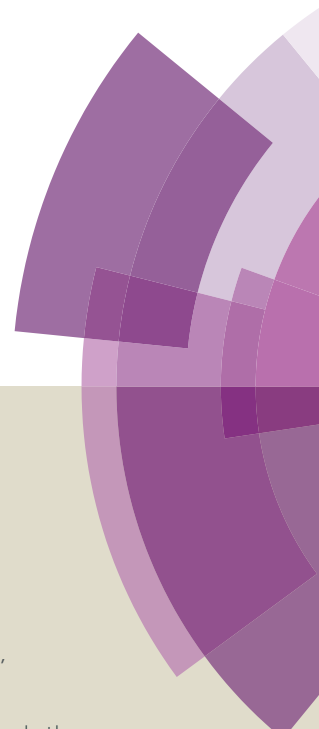


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ARTICLE TYPE

Supramolecular ionic networks with superior thermal and transport properties based on novel delocalized di-anionic compounds

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Supramolecular ionic networks based on highly delocalized dianions having (trifluoromethane-sulfonyl)imide, (propylsulfonyl)methanide and (cyano-propylsulfonyl)imide groups were developed and their physical properties were examined in detail. Most of the synthesized compounds were semicrystalline possessing T_m values close to 100 °C; however, amorphous networks were also obtained using aromatic asymmetric dianions. Rheological measurements in temperature sweep tests at a constant frequency confirmed two different behaviors: a fast melting close to the T_m for semicrystalline materials and a thermoreversible network to liquid transition for the amorphous supramolecular ionic networks. It was found the amorphous ionic networks showed significantly higher ionic conductivity (10^{-3} S/cm at 100 °C) than the crystalline ionic networks (10^{-6} S/cm) and previously reported amorphous citrate ionic networks (10^{-5} S/cm). The supramolecular ionic networks containing hydrophobic (trifluoromethanesulfonyl)imide groups demonstrated improved water stability and higher thermal stability than previously synthesized carboxylate ones. Noticeably, the obtained amorphous supramolecular ionic networks combine not only high ionic conductivity and thermal stability, but also self-healing properties into the same material.

Introduction

The introduction of new cations and anions coming from ionic liquids (ILs) chemistry is extending the properties and classical applications of ionic polymers.¹⁻⁴ This emerging ionic chemistry combined with supramolecular chemistry can also be translated to the development of supramolecular polymers based on ionic interactions. In comparison to other non-covalent counterparts, ionic interactions have unique properties as follows. Firstly, they are stronger and less-directional;⁵ secondly, they may form larger aggregated structures depending on the steric environment of the ion pair;^{6,7} thirdly, coulombic interactions are asymmetric and sensitive to the local constant of the medium they are in;⁸ and fourthly, ionic interactions are easily tunable through the combination of various anion (e.g. sulfonate vs. carboxylate) and cation structures (e.g. primary or secondary amine, quaternary ammonium), that are accessible through straightforward chemistry.⁹⁻¹²

Only six years ago, Grinstaff *et al.* reported the preparation of organic supramolecular ionic networks by mixing multi-cationic and multi-anionic compounds.¹³⁻¹⁶ In this case; complex molecules such as alkyl phosphonium dications were employed. More recently, we developed more simple pathways for the synthesis of supramolecular ionic networks by using multi-carboxylate anions and simple proton transfer reactions.⁹⁻¹² Among the investigated molecules citric acid showed great potential leading to supramolecular ionic networks with unique rheological properties when combined with a variety of dicationic compounds. Thus, a rapid soft solid network to liquid transition

(T_m) was revealed which facilitated the use of such supramolecular ionic networks in self-healing applications.⁹⁻¹¹

However, supramolecular ionic networks reported thus far possessed some intrinsic issues, related to the constituent carboxylate compounds, such as water sensitivity, poor thermal stability temperature and low ionic conductivity. Therefore the primary advantage of supramolecular ionic networks, which is the fact that they can combine self-healing and ionic conductive properties in one material, has not attained yet. Therefore the main goal of this work is to report the synthesis of a new family of supramolecular ionic networks having highly delocalized dianions which may overcome these limitations.

