LATVIJAS UNIVERSITĀTE, ĶĪMIJAS FAKULTĀTE
IMPERIAL COLLEGE LONDON, ĶĪMIJAS DEPARTAMENTS

MOLEKULĀRĀS MIJIEDARBĪBAS JONU ŠĶIDRUMOS

MAĢISTRA DARBS

Autors: **Eduards Baķis**
Apliecības №: eb09049
Darba vadītāji: profesors Toms Veltons, PhD,
Imperial College London
profesors Andris Zicmanis, Dr. hab. chem.,
Latvijas Universitāte

RĪGA
LONDONA
2014

UNIVERSITY OF LATVIA, FACULTY OF CHEMISTRY
IMPERIAL COLLEGE LONDON, DEPARTMENT OF CHEMISTRY

MOLECULAR INTERACTIONS IN IONIC LIQUIDS

MASTER THESIS

Authored by:	**Eduards Baķis**
Student ID:	eb09049
Supervided by:	Professor Tom Welton, PhD, Imperial College London
	Professor Andris Zicmanis, Dr. Hab. Chem., University of Latvia

RIGA
LONDON
2014

ANOTĀCIJA

Molekulārās mijiedarbības jonu šķidrumos. Baķis E., zinātniskais vadītājs prof., PhD Veltons T., Dr. hab. chem., prof. Zicmanis A. Maģistra darbs, 73 lappuses, 20 attēli, 1 tabula, 129 literatūras avoti. Angļu valodā.

Darbā veikti mēģinājumi izstrādāt jaunu ķīmisku instrumentu – sāli, kas sastāv no dikatjona un dianjona un veido lādiņa pārneses kompleksu, un izmantojams jonu pāru veidošanās pētījumiem jonu šķidrumos. Sintezēti vairāki jonu šķidrumi un 26 dažādi *N*,*N*-divaizvietoti bipiridīnija sāļi ar dažādiem anjoniem. Ar KMR palīdzību pētīta to šķīdība jonu šķidrumā 1-butil-3-metilimidazolija *bis*-(trifluormetānsulfonil)imīdā, un iegūtie dati skaidroti ar šo sāļu struktūras īpatnībām un kušanas temperatūrām. Tāpat pārbaudīta iespēja šķīdumā ievadīt trīs dažādus dianjonus.

JONU ŠĶIDRUMI, JONU PĀRI, LĀDIŅA PĀRNESES KOMPLEKSS, DIKATJONS, DIANJONS, ŠĶĪDĪBA

ABSTRACT

Molecular Interactions in Ionic Liquids. Baķis E., scientifical supervisor Prof. Welton, T., PhD, and Prof. Zicmanis, A., Dr. Hab. Chem. Master thesis, 73 pages, 20 figures, 1 table, 129 references. In English.

In this work development of a new chemical tool – salt, consistent from doubly charged ions that exhibit charge transfer properties, for ion pairing studies in ionic liquids was attempted. Towards this tool, several ionic liquids and 26 structurally diverse diquaternary bipyridinium salts with a range of anions were prepared. Their solubility in ionic liquid 1-butyl-3-methylimidazolium *bis*-(trifluoromethanesulfonyl)imide was studied by means of NMR and correlated with their structure and melting point. Also, three different dianions were tested for introduction in ionic liquid.

IONIC LIQUIDS, ION PAIRING, CHARGE TRANSFER COMPLEX, DICATION, DIANION, SOLUBILITY

CONTENTS

ABBREVIATIONS

$[C_nC_1im]^+$	1-alkyl-3-metylimidazolium cation
$[C_nC_1pyr]^+$	1-alkyl-1-metylpyrrolidinium cation
$[C_npy]^+$	1-alkylpyridinium cation
$[R_4N]^+$	tetraalkylammonium cation
$[C_1Him]^+$	1-methylimidazolium cation
BV^{2+}	boronium viologen-based dication
V^{2+}	4,4'-bipyridinium (viologen) dication

$[NTf_2]^-$	*bis*-(trifluoromathanesulfonyl)imide anion, bisimide
$[OTf]^-$	trifluoromethanesulfonate anion
$[BF_4]^-$	tetrafluoroborate anion
$[OAc]^-$	acetate anion
$[C_1C_1PO_4]^-$	dimethylphosphate anion
$[PF_6]^-$	hexafluorophosphate anion
$[DTC]^-$	α,α-dicyano-*p*-toluoylcyanamide anion

IL	ionic liquid
RT	room temperature
NMR	nuclear magnetic resonance
PTFE	polytetrafluoroethylene (teflon)
DMF	*N,N*-dimethylformamide
DMSO	dimethylsulfoxide
MeCN	acetonitrile
DCM	dichloromethane
TCNQ	tetracyanoquinodimethane
CT	charge transfer
$\Delta_{fus}G$	Gibbs free energy change of fusion, J
$\Delta_{solv}G$	Gibbs free energy change of solvation, J
ΔH	enthalpy change, $J \cdot mol^{-1}$
$\Delta_{latt}H$	lattice enthalpy change, $J \cdot mol^{-1}$
ΔS	entropy change, $J \cdot mol^{-1} \cdot K^{-1}$
$\Delta_{latt}S$	lattice entropy change, $J \cdot mol^{-1} \cdot K^{-1}$
F_C	Coulomb's force, N
ε	dielectric permittivity
ε_0	permittivity of free space, 8.85×10^{-12} F/m
χ	molar fraction
J	spin-spin coupling constant, Hz

ppm	parts per million
UV-Vis	ultraviolet – visible light
m.p.	melting point, °C
$h\nu$	energy of photon, J
λ	wavelength, nm
λ_{max}	wavelength of absorption maxima, nm

INTRODUCTION

First most deeply studied topics in chemistry where connected with changes that human could observe directly using his senses. Thereby L. Pasteur discovered stereoisomerism by manually picking the tartaric acid ammonium – sodium salt crystals of similar shape under magnification [1]. Also M. Tsvet found plant pigments separating into distinct colourful components if passed through a column of sorbent – the process nowadays known as chromatographic separation [2].

At the same time research of equilibrium processes requires indirect methods, for example, measurement of pH, what nowadays is well understood. However, most of these processes allow looking into the system only through a specific “keyhole” as, for instance, use of NMR measurements, various mass pectrometric techniques or other relatively recently developed principles.

This work is focused of finding a suitable chemical instrument for exploration of ion pairing in the relatively recent and little studied class of solvents – ionic liquids. Employing the physicochemical properties of charge transfer complexes one could answer the fundamental question if there are specific interactions known as solvation in ionic liquid solutions if ionic solutes with double unit charges are dissolved. So far it is known that ionic solutes A^+B^- with similar unit charges to those of ionic liquid X^+Y^- are distributed in solution only by entropy-driven mixing [3]. This phenomenon should be now examined in case of solutes $A^{2+}B^{2-}$ – with unit charges doubled. **The objective of this work** is to find a suitable charge transfer complex $A^{2+}B^{2-}$ for ion pairing studies in ionic liquid media. To reach this goal, **several tasks** should be performed: **(1)** synthesis of high quality ionic liquids, **(2)** finding of appropriate dication – charge transfer acceptor, **(3)** finding of dianion with charge transfer donor properties in solution to the chosen dication and a way for introducing them in solution, **(4)** estimation of correlation between charge transfer absorption band intensity and its concentration in ionic liquid solution, giving the insight about ion pairing.

1. LITERATURE REVIEW

1.1. Ionic Liquids

Ionic liquids, in addition to molecular liquids, are organic fluids that are entirely formed from ions. Although the use of ILs as reaction medium is not their only application [4–6], it is essential to examine this group of compounds exactly as solvents, since more than a few benefits lay in their properties –

- NEGLIGIBLE VAPOUR PRESSURE [7, 8], resulting in non-volatility at broad pressure range;
- EXTENDED THERMAL STABILITY [9], accompanied by wide liquid-state temperature range;
- HIGH FLASH-POINT AND IGNITION TEMPERATURES [10], ensuring non-flammability;
- UNUSUAL DISSOLUTION PROPERTIES [11–13] including solubilisation of gases and bio-polymers;
- EASILY ADJUSTABLE POLARITY CHARACTERISTICS [14] by the design of IL's structure.

