We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,000
Open access books available

147,000
International authors and editors

185M
Downloads

Our authors are among the

154
Countries delivered to

TOP 1%
most cited scientists

12.2%
Contributors from top 500 universities

BOOK CITATION INDEX INDEXED
CLARIVATE ANALYTICS

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com

Chapter

High Ionic Conductivities of Ionic Materials as Potential Electrolytes

Pradip K. Bhowmik, Si L. Chen, Haesook Han,
Khairul A. Ishak, Thamil Selvi Velayutham, Umama Bendaoud
and Alfonso Martinez-Felipe

Abstract

Ionic liquids (ILs) are salts consisting of organic cations and inorganic/organic anions having melting transitions lower than 100°C. They hold promise as engineered materials in a variety of modern fields. They are used as green solvents or catalysts for chemical reactions, biocatalysts, biopolymers processing, active pharmaceutical ingradients in medicine, even as electrolytes for batteries. For batteries applications, ionic liquids must have high ionic conductivity, but most of the ionic liquids (monocationic) have low conductivities. To address this limitation, we describe in this chapter dicationic ionic liquids based on extended viologens. The colossal conductivities, $\sigma_{dc} \sim 10^{-1.5} \cdot$S cm^1 of new diatonic ionic liquids in the same range of benchmark materials/electrolytes applied in fuel cells and batteries is reported. The relatively new class of ionic liquids consist of extended viologen bistriflimides containing oligoethyleneoxy groups were prepared via Zincke reaction under mild conditions and are excellent candidates as components in devices for energy conversion and storage applications. The synthesis and ionic conductivities of other ionic liquids and dicationic organic salts will be contrasted with dicationic ionic liquids in this chapter.

Keywords: extended viologens, ionic liquids, Zincke salt, dicationic ionic liquid crystals, ionic conductivity, dielectric impedance spectroscopy

1. Introduction

Ionic liquids (ILs) are salts consisting of organic cations and inorganic/organic anions having melting transitions (T_m) lower than 100°C, and even below ambient temperatures, and with cryogenic glass transition temperatures (T_g). ILs can be engineered for a variety of modern applications, including green solvents or catalysts [1, 2], biocatalysts [3], biopolymers [4–7], pharmaceutical ingredients [8], and electrolytes for batteries [9–11]. Despite they were discovered over 30 years ago, interest by researchers and industrialists in ILs continues to grow due to their versatility.

The introduction of multiple charges in low-molar ionic liquids and poly(ionic liquid)s widens the range of physical properties, leading to improvements in density, surface tension and viscosity, facilitated by their higher molecular weights [12, 13]. The large charge densities and electrostatic interactions normally increase the ILs

thermal stabilities [14, 15] and electrical capacities [16, 17], and results in better performance as antimicrobial agents [18] and stationary phases for gas chromatography [19], among others [20, 21].

Multi-charged ILs are particularly attractive as electrolytes used in energy storage and conversion materials and devices, 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 include ammonium, phosphonium, imidazolium, pyridinium, pyrrolidinium, piperidinium, triazolium and 4,4′-bipyridinium (viologen) cations, but the perspectives for new and tailored materials are almost unlimited.

In this chapter, we showcase the potential of three series of different ionic liquids as electrolytes in energy applications, by correlating their ionic conductivities to structural effects.

2. Conductivity measurements

The conductivity of the ionic liquids was studied by impedance spectroscopy [22]. Small amounts (few mg) of molten samples were inserted into commercial indium tin oxide (ITO) cells, *via* capillary method (Instec Inc.). The parallel capacitance C_p and the dielectric loss tangent ($\tan(\delta) = \varepsilon''/\varepsilon'$, where ε'' is the dielectric loss factor, and ε' the dielectric modulus) were measured in frequency sweeps ranging between f = 0.1 Hz and 10^6 Hz, and at different temperatures. Two instruments were used and combined for these impedance measurements: a laboratory-made dielectric spectrometer (10^{-1}–10^4 Hz) and a commercial impedance analyser (Agilent 4294A) (10^2–10^6 Hz). The results were analysed in terms of the complex permittivity, $\varepsilon^*(\omega) = \varepsilon' - j\varepsilon''$, and conductivity, $\sigma^*(\omega) = \sigma' - j\sigma''$, where $\sigma' = \omega\varepsilon_O\varepsilon''$ and $\sigma'' = \omega\varepsilon_O\varepsilon'$ with ω = $2\pi f$ is the angular frequency (rad·s^{-1}).

3. Results: materials preparation and conductivity

We have prepared and assessed three series of dicationic salts as novel ionic liquid electrolytes: dicationic stilbazolium salts, dicationic asymmetric viologens, and dicationic ionic liquids. Our general strategy for their synthesis is based on quaternization by S_N^2 aka Menshutkin reactions, followed by metathesis of anions [12–21, 23].

3.1 Dicationic stilbazolium salts and their ionic conductivities

The dicationic stilbazolium salts (**I-1 – I-4**) were prepared by the reaction of *trans*-4-octyloxy-4-stilbazole with α,ω-methylene ditosylates by S_N^2, followed by metathesis reaction of the corresponding ditosylates salts with lithium triflimide salt to yield the dicationic stilbazolium bistriflimide salts (**II-1- II-4**), as shown in **Figure 1**. The detailed synthetic procedures were described elsewhere [24]. Their chemical structures were established by using ^{1}H, ^{13}C and ^{19}F nuclear magnetic resonance (NMR) spectra and elemental analysis [24].
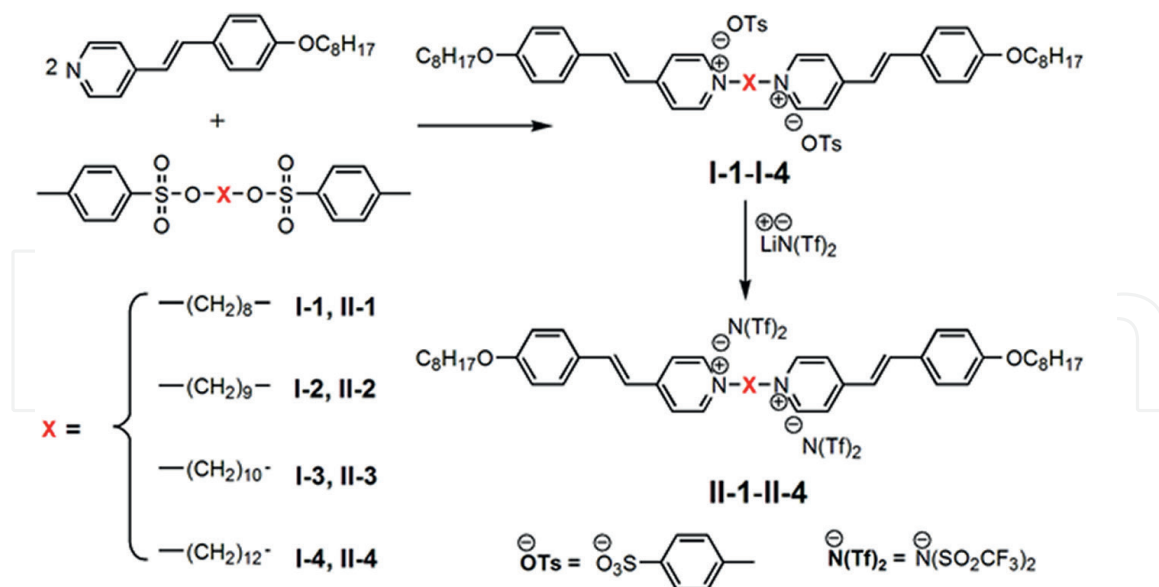
Figure 1.
Synthesis of dicationic stilbazolium dicationic salts containing bistosylate and bistriflimide counterions.

