



# Enhanced ionic mobility in Organic Ionic Plastic Crystal – Dendrimer solid electrolytes



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## ABSTRACT

We report the first study of the characterisation of the organic ionic plastic crystal (OIPC) *N*-ethyl-*N*-methylpyrrolidinium tetrafluoroborate ( $C_2mpyrBF_4$ ) upon mixing with a dendrimer additive. Whereas previous reports of OIPC composite formation (i.e. with ceramics and polymers) have typically reported a decrease in the conductivity when lithium salt had been added, the addition of dendrimer is shown to lead to a substantial enhancement in the lithium containing system, approaching 3 orders of magnitude at 30 °C. Mechanical analysis indicates that dendrimer addition leads to a softer more ductile material while microscopy shows that the dendrimer is uniformly distributed and that the crystal microstructure is substantially disrupted, ultimately adopting a dendritic microstructure at 1 mol% dendrimer content. Thermal analysis indicates a new phase in the lithium OIPC system, the crystallisation of which is suppressed in the presence of dendrimer. Instead, a decrease in the phase transition enthalpies indicates a large increase in the amorphous component of the Lithium OIPC, particularly for the most conductive system  $-C_2mpyrBF_4 + 10 \text{ mol}\% \text{ LiBF}_4 + 0.1 \text{ mol}\% \text{ dendrimer}$ . Variable temperature powder X-ray diffraction confirms the presence of a new distinct phase and its absence in the presence of dendrimer. A change in the progression of the thermal phase behaviour of the OIPC in the presence of dendrimer is also shown, exhibiting the phase I (high temperature) structure at temperatures below the phase II-I transition.

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## 1. Introduction

Organic ionic plastic crystals (OIPCs) are an exciting new class of materials that have attracted great interest over the last decade since it was discovered that significantly high ionic conductivities can be achieved with the addition of dopants like  $Li^+$  [1]. Thus, OIPCs are promising materials around which the next generation of all-solid-state high energy electrochemical devices can be developed with high levels of safety and performance that cannot yet be achieved through current technologies. Examples of the demonstration of OIPC application in lithium batteries [2–6], dye sensitised solar cells (DSSCs) [7–10] and as fuel cell electrolytes [11,12] highlight the increasing relevance of these materials as alternative electrolytes, offering a solution to issues such as

electrolyte leakage, safety, thermal stability and electrochemical stability. A recent perspective provides a summary of research in both fundamental and device-oriented aspects of OIPCs [13]. Despite such promise, critical properties of OIPCs, for instance mechanical ‘toughness’ and flexibility and ‘not-quite-high enough’ ionic conductivity, are major barriers to the further development of OIPCs in energy applications.

Attempts to improve the properties of OIPCs, for instance the ionic conductivity, by forming composite structures by combining the OIPC with a ‘filler’ material such as ceramic nanoparticles [14–17], ionic conducting polymers such as PEO [18], and polymer nanofibre mats [19] have demonstrated significant enhancements in the OIPC composite. However in these works, almost without exception, the combination of lithium doping and composite additions has resulted in reduced conductivity compared with that of the lithium doped material.

In this report, we explore a new approach to the modification and optimisation of OIPC material properties through the incorporation of polymeric dendrimers into the OIPCs. Dendrimers

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are hyperbranched polymer molecules formed of dendritic ‘trees’ of repeating, branching segments that are often symmetric around a core, which gives them a spherical molecular morphology [20,21]. As a result, dendrimers are atomically dense and small in size for their molecular weight compared to traditional linear polymers.

Linear polymers, when dissolved in a medium, typically form loose, extended coils which may not easily integrate into an OIPC crystal lattice structure and thus have a tendency to be expelled into the grain boundaries between crystal grains [18,22]. On the other hand, the density, monodispersity, and essentially spherical morphology of dendrimers [23] gives them a size and shape that is more compatible and more likely to allow integration into the OIPC crystal lattice structure rather than being forced to the grain boundaries.

The ionic conductivity of OIPC materials is known to be governed by factors facilitating the ion mobility. The principal factor influencing plastic crystal phase formation, and hence ion mobility, is the rotational motion of the individual ions in the OIPC. Chen et al. [24] have recently applied molecular simulation and solid-state NMR spectroscopy to the N-ethyl-N-methylpyrrolidinium tetrafluoroborate ( $C_2\text{mpyrBF}_4$ ) OIPC system to describe the interionic configurations and likely disorder modes which give rise to the observed solid-solid thermal phase transitions in this system. However, other factors such as the presence of structural defects (e.g. dislocations and vacancies), ion spacing, grain structure, grain boundaries, and the degree of crystallinity are known to also significantly affect ion mobility in plastic crystals, [13,25–32]. The integration of large spherical dendrimers into the OIPC crystal structure is expected to have several effects that may benefit ion mobility. First, the size of the dendrimer molecule is large with respect to the individual ions that make up the lattice, but still small enough that the ions cannot easily form an ordered structure around it. In this respect, the dendrimer can function as a large structural defect that can introduce significant lattice strain and geometric frustration as the ions attempt to form an ordered crystal structure around the highly curved, spherical object. This increased strain and frustration of the crystal lattice structure is expected to increase the amount of amorphous phases in the OIPC material and increase the size and number of structural vacancies into which small ions such as  $\text{Li}^+$  can migrate resulting in enhanced conductivity. Second, the increased frustration in the crystal packing order is likely to increase the spacing between ions in the