However, the ILs must not be overvalued as several limitations could be considered while dealing with them:

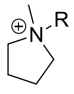
- HIGH VISCOSITY in comparison with molecular liquids what may result in decrease of the rate of particular reactions [15] and difficulties of handling;
- QUALITY AND PURITY;
- PRICE AND AVAILABILITY;
- CONTROVERSIAL GREENNESS due to the lack of sustainable routes for their preparation.

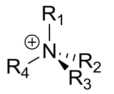
1.1.1. General Properties and Structural Diversity

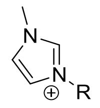
Regarding the historical development of this concept [16], nowadays ILs are defined as salts melting below 100 °C, while these liquid at room temperature are called room-temperature ILs (RT-ILs) [17]. Primary ammonium salts – ethanolammonium nitrate [18] with melting point 52-55 °C (1888, Gabriel) and ethylammonium nitrate [16], melting at 12 °C (1914, Walden), are within the first examples reported. The salts liquid above 100 °C are considered as molten salts and not ILs.

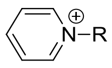
Many properties of ILs correlate with both the cation and anion structure. In general, unsymmetrical, charge-diffuse and conformationally rich ions lower the melting points of the salts.

The vast majority of IL cations are based on quaternized nitrogen framework including aliphatic as well as aromatic cores [19]. Alyphatic 1-alkyl-1-methylpyrrolidinium $[C_nC_1pyrr]^+$, tetraalkylammonium $[R_4N]^+$ and aromatic 1-alkyl-3-methylimidazolium $[C_nC_1im]^+$, 1-alkylpyridinium $[C_npyr]^+$ cations are common examples:


$[C_nC_1pyrr]^+$


$[NR_4]^+$


$[C_nC_1im]^+$


$[C_npyr]^+$

To answer the question of why ILs melt at relatively low temperatures [20] and predict their melting points prior the synthesis [21–23], several studies have been carried out. A reasonable explanation has been given by Krossing *et. al.* by assessing the Gibbs free energy of fusion $\Delta_{\text{fus}}G$ for the process $IL_{(s)} \rightarrow IL_{(l)}$ which relates to the melting point of the IL. Employing the volume-based thermodynamics and computational calculations, negative $\Delta_{\text{fus}}G^{\text{O}}$ values at 298.15 K and 10^5 Pa have been obtained for 14 common RT-ILs. This supports the hypothesis that ILs are liquid at ambient conditions because the liquid state is thermodynamically favourable.

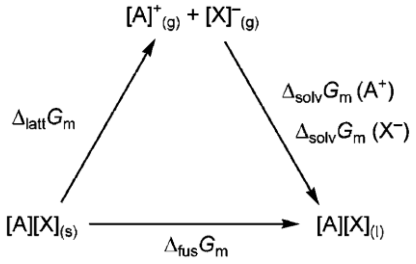


Fig. 1.1. *The Born-Fajans-Haber Cycle for Calculation the Molar Gibbs Energy of Fusion, $\Delta_{fus}G$, from the Lattice Gibbs Energy $\Delta_{latt}G$, and the Gibbs Energy of Solvation $\Delta_{solv}G$*

According to **Eq. 1.1**, this is the case because the lattice enthalpies $\Delta_{\mathrm{latt}}H$ (overall 411-492 kJ · mol^{-1}) and the large differences in entropies $\Delta_{\mathrm{latt}}S$ between the solid and gaseous state (0.324-0.387 kJ · mol^{-1} · K^{-1}) in ILs can be overcome by the solvation free energy of the individual ions in the bulk molten salt ($\Delta_{\mathrm{solv}}G$).

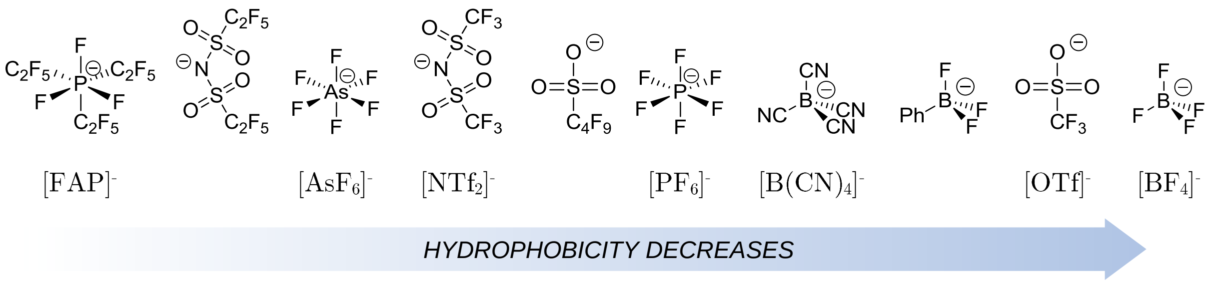
$$\Delta G = \Delta H - T\Delta S \qquad (1.1)$$

In typical salts such as NaCl the large $\Delta_{\mathrm{latt}}H$ (800 kJ · mol^{-1}) and small $\Delta_{\mathrm{latt}}S$ (0.158 kJ · mol^{-1} · K^{-1}) give a $\Delta_{\mathrm{latt}}G$ that is too large to be overcome by forming a molten salt, and thus the solid state is favoured [24].

According to the Coulomb's law, (**Eq. 1.2**) larger distance *r* between charged particles results in lower attractive forces. In the case of ionic liquids lower lattice energies should be caused by relatively large size of ions, and charges as low as ±1. The charge density is further minimized if delocalization over conformationally loosen conjugated system is possible.

$$F_C = \frac{z^+z^-}{4\pi\varepsilon_0 r^2} \qquad (1.2)$$

In water miscibility and other physicochemical properties of ILs, anion identity is of the foremost importance [25]. Due to the demand on anhydrous conditions hydrophobic IL's are under extended interest in many chemical processes. Ranke *et. al.* has showed the possibility to arrange the anions commonly incorporated in ILs in the sequence of hydrophobicity decrease [26–28] as follows:



This sequence, based on unit-less hydrophobicity parameter c_a, is derived from IL water solubility and reversed-phase chromatographic sorption measurements. Together with similar cation parameter c_c it precisely allows to predict the water solubility for a range of ion combinations [27]. However, this approach works if the IL considered is only partially water miscible.

Apparently, incorporation of fluorine in the structure of anion correlates with low melting points and water immiscibility and often points to the non-coordinative character of the anion [29]. The art of constructing the ultimate non-coordinating anion is to realize a structure without an accessible basic site. This may be achieved by a combination of steric as well as electronic effects [30, 31] and has led the fluorinated ILs to being under enhanced interest [32]. A typical example fulfilling the aforementioned requirements is *bis*-(trifluoromethanesulfonyl)imide anion, $[NTf_2]^-$. The corresponding acid, $HNTf_2$, is extremely strong thus making basicity of the anion low, and the electron-withdrawing trifluoromethyl- and sulfonyl- groups further enhance the charge delocalization. Besides, the di-substituted nitrogen formally bearing two pairs of unshared electrons extends the conformational freedom allowing two distinct conformers to exist in equilibrium (**Fig. 1.2.**) [33, 34]. If $[NTf_2]^-$ is replaced by its nonfluorinated homologue, *bis*-(methanesulfonyl)amide, there is a notable rise in viscosity and a decrease in thermal and electrochemical stability [29], highlighting the advantages of perfluorinated anions.

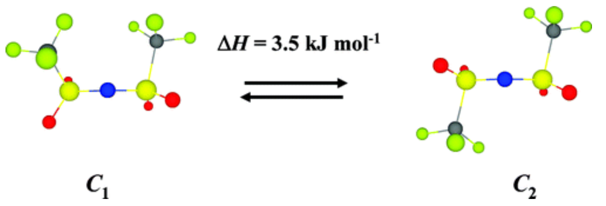


Fig. 1.2. *Conformational Equilibrium of $[NTf_2]^-$ Ion* [33]

Water sorption experiments have shown the contribution of imidazolium cation in hydrophobicity that increases with increasing the length of alkyl side-chains and substitution at imidazolium ring C-2 position [35]. However, these properties are temperature-dependant and phase separation may occur in aqueous IL solutions with temperature changes, as observed for $[BF_4]^-$ ILs [36].

