Dicationic Ionic Liquids based on Bis(4-oligoethyleneoxyphenyl) Viologen Bistriflimide Salts Exhibiting High Ionic Conductivities

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ABSTRACT

We report colossal conductivities, $\sigma_{dc} \sim 10^{-1.5} \cdot$S cm^{-1}, of new dicationic ionic liquids, close to the range of benchmark materials/electrolytes applied in fuel cells and batteries. The new ionic liquids consist of extended viologen bistriflimides containing oligoethyleneoxy groups, were prepared *via* Zinke reaction under mild conditions, and are excellent candidates as components in devices for energy conversion and storage applications.

Keywords: Extended viologen salts; Ionic liquids; Zincke reaction, Differential scanning calorimetry; Ionic conductivity, Dielectric impedance spectroscopy

Ionic liquids (ILs) are salts consisting of organic cations and inorganic/organic anions having melting transitions (T_m) lower than 100°C. Indeed, many ILs melt well below ambient temperatures, with typical glass transition temperatures (T_g) in the range from -93 to -53°C. They hold promise as engineered materials in a variety of modern fields, including green solvents or catalysts for chemical reactions [1,4], biocatalysts [5], biopolymers processing [6-9], active pharmaceutical ingredients in medicine [10], and electrolytes for batteries [11-13]. Multi-charged ILs and poly(ionic liquid)s exhibit a wider range of physical properties than their mono-charged analogues, e.g., higher density, T_g, T_m, surface tension and viscosity, due to their higher molecular weights [14-19]. These result in superior properties, such as, higher thermal stabilities [20-23], better antimicrobial activity [24], higher electrical capacities [25-27], better performance as stationary phases for gas chromatography [28-30], among others [31-36]. Multi-charged ILs are particularly attractive due to their combination of low viscosity (like traditional ILs) and high ionic conductivity (like poly(ionic liquid)s). The physical properties of multi-charged ILs can be fine-tuned by combining different cations and anions, with well-defined chemical structures that avoid polydispersity issues. Current multi-charged ILs range ammonium, phosphonium, imidazolium, pyridinium, pyrrolidinium, piperidinium, triazolium and 4,4′-bipyridinium (viologen) cations. The majority of these multi-charged ionic liquids are synthesized *via* quaternization S_N2 Menshutkin reactions, followed by metathesis of anions [14-38].

In the search of new ionic liquid electrolytes for energy applications, we have recently studied the conductivity of a series of multi-charged ionic liquids with different cationic structures, containing triflimide anions, $(Tf)_2N^-$ (see Fig. 1(a)) [39].

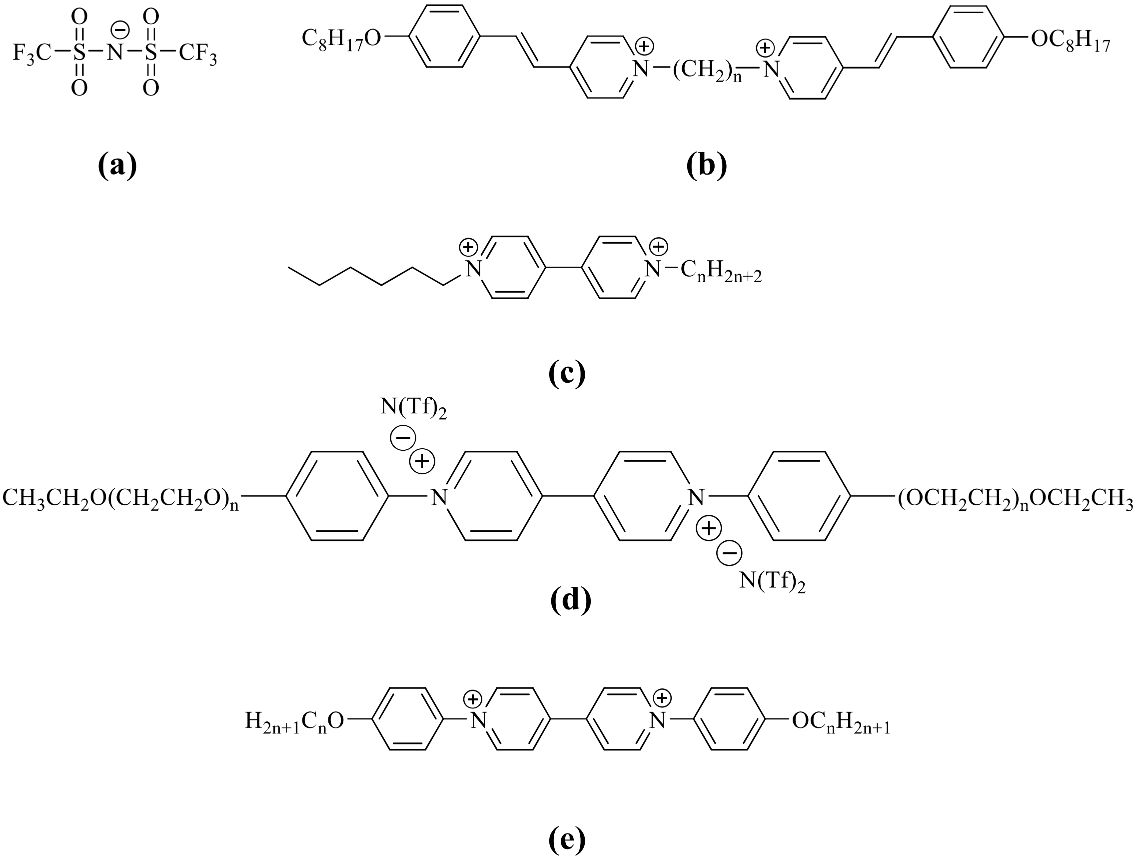

Fig. 1 Different cationic structures containing (a) triflimide anion, $(Tf)_2N$; (b) stilbazolium salts, *n* =10, 12 [39]; (c) asymmetric viologens, *n*= 7, 11, 14 [40]; (d) Ionic salts prepared in this work, ***1*** (*n*=1), ***2*** (*n*=2) and ***3*** (*n*=3); and (e) Alkoxy-terminated viologens [51].

We found that dicationic stilbazolium salts (refer to the structure in Fig. 1(b)) reached direct current conductivities in the $\sigma_{dc} \sim 10^{-4.5}$ S·cm^{-1} range, well above room temperature (T > 80 ºC) and activated by the larger free volume [39] available beyond their glass transitions, T_gs. On the other hand, we reported maximum values of σ_{dc}~$10^{-2.5}$ S·cm^{-1} for asymmetric viologen bistriflimide salts (refer to Fig. 1(c)) [40] associated with the formation of liquid crystalline smectic-T phases and correlated to short-range motions around the rod-like aromatic units [40]. It seems that the (close) location of the N^+ sites, and their capability to form π-π aggregates may benefit ionic conductivity. These results have prompted us to investigate new triflimide viologens with extended core structures, and herein we assess the conducting properties of new viologens, ***1*** to ***3***, prepared *via* Zincke reactions (refer to Fig. 1(d)).