Despite the presence of mesogenic units, these salts do not display mesomorphic properties, and instead solely exhibit crystalline polymorphism, confirmed by the presence of several peaks in the differential scanning calorimetric thermograms (DSC), **Figure 2**.

We found that the salts containing tosylate ions (**I-***n*) display stronger dielectric response than the triflimide analogues (**II-***n***, see Figure 3(a)**), and show more complex profiles, associated to the additional aromatic groups. All these dielectric relaxations promote short-range conductivity in the salts, see **Figure 3(b)**, associated to local displacements of the charges. Despite the strong ε "response, the tosylate salts did not develop signs of direct conductivity (σ_{dc}) in the range of temperatures and frequencies under study. We hypothesise that the presence of bulky aromatic groups may hinder long-range transport of ionic charges in these compounds. The triflimide salts, alternatively, show DC values that reach the $10^{-4.5}$ S·cm^{-1} range in the isotropic

Figure 2.
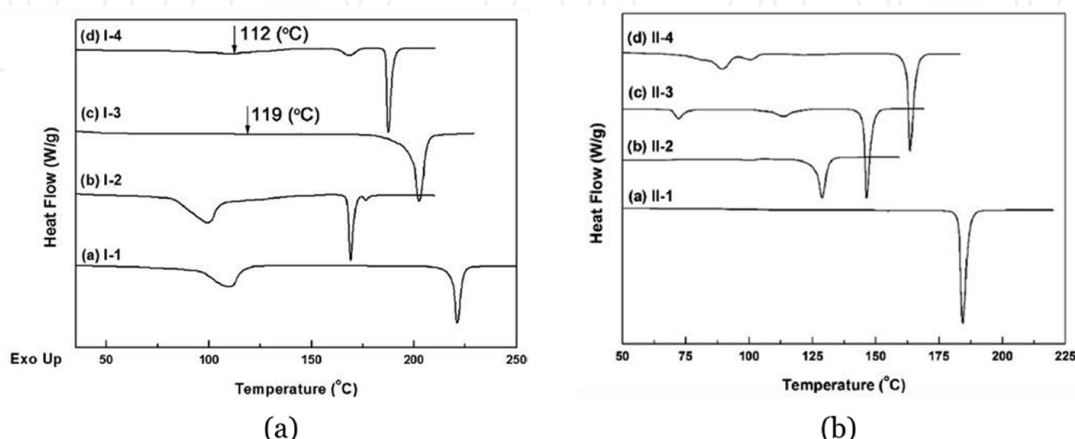*Differential scanning calorimetry thermograms (DSC) obtained on heating at 10°C·min^{-1} for the bistosylate (a) and bistriflimide (b) salts.*

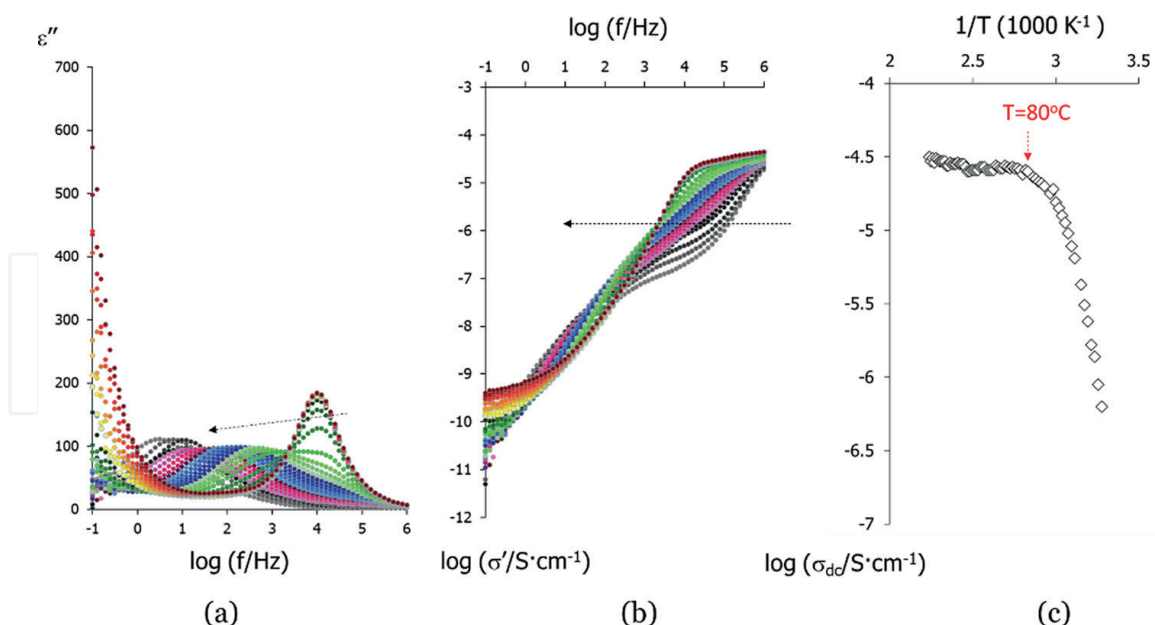**Figure 3.**
*Dielectric results obtained from the impedance frequency sweeps of dicationic stilbazolium salts: (a) dielectric loss factor, ε'' and (b) real component of the complex conductivity, σ' of **II-3**; (c) Arrhenius plots for the direct current conductivity (σ_{dc}) obtained for **II-4**.*

phase, see **Figure 3c**), but then fall rapidly following a Vogel- Fulcher-Tammann, VFT, profile [24–26].

These correlations between conductivity and structure highlight that the transport of ionic charges in these salts may require an amorphous environment, even if they involve short molecular range. The strong temperature dependence of σ_{dc} also confirms that the conductivity response is strongly coupled to segmental viscous-like motions.

