivity; R is the resistance; and l and A are the thickness and area of the sample, respectively.

Results and Discussion

Fig. 1 shows the synthetic route of supramolecular ionogels. Both

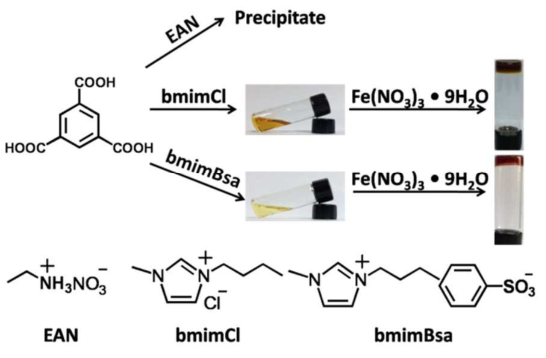
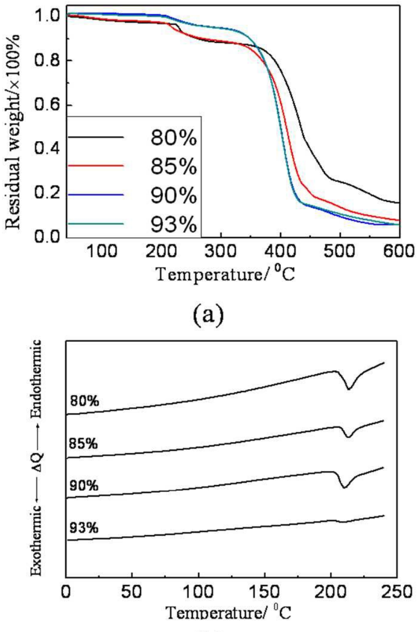


Fig. 1 Schematic representation for the synthesis of ionogels.

H_3BTC and $Fe(NO_3)_3$•$9H_2O$ can dissolve in bmimBsa and bmimCl well after heating to 70 °C, respectively. But neither H_3BTC nor $Fe(NO_3)_3$•$9H_2O$ can form gels by itself when dissolved in bmimBsa and bmimCl. After the addition of $Fe(NO_3)_3$•$9H_2O$ to transparent bmimBsa or bmimCl solutions of H_3BTC, the gels were formed within several seconds. The formation of ionogels and minimum gelator concentration were confirmed by a simple inverted-bottle test (Fig S1). It can be seen from Fig S2 that the ionogel Fe-H_3BTC-bmimCl has been destroyed at 100 °C. However, the ionogel Fe-H_3BTC-bmimBsa can remain stable at 150 °C. To the best of our knowledge, this is the first example of supramolecular conducting ionogels prepared by low molecular weight gelator that can remain gel state at such high temperature. As reported, there is π–π stacking interaction between imidazole ring and benzene ring.[48,50] Thus, strong π–π stacking interaction exists between H_3BTC and bmimCl or bmimBsa. For comparison, we found that H_3BTC cannot be dissolved in EAN (Fig. 1). Moreover, due to the presence of π–π stacking interaction between benzene rings, there is stronger π–π stacking interaction between bmimBsa and H_3BTC than that between bmimCl and H_3BTC. We believe that the high temperature durability of the ionogels Fe-H_3BTC-bmimBsa may result from the strong π–π stacking interaction between H_3BTC and bmimBsa. And then, these ionogels Fe-H_3BTC-bmimBsa are characterized in detail.



(a)

(b)

Fig. 2 (a) TG curves and (b) DSC curves of the supramolecular conducting ionogels Fe-H_3BTC-bmimBsa with the ionic liquid content varying from 80 wt% to 93 wt%.

The thermal properties of ionogels Fe-H3BTC-bmimBsa are further investigated through TG and DSC. All the ionogels Fe-H_3BTC-bmimBsa exhibit high thermal stability. Fig. 2 shows the TG and DSC curves of the supramolecular ionogels with the content of ionic liquids ranging from 80 wt% to 93 wt%. TG curves of all the supramolecular ionogels show the same variation trends. The first weight loss at about 220 °C corresponds to elimination of solid scaffold, while the abrupt weight loss at 360 °C corresponds to the decomposition of ionic liquids. Thus, the residual weight of each supramolecular ionogel at temperature higher than 400 °C corresponds to metal compounds. The high temperature durability of these ionogels is also demonstrated by DSC curves. There is no peak existing in the DSC curves of all the conducting ionogels below 200 °C. Exothermic peaks around 210 °C to 220 °C show the decomposition temperature (T_{dec}) of solid scaffold, which closely matches the first weight loss at about 220 °C in the TG profiles. Exothermic peaks are shifted towards higher temperature slightly when increasing the ionic liquid content in the composite, indicating enhanced thermal stability of the solid scaffolds and the corresponding supramolecular ionogels.