Viologens and their multitude derivatives have already been postulated as functional materials in electrochromic devices, diodes and transistors, memory devices, molecular machines, and dye-sensitized solar cells [41-48]. The reason to introduce the oxyethylene(s) terminations is two-fold. On the one hand, we aim to offset (at least partially) the rigidity of the four-ring phenyl core (which could increase viscosity). Besides, the presence of polar chains can help delocalize the triflimide anions and avoid complexation, which would ultimately inhibit ion mobility [49].

The 4-oligoethyleneoxypheylanilines were prepared according to modified literature procedures [50,51]. The synthesis of bis-(4-oligoethyleneoxyphenyl)-4,4′-bipyridinium dichlorides (**P1-P3**) with different ethyleneoxy groups, is summarized in **Scheme 1** (SI). The method involved: (i) the aromatic nucleophilic substitution between the 1-chloro-2,4-dinitrobenzene and 4,4′-bipyridine in acetonitrile under reflux, to yield the so-called Zincke salts [52,53] (steps 1 and 2); and (ii) subsequent anionic ring opening and ring closing reactions (ANROC) with the corresponding 4-oligoethyleneoxypheylanilines, in N,N-dimethylacetamide (DMAc) at room temperature (steps 3 and 4). Detailed synthetic procedures and analyses are also given as Supplementary Information (SI). Lastly**, P1-P3** were converted to the **1-3** salts under study by metathesis with lithium triflimides in methanol [54] (step 5). Each of the prepared salts was in brown powdered form. The chemical structures of the intermediates and final products were confirmed by Fourier transform infrared (FT-IR) spectroscopy, ^{1}H, ^{13}C, and ^{19}F nuclear magnetic resonance (NMR) obtained in CD_3OD (**Figs. S1-S9**), and their purities were determined by elemental analysis. To our knowledge, these are the first examples of ionic liquids prepared *via* Zincke reactions.

The thermal properties and phase behavior of the new salts were determined by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and polarized optical microscopy (POM). The three salts display less than 5% weight loss up to 300 ºC (degradation temperatures, T_d~311-334 °C) under nitrogen atmosphere (**Fig. S10, Table S1**). Whilst it was expected that the bistriflimide ions conferred high thermal stabilities, the high T_d values confirm that the presence of flexible oxyethylene groups do not have a destabilizing effect on our salts.

Fig. 2 shows the DSC thermograms of the three salts, corresponding to their first heating scans obtained at 10 $°C \cdot min^{-1}$ rates. While **1** and **2** display first-order endotherms associated to crystal to crystal (**2**) and melting (**1** and **2**) processes, **3** only displays a glass transition at low temperature (T_g = -6 °C) [1-13]. According to these results, both **1** and **2** act as ionic liquids that melt on heating (as expected, an increase in the oxyethylene termination length reduces the melting point). The absence of first-order transitions in the corresponding thermogram indicates that **3** behaves like an amorphous salt, due to inhibition of crystalization at sufficiently long ethyleneoxy chains, n=3. It is worth noting that there are no further thermal events visible in subsequent heating and cooling scans of **1** and **2**, suggesting that crystallization of these samples must be a slow process, see **Figs. S11-S13.** The absence of liquid crystal behavior contrasts with the formation of smectic phases by analogous alkoxy-terminated ($n \geq 6$) viologens recently reported by our own group [54] and others [55-57]. Even though we could have expected that comparable lengths of terminal chains (refer to Fig. 1(e)) [51] would promote microphase separation and smectic behavior in **1-3**, the formation of stronger interactions by the ethyleneoxy groups may restrict the local mobility required to yield liquid crystallinity. The effect of the terminal chain lengths on nanosegregation between the polar chains and the aromatic cores in similar viologens is the object of further ongoing research.

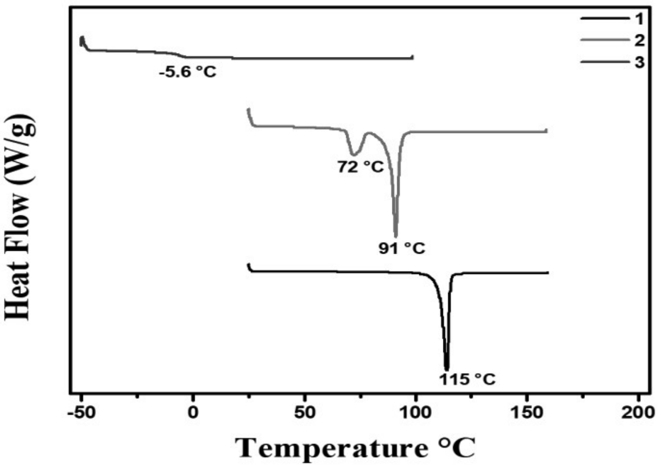

Fig. 2. DSC thermograms of **1-3** obtained at a heating rate of 10 °C·min^{-1} in nitrogen. Exo up.

We now focus on the conductivity response of the viologens under study, and **Fig. 3** shows their dielectric loss factor, ε'', obtained as a function of the temperature and frequency, and measured in isothermal steps on heating from room temperature, see the supplementary information for further details. The values are remarkably high for organic media, which is attributed to the strong polar character of ionic liquids and salts [40]. All double logarithmic ε'' plots show linear drops (with slopes ~-1) that denote the rise of direct current (DC) conductivity at sufficiently low frequencies [58]. This DC component overshadows any potential dielectric relaxation, even though some peaks are observed for **2** and **3** in **Fig. 3(b)** and **3(c),** respectively. For these ionic liquids, the isotherms shift with temperature, denoting thermal activation effects that will be reviewed later [59]. The salt **3,** on the other hand, depicts the highest ε'' values among the three salts, see **Fig. 3(c)**. The occurrence of direct current conductivity is confirmed by the formation of plateaus in the double logarithmic σ' vs f plots in **Fig. 4**, which have similar temperature dependences as the corresponding dielectric loss moduli depicted in **Fig. 3** [60,61]. The DC conductivity values, σ_{dc}, can be estimated by extrapolating the constant σ' ranges to $f \rightarrow 0$ at each temperature, and the resulting Arrhenius plots are shown in **Fig. 5.** The activation energies of the conductivity process from the Arrhenius plot, E_a, are calculated using the equation; $\sigma_{dc} = \sigma_0 \exp(E_a/RT)$, where R is the gas constant, 8.31 $J \cdot mol^{-1} \cdot K^{-1}$, T is the absolute temperature, and σ_o is a pre-exponential term.