Our strategy to develop supramolecular ionic networks with superior properties first involves the development of novel delocalized dianionic compounds (Scheme 1). Although, ionic liquids of dicationic type are well known,^{17,18} dianionic systems having typical anions such as sulfonamides have not been synthesized yet. Recently, Shaplov *et al.*¹⁹ and Armand *et al.*²⁰ have shown the synthetic pathway for the preparation of methacrylate and 4-vinylbenzene ionic liquid like monomers with highly delocalized attached trifluoromethane-sulfonyl)imide, (propylsulfonyl)methanide and (cyano-propylsulfonyl)imide anions. This approach was taken into consideration and allows us to design and synthesize a series of highly delocalized dianionic compounds. These novel dianions were combined with geminal di-imidazolium dications as the building blocks for the preparation of supramolecular ionic materials. In this paper we also present the superior thermal and transport properties of these materials that make them promising candidates as electrolytes for electrochemical devices with intrinsic self-healing properties that may offer advantageous in terms of safety.

Results and Discussions

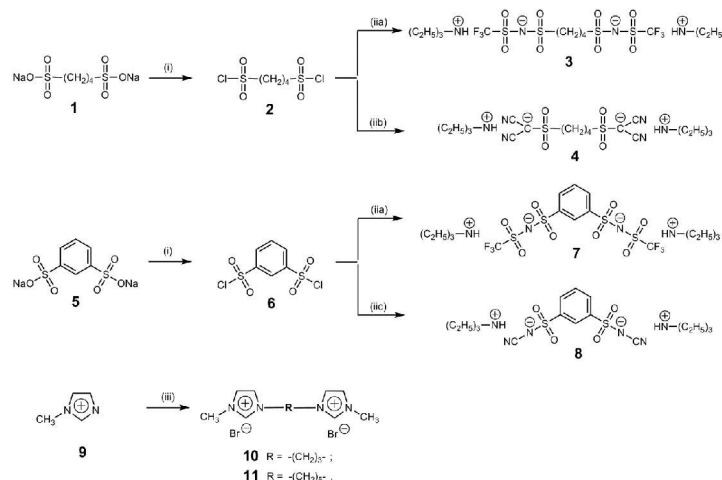
Synthesis and characterization of novel delocalized dianionic compounds

The design of novel dianionic monomers involves the chemical modification of the sulfonate group to highly delocalized anions having (trifluoromethane-sulfonyl)imide, (propylsulfonyl)methanide or (cyano-propylsulfonyl)imide groups. For this purpose, two different disulfonate sodium salts were chosen (Scheme 1, compounds **1** and **5**). While **1** is representative of aliphatic compounds, **5** belongs to the 1,3-substituted aromatics. The choice of the latter was driven by the desire to reduce the asymmetry and subsequent melting point of the final ionic monomers. The two steps synthetic route of **3**, **4**, **7** and **8** was similar to the procedure published by some of us previously¹⁹ in the case of methacrylic anionic monomers. On the first stage 1,4-butanedisulfonic acid disodium salt or benzene-1,3-disulfonic acid disodium salt were converted into their respective sulfonyl chloride derivatives by reaction with thionyl chloride in the presence of DMF as a catalyst. Both bis-sulfonyl chlorides (Scheme 1, **2** and **6**) were obtained as solid crystalline products. It was noticeable that aromatic compound **6** undergoes vacuum sublimation at low temperature and can thus be further purified. The second stage consisted of the reaction of **2** or **6** with trifluoromethanesulfonamide (Scheme 1, **3** and **7**), malononitrile (Scheme 1, **4**) or cyanamide (Scheme 1, **8**) in the presence of a 2.2 molar excess of triethylamine in anhydrous THF. Unexpectedly, in contrast to respective charged methacrylate¹⁹ or styrene²⁰ derivatives, all dianionic monomers **3**, **4**, **7** and **8** along with reaction byproduct (triethylammonium hydrochloride) precipitated during synthesis. Taking into account the nature of the cations, the separation process of the main reaction and its byproducts represented quite a difficult task. An elegant solution was found in the difference in solubility of **3**, **4**, **7**, **8** and triethylammonium hydrochloride. The insolubility of the latter in anhydrous DMF allowed its nearly quantitative separation from the main reaction products.