The opposite requirement – hydrophilic ILs – is met in findings to satisfy the demand of renewable feedstock using biomass [37]. The hydrophilic properties are mainly dictated by anion character and are based on properties of oxo-anions of weak acids to act as strong hydrogen-bond acceptors. Two anions of superior hydrophilicity are considered to be acetate $[OAc]^-$ and dimethylphosphate $[C_1C_1PO_4]^-$ [38]. The cation's impact on the hydrophilicity mainly appears in case of hydroxy-functionalization, e.g. 1-(2-hydroxyethyl)-3-methylimidazolium $[(HO)^2C_2C_1im]^+$ and ethanolammonium $[((HO)^2C_2)NR_3]^+$ cations.

1.1.2. Ionic Liquids as Solvents from the Aspect of Green Chemistry

The solvent is requirement for most chemical transformations known excluding those classified as gas- or solid-phase reactions. It must be clear that there always is a reaction component playing the role of solvent, even if only reactants are present [39]. The idea of "green" solvents expresses the goal to minimize the environmental impact resulting from the use of solvents in chemical production [40]. Unquestionably, the advance of ILs highlighting them over molecular solvents is their negligible vapour pressure that makes atmospheric emission and respiratory exposure issues non-existent.

Reduction of environmental impact here is understood as (1) increasing the efficiency of chemical processes and (2) reducing the possible hazards to the chemist using ILs. Thus, the chemical company BASF has introduced BASIL™ process for the production of alkoxyphenylphosphines (generic photoinitiator precursors): after scavenging the acid by-product with 1-methylimidazole, it separates as a discrete ionic liquid $[C_1Him]^+$ phase rather than forms an insoluble paste that was the case before the substitution of triethylamine was made. The productivity of whole process is therefore increased by factor of 86 000 and is run on a multi-ton scale confirming that ionic liquids can rise the efficiency and be handled on industrial scale [41]. In another example carried out in BASF high reaction selectivity and hazards are significantly reduced by replacing phosgene $COCl_2$ with hydrogen chloride in synthesis of 1,4-dichlorobutane starting from the corresponding diol: solely the use of ionic liquid in this way achieved the only product to be the dihaloalkane with 98% yield fully avoiding the formation of by-products tetrahydrofuran, symmetric halo-ether or monosubstituted alcohol [42].

The biodegradability of ILs can be predicted from their structure with a trivial precision according to the same biodegradation pathways as for other chemicals [43, 44]. The OECD test has shown the octylsulfate anion and imidazolium cation that contains the ester linkages in side-chains are prone to degradation while those bearing pure alkyl-substituents are not. In addition, pyridinium ILs appeared to be more biodegradable than imidazolium ILs [45], ease of degradation following the alkyl chain length sequence $n=8>6>4$. Rorije *et. al.* has explained the resistance of imidazolium with *N*-substitution that apparently blocks attack by enzymes in the urocanase pathway of histidine metabolism [46]. Therefore, it is only obvious that naturally occurring anions and cations are the most biodegradable placing cholinium carboxylates as a typical example [47]. Nevertheless, ILs are classified as salts assuming that in environment the cation and anion will behave independently, what means cytotoxicity of ILs cannot be systematically estimated by a summation of the independent effects of the cation and anion – they both might interact with other ions present in environment thus complicating the study [48].

The other side of greenness of ILs lays in their tuneable properties. It has been approximated that ca. 10^6 binary ionic liquid structures are possible thus allowing to optimize the yield, selectivity, substrate solubility, product separation, and even enantioselectivity – to design a solvent for a specific reaction and not vice versa. Indeed, only ca. 600 common organic solvents are in use today [49]. Despite the beneficial properties of ILs, yet true ‘‘greenness’’ should incorporate a sustainable synthesis [50], low toxicity, and limited environmental persistence [51]. These aspects are still to be comprehensively considered for the majority of ionic liquids. The previous knowledge on compound stability is also referable to the ILs: higher the nitrogen content in formula unit, more likely to expect an aggressive decomposition if enough activation energy is supplied. Thus, some protic nitrate or tetrazole-anion containing ILs are experienced to be combustible, oxidizing or even explosive [52, 53].

It should be made clear, from the outset, that the common generalisations that ionic liquids are either ‘‘green’’ or ‘‘toxic’’ solvents should be avoided: both extremes are totally misleading [48]. The substitution of molecular solvents with ILs in laboratory is less likely to ever happen, they rather have a potential to be used in large-scale industrial processes to be worth.

1.2. Studies of Ion Pairing in Ionic Liquids

According to the IUPAC, an ion pair is a pair of oppositely charged ions held together by Coulomb attraction without formation of a covalent bond. Experimentally, an ion pair behaves as one unit in determining conductivity, kinetic behaviour, osmotic properties, etc. [54]. According to the Coulomb's law (**Eq. 1.2**), the attraction force between oppositely charged particles is inversely proportional to the dielectric permittivity of medium, thus, one could expect ion pairing at greater extent in low polarity solvents like chloroform, tetrachloromethane or dichloroethane than that in high-permittivity solvents like dimethylsulfoxide or primary alcohols.

For instance, in chloroform solution the ion-pair $[C_2C_1im]^{\cdots}[NTf_2]$ is sufficiently long-lived to distinct separate signals in ^{1}H-NMR spectra [55]. In gas phase only neutral ion pairs are implied as shown in high vacuum mass spectrometric studies by Armstrong *et.al.* [56]. Existence of ion pairs in gas-phase is also quantum-chemically proposed. For the common $[C_4C_1im]^{\cdots}Cl$ ion pair the lowest energy conformers are those *front-met*, *front-but* and *top* (**Fig. 1.3.**).

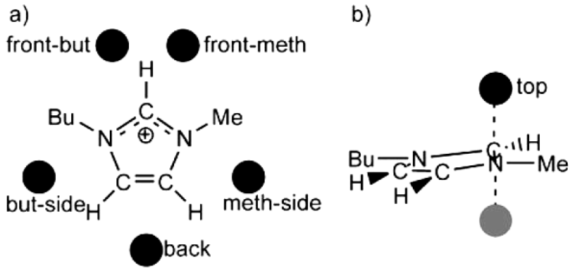


Fig 1.3. *Location of Primary Cation–anion Interaction Sites for $[C_4C_1im]Cl$: a) Cl Anion In-plane;* b) *Cl Anion Out-of-plane* [57]

For sure, spherical anions X^{-} with suitable radius almost always will tend to form the essentially ionic C^2—H$^{\cdots}$X bridge with nonsubstituted imidazolium ring [57]. By contrast, the role of hydrogen bonding with C^2—H with voluminous anions like $[PF_6]^-$, $[NTf_2]^-$ and $[BF_4]^-$ so far remains controversial [58].

The ε values of some common RT-ILs [59] and molecular solvents (**Fig. 1.4.**) affirm that the structure and composition of ionic liquids have no significant impact on their dielectric permittivity, which in overall is relatively low.

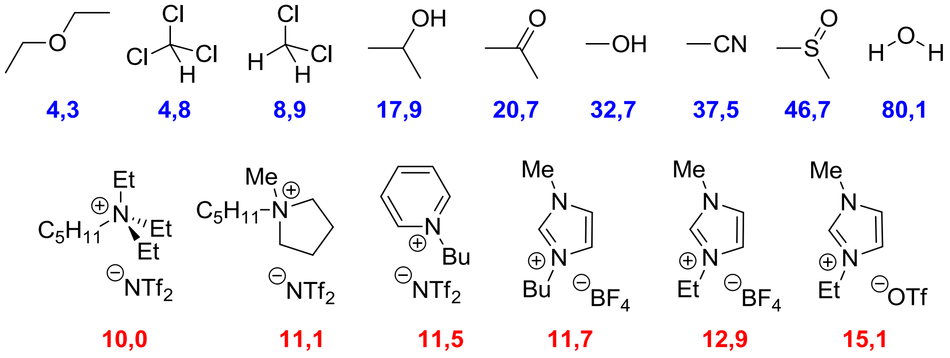


Fig 1.4. *Dielectric Permitivity* ε *of some Molecular Solvents and RT-ILs* [59]

Unfortunately dielectric permittivity does not representatively characterize the medium's solvent nature; it rather describes the bulk system properties [58] instead of its ability to solubilize other solutes.

