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A single cation or anion dendrimer-based liquid electrolyte

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We propose here a novel liquid dendrimer-based single ion conductor as a potential alternative to conventional molecular liquid solvent-salt solutions in rechargeable batteries, sensors and actuators. Specific change from ester (-COOR) to cyano (-CN) terminated peripheral group in generation-one poly(propyl ether imine) (G₁-PETIM)-lithium salt complex results in a remarkable switchover from high cation ($t_{Li^+} = 0.9$ for -COOR) to an anion ($t_{PF_6^-} = 0.8$ for -CN) transference number. This observed switchover draws an interesting analogy with the concept of Heterogeneous Doping, applied successfully to account for similar changes in ionic conductivity arising out of dispersion of insulator particle inclusions in weak inorganic solid electrolyte. The change in peripheral group simultaneously affects the effective ionic conductivity, with the room temperature ionic conductivity of PETIM-CN ($1.9 \times 10^{-5} \Omega^{-1} \text{cm}^{-1}$) being an order higher than PETIM-COOR ($1.9 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$). Notably, no significant changes are observed in the lithium mobility even following changes in viscosity due to the change in the peripheral group. Changes in the peripheral chemical functionality directly influences the anion mobility, being lower in PETIM-COOR than PETIM-CN, which ultimately becomes the sole parameter controlling the effective transport and electrochemical properties of the dendrimer electrolytes.

Introduction

One of the important strategies towards building stable and safe rechargeable batteries has been to develop newer forms of electrolytes as potential alternative to conventional liquid molecular solvent-salt solutions.^{1,2} In this line of thought, various electrolyte systems ranging from solid crystalline electrolytes to “solid-like” soft organic electrolytes have been explored as alternatives to conventional liquid electrolytes focused mainly for applications in lithium-based battery chemistries.³⁻⁷ Polymer electrolytes, which exhibits interesting compliant mechanical properties in addition to high ionic conductivity, have shown greater potential than solid crystalline electrolytes in diverse electrochemical devices viz. batteries,^{8a} fuel cells,^{8b} actuators,^{8c} sensors⁹. Design of novel polymer architectures (e.g. network, branched polymers) has been one of the important strategies for the development of high ion conducting polymer electrolytes.¹⁰ The major drawback with various polymer-based electrolytes is that the cations and anions contribute to specific conductivity and thus the specific ion i.e. cation or anion transference number is not high. Especially the cation ion transference number, which is of

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practical interest for various rechargeable battery chemistries, is typically low in the range $t_e = 0.2-0.5$.^{10,11} There have been several strategies to design polymer electrolytes with high transference number without significantly compromising the effective ionic conductivity. Majority of these approaches have been applied on polymers in the solid form viz. via chemical manipulations of the constituting units of the polymer or form single ion conductors where ion of one type (say anion) is immobilized on the polymer backbone as in block or copolymer units. The other major concern with solid-like electrolytes is related to poor charge transport kinetics at the electrode|electrolyte interface which leads to poor device efficiency. Apart from a few glowing examples an overwhelming majority of the polymer electrolytes and in general, solid electrolytes have not been able to successfully transcend beyond the precincts of laboratory-scale demonstrations. This has led to the continued persistence of the conventional liquid electrolytes in majority of modern day electrochemical devices including rechargeable batteries.

Dendrimers are a special class of mono-dispersed branched polymers, containing a large number of branched flexible chain-ends emanating from a core or linker molecules. This unique architecture has attracted considerable attention in biomedicine, catalysis, sensing and energy storage.¹² The mechanical consistency of dendrimers is intermediate between low viscosity molecular solvents ($\eta \approx 10^{-3}$ Pa.s) and high viscosity polymer gel or polymer-salt complex (very high η ; $\eta \rightarrow \infty$) electrolytes. Due to higher viscosities of dendrimers compared to typical molecular solvents, the ionic mobility and hence the effective ionic conductivity of dendrimer electrolytes expectedly will be lower compared to molecular solvent - salt liquid solutions. In the context of the vast volume of work accomplished with regard to solid polymers with high ionic conductivity¹³, viscosity cannot be the sole criteria for the determination of ionic mobility and effective ionic conductivity. Similarly, high viscosity of the dendrimers should not be a deterrent for exploring their application in electrochemical devices. The high degree of branching in the dendrimer network leads to multiple advantages viz. larger free volume, higher amorphocity and low glass transition temperatures (implying higher chain flexibility).¹⁴ These coupled with the flexibility to freely tune the chemical composition and conformation as a function of generation number also significantly affect the ion solvating ability and host-guest interaction with various metal salts including alkali-metal salts which are of direct relevance to rechargeable batteries. These advantageous features should make dendrimers an attractive alternative liquid matrix to conventional liquids, ionic liquids, solid polymers for synthesis of ion conductors tailored to perform specific tasks in various electrochemical devices. Of specific interest is whether dendrimer can be employed to produce electrolytes with high ion transference number of a single ion-type. To the best of our knowledge there have been no such efforts undertaken in this direction. Additionally, there have been no detailed and conclusive studies undertaken on the correlation of various chemical functional parameters on ion transport mechanism in

dendrimers in spite of their anticipated potential in various electrochemical applications. Studies in these directions will supposedly throw more light on the ion transport mechanism in dendrimers and identify key parameters for the development of dendrimers based ion conductors for various applications such as rechargeable batteries, sensors, and actuators.^{14,15} We present here for the first time, a detailed study of the influence of the chemical nature of peripheral end functional groups on ionic conductivity, diffusion and transference number in the generation-1 poly(propyl ether imine) (G_1 -PETIM)-lithium salt mixtures. We demonstrate here that the end peripheral chemical functionality is a very important parameter to optimize the effective transport as well as the electrochemical properties of the dendrimer electrolyte.