The structure and purity of **3**, **4**, **7** and **8** were determined by ¹H, ¹³C and ¹⁹F NMR, IR spectroscopy and elemental analysis. Three dianionic monomers represented solid crystalline or wax like products with a melting point equal to 40-43, 73-74 and >150 °C for **7**, **3** and **4** respectively. Only compound **8** was an ionic liquid at room temperature.

Synthesis of supramolecular ionic networks using delocalized dianionic and dicationic compounds

In the second step, supramolecular ionic networks were prepared via two synthetic pathways as illustrated in Scheme 2. In all the cases, reactants were mixed in equimolar amounts at room temperature in water as a solvent. The synthesis of supramolecular ionic networks based on di-anionic compounds having (trifluoromethane-sulfonyl)imide group, was simple. By mixing with dicationic compounds (**10** or **11**), the resultant ionic networks **iNet-1**, **iNet-2** and **iNet-3** precipitated in water which allowed for their easy separation and purification. This fact was a good indication of the diminished aqueous sensitivity of these



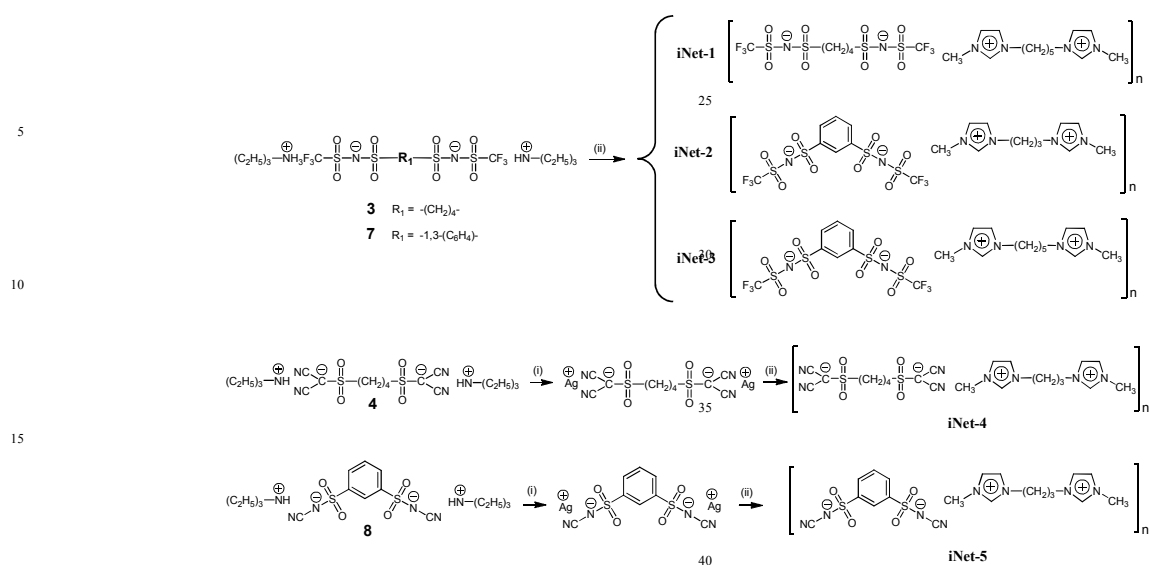
Scheme 1 Synthetic route for the preparation of ionic monomers

Reagents and conditions: (i) SOCl₂, THF/DMF, 0°C→RT; (ii) NH₂SO₂CF₃, THF, NEt₃, 0°C→RT; (iib) CH₂(CN)₂, THF, NEt₃, 0°C→RT; (iic) NH₂CN, THF, NEt₃, 0°C→RT; (iii) Br-(CH₂)₃-Br or Br-(CH₂)₅-Br, MeOH, 0→55 °C.

materials in comparison with previous supramolecular ionic networks based on the carboxylate anion, which were water soluble in most cases.⁹⁻¹²