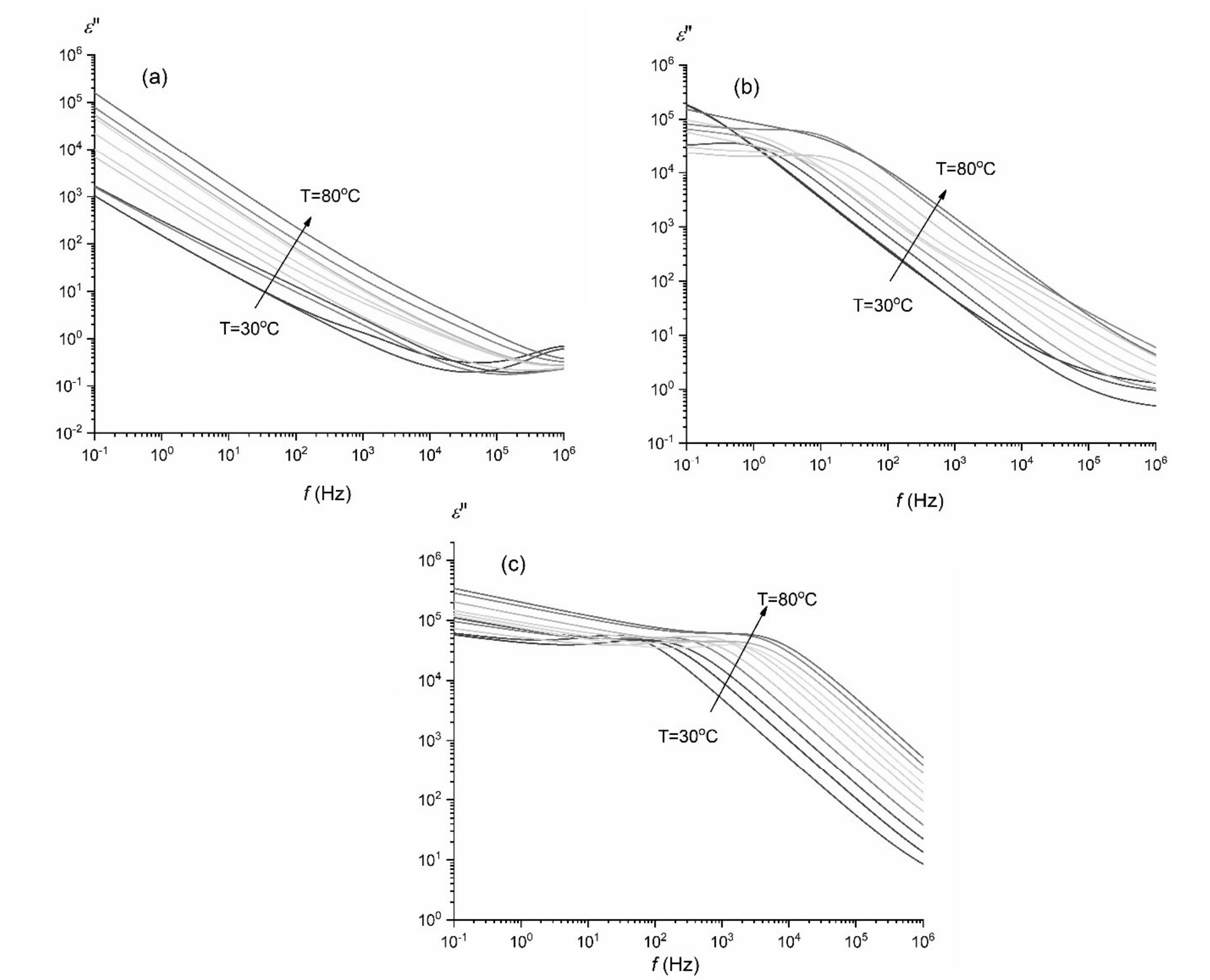

Fig. 3. Dielectric loss modulus, ε'', obtained at isothermal steps for **1** (a), **2** (b), and **3** (c), on heating from room temperature (see arrows).