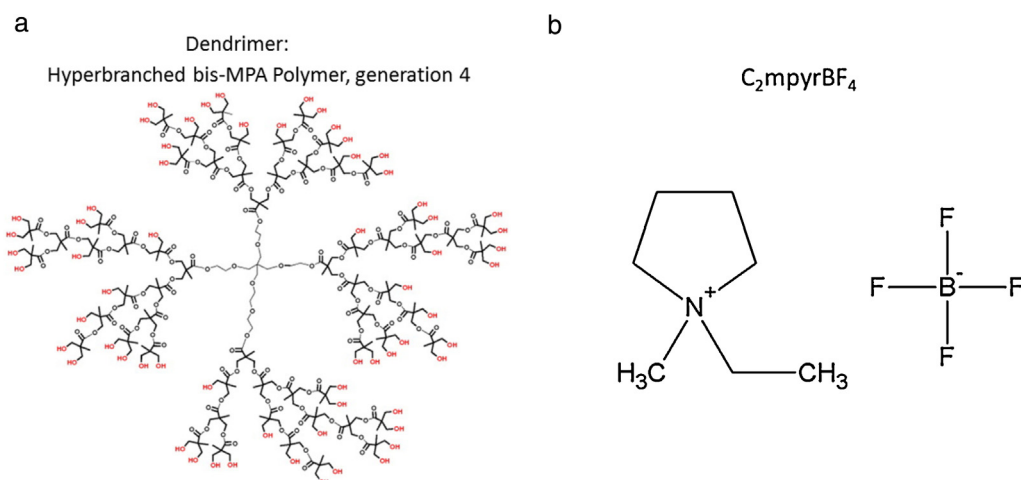
frustrated regions allowing for more rotational freedom and greater mobility of ions.

Thus, this manuscript describes the first report of an investigation into the ion dynamics, phase behaviour and bulk properties of a ternary OIPC-Li salt-dendrimer system as an approach to improving the properties of OIPCs for application as solid-state electrolytes. The OIPC chosen was N-ethyl-N-methylpyrrolidinium tetrafluoroborate ( $C_2\text{mpyrBF}_4$ ) due to recent reports describing its application in high temperature batteries together with detailed descriptions of its thermal phase behaviour, local structure and ion dynamics [5,24,33]. The dendrimer chosen was hyperbranched bis-MPA Polymer, generation 4 (D4) due, in part, to its ready commercial availability and near monodispersity [23]. This dendrimer was also chosen for its general electrochemical stability as well as its limited chemical interactions in the OIPC. The generation 4 dendrimer was chosen for this study because it was the largest of the generations readily available and was thus most likely to produce structural disruptions of the packing order. The terminal hydroxyl functionality on the dendrimer was also purposely chosen to provide a future means of functionalization (e.g.  $-\text{SO}_3\text{Li}$ ) and hence the present study will underpin future studies geared toward understanding the role of chemical functionality in these systems.

## 2. Experimental

### 2.1. Materials

Hyperbranched bis-MPA Polymer, generation 4 (i.e. ‘D4’;  $\text{MW}=7323.3$ ) dendrimer was purchased from Sigma–Aldrich and dried under vacuum at  $50^\circ\text{C}$  overnight (see Fig. 1). N-ethyl-N-methylpyrrolidinium tetrafluoroborate ( $C_2\text{mpyrBF}_4$  –98%) was purchased from io-li-tec (see Fig. 1). The OIPC was purified by recrystallisation from dry acetonitrile (Merck) in two steps: precipitation overnight in the refrigerator and stirring overnight in the presence of activated carbon at room temperature. The filtered solid from both steps was dried under reduced pressure for 48 hrs. Lithium tetrafluoroborate,  $\text{LiBF}_4$  (99.998%) was purchased from Sigma–Aldrich. The pure OIPC was doped with 10 mol%  $\text{LiBF}_4$  by dissolving both materials in dried acetonitrile (Merck) and mixing for 4 hrs under a nitrogen atmosphere. The solvent was removed using a rotary evaporator followed by drying in high vacuum at  $50^\circ\text{C}$  overnight. The concentration used here was



**Fig. 1.** Schematics illustrating the chemical structures of (a) the Hyperbranched bis-MPA Polymer, generation 4 (a.k.a. ‘D4’) and (b) the  $C_2\text{mpyrBF}_4$  OIPC used in these experiments.

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