In contrast, supramolecular ionic networks **iNet-4** and **iNet-5**, based on di-anionic compounds having (propylsulfonyl)methanide and (cyano-propylsulfonyl)imide groups, were soluble in water. As a result, an alternative synthesis route was developed in this case (Scheme 2b). This route consisted of two reaction steps. Thus, in the first stage the silver salts of the respective monomers **4** and **8** were obtained and quantitatively isolated, whereas in the second stage they were allowed to react with aqueous solution of **10** or **11** providing **iNet-4** and **iNet-5** in a pure form, after the removal of precipitated AgBr. Aliphatic chains between imidazolium rings in compounds **10** or **11** was chosen to provide a direct comparison with our previous supramolecular network with same type of dicationic molecules.¹²

The structure and purity of the supramolecular ionic network products were confirmed by ¹H and ¹³C NMR and IR spectroscopy. Except for **iNet-3** that was obtained as a transparent amorphous material, all other products represented crystalline solids at room temperature as confirmed by powder X-Ray diffraction (PXRD) experiments. According to X-Ray analysis a crystallinity degree of > 90 % for **iNet-1**, **iNet-2**, **iNet-4** and **iNet-5** was revealed. Thus most of the synthesized supramolecular ionic networks (four among five) with highly delocalized dianions were found to be highly crystalline. This was not the case for ionic networks based on citrate, which were mostly amorphous. Whereas using other types of carboxylates, having very rigid and regular structures, such as malonate and terephthalate dicarboxylates, will lead to crystallization, avoiding the formation of 3D ionic networks.⁹



Scheme 2 Synthetic route for the supramolecular ionic networks preparation. *Reagents and conditions:* (i) AgNO₃, H₂O, RT; (ii) **10** or **11**, H₂O, RT.

Thermal and rheological properties

The thermal properties of supramolecular ionic networks were investigated by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). By DSC it was observed that all the crystalline networks showed a melting point in the first heating cycle at 101, 94, 116 and 109 °C for **iNet-1**, **iNet-2**, **iNet-4** and **iNet-5**, respectively (Table 1). While, in the second heating cycle only a glass transition temperature in the range of $T_g = -1 \div -22$ °C (Table 1, entries 1-2 and 4-5) was observed. In contrast, amorphous **iNet-3** demonstrated only a glass transition at -20 °C in both heating cycles. DSC curves of **iNet-3** along with crystalline **iNet-1** are shown in Fig. 1 for comparison. It can be concluded that a change of the aliphatic dianion into its aromatic analogue leads to a more amorphous behavior (Table 1, entries 1 and 3). When the same dianion monomers are used, an increase of the spacer between two imidazolium cations also appears to avoid crystallinity (Table 1, entries 2 and 3).

Thermal stability of novel supramolecular ionic networks was estimated by TGA. It was revealed that their onset decomposition temperatures in air vary from 200 to 295 °C (Table 1, Fig. 2). In terms of thermal stability, the obtained products could be arranged in the following order: **iNet-2** \approx **iNet-3** > **iNet-1** > **iNet-5** > **iNet-4**. Thus, **iNet-2** and **iNet-3** based on aromatic **7** with bis(trifluoromethylsulfonyl)amide anions demonstrated the highest T_d among the investigated networks (Table 1, entries 2 and 3). The transfer from an aromatic spacer (**7**) to an aliphatic one (**3**) results in a decrease of thermal stability by ~ 40 °C (Table 1, entries 1 and 3). It is known that, the bis(trifluoromethylsulfonyl)amide anion usually imparts higher thermal stability to the ILs in comparison with dicyanamide based salts ($T_d = 390 \div 420$ °C²² and $290 \div 335$ °C²³, respectively). Following the same general tendency, the thermal

stability of **iNet-2** and **iNet-3** is higher than of **iNet-5** (Table 1, entries 2, 3 and 5), while T_d of **iNet-1** exceeds the onset decomposition temperature of **iNet-4** (Table 1, entries 1 and 4). Thermal behavior of our previously synthesized supramolecular network based on the carboxylate anion¹² was also included in Fig. 2 (Table 1, entry 6). As can be clearly observed, these new supramolecular ionic networks based on delocalized anions showed an improved thermal stability of between 60 to 160 °C.