Undoubtedly, bulk IL is entirely different medium from separate ion pairs. Conductivity measurements speak in favour to the existence of ion pairing and do not conform to expectations for fully dissociated systems [60–62]. However, the net charge of the particles greatly complicates the understanding of the electrostatic interactions:

the charged neighbours around a given particle screen its electrostatic interactions with particles that are located further away. Molecular dynamics simulations have shown, as a result, the dipole–ion and dipole–dipole interactions scarcely exceed two solvation shells [63, 64] what is in strong contrast to the molecular solvents.

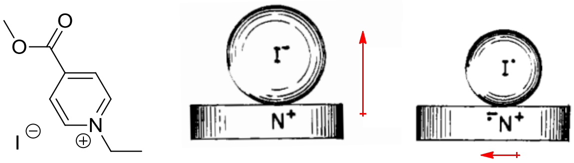
1.2.1. Charge Transfer Phenomenon - Terms and Definitions

CT is an electron-donor–electron-acceptor complex, characterized by electronic transition(s) to an excited state in which there is a partial transfer of electronic charge from the donor to the acceptor moiety [54, 65]. When two compounds in solution are brought together and a new optical absorption band is formed that was not present in the spectrum of either component, then it is likely that a CT complex has been formed:

$$\underset{\textit{colourless}}{\mathbf{A}} + \underset{\textit{colourless}}{\mathbf{D}} \rightleftharpoons \underset{\textit{coloured}}{\mathbf{AD}} \qquad (1.3)$$

This is particularly true when one of the components is good electron donor (has a low ionization potential) and the other is a good electron acceptor (has a high electron affinity) [66]. It also correlates with the relative energies of molecular orbitals – in case if acceptor's LUMO energy is lower than HOMO energy of the acceptor, and their orbitals are compatible in space, charge migration to acceptor occurs. Of course, transfer of the charge of whole electron would lead to irreversible oxidation, so the charge transferred usually is equal to 0.02–0.074 e^- like in CT complexes of 4,4'-bipyridinium cations [67].

On the way towards the spectroscopically active CT species in solutions of ionic compounds, what is the case of Kosower's salt 1-ethyl-4-methoxycarbonylpyridinium iodide **1**, the first step is formation of ground state complex – ion pair **1a** (**Fig. 1.5.**). Upon excitation (i.e,. light absorbtion), the charge is transferred thus changing the direction of dipole in the excited complex **1b** and lowering its magnitude [68].



1 **1a** **1b**

Fig 1.5. *CT Complexation in Kosower's Salt: its Ground (**1a**) and Excited (**1b**) State* [68]

It is noteworthy to emphasize that only spectroscopically active units like **1b** obeys the Beer—Lambert's law,

$$A = \varepsilon\, C\, l \tag{1.4}$$

while it cannot be said about all the salt **1** present in solution. In other words C in eq. **1.4** states only for the ions within the intimate ion pairs. The fraction of ions viable to take part in this process is strongly concentration dependant: at low concentrations all the ions are solvated by solvent molecules and cannot take part in ion pairing, while at high concentrations this equilibrium shifts towards left (Eq. **1.5**).

$$\underset{\textit{intimate ion pair}}{\mathbf{[Py]I}} \overset{K_1}{\rightleftharpoons} \underset{\textit{solvent separated ion pair}}{\mathbf{[Py]^{+} \,||\, I^{-}}} \overset{K_2}{\rightleftharpoons} \underset{\textit{free ions}}{\mathbf{[Py]^{+}, I^{-}}} \tag{1.5}$$

Thus ε calculated from the absorption serves as a measure of ion pairing in examinated media.

1.2.2. Ionic Liquid Systems with Singly Charged Ionic Solutes

In view of the before mentioned circumstances the question is proposed whether there is ion pairing in ionic liquids if they are employed as solvents for ionic solutes. The investigations by Welton *et. al.* have led to the main insights about the state of ionic solutes $A^{+}B^{-}$ in ILs $X^{+}Y^{-}$. Owing to the physicochemical properties of the Kosower's salt 1-ethyl-4-methoxycarbonylpyridinium iodide (**1**), it has been demonstrated there are no specific interactions known as ion pairing in a bulk IL while it is obvious in common molecular organic solvents such as dichloroethane, acetonitrile and butanol-1. This is proved by the different trends in changes of ε with increasing the total concentration of Kosower's salt in solution – in molecular solvents equilibrium (Eq. **1.5**) takes place and curve is observed (**Fig. 1.6.**) while in ionic liquids ε increases linearly. Thus, also in IL pyridinium and iodide ions unavoidably get in contact with each other; the frequency of these collisions increases with concentration only because the probability of two ions to collide increases just if greater number of these ions is present, without regard to the different chemical entities of all ions in solution [3, 69].

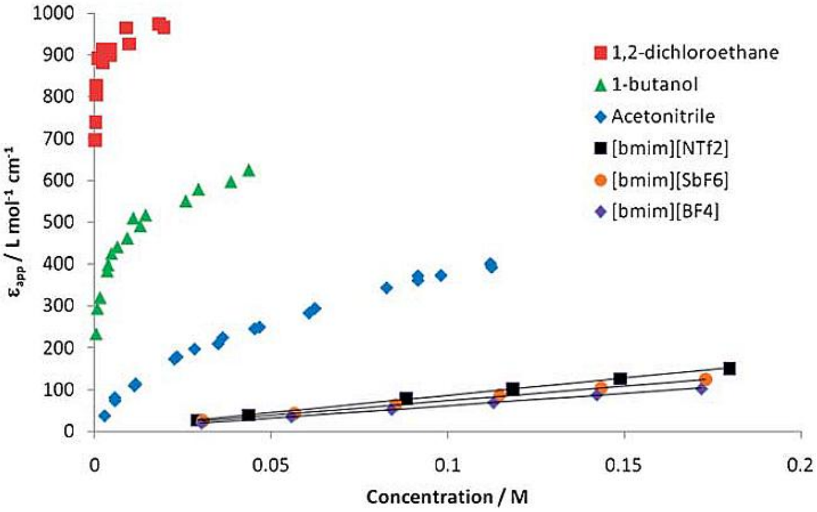


Fig 1.6. *Molar Absorptivity of Kosower's Salt in Different Solvents versus its Concentration* [70]

2. RESULTS AND DISCUSSION

2.1. Synthesis of the Ionic Liquids

In this work, ionic liquids for different purposes were prepared. First of all, these were the solvents whose properties were studied, and included [C_4C_1im][NTf_2], [C_4C_1pyrr][NTf_2], [C_4C_1im][OAc] and [C_4C_1im][$MeSO_4$]. Another role of IL's was as the source of the di-anions that could be easily introduced into solution due to their miscibility with each other. The assumption that all the ILs are necessarily miscible can't be accepted as a rule, especially if their component-ions bear different unit charges. There are several examples in literature when two ILs are immiscible and forms multiphasic mixture [71]. Nevertheless, this was not the case here.

***bis*-(Trifluoromethylsulfonyl)imide-based ILs.** The chosen synthetic route for *bis*-imide ILs was based on accepted principles for ILs with non-hydrogen bonding anions, and included two separate steps and purification after each of them (**Fig. 2.1.**).

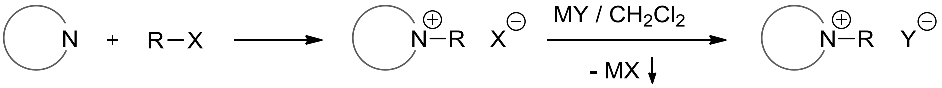


Fig. 2.1. Scheme of Typical Synthetic Route for Hydrophobic ILs

Using 1-chlorobutane and corresponding amines, quaternary ammonium chlorides were prepared applying relatively low temperatures and allowing the alkylation to proceed for several days in ethyl acetate. Apart from purifying starting materials, mild reaction conditions are another precondition [72] to reduce the colour of final ILs, thus making them suitable for UV-Vis spectroscopic examination.