Results and Discussion

Ion transport in polymer electrolytes largely depend on the chemical characteristics of the polymer such as branching, network, functionality of the side chains.^{8a,16,17} Different functional groups exhibit different binding abilities due to varying polarity of the groups and this influences the ion solvation via dissociation of the salt. On the other hand, their spatial distributions, size of end chains affect both cation and anion mobility resulting in large differences in respective ion transference number.¹⁷ The above stated issues on ionic conductivity and transference number are systematically probed here in the context of G_1 -PETIM dendrimers. The G_1 -dendrimers are synthesized with different end functional groups (-COOH, -COOR, -OH, -CN) maintaining the same linker (viz. ether) and branching points (viz. tertiary amine; c/f schematic Fig. 1). The study here focuses only on the first generation dendrimers primarily due to the following reasons. Firstly, the viscosity (0.1-6 Pa.s) of G_1 -PETIM dendrimer, though higher than the viscosity of a typical liquid molecular solvent (0.5-10 mPa.s),¹⁸ are much lower than the higher generations G_n -PETIM dendrimers ($n=2-4$). So, the influence of viscosity on ionic conductivity will be much less in G_1 -PETIM compared to G_n -PETIM dendrimer liquid electrolytes. The magnitude of ionic conductivity of some of the G_1 -dendrimers will not be significantly lower compared to a typical molecular liquid solvent-salt solutions¹⁷ of relevance to rechargeable batteries (typically: $>10^{-3}-10^{-2} \Omega^{-1}\text{cm}^{-1}$). Secondly, in G_1 -dendrimer the number density of the linker and branching moieties is lower compared to a higher generation dendrimer. Hence, the non-trivial influence due to the linker and branching moieties on solvation and ion mobility anticipated in the higher generation will be minimal and assumed constant in the G_1 -dendrimer. The ion transport in the G_1 -dendrimer electrolytes can then be directly correlated to the nature of the peripheral chemical functionality.

Temperature dependent ionic conductivity and viscosity of first generation dendrimers (with different functional groups) - 0.1 M LiPF_6 in the temperature range from (0-60) °C are shown in Fig. 2a and 2b respectively. Ionic conductivity of first generation nitrile terminated PETIM dendrimer electrolyte (G_1 -

CN-0.1 M LiPF₆) exhibits the highest room temperature ionic conductivity of $1.9 \times 10^{-5} \Omega^{-1} \text{cm}^{-1}$, whereas G₁-OH-0.1 M LiPF₆ shows the lowest conductivity of $9 \times 10^{-7} \Omega^{-1} \text{cm}^{-1}$. The conductivities of G₁-COOR-0.1 M LiPF₆ and G₁-COOH-0.1 M

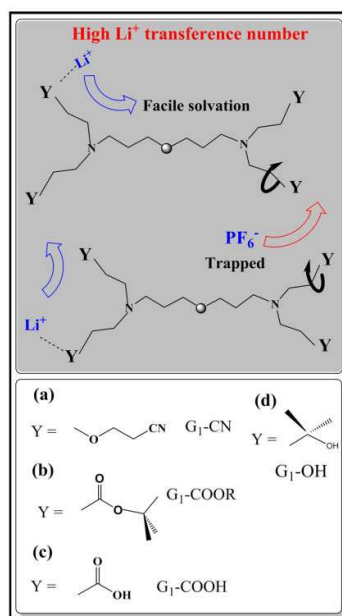


Fig. 1 Schematic representation of ion transport mechanism in G₁-PETIM dendrimers with different peripheral functional groups: (a) G₁-CN, (b) G₁-COOR, (c) G₁-COOH, (d) G₁-OH.

LiPF₆ at 25 °C are intermediate to G₁-CN-0.1 M LiPF₆ and G₁-OH-LiPF₆, being $1.9 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$ and $9.8 \times 10^{-7} \Omega^{-1} \text{cm}^{-1}$ respectively. The measured ionic conductivity of the various dendrimer electrolytes, which are at par with many single ion conductors^{10a, 19}, has the following trend: $\sigma_{\text{G}_1\text{-CN}} > \sigma_{\text{G}_1\text{-COOR}} > \sigma_{\text{G}_1\text{-COOH}} \sim \sigma_{\text{G}_1\text{-OH}}$. This variation in conductivity between the various dendrimer electrolytes by more than one order of magnitude indicates a strong correlation between chemical nature of peripheral functionalization and ion transport. The activation energies of conductivity are obtained by a linear fit of the conductivity data using Arrhenius equation: $\sigma = Ae^{-E_a/kT}$ where A, E_a, k, T are the pre-exponential factor, activation energy, Boltzmann constant and temperature respectively (c/f fitting parameters in Table ST2). In spite of notable differences in ionic conductivities between G₁-CN, G₁-COOR and G₁-COOH interestingly, no significant differences exist in the estimated activation energies between G₁-CN (E_{σ_{G₁-CN}} = 0.54 eV), G₁-COOR (E_{σ_{G₁-COOR}} = 0.58 eV) and G₁-COOH (E_{σ_{G₁-COOH}} = 0.58 eV). The VTF fitting²⁰ parameters of the conductivity plot (Fig. 2a) is tabulated in Table ST3. However, it is strongly felt that VTF fitting of the conductivity results is inappropriate for the present study. This is mainly attributed to the simpler chemical structure of the first generation dendrimers compared to higher generation dendrimers and polymers. The conductivity behaviour is correlated to temperature dependent fluidity (1/η, where η is the viscosity) shown in Fig. 2b.