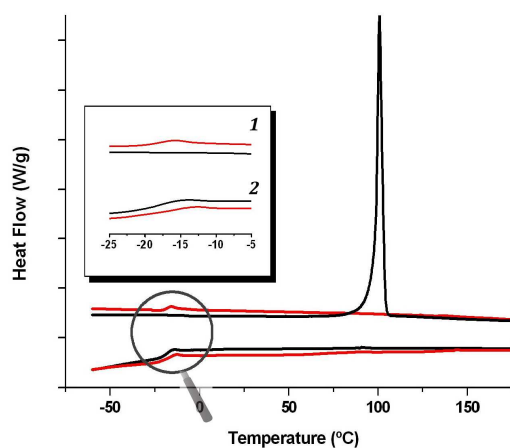


Fig. 1 DSC profiles of **iNet-1** (1) and **iNet-3** (2), first heating cycle (black color) and second heating cycle (red color), the figure in the inset shows magnified glass transition temperature for both materials.

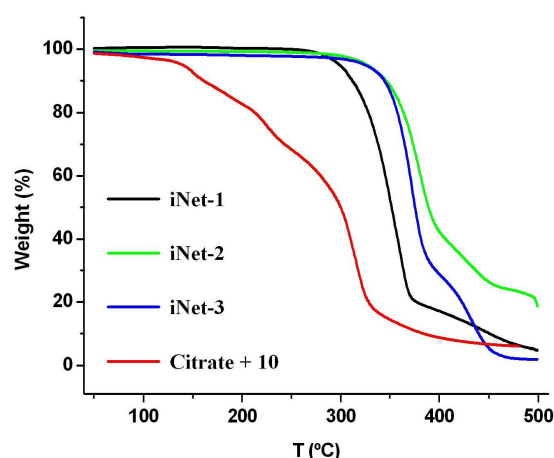


Fig. 2 Thermal gravimetric analysis (TGA) curves of **iNet-1**, **iNet-2** and **iNet-3** as well as the supramolecular ionic network based on citrate anion and 10

Rheological analysis of the ionic networks was carried out using temperature sweeps in small-amplitude oscillatory flow measurements. The temperature dependences of storage (elastic) G' and loss (viscous) G'' moduli at constant frequency of 1 Hz are shown in Fig. 3. As can be seen from Fig. 3, at temperatures below -10°C the ionic interactions in amorphous **iNet-3** brought about a soft solid characterized by a high elastic modulus with a constant value of $G_e = 7.2 \times 10^6$ which became a viscoelastic liquid with $G'' > G'$ values as the temperature increased. G_e reflects the equilibrium elasticity of the network. This transition from network to liquid state is characteristic for the majority of supramolecular ionic networks developed previously.⁹⁻¹² As an indicator of this transition, the crossover temperature at which $G' = G''$, or the temperature for the maximum in G'' , can be taken. The thermoreversible character of this supramolecular network is also analyzed in this measurement. Approximately the same G' and G'' values were obtained on a continuous cooling cycle, without any significant hysteresis being observed. The latter can indicate the rapid thermal reversibility of the network that can be explained by the non-covalent nature of the involved interactions, and the rapid dissociation and subsequent recovery of these interactions.

On the other hand in rheological experiments **iNet-1** demonstrated an almost constant elastic modulus G' (Fig. 3). It is noticeable that in the temperature range of 40 to 100°C , i.e. below **iNet-1** melting point, its G' was always higher than the associated loss modulus G'' . Such behavior is typical for a soft solid material and additionally confirms the crystalline nature of the network. Upon melting, both moduli decreased dramatically, indicating flow of the sample. This drastic decrease in modulus represents the melting transition. Although the cooling cycle was performed with the same temperature ramp rate, the rapid thermal reversibility was not observed, possibly due to the longer times needed for solidification. **iNet-4** and **iNet-5** showed the same behavior as for **iNet-1** in the rheological experiments except that the sharp drop in both moduli occurred at their corresponding melting points. **iNet-2** exhibited crystalline behavior during the

heating cycle again similar to **iNet-1**, however, during the cooling cycle after the melt transition, this material remained amorphous within the timescale of the measurement and a transition from liquid state to a network state was observed at $T_{ln} = 8^\circ\text{C}$.