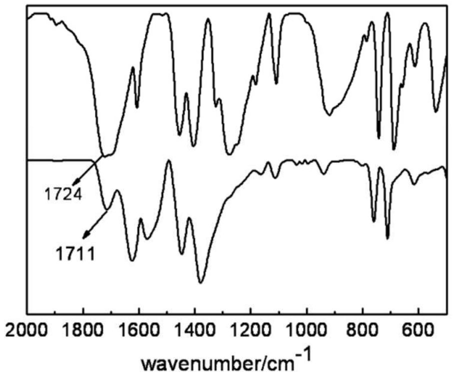


Fig. 3 Comparative FT-IR spectra of Fe-H3BTC-bmimBsa xerogels (bottom) and benzenetricarboxylic acid (top).

To investigate the microstructure and the formation mechanism of the supramolecular ionogels, SEM and FT-IR were preformed. As expected, FT-IR spectra (Fig. 3) of the ionogels showed the C=O stretching bands (asymmetric vibration) shifted to lower frequencies with respect to the free ligand due to the metal coordinated metal-coordinated carboxylates (Δ=13cm^{-1}).[51] Additional peaks at 1442, 1569 and 1624 cm^{-1} correspond to C-H stretching of benzene rings.

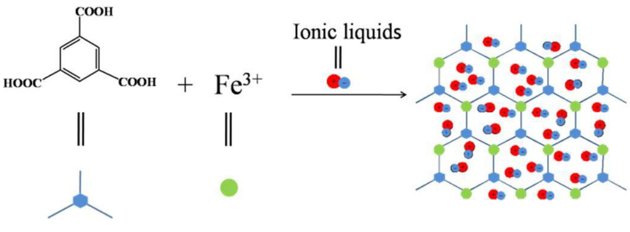


Fig. 4 A schematic representation of the formation of the supremolecular ionogels.

SEM images show the microstructure of the supremolecular ionogels. It can be seen from the SEM images (Fig. 5) that highly porous microstructures are formed by stacked sphere particles, which is namely the scaffold of the conducting ionogels. The formation of the supramolecular ionogels may consist of the following two steps, similar to the metal-organic gel formation mechanism described in the literatures.[52,53] Firstly, the coordination polymers between H_3BTC and $Fe(NO_3)_3$•$9H_2O$ via M–O (Fe-carboxylate) coordination suggested by FT-IR formed spheres in order to minimize interfacial free energy.[54] With the concentration of these coordination polymer spheres increasing, these spheres then condense together to form continuous, porous microstructure, which is confirmed by SEM images.

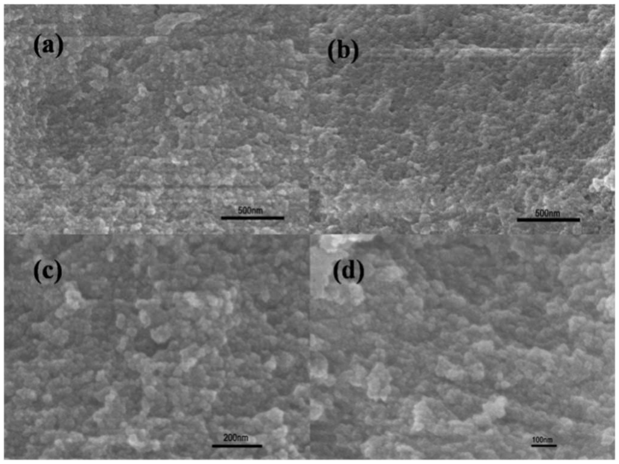
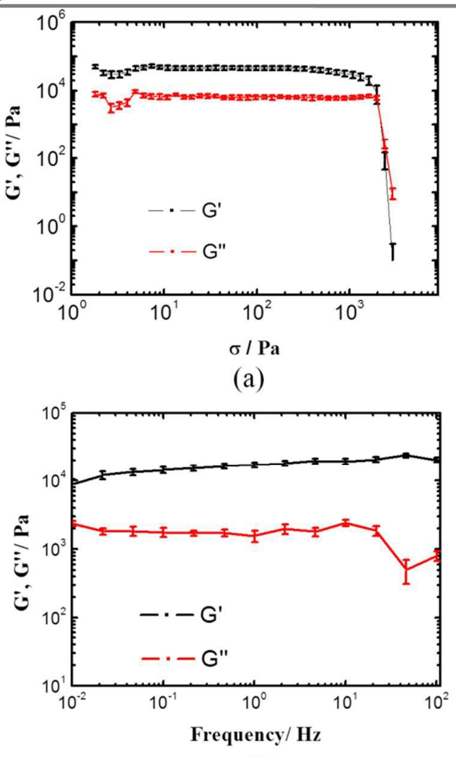


Fig. 5 SEM images of Fe-H_3BTC-90%bmimBsa xerogels.



(a)

(b)

Fig. 6 (a) The G' and G'' of ionogel Fe-H_3BTC-80%bmimBsa as a function of the applied stress at a constant frequency of 1 Hz at 25.0 °C. (b) The G' and G'' of ionogel Fe-H3BTC-80%bmimBsa as a function of frequency at 25.0 °C.