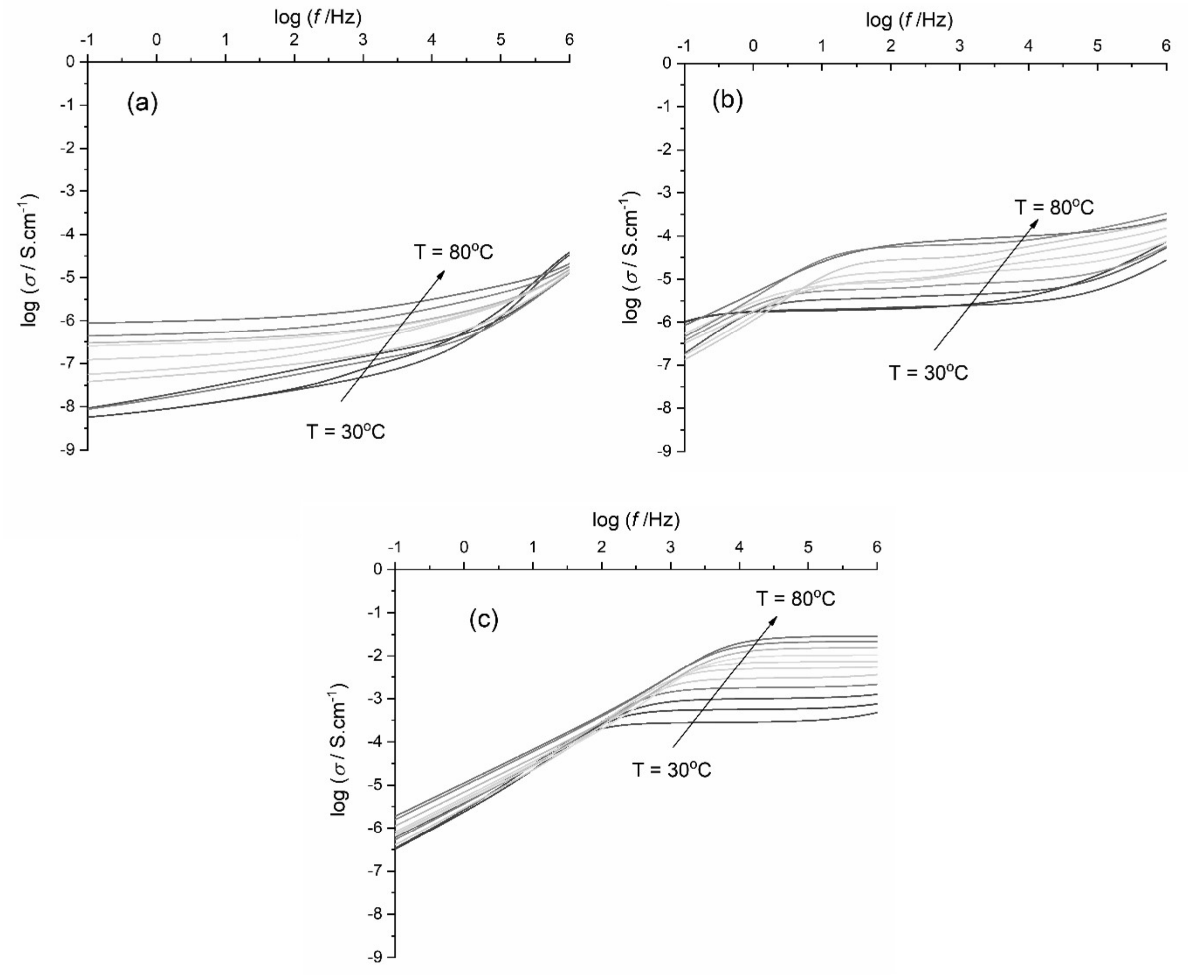

Fig. 4. Real component of the complex conductivity, σ', obtained at isothermal steps for **1** (a), **2** (b) and **3** (c), on heating from room temperature (see arrows).

The Cole-Cole plot of **3** is shown in **Fig.S14**. The AC oscillation voltage was 0.5 V. The results indicate that longer ethyleneoxy terminal chains promote conductivity in the salts. Indeed, **3** shows exceptional σ_{dc} values (between $10^{-3.5}$ and $10^{-1.5}$ $S\cdot cm^{-1}$) comparable to bench electrolytes used in fuel cells [62] and batteries [63]. To our knowledge, this material is one of the few examples of an organic salt exhibiting such large conductivities under anhydrous conditions, and at mild temperatures, even close to room temperature [11,64-68]. The activation energies estimated from the Arrhenius plots of the samples are $E_a = 95.\ 9$ $kJ\cdot mol^{-1}$ for **1**; $E_a = 84.5$ $kJ\cdot mol^{-1}$ for **2**; and E_a

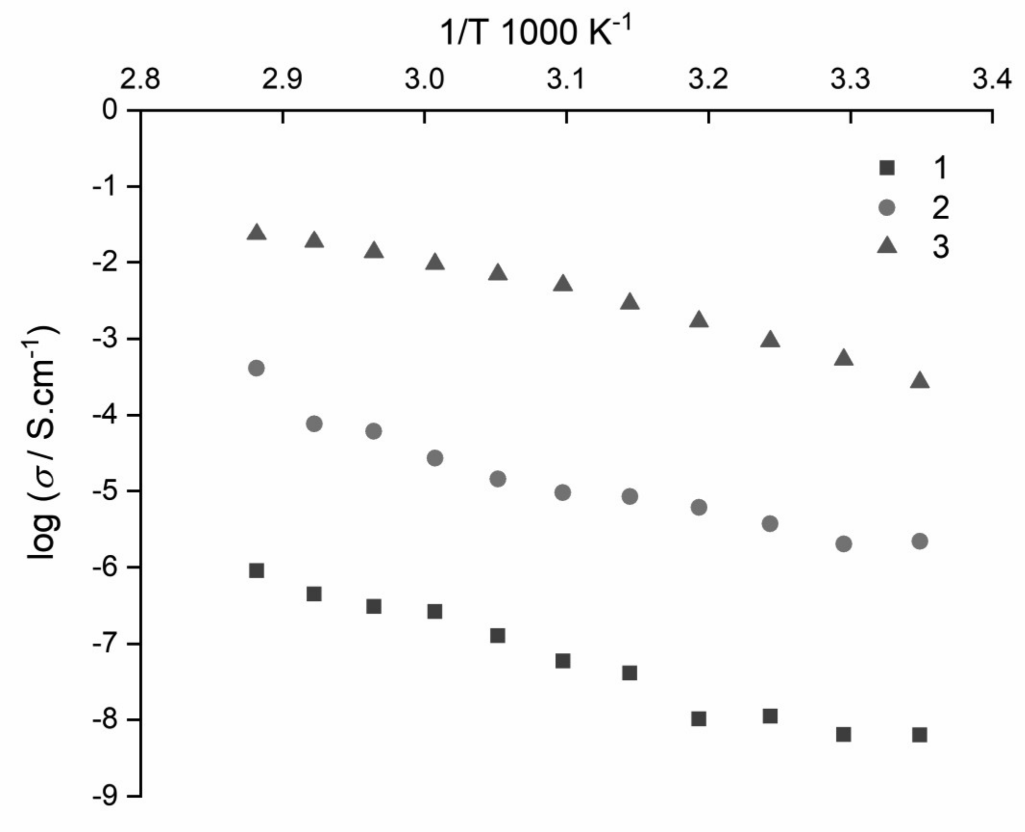

Fig. 5 Arrhenius plots (base 10) of **1-3** corresponding to the direct current conductivity, σ_{dc}, estimated from the plateaus in the double logarithmic σ' *vs* frequency plots.

= 79.4 kJ·mol^{-1}, for **3.** These values are considerably high for locally activated processes and are in good agreement with the occurrence of so-called β-relaxations, involving the rotation of rod-like molecules (extended viologen moieties) around their long axis within the crystal lattice [40,69]. It seems that, when the -(CH_2CH_2O)- terminal chains are short, the conductivity process is dominated (and partially hindered) by the motions around the bulky four-phenyl core [58,70-72]. In salt **3,** alternatively, the plasticizing effect of the longer terminal chains endows in the formation of a rubbery phase above its low glass transition (T_g ~ -6 ºC, see **Fig. 2**), with large free volumes that facilitate ionic motion (resulting in high σ_{dc} values and slightly lower activation energy) [73-74].

In conclusion, we have prepared new viologens using Zincke reactions, resulting in ionic liquids and salts with strong dielectric responses, attributed to the presence of both flexible oxyethylene groups and triflimide ions. Sufficiently long terminal chains promote exceptionally high ionic conductivities at room temperature, comparable to benchmark electrolytes used commercially, highlighting their potential use in energy devices, such as, fuel cells, batteries, supercapacitors, or solar cells. This work opens new horizons for designing ionic liquids with tuned electrostatic interactions and nanostructures by extending the central rigid core, exchanging different cations, or modifying the length of the oxyethylene terminations.