Regarding the miscibility of starting materials with ethyl acetate and insolubility of the product in it, such a choice of solvent offers a simple removal of any unreacted starting material after the completion of reaction. However, an excess of alkylating agent was used to avoid any residual 1-methylimidazole, that often makes the purification of the products difficult, even if present in trace amounts, and causes significant changes in physicochemical properties of the final [C_4C_1im] ILs, especially lowering of π^* value [38].

As the next step, anion exchange was performed. Employing the very hydrophobic and charge diffuse character of *bis*-(trifluoromethylsulfonyl)imide anion [34], it was possible to perform direct metathesis in DCM/aqueous solution. The choice of Li[NTf_2] as a source of desired anion apart from commercial availability is accompanied by benefits of oxophilicity of lithium cation, that ensures the good water solubility of this salt. Both being hard ions and interacting with water to the maximum extent from all the ions present in solution, Li^+ and Cl^- separates during the metathesis within aqueous phase, while the hydrophobic and charge diffuse ammonium and $[NTf_2]^-$ ions create an isolated, denser ionic liquid phase. Considering the circumstance there is no trivial and rapid method known so far to confirm the presence/absence of residual $[NTf_2]^-$ ions, what cannot be said for Cl^-, a slight excess of corresponding ammonium chlorides was taken for metathesis. After separation from the aqueous phase, formed *bis*-imide ionic liquids were thoroughly washed with several portions of water to remove any residual chlorides, whose presence was checked by $AgNO_3$ test. The lack of precipitate or turbidity after addition of Ag^+ to aqueous washings is a straightforward and reliable test for chloride content in ionic liquid, and certifies [Cl^-] being lower than 7 ppm, as results from the K_{SP} of AgCl [73].

The resulting colourless and viscous liquids were finally treated with powder of activated charcoal in order to ensure removal of nonpolar impurities, and then filtered through a short pad of basic and acidic alumina to remove charcoal and bind any acidic and basic contaminants [74]. Care must be taken before using thereafter obtained ILs – although visible particles of sorbent were not present, the neat salts were passed through 0.45 μm PTFE filter in order to achieve alumina-free products [75] and avoid deviations from proper elemental composition, as suggested by A.J.S. McIntosh from his personal experience.

It is well known that majority of ionic compounds containing $[NTf_2]^-$ are characterised by low water solubility, so the overall hygroscopicity of the *bis*-imide IL is determined by the nature of cation. The above-mentioned ILs are capable to adsorb up to 2.5% by weight [76, 77] of water, what in case of $[C_4C_1pyrr][NTf_2]$ is equal to molar fraction of $\chi(H_2O) = 0.2$ [77], so drying at elevated temperature under vacuum and magnetic stirring was performed.

1-Butyl-3-methylimidazolium Acetate. Seemingly the most economically favourable synthetic route to this IL utilizing metathesis of $[C_4C_1im]Cl$ with NaOAc would not lead to success. When desired anion's hydrogen-bonding strength is high, metathesis in DCM reaches equilibrium giving the mixture of anions Cl^- and $[OAc]^-$. The purification of the mixture is problematic and surely excludes continuous extraction due to the strong preference of $[OAc]^-$ to the aqueous phase. The demand for other approaches is still under interest. Here, the regular acid-base neutralization reaction was employed. To the aqueous $[C_4C_1im]OH$ a slight excess of AcOH was added. The water and residual acid were then removed under reduced pressure yielding the desired IL.

1-Butyl-3-methylimidazolium Methylsulfate. Undoubtly, 1-alkyl-3-methyl imidazolium methylsulfates can be suggested as ones that are the easiest to prepare. Typically known as a cheap and powerful alkylating agent, dimethyl sulfate here acts both as the quaternizing agent and a source of anion. Obviously, in this case starting imidazole already must be *N*-substituted with the desired non-methyl side-chain. This can be the limiting economic obstacle to employ the above-mentioned route in industry, due to different ways how *N*-methyl- versus other *N*-alkyl-imidazoles are produced [78], and results in distinct costs.

Apart from precautions that must be taken using the poisonous and carcinogenic dimethylsulfate, the reaction is easily carried out at room temperature in toluene, and finally gives a separate layer of ionic liquid. A thorough washing with multiple portions of toluene necessarily was performed since the reaction did not proceed to completion at selected conditions, and some starting materials were left. Obtained $[C_4C_1im][MeSO_4]$ was further worked up in the same way as *bis*-imide ILs.

1-Butyl-3-methylimidazolium Hydrogensulfate. The ester functionality of methylsulfate anion may serve as a useful starting material on the way to ILs with various anions which have stable corresponding Brønsted acids available (**Fig. 2.2**). The hydrolysis of mentioned $[C_4C_1im][MeSO_4]$ required harsh reaction conditions, but still coincided with the general principles of hydrolysis of esters, – presence of acid catalyst, excess of water and removal of the formed alcohol.

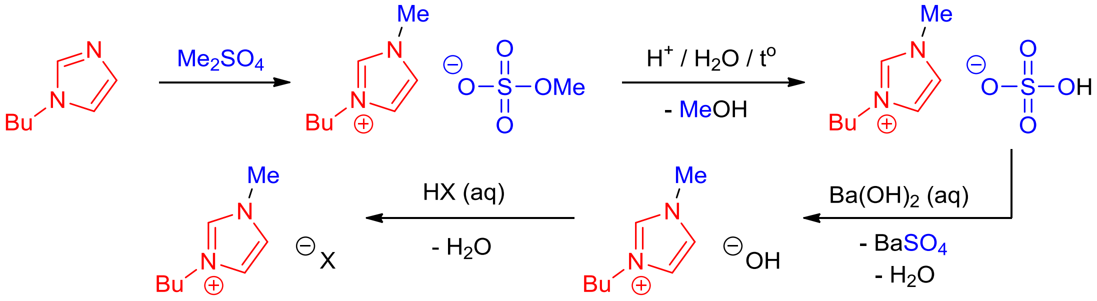


Fig. 2.2. Scheme for the Synthesis of ILs using Dimethyl Sulfate

In this case only an acid can be selected as a catalyst; the presence of a strong base in the neat imidazolium ionic liquid may lead to the formation of *N*-heterocyclic carbene [79, 80], which is known as a reactive nucleophile and therefore may cause a complex contamination [81]. Thence, a catalytic amount of sulphuric acid was added to the aqueous solution of $[C_4C_1im][MeSO_4]$, and it was heated until the temperature reached c.a. 170 °C, allowing the methanol to leave the reaction medium. Water was repeatedly added till the complete disappearance of methyl sulphate signal in the NMR spectrum.

It is an interesting fact indeed, why and how exactly the hydrolysis of methyl sulphate anion does occur. From the first look the initial site of protonation in methyl sulphate anion expected could be the negative oxygen anion. That, of course, would exclude the possibility of hydrolysis, especially knowing the significant excess of methyl sulphate ions over the amount of sulphuric acid present. It means methyl sulphuric acid must be stronger than sulphuric acid in order to get the reaction to proceed.

In spite of the high structural similarity between hydrogen sulphate and methyl sulphate anion, corresponding acids differ in the number of acidic protons they owe. While methyl sulphuric acid takes part in protolytic equilibria with one proton only, ionisation of sulphuric acid involves two protons. At the same concentration of acid, the number of water molecules to interact with protons of the acid remains the same, so the statistical factor might be a feasible issue and somehow make the only proton of methylsulfuric acid higher ionizable.

More reasonable might be explanation regarding the differences in structure. Apart from the ionizable oxygen – hydrogen bond, the diversity between both molecules lays in unequal electronegativities of hydrogen versus carbon (**Fig. 2.3.**). While REN of oxygen is 3.44, this value for hydrogen and carbon is 2.20 and 2.55, respectively [82]. Although not serious, this circumstance causes more negative inductive effect in H_2SO_4 and significant difference in dipole moments of both molecules. It results in O—H bond being more polar and therefore more ionizable in methyl sulfuric acid than in sulphuric acid. Also crystallographic and computational bonding studies of the octet rule violating sulfonyl-compounds confirms this judgment [83].