It is worth to mention that the amorphous supramolecular ionic network **iNet-3** shows the typical rheological properties associated with self-healing behavior. This was observed before in other supramolecular ionic systems where this rheological behavior was translated into self-healing by a slight temperature change before and after the T_{nl} transition. Below the T_{nl} the material shows a solid film like properties, when a crack is provoked the material healed itself in some minutes even without the need of applying a heat and recovers its initial shape/aspect.

Table 1 Thermal Characterization of supramolecular ionic networks

Supramolecular ionic network	T_g^a ($^\circ\text{C}$)	T_m^b ($^\circ\text{C}$)	T_d^c ($^\circ\text{C}$)	T_{nl}^d ($^\circ\text{C}$)	T_{ln}^d ($^\circ\text{C}$)
iNet-1	-19	101	260	-	-
iNet-2	-1	94	290	-	8
iNet-3	-20	-	295	-12	-13
iNet-4	-17	116	200	-	-
iNet-5	-22	109	240	-	-
Citrate + 10	-14	-	135	21	20

^a By DSC. ^b By DSC. ^c Onset loss temperature by TGA. ^d The transition temperatures from the network to the liquid state, T_{nl} , and from the liquid to the network state, T_{ln} , obtained from temperature scans at $\omega = 6.28$ rad/s.

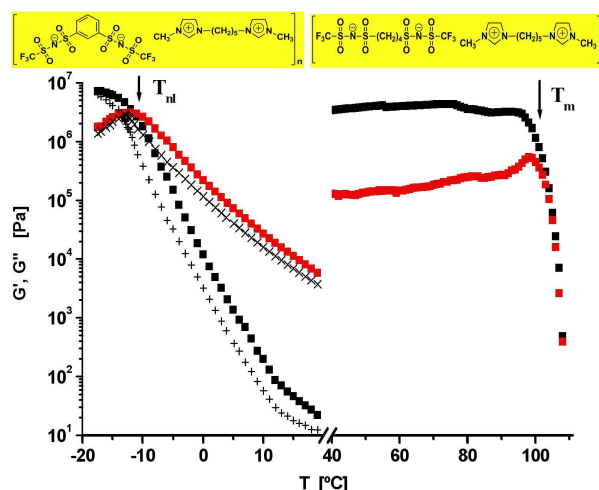


Fig. 3 Temperature dependence of dynamic storage modulus G' (heating \blacksquare & cooling \blacktriangle) and loss modulus G'' (heating \blacksquare & cooling \times) for **iNet-3** (left) and **iNet-1** (right) Arrows in the figure indicate the melting point (T_m) and network to liquid transition (T_{nl}).

Ionic conductivity

The ionic conductivity of supramolecular ionic networks was measured by AC impedance spectroscopy. It was revealed, that depending on the monomer's combination the ionic conductivity of networks varies in the range of 7.7×10^{-12} and 7.3×10^{-7} S cm⁻¹ at 30 °C. The increase of spacer between two imidazolium cations results in an increase in respective network's conductivity. The change of aliphatic dianion to its aromatic analogue leads to an increase in conductivity of nearly three orders of magnitude. The comparison of ionic conductivity for networks based on monomers having trifluoromethane-sulfonylimide, (propylsulfonyl)methanide and (cyano-propylsulfonyl)imide does not show a clear effect.

The temperature dependence of conductivity was also investigated. Fig. 4 shows representative results for a crystalline supramolecular ionic network (**iNet-1**), a citrate based amorphous supramolecular ionic network⁹ and an amorphous supramolecular ionic network based on delocalized anions (**iNet-3**). At temperatures below 70 °C crystalline **iNet-1** demonstrate nearly linear behavior (Arrhenius behavior) with the conductivity increasing from 1.3×10^{-10} to 4.4×10^{-9} S cm⁻¹. However, at temperatures close to the melting transition, T_m , a more rapid increase in ionic conductivity, equal to three orders of magnitude, was observed (Fig. 4). The temperature dependence of ionic conductivity for amorphous **iNet-3** was different (Fig. 4) to the two crystalline materials. The behavior for **iNet-3** appears predominantly linear and shows the highest values of ionic conductivity (between 10^{-6} and 10^{-3} S cm⁻¹) for the entire temperature range (30-100 °C) in comparison with crystalline **iNet-1**. Furthermore, the effect of lithium doping was investigated by adding 10 % LiTFSI to the amorphous **iNet-3**. The doped materials showed very similar values of ionic conductivity than the original **iNet**. In fact, the doped material showed a slightly higher ionic conductivity value at low temperatures which is the typical behavior of polymer electrolytes (Fig. 4). However at high temperatures where the viscosity drops, the ionic conductivity is lower in the case of the doped sample. This behavior is actually the typical one of ionic liquids where addition of a lithium salt decreases the overall ionic conductivity value.