The viscosities of PETIM dendrimers, calculated from the static viscosity versus shear rate measurements, are shown in Table ST2. The viscosity increases nearly two times from 0.15 Pa.s for

G₁-CN to 0.30 Pa.s for G₁-COOR. The viscosity at 30 °C for G₁-OH-0.10 M LiPF₆ and G₁-COOH-0.10 M LiPF₆ are even higher, being 4.5 Pa.s and 6.5 Pa.s respectively. The viscosity showed the following trend: $\eta_{\text{G}_1\text{-CN}} < \eta_{\text{G}_1\text{-COOR}} < \eta_{\text{G}_1\text{-OH}} < \eta_{\text{G}_1\text{-COOH}}$. The higher viscosity of ester dendrimer (G₁-COOR) compared to G₁-CN is attributed to more polar nature of COOR group compared to -CN group and steric hindrance exerted by the bulkier -COOR (R = *t*-butyl) group implying higher dragging force compared to the linear -CN in G₁-CN. Differences in viscosity between G₁-carboxyl groups (i.e. COOR, COOH and OH) and G₁-CN can also be accounted on the basis of the intra or inter molecular hydrogen bonding. The strength of hydrogen bond is significantly higher in G₁-COOH and G₁-OH resulting in significantly higher viscosity compared to G₁-CN and G₁-COOR. An increase in viscosity for carboxyl groups (G₁-COOR and G₁-COOH) and hydroxyl (G₁-OH) terminated dendrimers results in decrease in ionic conductivity compared to G₁-CN dendrimer. Activation energy of viscosities obtained by fitting the temperature dependent fluidity (1/η) (Fig. 2b) using Arrhenius equation are tabulated in Table ST2. Similar trend in activation energies for both temperature dependent conductivity and viscosity indicates that the underlying mechanism for conductivity and viscosity is thermally activated. However, the observed trends in viscosity cannot be correlated one-to-one with the conductivity trends. This is especially true for the -COOH terminated dendrimer. Logical interpretation of the observed trends in conductivity and (viscosity) can only be achieved by simultaneously studying the diffusion behavior of the various participating entities viz. Li⁺, PF₆⁻ and H (dendrimer). The G₁-COOH and G₁-OH have been excluded from additional studies as both have lower ionic conductivities and higher viscosities compared to G₁-CN and G₁-COOR in the measured temperature range. G₁-COOR is selected as the representative among the two carboxyl groups as an understanding of the mechanism in -COOR will also aid in accounting for the experimental observations in -COOH. Ion solvation in G₁-CN-LiPF₆ and G₁-COOR-LiPF₆ electrolytes is studied by FTIR spectroscopy at various salt concentrations (ranging from 0-0.1 M) and temperatures (from room temperature to 70 °C). The FTIR spectra for both the electrolytes in the wavenumber region 800-920 cm⁻¹ (normalized with respect to the highest intensity peak at 1118 cm⁻¹ for G₁-CN and 1154 cm⁻¹ for G₁-COOR) are shown in Fig. 3. The area under the peak is calculated by fitting the spectra with Gaussian function. Fig. 3a and 3b depicts the FTIR spectra of G₁-CN-xM LiPF₆ and G₁-COOR-xM LiPF₆ respectively with varying salt concentration (x) ranging from 0-0.10 M. Both pristine G₁-COOR and G₁-CN exhibit the characteristic symmetric stretching vibration of C-O-C group of the aliphatic ether present in the dendrimer core at 848 cm⁻¹ (splitting in C-O-C symmetric stretch in G₁-CN leads to additional band appeared at 830 cm⁻¹, possibly due to presence of two types of ether groups in core and periphery).²¹

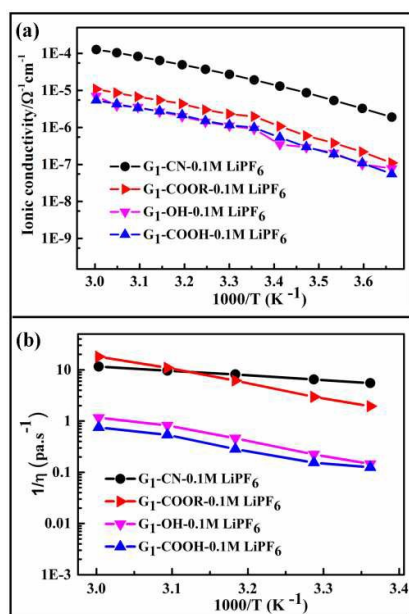


Fig. 2 (a) Temperature dependent ionic conductivity and (b) fluidity (η^{-1}) of G_1 -dendrimers with different peripheral functional groups.

This band is observed to merge with the strong band also appearing at 848 cm^{-1} corresponding to P-F vibration of the free PF_6 ion of the salt²² in G_1 -xM LiPF_6 . A weak band appearing at 875 cm^{-1} for G_1 -CN-xM LiPF_6 is assigned to the associated tri-dented ion pair of LiPF_6 salt and this is in good agreement with the earlier reports.²² With increasing salt concentration, the band area of the weaker band at 875 cm^{-1} is observed to intensify (inset of Fig. 3a) with respect to the stronger band (at 848 cm^{-1}) for G_1 -CN-xM LiPF_6 . This suggests presence of ion pairs in G_1 -CN-xM LiPF_6 . The intensity of this shoulder band at 875 cm^{-1} decreases with increasing temperature from RT to 70°C (Fig. 3c), signifying dissociation of ion pairs with increasing temperature. In the case of pure G_1 -COOR, the observed IR band at 898 cm^{-1} (Fig. 3b) is attributed to the C-C stretching frequencies of ester group (O-C-C) or ether group,²¹ which is affected by addition of the salt as well as temperature. No additional bands corresponding to ion-pairs are observed in G_1 -COOR-xM LiPF_6 (Fig. 3b) at various salt concentration, signifying facile salt dissociation in ester functionalized dendrimers. Stronger interaction of oxygen atom of ester group to Li^+ ion, compared to -CN group, leads to higher dissociation of ion pairs in G_1 -COOR. To support the FTIR observations, the Stokes equation (c/f Supporting Information) for both the dendrimers have been investigated (Fig. S3). Fig. S3 shows the product of dc-conductivity (related to number of free charges from Stokes equation) and viscosity at various temperatures for both the dendrimers. Constancy of this product (i.e. $nq^2/6\pi r$) in equation S1 in ESI) at various temperatures for G_1 -COOR signifies no change in free charges with increase of temperature, which is true for electrolyte with a fully dissociated salt. In case of G_1 -CN, an increase in free charges is observed with increase in temperature (in Fig. S3 in