3.2 Dicationic asymmetric viologens, 6BP*n*(s)

The synthesis of asymmetric viologens with hexyl terminal groups and different alkyl chain lengths, and their synthetic routes are shown in **Figure 4**. The detailed synthetic procedures were described elsewhere, and their chemical structures were determined by using ^{1}H, ^{13}C and ^{19}F NMR spectra and elemental analysis [27].

The **6BPn(s)** exhibit Smectic T phases in a broad range of temperatures, including room temperature, confirmed by polarised optical microscopy and X-ray diffraction, see **Figure 5**.

The **6BPn(s)** undergo one main dielectric relaxation, **Figure 6(a)**, associated to the rotation of the molecular core, and high frequency conductivity, **Figure 6(b)**, related to short-range triflate ion-hoping. The materials reach direct current conductivities (σ_{dc}) in the 10^{-5} to 10^{-3} S cm^{-1} range, **Figure 6(c)**, which are very promising for organic media. These dielectric processes depict a clear Vogel-Fulcher-Tammann (VFT) behaviour, indicating that the dielectric and conductivity response of these LCIs is strongly coupled to segmental-type motions [27].

3.3 Dicationic extended viologens and their ionic conductivities

The dicatonic extended viologens **1–3** were prepared according to the **Figure 7** (vide infra). The 4-oligoethyleneoxypheylanilines were prepared according to
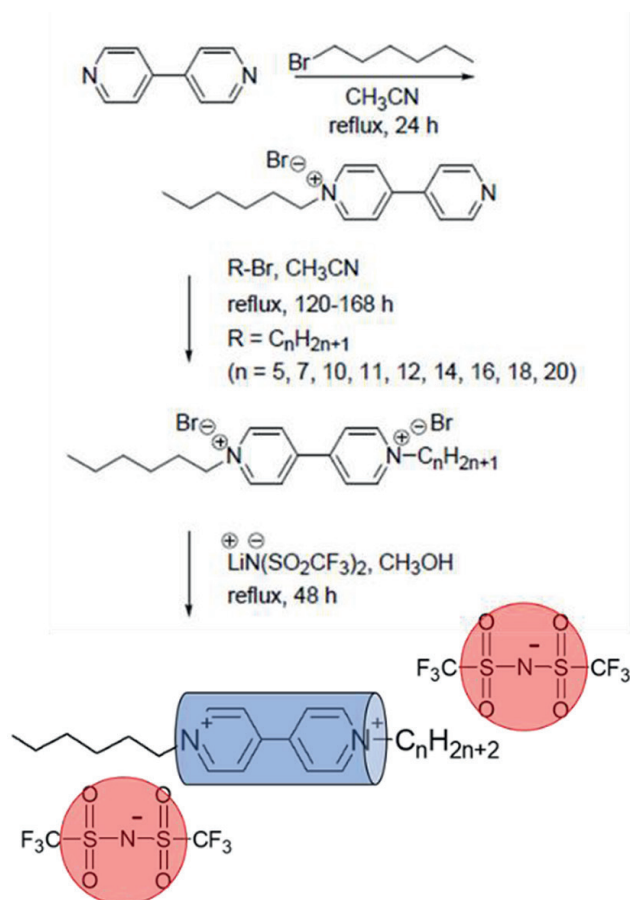
Figure 4.
Synthetic routes for the asymmetric viologen bistriflimide salts of a 4,4′-bipyridinium core (BP) alkylated with hexyl group with n = 5, 7, 10, 11, 12, 14, 16, 18 and 20.
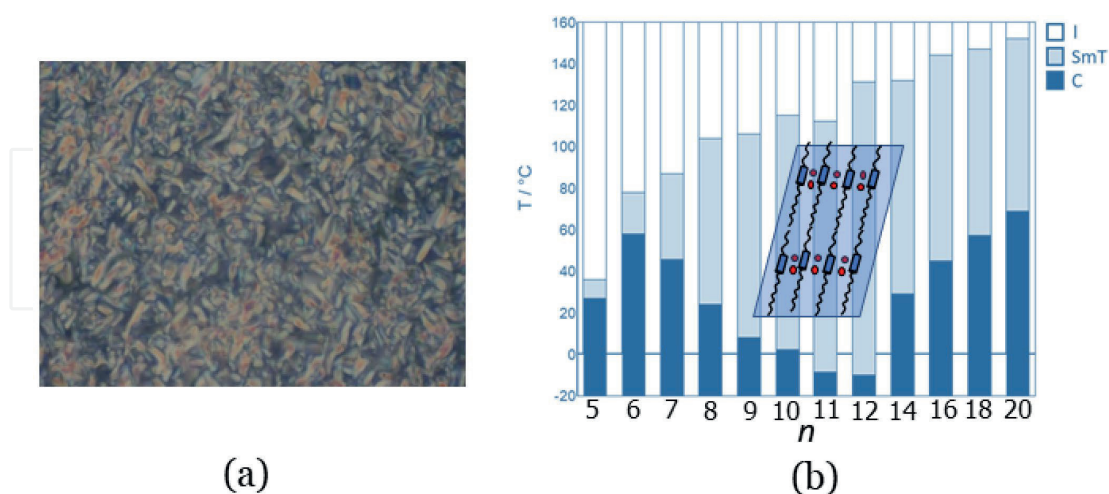

(a) (b)

Figure 5.
*(a) Photomicrograph of **6BP16** obtained under the polarised optical microscope, showing the SmT phase; (b) phase diagram of the **6BPn(s)** as a function of terminal chain, n, showing a sketch of a proposed SmT structure.*