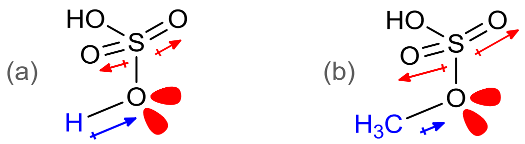


Fig. 2.3. Structure of (a) Sulphuric Acid and (b) Methylsulphuric Acid

Indeed, pK_{a1} of H_2SO_4 is -2.8±0.5, while for $MeSO_3OH$ it is -3.4±0.5 [84]. For sure, a competition between the sites of protonation probably exists, as the difference of pK_a values is small, and ester-anion hydrolysis is probably also favoured by loss of the volatile methanol (**Fig. 2.4.**).

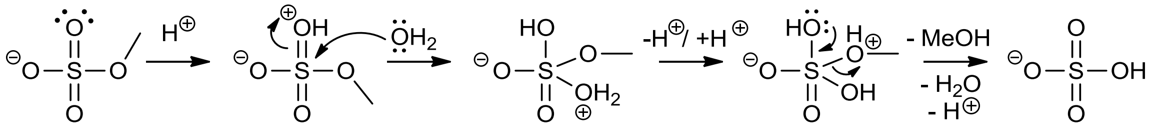


Fig. 2.4. Hydrolysis of Methyl Sulfate Anion

1-Butyl-3-methylimidazolium hydroxide. The hydrogensulfate anion, partially being acid, can be neutralized with metal hydroxide, and resulting sulphate anion precipitated leaving OH^- as an anion. There are two general requirements for this metal hydroxide:

- high enough water solubility to avoid dealing with large volumes of diluted aqueous solutions;
- low enough solubility of corresponding metal sulphate salt to avoid contamination of the final solution.

Owing to the good water solubility of group IA metal salts, these can't be considered as the hydroxides of choice, therefore some of the group IIA elements should be employed. The only appropriate hydroxide in terms of solubility is $Ba(OH)_2$, whose saturated solution at 80 °C contains 50% of this compound. Furthermore, the solubility product K_{SP} of $BaSO_4$ is $1.10 \cdot 10^{-10}$, what ensures concentration of Ba^{2+} and SO_4^{2-} being only about 10^{-5} M in saturated solution [85].

In order to obtain particles of $BaSO_4$ as large as possible and significantly facilitate the filtration, both solutions of reactants were mixed almost boiling. It was observed that the use of boiling solutions – although aqueous – caused $[C_4C_1im]OH$ solution to be coloured what means the final ILs will not be colourless. After repeating the same procedure with room-temperature solutions, separation of $BaSO_4$ was found to be doable.

The $[C_4C_1im]OH$ solution was potentiometrically titrated with hydrochloric acid before the use and utilized in preparation of $[C_4C_1im][OAc]$.

2.2. Preliminary Findings of Desired Charge Transfer Complex

There are several different properties of desired CT salt that are required for it to be suitable for solvation phenomenon studies. Apart from (1) having CT character in solution, the salt (2) needs to be soluble in ionic liquids in a concentration range wide enough to observe the trend of molar extinction change. Most ILs are composed of monocation and monoanion, what obviously is essential property for the dye regarding similarity that Kosower's dye owe, and results in even greater its solubility in ionic liquids than in molecular solvents [3]. Unlike this case, **(3)** dye for further studies of ionic liquids X^+Y^- above all requires being doubly charged, $A^{2+}B^{2-}$. That could result with problems in solubility because of more preferential Coulombic interactions between doubly charged particles rather than singly charged, in this way favouring the crystalline state. On the other hand, the doubly charged ions could be better solubilized by the ions of IL, thereby ensuring dissolution but weakening intensity of CT.

The other part of „like dissolves like" approach should regard similar specific interactions that neat ionic liquids have. IL cation usually contains linear alkyl chains that might interact with supposed alkyl chains in dye's cation via hydrophobic interactions, thus, increasing solvation of cation and solubility as well. The other inherent interaction to utilize is hydrogen bonding ability. On the first look, the bipyridinium moiety, what is structurally highly related to Kosower's dye, itself contains neither hydrogen bond donating, nor accepting sites; the double positive charge is delocalized over the conjugated system. Apart from that, easily functionalizable side-chains on nitrogen atoms could contain both hydrogen bond donating and accepting functional groups.

It may be worth of considering to force the so-called π-π stacking what is characteristic for bipyridinium salts in crystalline state [86]. Introducing sterically bulky substituents, *tert*-butyl representing the most common example with this character, might be another choice. However, inspecting the previous attempts to synthesize the corresponding bipyridinium salt, low yields and harsh reaction conditions appears what is probably due to the steric hindrance around the centre of nucleophilic attack. What is more important, the corresponding bromide appears to be a white solid, what purports to the lack of charge transfer. Presumably anion cannot reach the bipyridinium moiety close enough to ensure the CT.

Finally, **(4)** the chemical compatibility with solvent and stability under laboratory conditions is compulsory requirement since a large number of measurements afterwards will have to be performed.

Considering the above-mentioned challenges one might meet, it was decided to introduce both components – cation A^{2+} and anion B^{2-} – in solution separately regarding that the synthesis of the desirable $A^{2+}B^{2-}$ with previously unknown composition would require too much effort. The bipyridinium cation A^{2+} was decided to introduce in IL in the form of some of its diquaternized salt, whereas anion B^{2-} – as the corresponding $[C_4C_1im]^+$ salt thus providing the same chemical composition of the system as if the authentic compound $A^{2+}B^{2-}$ would have been introduced (**Fig. 2.5.**).

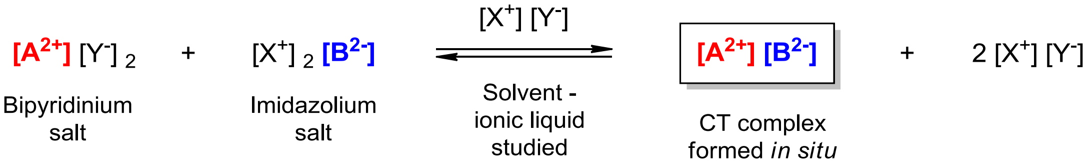
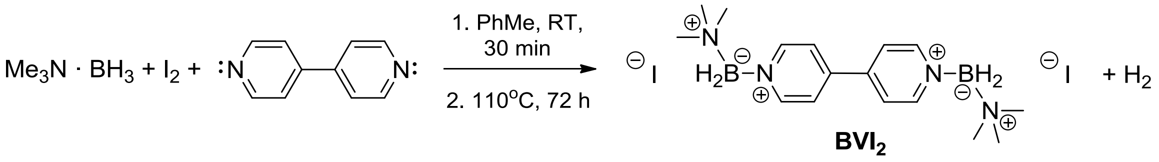


Fig. 2.5. The Chosen Approach for the Formation of Solvent – Solute System

2.3. Design of the Dication

2.3.1. Boronium Viologen-based Salts

The first CT dication chosen to test was boronium-based viologen in form of its diiodide BVI_2. The synthesis was carried out according to the only procedure described in literature [87] although the property of borane-amine complexes to form bisamine complexes is well known [88]. Starting from 4,4'-bipyridyl, trimethylamine—borane adduct and elemental iodine synthesis proceeded according to the reaction: **(2.1)**



As can be seen from the crystal structure (**Fig. 2.6.**) [87], the choice of this dication is not just circumstantial: both pyridinium rings are located in plane and the charge is further delocalised over the trimethylammonium–boron "-ate" moieties. The cation's geometry is expected to favour charge acceptor properties. Indeed, the solid salt exhibits bright-orange colour what could be associated with iodide to bipyridinium CT.

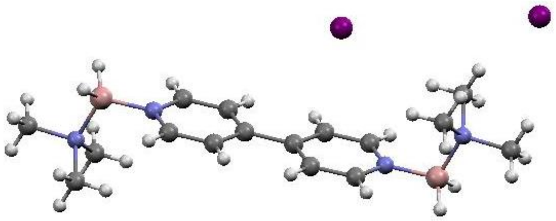


Fig. 2.6. Crystal Structure of BVI_2

In order to test if CT also occurs in solution, UV-Vis spectroscopic measurements were performed. Unfortunately, neither of the solvents - 1,2-dichloroethane and acetonitrile - used in previous study with Kosower's salt were capable to solubilize BV iodide well enough so alternative solvents were considered. As expected, nitromethane proved to dissolve BV iodide with ease, but due to its possible chromophore behaviour and safety concerns was refused. As an alternative, *N*,*N*-dimethylformamide was chosen exhibiting the solubility of BV iodide up to $1.6 \cdot 10^{-2}$ M.