ESI), which is attributed to an increase in salt dissociation with increasing temperature.

The self-diffusion coefficients, characterizing long range macroscopic transport of ^7Li , ^{19}F and ^1H nuclei are obtained from multinuclear PFG-NMR experiment using $\ln I/I_0 = -D^{\text{NMR}} \gamma^2 (\Delta \delta / 3) l^2 g^2$,²³ where I and I_0 are the signals in the presence and absence of the gradient respectively, γ is the gyromagnetic ratio of the nucleus studied, Δ is the interval between the gradient pulses, δ is the length of the gradient pulse, and g is the magnitude of the gradient pulse. Self-ionic diffusion coefficients in the temperature range (0 - 60°C) are shown in Fig. 4a.

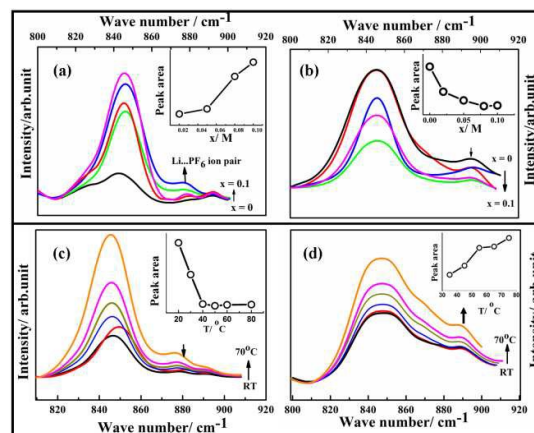


Fig. 3 FTIR spectra of G_1 -CN- LiPF_6 (a) and G_1 -COOR- LiPF_6 (b) at different salt concentrations [$x= 0$ (black), 0.01 (red), 0.02 (magenta), 0.05 (green), 0.1 (blue)]. FTIR spectra of G_1 -CN- LiPF_6 (c) and G_1 -COOR- LiPF_6 (d) at temperatures [$T= \text{RT}$ to 70°C , with $x= 0.1$]. [$T= \text{RT}$ (black), 30°C (red), 40°C (blue), 50°C (green), 60°C (magenta), 70°C (orange)].

The G_1 -CN- 0.1 M LiPF_6 exhibits much higher ^1H diffusion coefficients (varying from $1.9 \times 10^{-12}\text{ m}^2\text{ s}^{-1}$ - $6.3 \times 10^{-11}\text{ m}^2\text{ s}^{-1}$ between 0 to 60°C), nearly one order in magnitude higher compared to G_1 -COOR- 0.1 M LiPF_6 ($2.5 \times 10^{-13}\text{ m}^2\text{ s}^{-1}$ - $1.8 \times 10^{-11}\text{ m}^2\text{ s}^{-1}$ between 10 to 60°C). Following Stokes-Einstein equation ($D = kT(6\pi\eta r_s)^{-1}$, where η , D , r_s are viscosity, self-diffusion coefficient and effective hydrodynamic (Stokes) radius respectively), higher viscosity (0.3 Pa.s) of G_1 -COOR- 0.1 M LiPF_6 compared to G_1 -CN- 0.1 M LiPF_6 (0.15 Pa.s) results in lower ^1H diffusion coefficients for the ester dendrimer. ^{19}F self-diffusion coefficients for both the G_1 -CN- 0.1 M LiPF_6 ($1.36 \times 10^{-12}\text{ m}^2\text{ s}^{-1}$ - $7.8 \times 10^{-11}\text{ m}^2\text{ s}^{-1}$ between 0 to 60°C) and G_1 -COOR- 0.1 M LiPF_6 ($3.5 \times 10^{-13}\text{ m}^2\text{ s}^{-1}$ - $1.1 \times 10^{-11}\text{ m}^2\text{ s}^{-1}$ between 20 to 60°C) are found to be in close proximity to their respective ^1H diffusion coefficients values. The similarities in diffusion coefficient values between ^{19}F and ^1H nuclei for both G_1 -COOR and G_1 -CN signify correlated PF_6 anion motion with the dendrimer molecules. Lower viscosity of G_1 -CN- 0.1 M LiPF_6 results in nearly one order higher ^{19}F diffusion coefficient for G_1 -CN- 0.1 M LiPF_6 ($1.3 \times 10^{-11}\text{ m}^2\text{ s}^{-1}$ at 30°C) compared to that of G_1 -COOR- 0.1 M LiPF_6 ($1.1 \times 10^{-12}\text{ m}^2\text{ s}^{-1}$ at 30°C). The estimated $R_{\text{PF}_6^-}$ ($= D_{\text{H}}/D_{\text{F}}$) for ^{19}F in G_1 -CN (0.6) and G_1 -COOR (0.8) supports a stronger solvent correlated PF_6 motion in G_1 -COOR compared to G_1 -CN. The reason behind this correlation is possibly due to stronger steric hindrance posed by bulkier *t*-butyl group to PF_6 mobility²⁴ in G_1 -COOR compared to linear -

