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Ionic conductivity and molecular dynamic behavior in supramolecular ionic networks; the effect of lithium salt addition

M.Ali Aboudzadeh [a], Haijin Zhu [b,*], Cristina Pozo-Gonzalo [b,*], Alexander S. Shaplov [c], David Mecerreyes [a], Maria Forsyth [b]

[a] *POLYMAT, University of the Basque Country UPV/EHU, Joxe Mari Korta Center, Avda. Tolosa 72, 20018 Donostia-San Sebastian, Spain*
[b] *IFM, Deakin University, Burwood, VIC 3125, Australia*
[c] *A.N Nesmeyanov Institute of Organoelement Compounds Russian Academy of Sciences (INEOS RAS), Vavilov str. 28, 119991, GSP-1, Moscow, Russia*

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ABSTRACT

Supramolecular ionic networks combine singular properties such as self-healing behaviour and ionic conductivity. In this work we present an insight into the ionic conductivity and molecular dynamic behaviour of an amorphous and semicrystalline supramolecular ionic networks (iNets) that were synthesised by self-assembly of difunctional imidazolium dicationic molecules coupled with (trifluoromethane-sulfonyl) imide dianionic molecules. Relatively low ionic conductivity values were obtained for the semicrystalline iNet below its melting point (T_m = 101 °C) in comparison with the amorphous iNet for which the conductivity significantly increased (~3 orders of magnitude) above 100 °C. Upon LiTFSI doping, the semicrystalline iNet reached conductivity values ~ 10^{-3} S cm^{-1} due to enhanced mobility of the network which was supported by solid-state static NMR. Furthermore, the overlapping of ^{19}F and ^{7}Li resonance lines from both the semicrystalline network and the LiTFSI suggests fast molecular motions.

1. Introduction

The recent strategies of self-assembly and supramolecular chemistry are opening new opportunities for the bottom-up design of functional materials [1–7]. For over a decade, functional supramolecular materials assembled via non-covalent interactions, such as hydrogen bonding, π - π stacking or metal-ligand bonds have been attracting a great deal of attention [8–10]. Among non-covalent interactions, ionic interactions are an attractive, unexplored and viable approach to the construction of supramolecular materials. The early history of ionic interactions in polymers dates back to the developments of polyelectrolytes and ionomers. Polyelectrolytes possess a high content of ionic groups that afford them properties such as ionic conductivity, enabling a variety of potential applications such as solid-state polymer electrolytes in Li-ion battery and fuel cells, and so on [11–13].

In the last years, new types of polyelectrolytes and ionic materials have been developed by introduction of new cations and anions that come from ionic liquid chemistry [14,15]. For instance, the preparation of supramolecular ionic networks was reported by conbining multi-cationic and multi-anionic compounds [16–19]. In this case, complex molecules such as alkyl phosphonium dications were employed together with multicarboxylate molecules. Recently, some of us reported examples of using simple acid-base ionic complexes for the generation of supramolecular ionic networks [20–23]. The materials were similar than protic ionic liquids where multifunctional carboxylic acids such as citric acid and diamines were combined. In these works, the resulting ionic networks demonstrated sharp changes in rheological and conductivity properties through a temperature range of 30 to 80 °C. This fact suggested their potential use as self-healing materials as well as ion conducting materials [20]. However, the supramolecular ionic networks possessed some intrinsic issues, related to the constituent carboxylate compounds, such as water sensitivity, poor thermal stability and low ionic conductivity.

More recently, we developed a new family of supramolecular ionic networks (iNet) based on highly delocalized di-anionic monomers that exhibited good thermal and water stability. These iNets formed by the self-assembly of difunctional imidazolium dicationic molecules coupled with (trifluoromethane-sulfonyl) imide dianionic molecules presented superior transport properties and self-healing type rheological behaviour [24]. Although, most of the synthesized compounds were semicrystalline, amorphous networks were also obtained using aromatic asymmetric dianions.

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* Corresponding authors. Tel.: +61392446634.
E-mail addresses: h.zhu@deakin.edu.au (H. Zhu), cpg@deakin.edu.au (C. Pozo-Gonzalo).

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These amorphous ionic networks showed a significantly higher ionic conductivity than the semicrystalline iNets. Following that study, the goal of this article is to understand the relationship between morphology and ionic conductivity of an semicrystalline and amorphous ionic networks using temperature and time-sweep tests. The impact of addition of lithium salt on the transport properties, in particular conductivity, of the semicrystalline networks is evaluated for the first time. Thermal and molecular dynamics behaviour of the neat and lithium doped semicrystaline network was investigated by impedance spectroscopy, differential scanning calorimeter (DSC) and static solid-state NMR spectroscopy.