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Dicationic Ionic Liquids based on Bis(4-oligoethyleneoxyphenyl) Viologen Bistriflimide Salts Exhibiting High Ionic Conductivities

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ABSTRACT

We report colossal conductivities, $\sigma_{dc} \sim 10^{-1.5} \cdot$S cm^{-1}, of new dicationic ionic liquids, close to the range of benchmark materials/electrolytes applied in fuel cells and batteries. The new ionic liquids consist of extended viologen bistriflimides containing oligoethyleneoxy groups, were prepared *via* Zinke reaction under mild conditions, and are excellent candidates as components in devices for energy conversion and storage applications.

Keywords: Extended viologen salts; Ionic liquids; Zincke reaction, Differential scanning calorimetry; Ionic conductivity, Dielectric impedance spectroscopy

Ionic liquids (ILs) are salts consisting of organic cations and inorganic/organic anions having melting transitions (T_m) lower than 100°C. Indeed, many ILs melt well below ambient temperatures, with typical glass transition temperatures (T_g) in the range from -93 to -53°C. They hold promise as engineered materials in a variety of modern fields, including green solvents or catalysts for chemical reactions [1,4], biocatalysts [5], biopolymers processing [6-9], active pharmaceutical ingredients in medicine [10], and electrolytes for batteries [11-13]. Multi-charged ILs and poly(ionic liquid)s exhibit a wider range of physical properties than their mono-charged analogues, e.g., higher density, T_g, T_m, surface tension and viscosity, due to their higher molecular weights [14-19]. These result in superior properties, such as, higher thermal stabilities [20-23], better antimicrobial activity [24], higher electrical capacities [25-27], better performance as stationary phases for gas chromatography [28-30], among others [31-36]. Multi-charged ILs are particularly attractive due to their combination of low viscosity (like traditional ILs) and high ionic conductivity (like poly(ionic liquid)s). The physical properties of multi-charged ILs can be fine-tuned by combining different cations and anions, with well-defined chemical structures that avoid polydispersity issues. Current multi-charged ILs range ammonium, phosphonium, imidazolium, pyridinium, pyrrolidinium, piperidinium, triazolium and 4,4′-bipyridinium (viologen) cations. The majority of these multi-charged ionic liquids are synthesized *via* quaternization S_N2 Menshutkin reactions, followed by metathesis of anions [14-38].

In the search of new ionic liquid electrolytes for energy applications, we have recently studied the conductivity of a series of multi-charged ionic liquids with different cationic structures, containing triflimide anions, $(Tf)_2N^-$ (see Fig. 1(a)) [39].

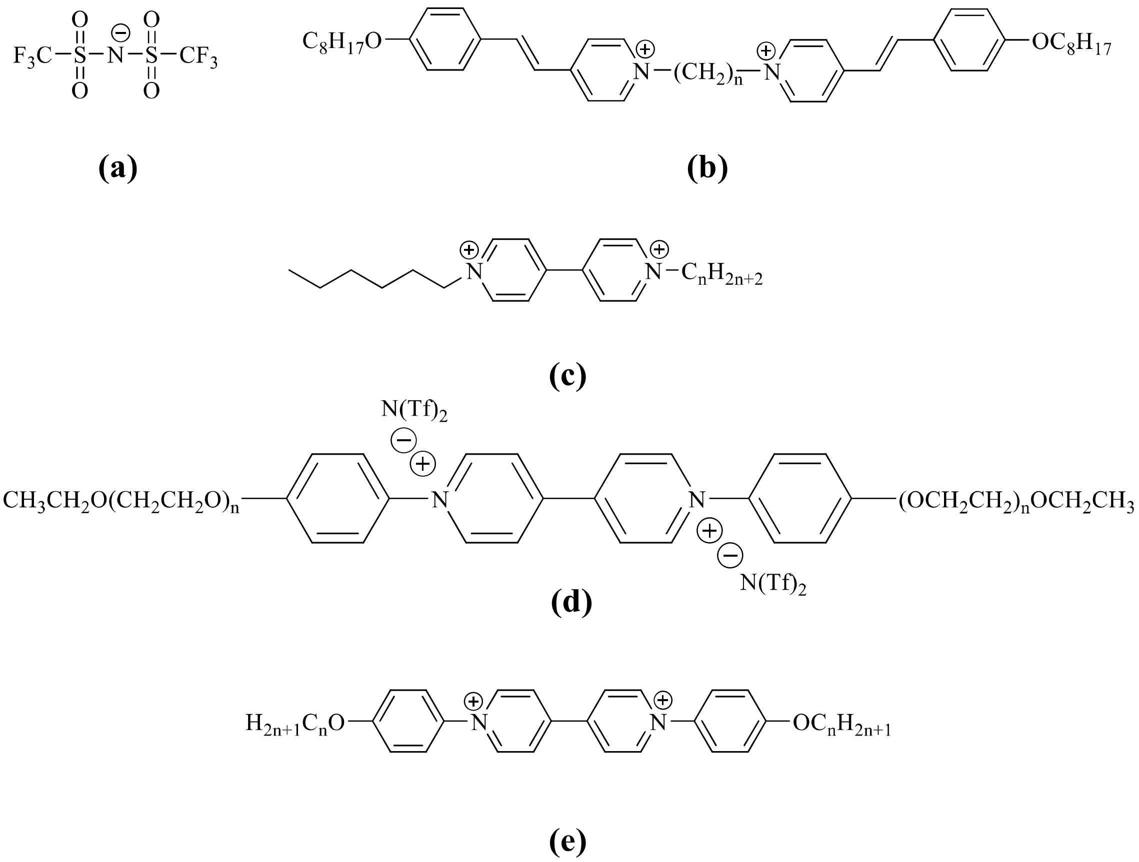

Fig. 1 Different cationic structures containing (a) triflimide anion, (Tf)2N; (b) stilbazolium salts, *n* =10, 12 [39]; (c) asymmetric viologens, *n*= 7, 11, 14 [40]; (d) Ionic salts prepared in this work, ***1*** (*n*=1), ***2*** (*n*=2) and ***3*** (*n*=3); and (e) Alkoxy-terminated viologens [51].

We found that dicationic stilbazolium salts (refer to the structure in Fig. 1(b)) reached direct current conductivities in the $\sigma_{dc} \sim 10^{-4.5}$ S·cm^{-1} range, well above room temperature (T > 80 ºC) and activated by the larger free volume [39] available beyond their glass transitions, T_gs. On the other hand, we reported maximum values of σ_{dc}~$10^{-2.5}$ S·cm^{-1} for asymmetric viologen bistriflimide salts (refer to Fig. 1(c)) [40] associated with the formation of liquid crystalline smectic-T phases and correlated to short-range motions around the rod-like aromatic units [40]. It seems that the (close) location of the N$^+$ sites, and their capability to form π-π aggregates may benefit ionic conductivity. These results have prompted us to investigate new triflimide viologens with extended core structures, and herein we assess the conducting properties of new viologens, ***1*** to ***3***, prepared *via* Zincke reactions (refer to Fig. 1(d)).