CN in G_1 -CN. On the contrary, lithium-ion diffusion is not at all influenced by the viscosity. Similar values of ^7Li self-diffusion coefficients are observed in both cases ($2.0 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ - $5 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ between 30 to 60 °C). Contribution of each Li^+ and PF_6^- towards total effective conductivity for G_1 -CN, calculated following Nernst-Einstein equation^{25a, 23} ($\sigma_i = Nq^2(kT)^{-1}D_i$ where σ_i and D_i are dc-ionic conductivity and diffusion coefficient of the i^{th} ion type), are $1.2 \times 10^{-5} \Omega^{-1} \text{ cm}^{-1}$ and $4.9 \times 10^{-5} \Omega^{-1} \text{ cm}^{-1}$ respectively.

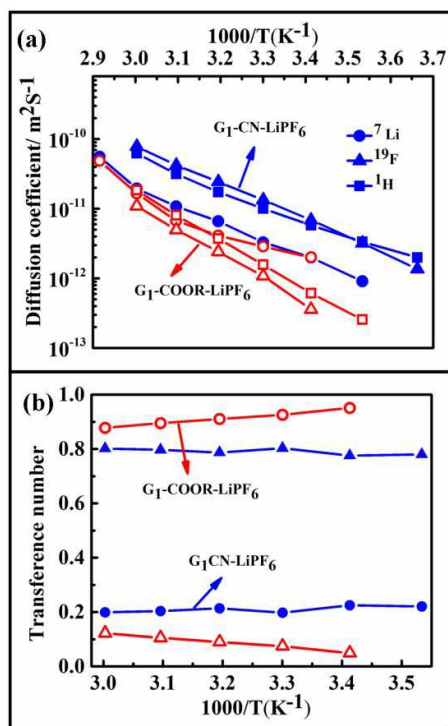


Fig. 4 (a) Self diffusion coefficients of ^1H (square), ^{19}F (triangle), ^7Li (circle) at various temperatures for G_1 -CN-0.1M LiPF_6 (blue, with closed symbols) and G_1 -COOR-0.1M LiPF_6 (red, with open symbols). (b) ^7Li and ^{19}F transference number of G_1 -CN-0.1M LiPF_6 (blue) and G_1 -COOR-0.1M LiPF_6 (red) at various temperatures.

Higher value of anion conductivity strongly suggests that G_1 -CN is predominantly an anion conductor. On the other hand, the lower contribution of ^{19}F ($\sigma = 3.9 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$ from NMR data) to total conductivity in G_1 -COOR compared to its ^7Li diffusion ($1.1 \times 10^{-5} \Omega^{-1} \text{ cm}^{-1}$) strongly suggests cation transport in ester dendrimer. Thus, trapping of anion by the peripheral bulkier ester group in G_1 -COOR makes it a single cationic conductor. Thus, the difference in effective ionic conductivity between G_1 -CN and G_1 -COOR is mainly due to the difference in the anionic conductivity between them. Manipulations in the chemical constitution of dendrimers via variation in the peripheral end group, which exert varying degree of steric hindrance to mobility of anion, results in transformation from anionic to cationic conductor. This approach is interesting as it becomes the organic analog to the concept of Heterogeneous Doping introduced by J. Maier.²⁶ Heterogeneous doping has been in the past successfully implemented to account for changes in effective ionic conductivity of solid-solid composites

comprising of dispersion of nanometer to micrometer sized oxide additives (e.g. Al_2O_3 , SiO_2) in a weak solid electrolyte e.g. LiI , TlCl_2 .²⁷ In this concept, the changes in conductivity has been attributed to the space-charge layer formed at the interface of the weak electrolyte-oxide insulator which directly influences the transition from an anion to cation conductor as demonstrated in $\text{TlCl}_2\text{-Al}_2\text{O}_3$. The concept with limited success was later extended to liquids where dispersions of fine oxide particle in liquid electrolyte lead to modest enhancements in the effective conductivity of the liquid.^{28, 29} To the best of our knowledge the heterogeneous doping concept has not yet been utilized to transform the nature of ion transport in liquids. It is envisaged that the approach presented here is the first of its kind to be adopted in the realm of liquids. This adopted approach is simpler and expected to be highly efficient and reproducible compared to addition of oxides, which display considerable non-uniformities in size and chemical functionality of the oxide additive.

In the case of G_1 -CN-0.1 M LiPF_6 , observed ^7Li diffusion coefficient is almost an order lower compared to its corresponding ^{19}F or ^1H diffusion coefficients signifying uncorrelated motion of lithium ion with the dendrimer molecule, as expected in the case of weak interaction between -CN and Li^+ . On the other hand, stronger binding between -COOR and Li^+ in G_1 -COOR- LiPF_6 , leads to close proximity of ^7Li to the ^1H diffusion coefficients at all temperature ranges, signifying a higher correlated motion of lithium-ion with the ester molecules. The correlated motion of Li^+ in G_1 -COOR is further supported by the estimate of the Stokes radius for lithium ($R_{\text{Li}} = D_{\text{H}}/D_{\text{Li}}$),^{25b} which is equal to 1.4 signifying an almost 1:1 co-ordination between G_1 -COOR and Li^+ .