modified literature procedures step 1 and step 2 [28, 29]. The synthesis of bis-(4-oligoethyleneoxyphenyl)-4,4′-bipyridinium dichlorides (**P1-P3**) with different ethyleneoxy groups is also summarised in **Figure** 7. The synthetic routes involved: (i) the aromatic nucleophilic substitution between the 1-chloro-2,4-dinitrobenzene
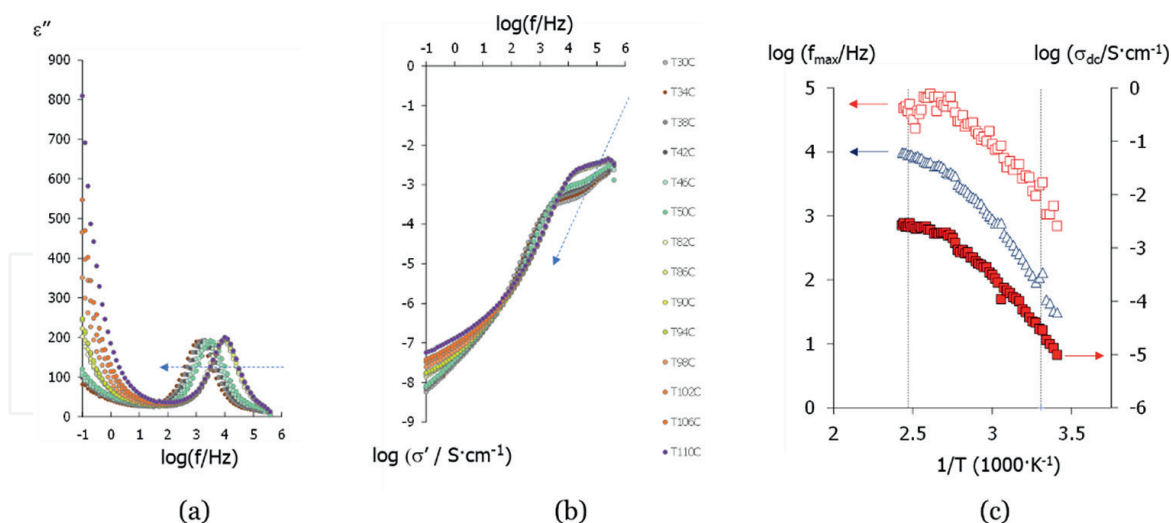
Figure 6.
Dielectric results obtained from the impedance frequency sweeps of **6BP14:** *(a) dielectric loss factor, ε''; (b) real component of the complex conductivity, σ'; (c) Arrhenius plots for the frequency dependence of ε'' and σ' maxima, and direct current conductivities (σ_{dc}).*

and 4,4′-bipyridine in acetonitrile on heating to reflux, to yield the so-called Zincke salts [30, 31] (step 3); and (ii) subsequent anionic ring opening and ring closing reactions (ANROC) with the corresponding 4-oligoethyleneoxypheylanilines, in N,N-dimethylacetamide (DMAc) at room temperature (step 4). Lastly, **P1-P3** were converted to **1–3** by metathesis with lithium triflimides in methanol [32] (step 5). Detailed synthetic procedures and analyses are also given elsewhere [33]. The chemical structures of the intermediates and final products were confirmed by their Fourier-transform infrared (FT-IR) spectra, ^{1}H, ^{13}C, and ^{19}F spectra in CD_3OD and their purity was determined by elemental analysis [33]. To our knowledge, these are the first examples of ionic liquids prepared *via* Zincke reactions.

Thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and polarised optical microscopy (POM) were used to determine the thermal properties and phase behaviour of these salts. The three salts' degradation temperatures, T_d, range from ~311 to 334°C, with less than 5% weight loss up to 300°C in nitrogen [33]. Although it was anticipated that bistriflimide ions would impart high thermal stabilities, the high T_d values demonstrate that the presence of flexible oxyethylene groups has no destabilising effect on these salts.

The DSC thermograms of salts **1** and **2** exhibit first-order endotherms associated with crystal-to-crystal (**2**) and melting (**1** and **2**) processes, whereas salt **3** only exhibits a low-temperature glass transition ($T_g = -6°C$) [1–11, 34, 35]. Both **1** and **2** melt upon heating as expected where the increase in the oxyethylene termination length reduces the melting point. Due to inhibition of crystallisation at sufficiently long ethyleneoxy chains, n = 3, the absence of first-order transitions in the corresponding thermogram indicates that **3** behaves like an amorphous salt. In subsequent heating and cooling scans, there are no additional thermal events were visible for **1** and **2**, suggesting that crystallisation of these samples must be a slow process. The absence of liquid crystal behaviour in these salts, contrasts with the recent report of smectic phases by analogous alkoxy-terminated (n ≥ 6) viologens (see **Figure 8**) [32] and others [36–38]. Even though comparable lengths of terminal chains would have been expected to promote microphase separation and smectic behaviour in **1–3**, the formation of stronger interactions by the ethyleneoxy
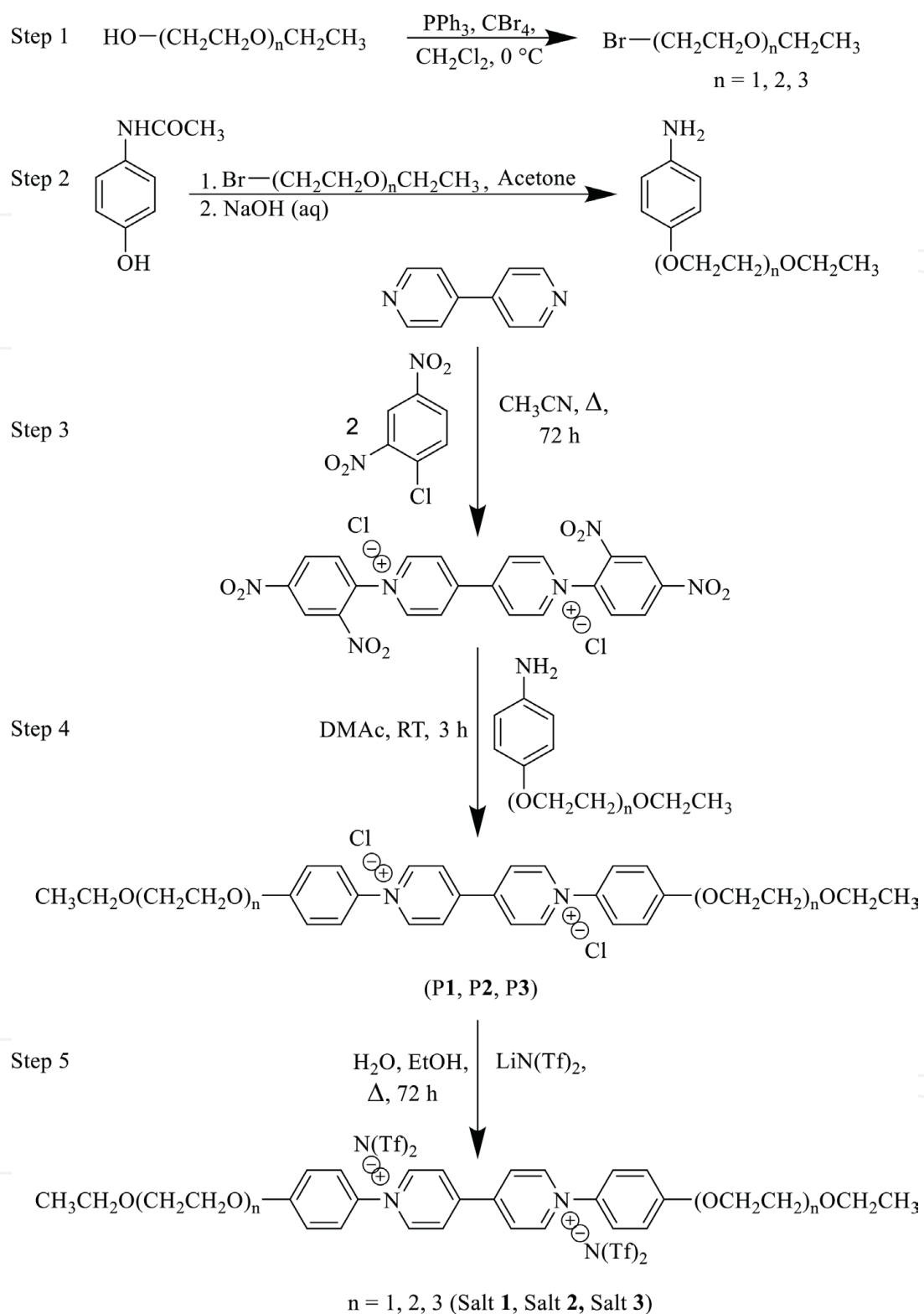
Step 1 $HO-(CH_2CH_2O)_nCH_2CH_3 \xrightarrow[\text{CH}_2\text{Cl}_2,\ 0\ °\text{C}]{\text{PPh}_3,\ \text{CBr}_4,} Br-(CH_2CH_2O)_nCH_2CH_3$