Viologens and their multitude derivatives have already been postulated as functional materials in electrochromic devices, diodes and transistors, memory devices, molecular machines, and dye-sensitized solar cells [41-48]. The reason to introduce the oxyethylene(s) terminations is two-fold. On the one hand, we aim to offset (at least partially) the rigidity of the four-ring phenyl core (which could increase viscosity). Besides, the presence of polar chains can help delocalize the triflimide anions and avoid complexation, which would ultimately inhibit ion mobility [49].

The 4-oligoethyleneoxypheylanilines were prepared according to modified literature procedures [50,51]. The synthesis of bis-(4-oligoethyleneoxyphenyl)-4,4′-bipyridinium dichlorides (**P1-P3**) with different ethyleneoxy groups, is summarized in **Scheme 1** (SI). The method involved: (i) the aromatic nucleophilic substitution between the 1-chloro-2,4-dinitrobenzene and 4,4′-bipyridine in acetonitrile under reflux, to yield the so-called Zincke salts [52,53] (steps 1 and 2); and (ii) subsequent anionic ring opening and ring closing reactions (ANROC) with the corresponding 4-oligoethyleneoxypheylanilines, in N,N-dimethylacetamide (DMAc) at room temperature (steps 3 and 4). Detailed synthetic procedures and analyses are also given as Supplementary Information (SI). Lastly**, P1-P3** were converted to the **1-3** salts under study by metathesis with lithium triflimides in methanol [54] (step 5). Each of the prepared salts was in brown powdered form. The chemical structures of the intermediates and final products were confirmed by Fourier transform infrared (FT-IR) spectroscopy, ^{1}H, ^{13}C, and ^{19}F nuclear magnetic resonance (NMR) obtained in CD_3OD (**Figs. S1-S9**), and their purities were determined by elemental analysis. To our knowledge, these are the first examples of ionic liquids prepared *via* Zincke reactions.

The thermal properties and phase behavior of the new salts were determined by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and polarized optical microscopy (POM). The three salts display less than 5% weight loss up to 300 ºC (degradation temperatures, T_d~311-334 °C) under nitrogen atmosphere (**Fig. S10, Table S1**). Whilst it was expected that the bistriflimide ions conferred high thermal stabilities, the high T_d values confirm that the presence of flexible oxyethylene groups do not have a destabilizing effect on our salts.

Fig. 2 shows the DSC thermograms of the three salts, corresponding to their first heating scans obtained at 10 $°C\cdot min^{-1}$ rates. While **1** and **2** display first-order endotherms associated to crystal to crystal (**2**) and melting (**1** and **2**) processes, **3** only displays a glass transition at low temperature (T_g = -6 °C) [1-13]. According to these results, both **1** and **2** act as ionic liquids that melt on heating (as expected, an increase in the oxyethylene termination length reduces the melting point). The absence of first-order transitions in the corresponding thermogram indicates that **3** behaves like an amorphous salt, due to inhibition of crystalization at sufficiently long ethyleneoxy chains, n=3. It is worth noting that there are no further thermal events visible in subsequent heating and cooling scans of **1** and **2**, suggesting that crystallization of these samples must be a slow process, see **Figs. S11-S13.** The absence of liquid crystal behavior contrasts with the formation of smectic phases by analogous alkoxy-terminated ($n \geq 6$) viologens recently reported by our own group [54] and others [55-57]. Even though we could have expected that comparable lengths of terminal chains (refer to Fig. 1(e)) [51] would promote microphase separation and smectic behavior in **1-3**, the formation of stronger interactions by the ethyleneoxy groups may restrict the local mobility required to yield liquid crystallinity. The effect of the terminal chain lengths on nanosegregation between the polar chains and the aromatic cores in similar viologens is the object of further ongoing research.

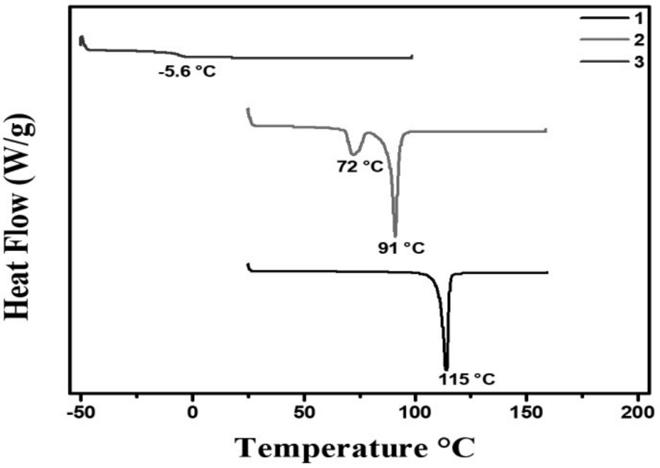

Fig. 2. DSC thermograms of **1-3** obtained at a heating rate of 10 °C·min^{-1} in nitrogen. Exo up.

We now focus on the conductivity response of the viologens under study, and **Fig. 3** shows their dielectric loss factor, ε'', obtained as a function of the temperature and frequency, and measured in isothermal steps on heating from room temperature, see the supplementary information for further details. The values are remarkably high for organic media, which is attributed to the strong polar character of ionic liquids and salts [40]. All double logarithmic ε'' plots show linear drops (with slopes ~-1) that denote the rise of direct current (DC) conductivity at sufficiently low frequencies [58]. This DC component overshadows any potential dielectric relaxation, even though some peaks are observed for **2** and **3** in **Fig. 3(b)** and **3(c),** respectively. For these ionic liquids, the isotherms shift with temperature, denoting thermal activation effects that will be reviewed later [59]. The salt **3,** on the other hand, depicts the highest ε'' values among the three salts, see **Fig. 3(c)**. The occurrence of direct current conductivity is confirmed by the formation of plateaus in the double logarithmic σ' vs f plots in **Fig. 4**, which have similar temperature dependences as the corresponding dielectric loss moduli depicted in **Fig. 3** [60,61]. The DC conductivity values, σ_{dc}, can be estimated by extrapolating the constant σ' ranges to $f \rightarrow 0$ at each temperature, and the resulting Arrhenius plots are shown in **Fig. 5.** The activation energies of the conductivity process from the Arrhenius plot, E_a, are calculated using the equation; $\sigma_{dc} = \sigma_0 \exp(E_a/RT)$, where R is the gas constant, 8.31 $J\cdot mol^{-1}\cdot K^{-1}$, T is the absolute temperature, and σ_o is a pre-exponential term.