The temperature dependent ionic diffusivity (Fig. 4a) is fitted using the Arrhenius equation and activation energies for ^7Li , ^1H and ^{19}F diffusions are tabulated in Table ST4 (c/f Supporting Information). The observed trend in activation energies for Li^+ and F^- diffusion is as follows: $E_{\text{D(Li)}}(G_1\text{-CN}) (= 0.53 \text{ eV}) \sim E_{\text{D(Li)}}(G_1\text{-COOR}) (= 0.53 \text{ eV})$ and $E_{\text{D(F)}}(G_1\text{-CN}) (= 0.50 \text{ eV}) < E_{\text{D(F)}}(G_1\text{-COOR}) (= 0.70 \text{ eV})$. This trend further suggests that the viscosity mainly influences the activation energy of ^{19}F diffusion and not ^7Li diffusion. Similarly, Li^+ diffusion activation energy ($E_{\text{D(Li)}}$) between G_1 -CN and G_1 -COOR leads to similar activation energy of conductivity, as obtained from ac-impedance spectroscopy (Fig. 2a). Hence, underlying mechanism of lithium conduction is similar to lithium diffusion mechanism and the difference in the effective conductivity is mainly determined by the differences in anion mobility. Temperature dependent viscosity (Fig 2b) and diffusion (Figure 4a) do not show a clear of VTF-like behaviour (i.e. curvature-like profile). So, employing the VTF analysis will not be appropriate for analyzing and correlating the diffusion, viscosity and conductivity data together. Additionally, first generation dendrimers are considered as viscous liquids with considerably simpler molecular architecture unlike the higher generation dendrimers (G_n , $n > 2$) or polymers. So, based on these aspects we considered a thermally activated diffusion, viscosity and conductivity (i.e. Arrhenius) rather than

segmental motion driven ion transport where VTF fitting will be more appropriate.

Transference number of ^7Li (t_+) and ^{19}F (t_-) are calculated from ionic diffusion coefficients following the equation: $t_+ = (1-t_-) = D_+(D_+ + D_-)^{-1}$ where D_+ and D_- are cationic and anionic diffusion coefficient respectively. Fig. 4b shows the temperature dependent cationic (Li^+) and anionic (PF_6^-) transference numbers for both $\text{G}_1\text{-COOR-0.1 M LiPF}_6$ and $\text{G}_1\text{-CN-0.1 M LiPF}_6$. $\text{G}_1\text{-COOR-0.1 M LiPF}_6$ exhibits extremely high lithium transference number (t_+) of 0.9 at all experimental temperatures, whereas Li^+ transference number of $\text{G}_1\text{-CN-0.1 M LiPF}_6$ is observed to be as low as 0.2, almost comparable to conventional PEO-based polymer electrolytes. Lower values of ^{19}F diffusion coefficient compared to Li^+ diffusion coefficient in $\text{G}_1\text{-COOR}$ electrolyte leads to extremely high Li^+ transference number, suggesting predominantly a cationic conductor. In comparison, $\text{G}_1\text{-CN}$ presents an opposite scenario, where a very high anionic transference number ($t_- = 0.8$) is observed compared to lithium, implying favorable anion transport. As discussed earlier, viscosity and steric hindrance of bulky peripheral $-\text{COOR}$ group affect mobility of larger anions and this trapping effect results in extremely high Li^+ transference number in $\text{G}_1\text{-COOR}$ in spite of the lower conductivity compared to $\text{G}_1\text{-CN}$ electrolyte. A significant difference in cationic transference number between $\text{G}_1\text{-CN}$ ($t_+ = 0.2$) and $\text{G}_1\text{-COOR}$ ($t_+ = 0.9$) further suggests that the present approach is highly effective in manipulating the nature of ion transport in dendrimer electrolytes. We attempted the estimation of transference number of Li^+ ion using the electrochemical method, proposed by Evans, Vincent, Bruce.^{20a, 30} This method has been predominantly employed to estimate cation transference number of liquid and polymer electrolytes. The molecular solvent-based liquid and polymer electrolytes exhibit both cation and anion conductivity in one system. The transference number of one ion type is usually greater than the other however, both are appreciably high and contributions to conductivity from the minority carrier cannot be neglected. So, the $\text{G}_1\text{-dendrimer}$ electrolytes do not exactly match the criteria for applicability of this method. The t_+ for $\text{G}_1\text{-CN-0.1 M LiPF}_6$ is estimated to be ≈ 0.4 which was higher compared to our estimates from NMR ($t_+ = 0.2$). Thus, both electrochemical and NMR measurements conclude that the $\text{G}_1\text{-CN}$ is an anion conductor. On the other hand, the t_+ of $\text{G}_1\text{-COOR-LiPF}_6$, estimated was 0.3 instead of 0.9 as predicted from the diffusion NMR measurements. The reason for wide discrepancy between the values in $\text{G}_1\text{-COOR}$ is due to combination of various factors. Higher viscosity leads to slower anion kinetics during polarization. Extremely slow anion diffusion coefficient also leads to uncertainties in maintaining the necessary condition of zero anion flux in the steady state. At this juncture, the possibility of an imminent application of the novel $\text{G}_1\text{-dendrimer}$ electrolyte in an electrochemical device is remote and non-trivial. However, it is strongly envisaged that the present dendrimer and similar such systems will have strong implications in various applications such as rechargeable batteries, sensors and actuators. The present dendrimers exhibit very high anion and cation transference number with the conductivities being at par with many polymer-based single ion conductors.^{10a, 19} The

remarkably high cation transference number ($t_+ = 0.9$) of $\text{G}_1\text{-COOR-LiPF}_6$ prompted us to perform electrochemical characterizations for potential application as electrolyte or as a co-solvent in rechargeable batteries. We discuss here some of the studies which may trigger electrolyte designs based on dendrimer, in general polymeric systems for rechargeable batteries based on lithium. The cell configurations and electrode assemblies employed for the studies are exactly similar to those used for molecular based solvent electrolytes.