$n = 1, 2, 3$

Step 2   1. $Br-(CH_2CH_2O)_nCH_2CH_3$, Acetone
      2. NaOH (aq)

Step 3 $CH_3CN, \Delta,$ 72 h

(P**1**, P**2**, P**3**)

Step 4   DMAc, RT, 3 h

Step 5 H_2O, EtOH, $LiN(Tf)_2$, Δ, 72 h

n = 1, 2, 3 (Salt **1**, Salt **2**, Salt **3**)

Figure 7.
*Multiple steps for the synthesis of the ionic liquids and salts **1–3**.*
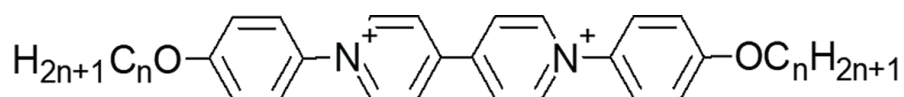
Figure 8.
General chemical structures of alkoxy-terminated viologens [32].

groups may limit the local mobility required to yield liquid crystallinity. The effect of terminal chain lengths on nanosegregation between polar chains and aromatic cores in similar viologens is being studied further.

Viologens and their countless derivatives have already been proposed as potential redox active functional materials for use in electrochromic devices, diodes and transistors, memory devices, molecular machines, and dye-sensitised solar cells [39–41]. The incorporation of the oxyethylene(s) terminations is warranted for not one but two distinct reasons. On the one hand, one of our goals is to reduce (at least partially) the rigidity of the four-ring phenyl core (which could increase viscosity). On the other hand, the presence of polar chains can help delocalize the triflimide anions and avoid complexation, both of which would inhibit ion mobility [42]. This is because polar chains have a higher dipole moment.

Figure 9 shows the dielectric and conductivity response of the extended viologens **1–3** as a function frequency measured at room temperature. The complex permittivity and conductivity values of these salts have been found to be extraordinarily high due to the highly polar nature of ionic liquids and salts [33]. The ε" plot demonstrates a linear increase (with slopes of −1) at sufficiently lower frequencies representing the increase in direct current (DC) conductivity [43]. This DC component dominates any potential dielectric relaxation, despite the presence of peaks in the salts **1** in **Figure 9(a)**. The third salt has the highest conductivity values of the three salts. The formation of plateaus in the double logarithmic σ' versus f plots in **Figure 9(b)** [22] confirms the existence of DC conductivity. The exemplary temperature plot of complex permittivity (ε^*) and conductivity (σ^*) of salt **2** is shown
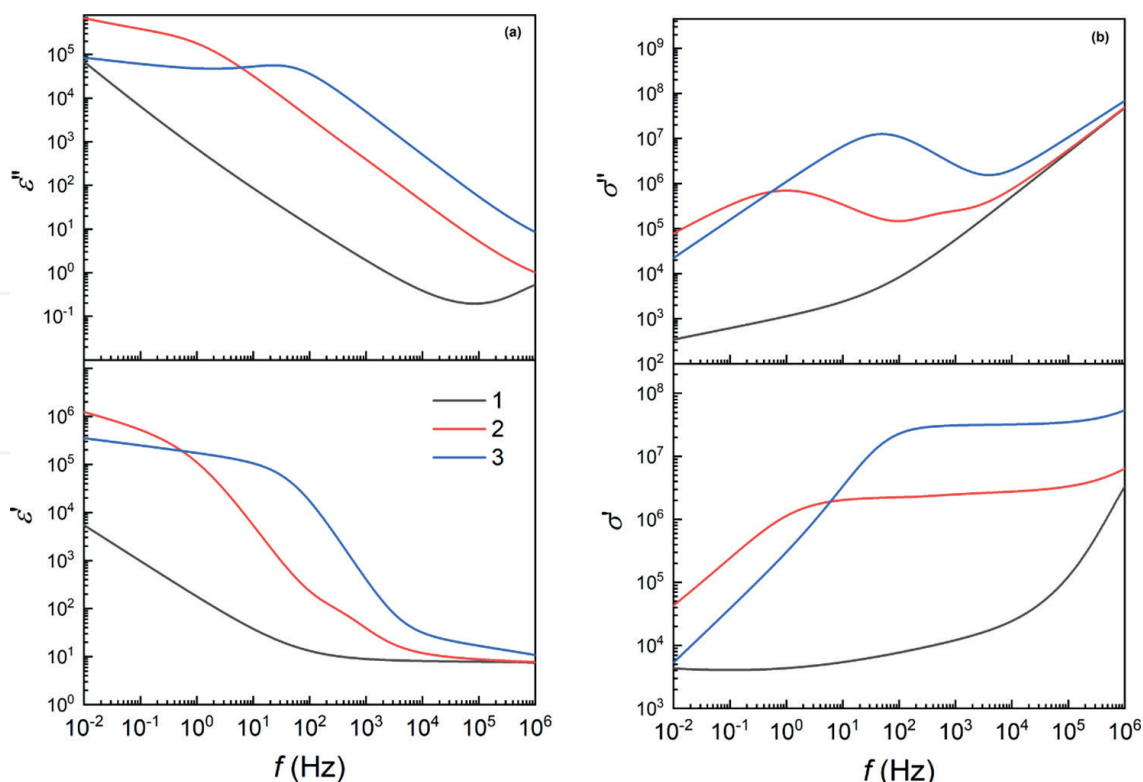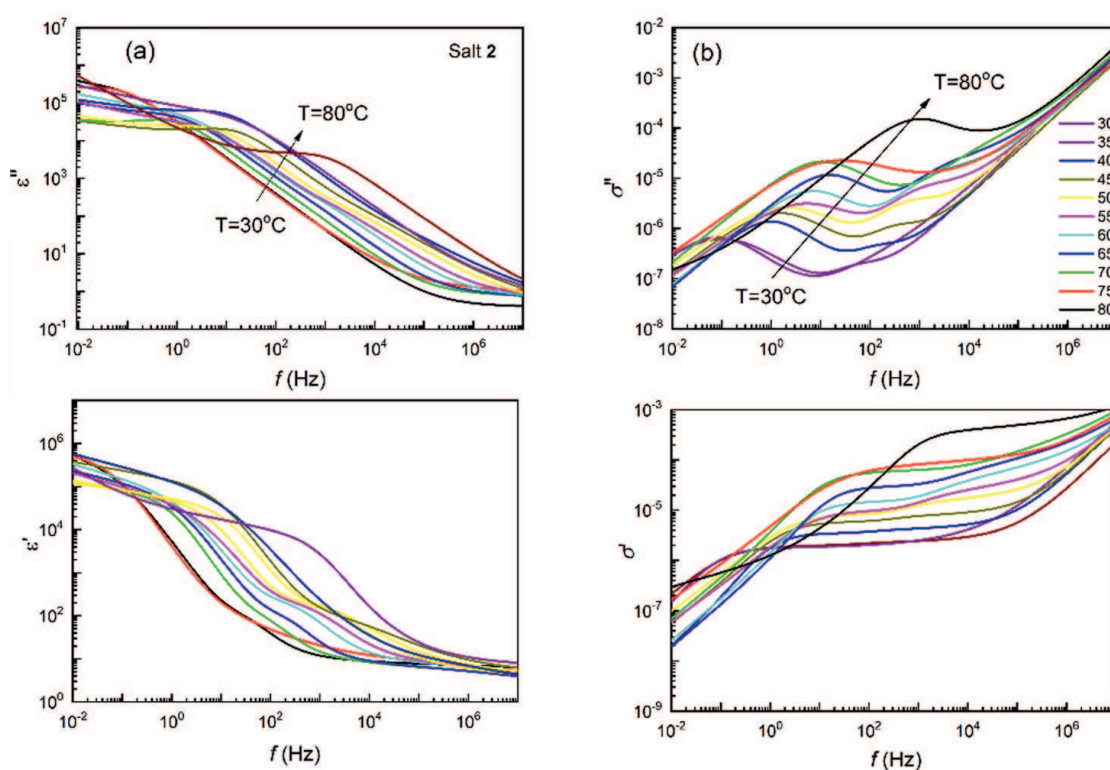