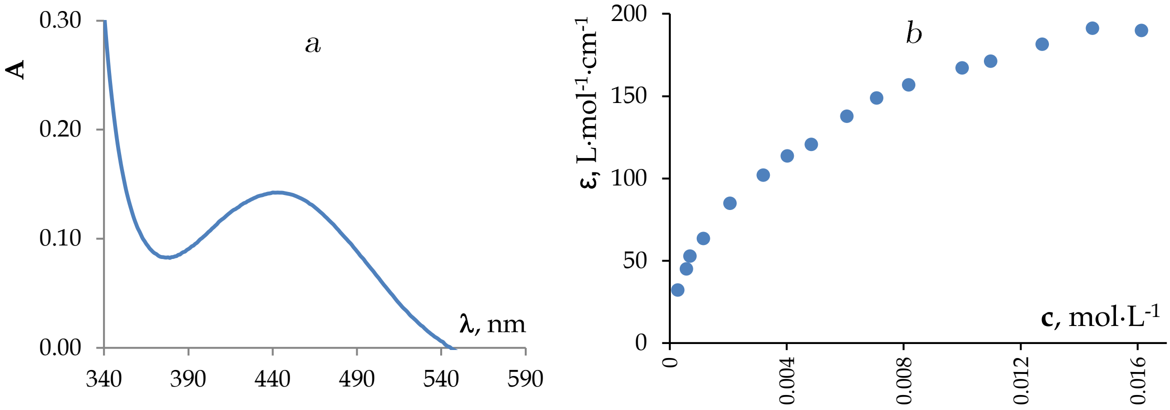


Fig. 2.7. *a* – UV-Vis absorbtion spectrum of BVI_2 in DMF, λ_{max}=433 nm
b – molar absorptivity of BVI_2 versus concentration of DMF solution

The BV iodide's UV-Vis spectrum in DMF (**Fig. 2.7.a**) exhibits an absorption maximum of 433 nm. This band was supposed to correspond to CT transition, so this assumption had to be proved by measuring a series of solutions: by knowing solution's concentration and absorbance one can easily calculate the molar absorptivity ε. The obtained trend of ε versus concentration confirms the presence of CT equilibrium in solution of BV diiodide (**Fig. 2.7.b**). For the first time this kind of relationship for iodide CT with dicationic acceptor is plotted thus affirming that in overall this phenomenon is similar to behaviour of Kosower's salt.

The following step was to examine this CT system in IL medium. From ionic liquids where ion pairing has been studied before, $[C_4C_1im]NTf_2$ was chosen, as it is widely known and is highlighted by hydrolytic an thermal stability, low viscosity and broad liquid-state range. Besides, the others – $[C_4C_1im]SbF_6$ and $[C_4C_1im]BF_4$ – are notorious with their tendency to undergo hydrolysis thus forming the hazardous HF [89].

Unfortunately, attempts to dissolve BV diiodide were not successful by unknown reason so it was decided to test the effect of anion on the dissolution of BV salt. Although "soft" and with a large radius, iodide still is conformationally definite – it is spherical. This consideration may be the reason of firm packing of ions in BV iodide crystal lattice thereby preferring solid state or making dissolution kinetically slow. The anion with completely opposite character is *bis*-(trifluoromethanesulfonyl)imide, $[NTf_2]^-$. Due to its hydrophobic character the corresponding BV salt was prepared with ease employing a simple metathesis in aqueous solution:

$$BVI_{2(aq)} + 2LiNTf_{2(aq)} \rightarrow BV(NTf_2)_{2(s)} + 2LiI_{(aq)} \tag{2.2}$$

The starting orange-red BV iodide formed almost colourless solution in water evidencing that strong solvation in the protic and strongly polar media takes place thus denying the formation of intimate ion pairs. After addition of $LiNTf_2$ an immediate evidence for the lack of CT in produced $BV(NTf_2)_2$ was observed – the desired salt appeared to be without any characteristic colour. Unfortunately, BV *bis*-(trifluoromethanesulfonyl)imide showed no enhanced solubility in comparison with iodide analogue – the solute signals were hardly noticeable in ^{1}H-NMR spectrum of its saturated $[C_4C_1im]NTf_2$ solution.

It is not clear if the solubility of ionic solutes in ionic liquids are expressed by solubility product constant K_{SP}. In case if the solubility equilibrium follows this rule, the failure of this attempt might be explicable with the so-called common ion effect from $[NTf_2]^-$ ion:

$$\mathrm{K_{sp}} = [\mathrm{BV}^{2+}][\mathrm{NTf}_2^-]^2 \tag{2.3}$$

2.3.2. 1,1'-Dialkyl-4,4'-bipyridinium-based Salts

Due to the lack of solubility of $BV(NTf_2)_2$, viologen dications were considered for further examination. Historically, the abbreviation "viologens" states for the salts of *N*,*N*-dialkyl-substituted 4,4'-bipyridine, and the most common example is herbicide paraquat dichloride (*N,N'*-dimethyl-4,4'-bipyridinium dichloride). Apart from being doubly charged, many viologen CT complexes with anions bearing high charges are known, these include $EDTA^{4-}$, $EDTAH^{3-}$, $[Fe(CN)_6]^{4-}$, S^{2-}, citrate^{2-}, oxalate^{2-} [67], acetate [90, 91] (complexation at solution-phase), $[CuCl_4]^{2-}$, $[FeCl_4]^{2-}$, $[Cu_2Br_4]^{2-}$, $[Ag_2I_4]^{2-}$ (complexation at solid-state) [67].

All the bipyridinium halides used in this work were prepared through the reaction of bipyridine with alkylhalides, also known as Anderson quarterisation [92]. As expected, the reactivity of alkyl halides in this reaction follows the order R—I > R—Br > R—Cl, and offers the access to various bipyridinium diiodides and dibromides. Unfortunately, dichlorides can't be obtained via this route as the nucleophilicity of the neutral nitrogen atom in bipyridine is diminished after the first quaternization takes place, and another C—Cl bond by the remaining neutral nitrogen is not cleaved.

In general, reaction conditions were similar for all substrates and typically required reflux of starting materials in polar solvent for 24 hours. Normally, the dipolar and aprotic acetonitrile as the S_N2 conditions favouring solvent was chosen.

However, the use of ethanol, rectificate or absolute, gave no significant differences. A slight excess of alkylating agent over the stoichiometrical amount (up to 2.5 eq) was always taken to ensure complete conversion of the starting bipyridyl.

In some cases other anions for bipyridinium cation such as $[OTf]^-$, $[NTf_2]^-$ were required (**Table 2.1.**), so ion exchange from halide to the desired anion was found to be the most straightforward route. The aqueous solutions of bipyridinium halides were treated with the corresponding silver salts, yielding insoluble silver halide by-product and leaving the product in the aqueous solution.

The purpose for choosing so different structures was to estimate if certain functionalities lead to enhancement in solubility. Basically, three groups of symmetrical viologen salts with similar features (**Table 2.1.**) can be distinguished.

A – Salts with side-chains containing only hydrocarbon-derived backbone. In general, the prolongation of alkyl chain length increases the degrees of conformational freedom thereby favouring entropy-controlled behaviour and weakening other possible ways of interaction. Also, as mentioned before, the presence of hydrophobic element in solute may specifically interact with solvent if it also bears moiety with this character. In case of imidazolium ILs this role is played by the often employed butyl side chain.

B – Salts containing ester functionality to evaluate if it possesses any effect on solubility behaviour of dicationic solutes. It must be noted that none of these examples contain the ester group conjugated with the cation; it acts only as the site for specific interactions owing to the moderate hydrogen-bond acceptor character. Also, various linker lengths and connections are chosen.

C – Salts with especially pronounced hydrogen-bond donor and acceptor functionalities.