Electrochemical potential window of $\text{G}_1\text{-CN-LiPF}_6$ and $\text{G}_1\text{-COOR-LiPF}_6$ electrolytes are studied via cyclic voltammetry with $\text{Li}|\text{G}_1\text{-Dendrimer-LiPF}_6|\text{SS}$ (stainless steel) cell configuration at scan rate of 1 mVs^{-1} and represented in Fig. 5a and 5b respectively. The cyclic voltammograms clearly shows that the $\text{G}_1\text{-CN}$ system does not support stable reversible cycling of Li , whereas, $\text{G}_1\text{-COOR}$ shows lithium stripping peak (at $\sim 2\text{V}$) followed by reductive deposition too. The higher cathodic (deposition currents) currents observed for $\text{G}_1\text{-CN}$ as compared to $\text{G}_1\text{-COOR}$, are consistent with higher conductivity of $\text{G}_1\text{-CN}$ compared to $\text{G}_1\text{-COOR}$. Improved reversibility in lithium cycling for $\text{G}_1\text{-COOR}$ compared to $\text{G}_1\text{-CN}$ is consequence of higher lithium transference number and faster ionic diffusion at lithium electrode. Both of these dendrimers show stable electrochemical window of 4 V as observed from cyclic voltammetry.

The electrochemical stability of $\text{G}_1\text{-COOR-LiPF}_6$ and $\text{G}_1\text{-CN-LiPF}_6$ electrolytes at lithium metal interfaces are investigated over a period of 35 days by ac-impedance spectroscopy in a lithium symmetrical $\text{Li}|\text{G}_1\text{-Dendrimer}|\text{Li}$ cell configuration, as shown in Fig. 5c. The lithium interface resistance (R_{Li}) is evaluated from the Nyquist plots as shown in Fig. S4. The lithium interfacial resistance (R_{Li}) of $\text{G}_1\text{-COOR-0.1 M LiPF}_6$ on the first day ($5.4 \times 10^4 \Omega$) is higher than that of $\text{G}_1\text{-CN-0.1 M LiPF}_6$ ($2.7 \times 10^4 \Omega$). However, a sudden increase in interfacial resistance is observed in case of $\text{G}_1\text{-CN-LiPF}_6$ after the 15th day. At the 30th day, R_{Li} of $\text{G}_1\text{-CN-0.1 M LiPF}_6$ increased to $2.2 \times 10^5 \Omega$ (10 times increase in magnitude compared to day 1). On the other hand, the $\text{G}_1\text{-COOR}$ electrolyte displayed a marginal increase over the same period reaching the value of $7.7 \times 10^4 \Omega$ on the 30th day (1.3 times increase in magnitude). This result indicates a slower rate of growth of the passivation layer at the lithium interface for $\text{G}_1\text{-COOR-0.1 M LiPF}_6$ compared to $\text{G}_1\text{-CN-0.1 M LiPF}_6$. The improved stability can be directly attributed to the high t_+ in $\text{G}_1\text{-COOR-0.1 M LiPF}_6$ which improves the charge transfer kinetics at the electrode|electrolyte interface. Following this, galvanostatic charge/discharge cycling measurements are performed (rate = $C/10$). The pristine dendrimer-salt system i.e. $\text{G}_1\text{-COOR-LiPF}_6$ (and $\text{G}_1\text{-CN-LiPF}_6$) exhibited poor galvanostatic cycling. The capacity faded to very low values within a few cycles. We attribute the failure to the high viscosity of the pristine dendrimer-salt system which resulted in poor charge kinetics at the electrode|electrolyte interface.

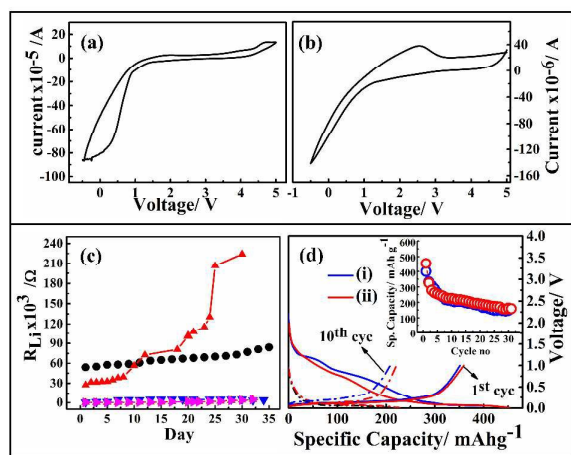


Fig. 5 Cyclic voltammogram of G_1 -CN-0.1M $LiPF_6$ (a) and G_1 -COOR-0.1M $LiPF_6$ (b) with stainless steel as working and lithium as reference and counter electrode. (c) Lithium interface stability of G_1 -CN (black circle), G_1 -COOR (red triangle), 50% G_1 -CN-(EC-DMC) (pink triangle), 50% G_1 -COOR-(EC-DMC) (blue triangle) dendrimer electrolytes. (d) Battery cycling performance of ternary 50% G_1 -CN-(EC-DMC- $LiPF_6$) (i) (blue) and 50% G_1 -COOR-(EC-DMC- $LiPF_6$) (ii) (red) electrolyte with Li/electrolyte/Graphite cell configuration at C/10 constant current rate. Inset figure shows specific capacity ($mAhg^{-1}$) vs cycle number for both ternary electrolytes.