Figure 9.
*Complex permittivity (a) and conductivity (b) obtained for compounds **1**, **2** and **3** measured at room temperature.*

Figure 10.
*Complex permittivity (a) and conductivity (b) obtained for compounds **2** measured on heating from 30°C (see the arrow).*

in **Figure 10**. The DC conductivity values, σ_{dc}, are estimated by extrapolating the constant σ' ranges to $f \rightarrow 0$ at various temperature. The resulting Arrhenius plots (not shown here) were used to evaluate the activation energy E_a of the conductivity process using the equation; $\sigma_{dc} = \sigma_0 \exp(E_a/RT)$, where R is the gas constant, 8.31 J. $mol^{-1}.K^{-1}$, T is the absolute temperature, and σ_0 is a pre-exponential term. Salts **1** and **2** have activation energies of 95.9 kJ/mol and 84.5 kJ/mol, respectively. These values are significantly higher for locally activated processes and are consistent with the occurrence of so-called β-relaxations, which involve the rotation of rod-like molecules (extended viologen moieties) within the crystal lattice around their long axis [33, 44]. When the -(CH$_2$CH$_2$O)- terminal chains are short, it appears that the motions around the bulky four-phenyl core dominate (and partially hinder) the conductivity process [43, 45–47]. On the other hand, salt **3** shows exceptional σ_{dc} values (~$10^{-1.5}$ S/cm) comparable to the bench electrolytes used in fuel cells [48] and batteries [49]. Longer ethyleneoxy terminal chains enhance conductivity in salts by a plasticizing effect, thereby promoting ionic motions in the material. Moreover, salt **3** is one of the few examples of an organic salt with such large conductivities under anhydrous conditions and at temperatures close to room temperature [9, 50–54]. The formation of a rubbery phase above its low glass transition $T_g - 6$°C (from DSC measurement) with large free volumes that facilitate ionic motion can explain the higher σ_{dc} values observed for **3** within the series [55, 56]. In this molten-like state, conductivity has very weak temperature dependence [57–59]. The ionic liquids **1** and **2**, on the other hand, remain in a glassy state throughout the temperature range under study, and the σ_{dc} values are lower.

4. Conclusions

We have prepared new viologens by using Zincke reactions, which led to the formation of ionic liquids and salts with strong dielectric responses. Our results confirm that a fine balance between local/charge interactions and mobility is needed to optimise phase behaviour and conductivity of the ionic liquids. In general terms, the formation of amorphous, liquid crystalline, or crystal phases, can be tuned by the aspect ratio of the rigid core and the flexible terminations.

Whilst compounds having alkyl terminations still fall some orders of magnitude below those exhibited by reference phosphonium or imidazolium-based ionic liquid electrolytes (10^{-2} S·cm^{-1}) [60, 61], we found that the presence of oxyethylene groups promotes high conductivities in the $10^{-1.5}$ S·cm^{-1} range, comparable to those required in commercial batteries or fuel cells [48, 49]. The presence of additional polar sites in these terminations may be the key to facilitate long-range transport in these materials. Interestingly, the presence of tosylate ions with a strong dielectric response does not promote long-range conductivity, and triflimide ions appear to be more suitable for ionic transport. Delocalisation of the charges can therefore be a key enabler for high σ_{dc} values.

These results highlight the potential use of these and other ionic liquids in energy devices such as fuel cells, batteries, supercapacitors, or solar cells. By extending the central rigid core, exchanging different cations, or modifying the composition and length of the terminations, this work opens new avenues for the design of ionic liquids with tuned electrostatic interactions and nanostructures.

Acknowledgements

Conflict of interest

The authors declare no conflict of interest.