The shear stress dependence and frequency dependence of the storage modulus (G') and loss modulus (G'') are shown in Fig. 6 (only the data of the system with 20.0 wt% gelator is shown in Fig. 6. The viscoelastic properties of other systems are similar to the system with 20.0 wt% gelator). When shear stress is below or equal to critical stress value (σ_c), both modulus are independent of the applied stress. And G' is bigger than G''. However, when applied shear stress is above critical stress value, both (G') and (G'') decrease rapidly, but (G') is smaller than (G''). It can be concluded that the elastic properties of ionogels are more evident than viscous properties at low stress, and become contrary at high stress. But the critical stress value of G'' exceeded that of G', which means their elastic properties could be changed easilier than viscous properties. Other ionogels with various ionic liquid contents show the same tendencies. The plate modulus (G_0) and stress values (σ_c) of all the samples were shown in Table 1. It can be seen that the plate modulus increase dramatically with the increase of gelator concentration, indicating the reinforcement of solid scaffolds.

The viscoelastic properties of the ionogels with different concentrations of ionic liquids were also characterized through non-destructive oscillatory measurements. Within the frequency range investigated, G' and G'' are also independent of frequency, and G' is thoroughly bigger than G'' about one magnitude. All the phenomena of ionogels are characteristic for a well-developed network.

Table 1 Plate modulus G_0 and critical stresses σ_c of ionogels Fe-H_3BTC-bmimBsa.

bmimBsa /wt%	G' [a]/Pa		G''[b]/Pa	
	G_0'	σ_c	G_0''	σ_c
93%	3587.8±132.1	129.4	674.9±28.5	362.8
90%	5147.7±155.7	216.7	996.9±30.8	607.5
85%	10753.5±280.3	362.0	1214.5±154.1	1704.0
80%	45941.7±600.5	398.8	6058.7±77.5	1974.0

[a] G' the storage modulus; [b] G'' the loss modulus.

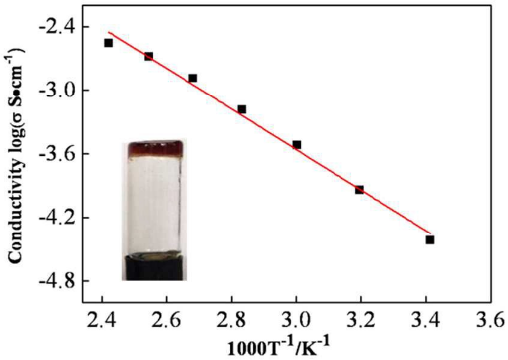


Fig. 7 The conductive Arrhenius plots of the ionogel Fe-H_3BTC-80%bmimBsa.

The conductivity (σ) is determined as a function of temperature for the ionogels, using impedance analysis (Fig. 7).[47,55] The conductivity of pure bmimBsa has been measured to be 1.13 mS cm^{-1} at 20 °C. As expected, the conductivity of ionogel is slightly lower than that of the pure bmimBsa. This can be explained by the reduced mobility of the ions in the gel state.[55,56] Along with the temperature increasing from 20 °C to 140 °C, the conductivity of the ionogel Fe-H_3BTC-80%bminBsa increases from 0.04 mS cm^{-1} to 2.80 mS cm^{-1}, monotonously. The activation energy of the supramolecular conducting ionogels can be calculated by Arrhenius plots of the conductivity. The resulting conductive activation energy of supramolecular ionogel is 33.13 kJ mol^{-1}, which is relatively lower than that of supramolecular ionogel reported in the literature.[57] In general, the activation energy is considered as the energy obstacle that the migration of ions must overcome. The smaller the activation energy is, the easier the movement of ion is.[58]

Conclusion

In this work, a facile strategy to prepare supramolecular conducting ionogels is developed based on two commercially available and inexpensive compounds: benzenetricarboxylic acid (H_3BTC) and iron(III) nitrate nonahydrate ($Fe(NO_3)_3 \bullet 9H_2O$). Gelators can form stable ionogels in bmimBsa and bmimCl *via* metal-coordination interaction within several seconds. *Via* this method, the time required for producing ionogels is reduced significantly. The prepared ionogels Fe-H_3BTC-bmimBsa can even remain gel state at 150 °C. This is the first example of supramolecular conducting ionogels prepared by low molecular weight gelators that can remain gel state at such high temperature. The high gel-sol transition temperature of ionogels Fe-H_3BTC-bminBsa may result from the strong π–π stacking interaction between the scaffolds and the ionic liquids. Moreover, these supramolecular ionogels exhibit high conductivity and relatively low activation energy. These results help to promote the applications of supramolecular ionogels in the area of the electrolyte.

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Facile prepared supramolecular ionogels can remain gel state at high temperature and exhibit high conductivity and relatively low activation energy.