2. Experimental

2.1. Preparation of lithium doped supramolecular ionic network

Lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) (Aldrich, 99%) was used as received. Supramolecular ionic networks **iNet-1** and **iNet-2** (Table 1) were synthesised by combining highly delocalised dianions with geminal di-imidazolium dications as the building blocks. Theses novel dianionic monomers were synthesised by the chemical modification of disulfonate sodium salts to highly delocalized anions (trifluoromethane-sulfonyl) imide. A more detailed synthesis has been reported in the previous study [24]

Doping was achieved by melting the supramolecular ionic network **iNet-1** with either 5 or 10 mol% LiTFSI in a high-purity argon environment glove box and stirring for 1 hour at 110 °C to ensure that the LiTFSI had completely dissolved.

2.2. Characterization

A Mettler Toledo differential scanning calorimeter (DSC) was used to investigate the thermal properties of the samples. Measurements were made from -70 °C to180 °C at cooling and heating rates of 10 °C/min. Samples weighed were ~ 9-12 mg. Glass transition temperature (T_g) was determined automatically by the instrument from the second heating trace and reported as the midpoint of the thermal transition.

The ionic conductivities of all samples were measured using AC impedance spectroscopy on a Solartron potentiostat equipped with modulab MTS software. Samples were dried overnight inside a vacuum oven at 70 °C prior ionic conductivity characterisation.

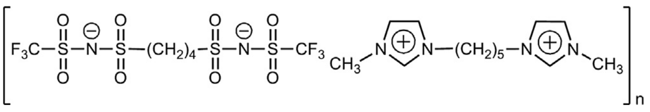
For solid samples, pellets, 0.8–1.0 mm thick and ~ 13 mm diameter were prepared by pressing in a KBr die under 3 tons of load for 5 minutes. The prepared pellets were sandwiched between two circular stainless steel electrodes in hermetically sealed conductivity cells (Advanced Industrial Services, Moorabbin, Australia). Data were collected over a frequency range of 100 mHz–1 MHz and specific temperature range for each sample were considered, in heating and cooling cycles, at 5 °C intervals under single sine wave acquisition mode at 100 mV signal voltage amplitude and auto current mode. The cooling cycle was carried out immediately after, and at the same rate as the heating cycle. The temperature was controlled using a Eurotherm model 3504 temperature controller and a 28 V/32 W heater (Helios Electroheat Pty Ltd Cheltenham, Australia). For liquid samples, a homemade conductivity cell was used, consisting of two platinum electrodes immobilized in a resin and embedded into a glass matrix. Each of the wires was electrically connected to the potentiostat. The cell was dipped into a glass vial containing the liquid sample while ensuring complete immersion of the wires and avoiding bubbles. Water and air were excluded from the sample using rubber seal and teflon tape. Conductivity standard KCl solution (concentration: 0.01 mol/l, conductivity: 1.413 mS/cm at 25 °C) was used to calibrate this conductivity cell. An interval of 20 min was allowed between each measurement temperature (i.e., after each 5 or 10 °C step). Multiple measurements were carried out to check for stability and reproducibility in the Nyquist plots for each of the samples. Nyquist plots of the impedance data were used to determine the sample resistance from the intercept (or the first touch-down) of the real axis.

All the ^{1}H, ^{7}Li, and ^{19}F static solid-state NMR experiments were performed on a Bruker Avance III 300 wide bore NMR spectrometer operating at 300.13 MHz. A 4 mm double resonance Magic Angle Spinning (MAS) probe head was used to record the spectra from both the MAS and stationary powder samples. For both ^{1}H and ^{19}F NMR experiments, the 90° pulse lengths were 2.5 μs corresponding to rf-field strengths of 100 kHz, and the recycle delays were 20 s to allow the system to recover to equilibrium. The 90° pulse lengths for ^{7}Li were 4 μs corresponding to rf-field strengths of 62.5 kHz, and recycle delay was 5 s (t_1 {^{7}Li} < 1 s). The sample temperatures for the variable temperature (VT) experiments were calibrated with lead nitrate, using the method described in the literature [25,26].

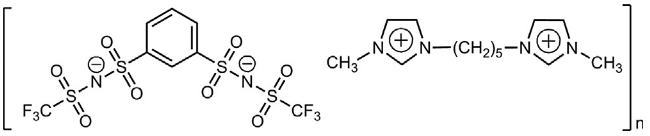
The static NMR measurements were performed by holding the temperature at 120 °C for 5 minutes before measurements to remove any thermal history, and then air-quenched to room temperature and equilibrated for approximately 10 min before NMR measurements. During NMR measurement, the temperature was increased from 20 °C to 70 °C, every 10 °C stepwise. Equilibration time of 5 min was allowed at each temperature before the measurements. Unless otherwise stated, the temperature procedures for all the following variable-temperature NMR experiments are the same.

The ^{1}H diffusion coefficients were measured with pulse-field gradient (PFG) NMR experiments on the same NMR spectrometer as the static NMR experiments, but equipped with a 5 mm diff50 pulse-field gradient probe. The samples were packed to a

Table 1
Supramolecular ionic networks iNets.



iNet-1



iNet-2