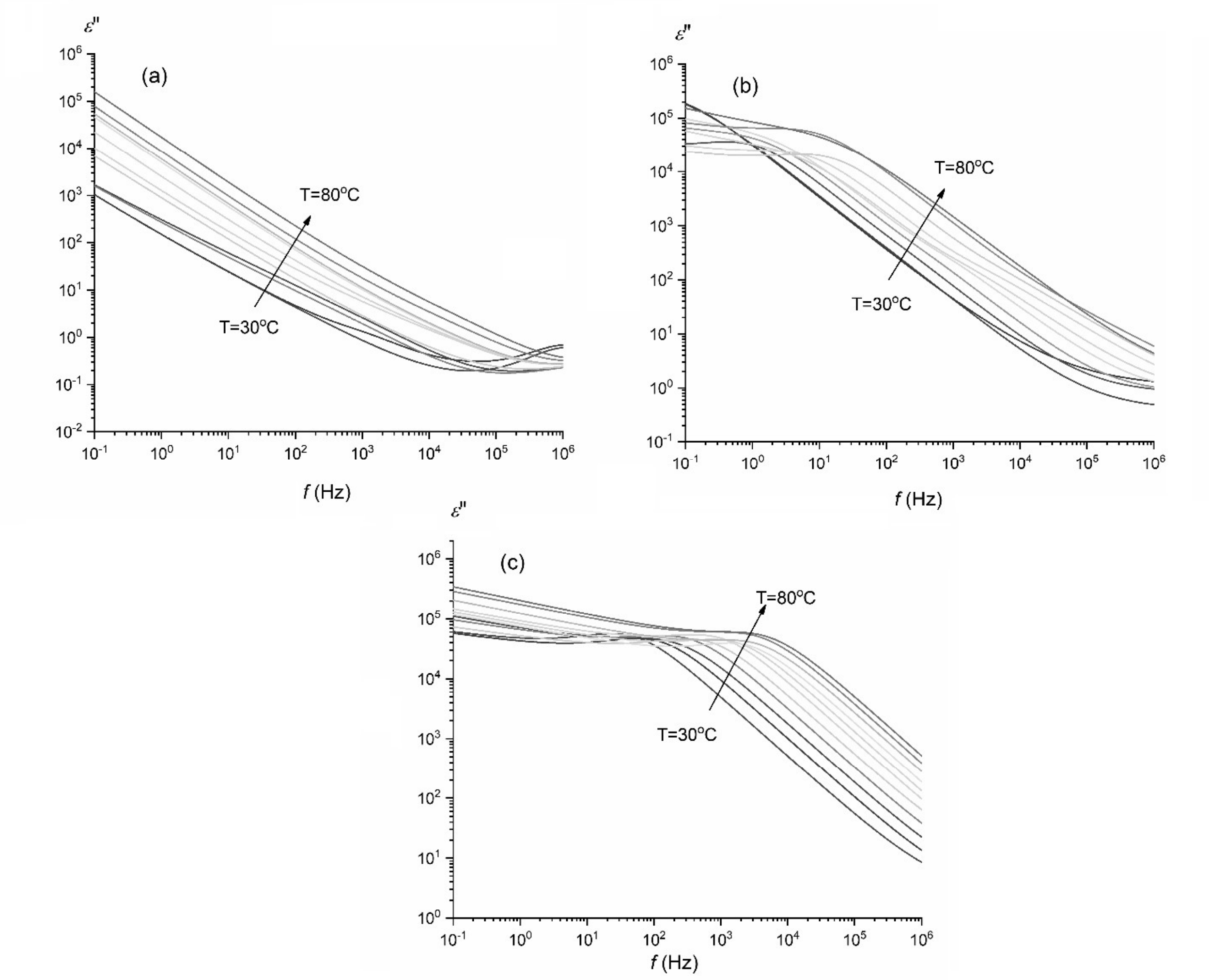

Fig. 3. Dielectric loss modulus, ε'', obtained at isothermal steps for **1** (a), **2** (b), and **3** (c), on heating from room temperature (see arrows).