Fig. 4 also compares the new supramolecular ionic networks based on delocalized anions with the conventional supramolecular ionic network materials based on carboxylates such as the citrate + diamine system. It is worth to remark that the new supramolecular ionic networks (**iNet**) showed a two to three order of magnitude improvement of its ionic conductivity with respect to previous amorphous supramolecular ionic networks based on citrate. The ionic conductivity value of 10^{-3} S/cm (at 100 °C) makes them of potential interest for real application in electrochemical devices such as batteries. However, the value of ionic conductivity at room temperature may not be enough for real applications. Further investigations are being carried out to replace the aliphatic groups by ethylene oxide units to improve the ionic conductivity of the supramolecular ionic networks.²¹

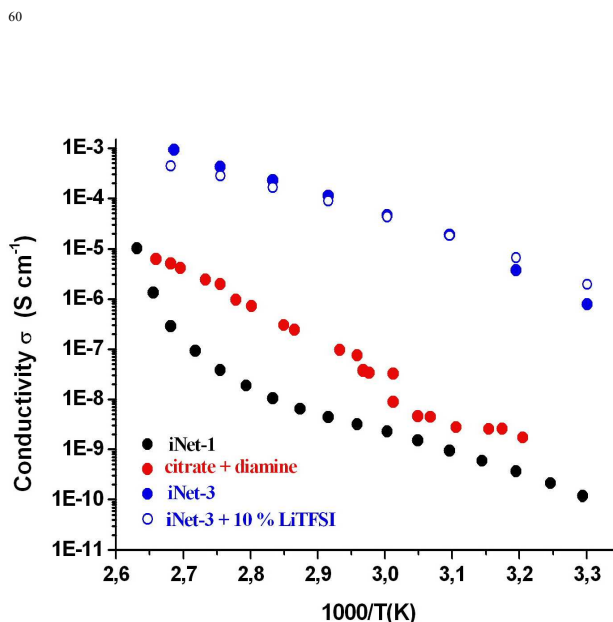


Fig. 4 Temperature dependence of the ionic conductivity for **iNet-1**, **iNet-3**, **iNet-3+10% LiTFSI** and supramolecular ionic network based on citrate

Conclusions

We have demonstrated a new synthetic route to supramolecular ionic networks based on highly delocalized di-anions. In particular, supramolecular ionic networks containing hydrophobic (trifluoromethane-sulfonyl)imide groups showed improved water stability and higher thermal stability than previously synthesized carboxylate ones. Although, most of the synthesized compounds were semicrystalline, amorphous networks were also obtained using aromatic asymmetric dianions. In this case rheological measurements in temperature sweep tests at a constant frequency confirmed a reversible network to liquid transition behavior associated with self-healing properties. Amorphous ionic networks showed high ionic conductivity, showing values close to 10^{-3} S/cm (at 100 °C). **i-Nets** reported here combine properties such as ionic conductivity and self-healing properties. This can be very interesting for applications like batteries for electric vehicles where security of the battery is a must and further optimization of the ionic conductivity of our materials could lead to an electrolyte for a battery that repairs itself.

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Notes and references

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¹⁵ † Electronic Supplementary Information (ESI) available: [Detailed experimental procedures include materials used, characterization methods, complete synthesis steps of the supramolecular ionic networks and methods used to evaluate their structure and purity, the rest of rheological and conductivity graphs]. See DOI: 10.1039/b000000x/

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Table of Contents

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