Author details

Pradip K. Bhowmik[1*], Si L. Chen[1], Haesook Han[1], Khairul A. Ishak[2],
Thamil Selvi Velayutham[3], Umama Bendaoud[4] and Alfonso Martinez-Felipe[4]

1 Department of Chemistry and Biochemistry, University of Nevada Las Vegas,
Las Vegas, NV, USA

2 Faculty of Science, Institute of Biological Sciences, Universiti Malaya,
Kuala Lumpur, Malaysia

3 Faculty of Science, Department of Physics, Low Dimensional Materials Research
Centre, Universiti Malaya, Kuala Lumpur, Malaysia

4 Chemical Processes and Materials Research Group, School of Engineering, Centre
for Energy Transition, King's College, University of Aberdeen, Old Aberdeen, UK

*Address all correspondence to: pradip.bhowmik@unlv.edu

IntechOpen

References

[1] Welton T. Room-temperature ionic liquids. Solvents for synthesis and catalysis. Chemical Reviews. 1999;**99**:2071-2084

[2] Kar M, Plechkova NV, Seddon KR, Pringle JM, MacFarlane DR. Ionic liquids –further progress on the fundamental issues. Australian Journal of Chemistry. 2019;**72**:3-10

[3] Sheldon RA. Biocatalysis in ionic liquids: State-of-the union. Green Chemistry. 2021;**23**:8406-8427

[4] Swatloski RP, Spear SK, Holbrey JD, Rogers RD. Dissolution of cellulose in ionic liquids. Journal of the American Chemical Society. 2002;**124**:4974-4775

[5] Zhang ZR, Song JL, Han BX. Catalytic transformation of lignocellulose into chemical and fuel products in ionic liquids. Chemical Reviews. 2017;**117**:6834-6880

[6] Ren F, Wang J, Xie F, Zan K, Wang S, Wang S. Applications of ionic liquids in starch chemistry: A review. Green Chemistry. 2020;**22**:2162-2183

[7] Shukla SK, Mikkola J-P. Use of ionic liquids in protein and DNA chemistry. Frontiers Chemistry. 2020;**8**:598662

[8] Egorova KS, Gordeev EG, Ananikov VP. Biological activity of ionic liquids and their applications in pharmaceutics and medicine. Chemical Reviews. 2017;**117**:7132-7189

[9] Watanabe M, Thomas ML, Zhang SG, Ueno K, Yasuda T, Dokko K. Application of ionic liquids to energy storage and conversion materials and devices. Chemical Reviews. 2017;**117**:7190-7239

[10] Yang QW, Zhang ZQ, Sun XG, Hu YS, Xing HB, Dai S. Ionic liquids and derived materials for lithium and sodium batteries. Chemical Society Reviews. 2018;**47**:2020-2064

[11] Yu LP, Chen GZ. Ionic liquid-based electrolytes for supercapacitor and supercapattery. Frontiers in Chemistry. 2019;**7**:272

[12] Guglielmero L, Mezzetta A, Guazzelli L, Pomelli CS, D'Andrea F, Chiappe C. Systemetic synthesis and properties evaluation of dicationic ionic liquids, and a glance into potential new field. Frontier in Chemistry. 2018;**6**:612

[13] Ikeda T. Facile synthesis of tetra-branched tetraimidazolium and tetrapyrrolidinium ion liquids. ACS Omega. 2021;**6**:19623-19628

[14] Ferdeghini C, Guazzelli L, Pometti CS, Ciccioli A, Brunetti B, Mezzetta A, et al. Synthesis, thermal behavior and kinetic study of N-morpholinium dicationic ionic liquids by thermogravimetry. Journal of Molecular Liquids. 2021;**332**:115662

[15] Clarke CJ, Morgan PJ, Hallet JP, Licence P. Linking the thermal and electronic properties of functional dicationic salts with their molecular structures. ACS Sustainable Chemistry and Engineering. 2021;**9**:6224-6234

[16] Matsumoto M, Shimizu S, Sotoike R, Watanabe M, Iwasa Y, Itoh Y, et al. Exceptionally high electric double layer capacitances of oligomeric ionic liquids. Journal of the American Chemical Society. 2017;**139**:16072-16075

[17] Maruyama Y, Marukane S, Morinaga T, Homma S, Kamijo T, Shomura R, et al. New design of polyvalent ammonium salts for a

high-capacity electric double layer capacitor. Journal Power Sources. 2019;**412**:18-28

[18] Pernak J, Skrzypezak A, Lota G, Frackowiak E. Synthesis and properties of trigeminal tricationic ionic liquids, Chemistry – A. European Journal. 2007;**13**:3106-3112

[19] Patil RA, Talebi M, Sidisky LM, Berthod A, Armstrong DW. Gas chromatography selectivity of new phosphonium-based dicationic ionic liquid stationary phases. Journal of Separation Science. 2018;**41**:4142-4148

[20] Cui J, Li Y, Chen D, Zhan T-G, Zhang K-D. Ionic liquid-based stimuli-responsive functional materials. Advanced Functional Materials. 2020;**30**:2005522

[21] Yoshida Y, Kitagawa H. Chromic ionic liquids. ACS Applied Electronic Materials. 2021;**3**:2468-2482

[22] Dyre JC. Some remarks on ac conduction in disordered solids. Journal of Non-Crystalline Solids. 1991;**135**:219-226

[23] Jordão N, Cruz H, Branco A, Pina F, Branco LC. Electrochromic devices based on disubstituted oxo-bipyridinium ionic liquids. ChemPlusChem. 2015;**80**:202-208

[24] Bhowmik PK, Koh JJ, King D, Han H, Heinrich B, Donnio B, et al. Dicationic stilbazolium salts: Structural, thermal, optical, and ionic conduction properties. Journal Molecular Liquids. 2021;**341**:117311

[25] Vogel H. The temperature dependence low of viscosity of fluids. Physikalische Zeitschrift. 1921;**22**:645-646

[26] Fulcher GS. Analysis of recent measurements of the viscosity of glasses-reprint. Journal of the American Ceramic Society. 1992;**75**:1043-1059

[27] Bhowmik PK, Noori O, Chen SL, Han H, Fisch MR, Robb CM, et al. Ionic liquid crystals: Synthesis and characterization via NMR, DSC, POM, X-ray diffraction and ionic conductivity of asymmetric viologen bistriflimide salts. Journal Molecular Liquids. 2021;**328**:115370

[28] Sudhakar S, Narasimha Swamy T, Srinivasan KSV. Synthesis, characterization, and thermal properties of 4,4′-bis(4-n-alkoxybenzoyloxy)benzylideneanilines and bis(4-benzylidene-4′-n-alkoxyaniline) terephthalates. Liquid Crystals. 2000;**27**:1525-1532

[29] Kim I-H, Tsai H-J, Nishi K, Kasagami T, Morisseau C, Hammock BD. 1,3-Disubstituted Ureas functionalized with ether groups are potent inhibitors of the soluble epoxide hydrolase with improved pharmacokinetic properties. Journal of Medicinal Chemistry. 2007;**50**:5217-5226

[30] Sharma GD, Saxena D, Roy MS. Studies on electrical and photoelectrical behaviour of ITO/ArV/In Schottky barrier device. Synthetic Metals. 1999;**106**:97-105

[31] Cheng W-C, Kurth MJ. The Zincke reaction. A review. Organic Preparations and Procedures International. 2002;**34**:585-608