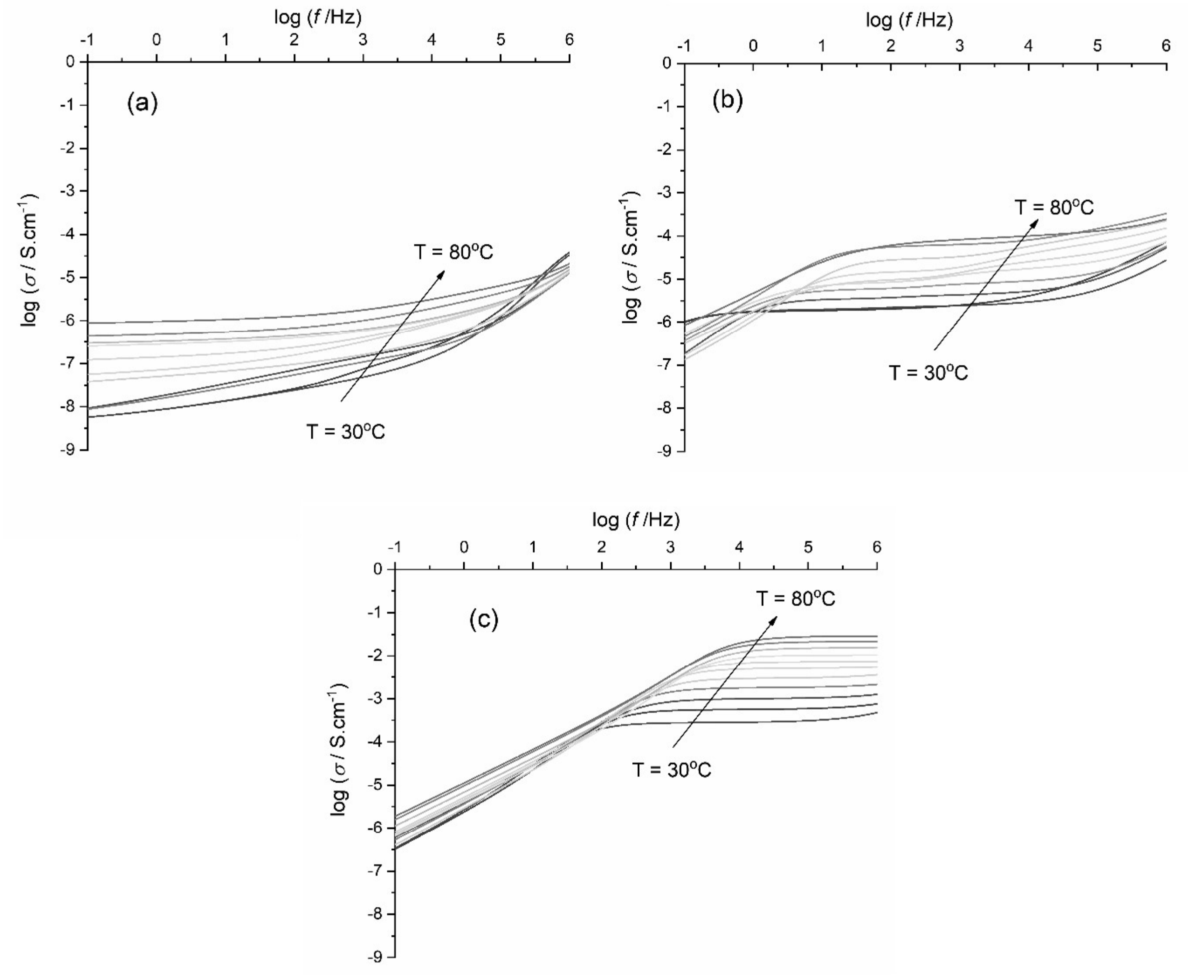

Fig. 4. Real component of the complex conductivity, σ', obtained at isothermal steps for **1** (a), **2** (b) and **3** (c), on heating from room temperature (see arrows).

The Cole-Cole plot of **3** is shown in **Fig.S14**. The AC oscillation voltage was 0.5 V. The results indicate that longer ethyleneoxy terminal chains promote conductivity in the salts. Indeed, **3** shows exceptional σ_{dc} values (between $10^{-3.5}$ and $10^{-1.5}$ $\mathrm{S \cdot cm^{-1}}$) comparable to bench electrolytes used in fuel cells [62] and batteries [63]. To our knowledge, this material is one of the few examples of an organic salt exhibiting such large conductivities under anhydrous conditions, and at mild temperatures, even close to room temperature [11,64-68]. The activation energies estimated from the Arrhenius plots of the samples are E_{a} = 95. 9 $\mathrm{kJ \cdot mol^{-1}}$ for **1**; E_{a} = 84.5 $\mathrm{kJ \cdot mol^{-1}}$ for **2**; and E_{a}

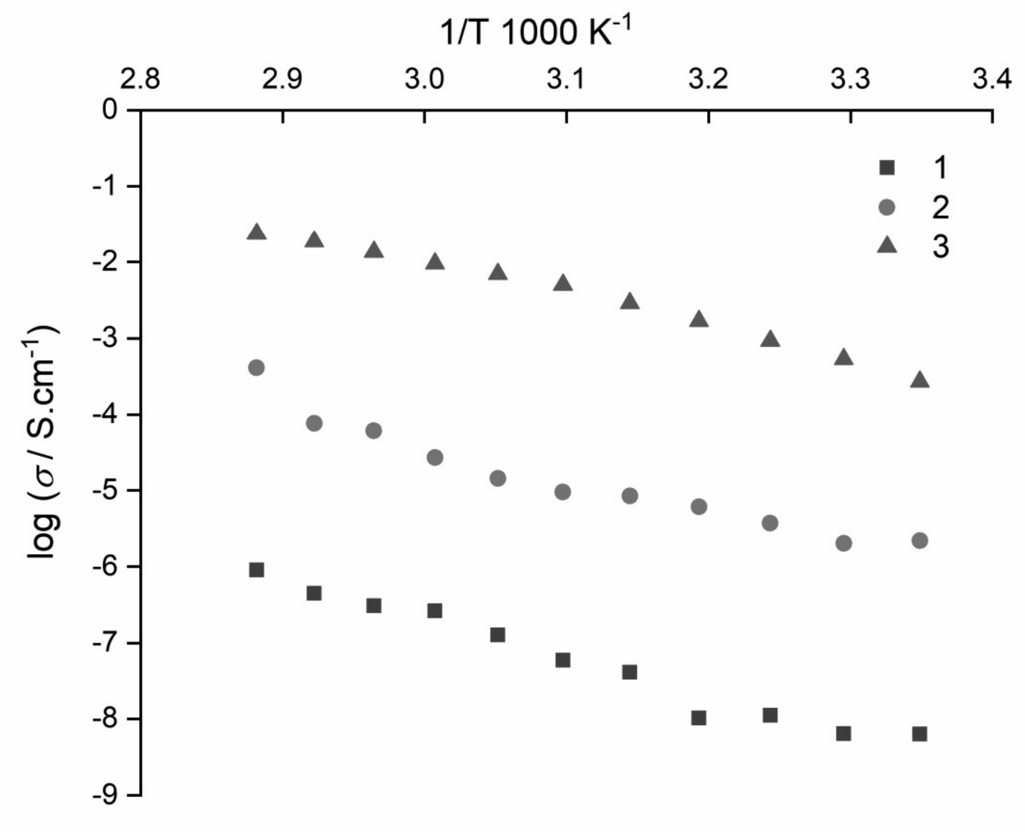

Fig. 5 Arrhenius plots (base 10) of **1-3** corresponding to the direct current conductivity, σ_{dc}, estimated from the plateaus in the double logarithmic σ' *vs* frequency plots.

= 79.4 kJ·mol^{-1}, for **3.** These values are considerably high for locally activated processes and are in good agreement with the occurrence of so-called β-relaxations, involving the rotation of rod-like molecules (extended viologen moieties) around their long axis within the crystal lattice [40,69]. It seems that, when the -(CH_2CH_2O)- terminal chains are short, the conductivity process is dominated (and partially hindered) by the motions around the bulky four-phenyl core [58,70-72]. In salt **3,** alternatively, the plasticizing effect of the longer terminal chains endows in the formation of a rubbery phase above its low glass transition (T_g ~ -6 ºC, see **Fig. 2**), with large free volumes that facilitate ionic motion (resulting in high σ_{dc} values and slightly lower activation energy) [73-74].

In conclusion, we have prepared new viologens using Zincke reactions, resulting in ionic liquids and salts with strong dielectric responses, attributed to the presence of both flexible oxyethylene groups and triflimide ions. Sufficiently long terminal chains promote exceptionally high ionic conductivities at room temperature, comparable to benchmark electrolytes used commercially, highlighting their potential use in energy devices, such as, fuel cells, batteries, supercapacitors, or solar cells. This work opens new horizons for designing ionic liquids with tuned electrostatic interactions and nanostructures by extending the central rigid core, exchanging different cations, or modifying the length of the oxyethylene terminations.

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Declaration of interests

☒The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Author Statement

All authors have equally contributed to the elaboration of this paper and have equal relevant credit roles.