Following the unsatisfactory battery cycling of the pristine dendrimer electrolytes, the cells are assembled with a mixture (by volume) containing 50% ethylene carbonate (EC)-dimethyl carbonate (DMC) (EC: DMC = 1:1 by v/v) and 50% of G_1 -COOR (G_1 -CN) and $LiPF_6$. The G_1 -COOR-EC-DMC- $LiPF_6$ (as well as G_1 -COOR-EC-DMC- $LiPF_6$) exhibited a voltage stability of 3 V with stainless steel (as working electrode) and lithium foil (Aldrich) as the counter and reference electrodes (Fig S5). The lithium metal is passivated even better in the case of G_1 -COOR-EC-DMC (or G_1 -CN-EC-DMC) compared to the pristine dendrimers. No significant change in the interface resistance is observed in the case of the ternary mixture G_1 -COOR-EC-DMC (and G_1 -CN-EC-DMC) (Fig. 5c). This strongly suggests that the G_1 -dendrimers with further chemical design modifications (leading to lower viscosity) can be employed as both alternative electrolyte and electrolyte additives in conventional liquid electrolytes. With regard to the latter issue, there have been a few interesting reports on boron-based additives³¹ aimed at stabilizing both the cathode/anode|electrolyte interfaces. While the boron-based additives aid in electron transport, the present dendrimer aid in ion conductivity. Hence, to the best of our knowledge the PETIM dendrimers are the first of its kind where the additive stabilizes the electrode|electrolyte interface via promotion of ion transport.

Fig. 5d represents the galvanostatic cycling performance of G_1 -CN-EC-DMC- $LiPF_6$ and 50% G_1 -COOR-EC-DMC- $LiPF_6$ with graphite as working electrode and lithium metal as reference and counter electrode respectively. The charge and discharge cycling are done at a constant current rate at C/10 over voltage ranges (0-2.5) V for dendrimers. In Fig. 5b, the first discharge curve shows two distinct reductive plateau in the range (0.5-0.8) V and (0.9-1.5) V corresponding to reductive degradation of both EC solvent (SEI formation) via single and double reduction process,³² which vanishes on further cycling in lithium insertion process. The broad plateau at (0.5-0.8) V

signifies decomposition of G_1 -CN molecule at the graphite surface. The charge plateau appears at 0.18 V corresponding to lithium de-insertion processes. The appearance of reductive and oxidative peaks agrees with cyclic voltammetry results (ESI Fig. S6). The G_1 -CN-EC-DMC- $LiPF_6$ shows a 1st discharge capacity of $400 mAhg^{-1}$ which decreases to $330 mAh g^{-1}$ in the 2nd cycle. In the 30th cycle, the capacity stabilized at $150 mAh g^{-1}$. The 1st charge capacity is equal to $354 mAh g^{-1}$ and this stabilized to $148 mAh g^{-1}$ in the 30th cycle. Coulombic efficiency increases from 88% (1st cycle) to 89% (5th cycle) and stabilized at 99% in the 30th cycle. The low Coulombic efficiency in the 1st cycle is a consequence of irreversible capacity loss during the formation of SEI film which stabilizes over successive cycling leading to higher coulombic efficiency over successive cycling. Similar cycling behavior for ternary G_1 -COOR-EC-DMC- $LiPF_6$ is observed except that the additional plateau at 0.9-1.5 V is absent in this case. The disappearance of this reductive plateau at (0.9-1.5) V indicates lesser decomposition of EC (suppression of two electron transfer process of EC)³² and better stability of G_1 -COOR dendrimer at the graphite electrode surface (clear from cyclic voltammetry in Fig. S5). The G_1 -COOR-EC-DMC- $LiPF_6$ specific capacity in the 1st discharge cycle is $453 mAhg^{-1}$ which decreases to $325 mAh g^{-1}$ in the 2nd cycle. In the 30th cycle, the capacity stabilized at $160 mAh g^{-1}$. The 1st charge capacity is $359 mAhg^{-1}$ and stabilized at $153 mAhg^{-1}$ in the 30th cycle. Coulombic efficiency increases from 79% (1st cycle) to 85% (5th cycle) and eventually stabilizing at 96% in the 30th cycle. Thus, the ternary dendrimer electrolyte can be successfully cycled with graphite electrode and may hold promise in lithium battery applications.

Conclusion

In conclusion, we have demonstrated here a novel dendrimer-salt based ion conductor with high ion transference for prospective applications as an electrolyte in diverse devices such as rechargeable batteries, sensors and actuators. The transference number achieved here is the highest reported so far in dendrimers and polymer electrolytes. We have comprehensively demonstrated for the first time that ion conductivity and transference number can be manipulated by varying the chemical nature of the dendrimer peripheral group. The chemical nature of the peripheral group completely determines the solvation i.e. quantum of free charge carriers, the mobility of the free charge carriers and the electrochemical properties. It is interesting to note that changes in peripheral chemical functional group which affects the viscosity of the solution do not at all influence the cation diffusivity. We anticipate similar observations for other alkali ions provided the anion remains same or bulkier than PF_6^- anion. In the case of other monovalent cations (K, Rb, Cs), factors specific to the metal-ions need to be considered to achieve similar trend in ion transport in dendrimer electrolytes. Given the advancements in polymer processing, it is strongly proposed that similar strategies as discussed here can also be adopted in designing novel solid polymers with a variety of metal salts single ion conducting polymer electrolytes.

Acknowledgements

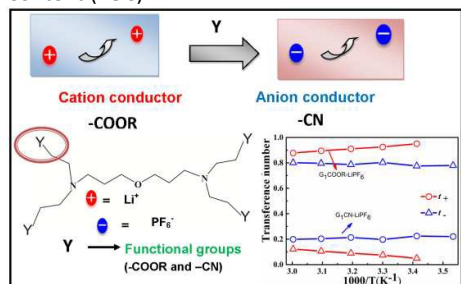
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Table of Content (TOC):



The proposed dendrimer based liquid electrolyte is a single-ion conductor where ion transport is altered by nature of chemical functionalities leading to large variation in anion diffusion and hence ionic transference number.