[32] Bhowmik PK, Al-Karawi MKM, Killarney ST, Dizon EJ, Chang A, Kim J, et al. Thermotropic liquid-crystalline and light-emitting properties of bis(4-alkoxyphenyl)viologen bis(triflimide) salts. Molecules. 2020;**25**:2435

[33] Bhowmik PK, Chen SL, Han H, Ishak KA, Velayutham TS, Bendaoud U, et al. Dicationic ionic liquids based on bis(4-oligoethyleneoxyphenyl) viologen bistriflimide salts exhibiting high ionic conductivities. Journal of Molecular Liquids. 2022;**365**:120126

[34] Hallet JP, T. Welton T. Room-temperature ionic liquids: Solvents for synthesis and catalysis. 2. Chemical Reviews. 2011;**111**:3508-3576

[35] Welton T. Ionic liquids: A brief history. Biophysical Reviews. 2018;**10**:691-706

[36] Haramoto Y, Yin M, Matukawa Y, Ujiie S, Nanasawa MA. A new ionic liquid crystal compound with viologen group in the principal structure. Liquid Crystals. 1995;**19**:319-320

[37] Wang R-T, Lee G-H, Lai CK. Anion-induced ionic liquid crystals of diphenylviologens. Journal Materials Chemistry C. 2018;**6**:9430-9444

[38] Veltri L, Cavallo G, Beneduci A, Metrangolo P, Corrente GA, Ursini M, et al. Synthesis and thermotropic properties of new green electrochromic ionic liquid crystals. New Journal of Chemistry. 2019;**43**:18285-18293

[39] Das G, Škorjanc T, Sharma SK, Gándara F, Lusi M, Shankar Rao DS, et al. Viologen-based conjugated covalent organic networks via Zincke reaction. Journal of the American Chemical Society. 2017;**139**:9558-9565

[40] Striepe L, Baumgartner T. Viologens and their application as functional materials. Chemistry A European Journal. 2017;**23**:16924-16940

[41] Ding J, Zheng C, Wang L, Lu C, Zhang B, Chen Y, Li M, Zhai G, Zhuang X. Viologen-inspired functional materials: Synthetic strategies and applications. Journal of Materials Chemistry 2019;A 7:23337-23360.

[42] Bishop AG, MacFarlane DR, McNaughton D, Forsyth M. Triflate ion association in plasticized polymer electrolytes. Solid State Ionics. 1996;**85**:129-135

[43] Brown AW, Martinez-Felipe A. Ionic conductivity mediated by hydrogen bonding in liquid-crystalline 4-n-alkoxybenzoic acids. Journal of Molecular Structure. 2019;**1197**:487-496

[44] Zentel R, Strobl GR, Ringsdorf H. Dielectric-relaxation of liquid-crystalline polyacrylates and polymethacrylates. Macromolecules. 1985;**18**:960-965

[45] Bojanowski Z, Knapik J, Diaz M, Ortiz A, Ortiz I, Paluch M. Conductivity mechanism in polymerized imidazolium-based ptotic ionic liquid [HSO$_3$-BVIm][OTf]: Dielectric relaxation studies. Macromolecules. 2014;**47**:4056-4065

[46] Concellón A, Hernández-Ainsa S, Barberá J, Romero P, Serrano JL, Marcos M. Proton conductive ionic liquid crystalline poly(ethyleneimine) polymers functionalized with oxadiazole. RSC Advances. 2018;**8**:37700-37706

[47] Liang SW, O'Reilly MV, Choi UH, Shiau H-S, Bartels J, Chen Q, et al. High ion content siloxane phosphonium ionomers with very low T-g. Macromolecules. 2014;**47**:4428-4437

[48] Mauritz KA, Moore RB. State of understanding of Nafion. Chemical Reviews. 2004;**104**:4535-4585

[49] Luntz AC, McCloskey BD. Nonaqueous Li-air batteries: a

status report. Chemical Reviews. 2014;**114**:11721-11750

[50] Bostwick JE, Zanelotti CJ, Yu D, Pietra NF, Williams TA, Madsen LA, et al. Ionic interactions control the modulus and mechanical properties of molecular ionic composite electrolytes. Journal Materials Chemistry C. 2022;**10**:947-957

[51] Devaki SJ, Sasi R. Ionic liquids/ionic liquid crystals for safe and sustainable energy storage systems. In: Handy S, editor. Progress and Developments in Ionic Liquids. Intech: London, UK; 2017. pp. 313-336

[52] Liu H, Yu H. Ionic liquids for electrochemical energy storage devices applications. Journal Materials Science and Technology. 2019;**35**:674-686

[53] Papović S, Gadžurić S, Bešter-Rogač M, Vraneš M. Effect of the alkyl chain length on the electrical conductivity of six (imidazolium-based ionic liquids + γ-butyrolactone) binary mixtures. Journal of Chemical Thermodynamics. 2016;**102**:367-377

[54] Xu C, Yang G, Wu D, Yao M, Xing C, Zhang J, et al. Roadmap on ionic liquid electrolytes for energy storage devices. Chemistry An Asian Journal. 2021;**16**:549-562

[55] Angell CA, Imrie CT, Ingram MD. From simple electrolyte solutions through polymer electrolytes to superionic rubbers: Some fundamental considerations. Polymer International. 1988;**47**:9-15

[56] Angell CA. Relaxation in liquids, polymers and plastic crystals-strong fragile patterns and problems. Journal of Non-Crystalline Solids. 1991;**131**:13-31

[57] Vanti L, Alauddin SM, Zaton D, Aripin NFK, Giacinti-Baschetti M, Imrie CT, et al. Ionically conducting and photoresponsive liquid crystalline terpolymers: Towards multifunctional polymer electrolytes. European Polymer Journal. 2018;**109**:124-132

[58] Alauddin SM, Ibrahim AR, Aripin NFK, Velayutham TS, Abou-Zeid OK, Martinez-Felipe A. New side-chain liquid crystalline terpolymers with anhydrous conductivity: Effect of azobenzene substitution on light response and charge transfer. European Polymer Journal. 2021;**146**:110246

[59] Alauddin SM, Aripin NFK, Velayutham TS, Martinez-Felipe A. Liquid crystalline polymers containing sulfonic and light-responsive groups: From molecular design to conductivity. Molecules. 2020;**25**:2579

[60] Jourdain A, Serghei A, Drockenmuller E. Enhanced ionic conductivity of a 1,2,3-triazolium-based poly(siloxane ionic liquid) homopolymer. ACS Macro Letters. 2016;**5**:1283-1286

[61] Maximean DM, Cîrcu V, Paul Ganea CP. Dielectric properties of a bisimidazolium salt with dodecyl sulfate anion doped with carbon nanotubes. Beilstein Journal of Nanotechnology. 2018;**9**:164-174