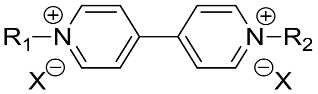
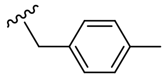
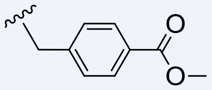
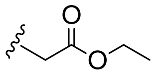
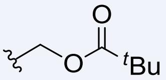
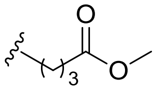
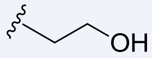
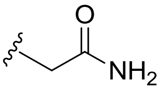


Table 2.1.

Viologen Salts $R_1R_2VX_2$ Synthesized and Corresponding Temperatures of their Melting or Decomposition

Group	Substituent R	*yellow*	*orange-red*	*colourless*	
		X^-; m.p.*	X^-; m.p.*	X^-; m.p.*	X^-; m.p.*
A	—Me		I^-; 320‡	$[NTf_2]^-$; 127	
	—Et	Br^-; 250‡			
	—^{n}Bu	Br^-; 266‡	I^-; 335‡	$[NTf_2]^-$; 86	$[OTf]^-$; 255‡
	—$^nC_8$	Br^-; 280	I^-; 280		
	—$^nC_{14}$		I^-; 290‡		
			I^-; 249‡		
B			I^-; 238‡		
		Br^-; 200‡	I^-; 195‡		
			I^-; 252‡	$[NTf_2]^-$; 131	
			I^-; 204‡	$[NTf_2]^-$; 90	$[OTf]^-$; 147‡
C		Br^-; 265‡	I^-; 255‡		
			I^-; 268‡		

* Temperature, °C, at which melting or decomposition (‡) was observed

At some point, the melting point of substance speaks about the energy of crystal lattice what needs to be overcome for the meltdown to proceed. The same amount of energy needs to be obtained via solvation interactions to ensure the dissolution. Unfortunately, bromide, iodide and triflate viologen salts undergo thermal decomposition upon heating what forbids correlating these temperatures with their solubilities. The only conclusion derived from the temperatures of decomposition of iodides is, that these viologens with shorter alkyl chains are more stable than their extended associates and their crystal energies most likely are higher compared to those of $[NTf_2]^-$ salts.

The mechanism of decomposition for dicationic viologen salts has been proposed and experimentally confirmed before: the example with acetate viologen salt showed the nucleophilic attack of the basic anion to the α carbon in *N*-substituent at room temperature in aqueous solution [91]. Thermal degradation of imidazolium ILs also follows similar pathway [93]. Here, the requirement for high temperatures is satisfied and appears a reasonable explanation even regarding the significantly lower basicity of Br^-, I^-, $[OTf]^-$ and the solid state of the salts.

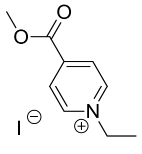
At the same time the $[NTf_2]^-$ viologen salts show smooth melting without any noticeable decomposition. Shorter side-chain length and conformationally more fixed, bulky substitution at the dication ensures higher melting points of the bisimide salts whereas extension of the side chain leads to increased degrees of conformational freedom despite their chemical entities, and the melting points of bisimide salts are thus lower. These observations are in full consistence with the relations determining the melting point of any ionic liquid.

The clear evidence for the anion CT donor properties is demonstrated by the colours of the respective viologen salts: $[NTf_2]^-$ and $[OTf]^-$ are colourless thus certifying they do not give CT to the viologen dication while all the iodides and bromides are strongly coloured.

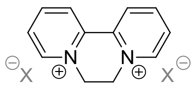
So far there are no obvious correlations comparing the salts within groups **A**, **B** and **C**.

2.3.3. 1,1'-Dialkyl-2,2'-Bipyridinium-based Salts

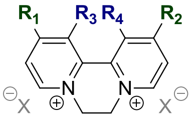
The highest similarity to Kosower's salt **1** can be attributed to the substituted derivative of diquat **4**. This dication, being conformationally more fixed than any of viologens, also possesses two ester-functionalities bonded to the pyridine ring. Obviously, it has increased departure from coplanarity in comparison with its methylene analogue **5** due to the ethylene bridge which attempts to adopt the pseudo-hexadiene-1,3 ring conformation [94]. Unfortunately, the obviously planar methylene-bridged 2,2'-bipyridinium dication **5** spontaneously undergoes the reduction and is not stable [95]. The demand for intramolecularly bridged dication is not a whim: with two individual molecules of alkylating agent rotation around the C^2—$C^{2'}$ axis would freely occur thereby distorting the planarity of cation what is necessary for CT to occur.



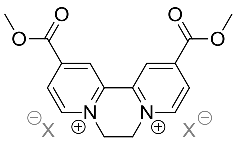
1



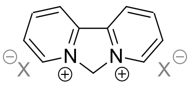
2



3



4



5

Many authors, including Kosower [68], justify the role of ester-funtionality in *Z*-scale dye **1** only as enhancer of its solubility in many solvents. To evaluate if ester functionalities may prove to be crucial for solubility also in dication, the non-functionalized diquat dibromide **2** (X=Br^-) was prepared [96]. Again, the reactivity of dichloroethane was not sufficiently high so the dibromoethane was used as an alkylating agent. Owing to that the reaction was carried out in neat dibromoethane without any dipolar solvent added, and that the formation of six-membered ring is thermodinamically favoured, no homo-coupling with another substrate molecule was observed.

The rough evaluation of bromide's solubility didn't show significant improvements compared to that of BVI_2, so necessitated to perform the anion metathesis with $LiNTf_2$ in a similar way as before. Unfortunately, this manipulation still did not lead to decent results; diquat bisimide **2** (X=$[NTf_2]^-$) exhibited the solubility in $[C_4C_1im][NTf_2]$ of only 1.40±0.19 mol%.

These results urged to continue with synthesis of the ester-functionalized analogue. The route was based on the three-step synthesis with the first two steps reported before (**Fig. 2.8.**). The direct synthesis starting from the ester-functionalized 2,2'-bipyridyl was not possible due to the absence of commercial sources of the substrate.

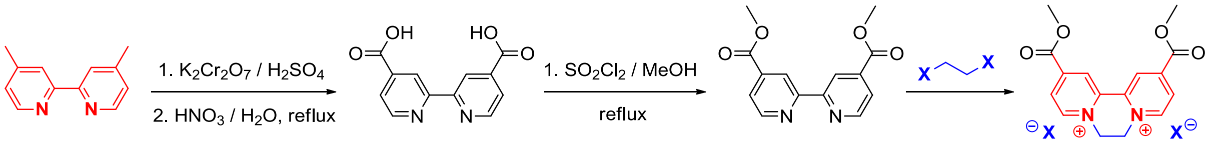


Fig. 2.8. *The Synthetic Route to the Ester-functionalized Diquat*

The pathway to the ester-functionalized diquat proceeded smoothly and yielded the desired product in two steps with 77% yield after purification [97, 98]. Unfortunately, the following step of diquaternization was problematic. The reaction with dibromoethane in similar conditions as for the preparation of diquat dibromide did not progress at all even after 19 h reflux in neat dibromoethane, as evinced by ^{1}H-NMR. Addition of DMF to the reaction mixture led to the formation of unidentifiable, crystalline and completely insoluble (MeCN, DMSO, DMF, H_2O) substance – presumably the polymeric homo-coupling product was formed.

It is mandatory for the monoalkylated intermediates to be even a little soluble in reaction medium thus making them available for further reaction [99], so similar reaction was repeated in a solvent with higher polarity than that of dibromoethane but lower than of DMF, respectively, in DCM. Even when the more reactive alkylating agent, 1,2-diiodoethane, was taken no progress of the reaction was observed after 72 h at the boiling point of DCM.

This failure could be explained with the reduced nitrogen nucleophilicity due to the electron-withdrawing methoxy-carbonyl-functionalties in *para* positions of 2,2'-bipyridine. Moreover, the extended conjugation of the aromatic system reduces electron density even more. Several literature examples on preparation of substituted diquats **3** are known:

$\mathbf{R}_1$=$\mathbf{R}_2$=Me, X=[OTf]$^-$ [100];

$\mathbf{R}_1$=Me, $\mathbf{R}_2$=CH_2Br, X=[OTf]$^-$ [100];

$\mathbf{R}_1$,$\mathbf{R}_2$=$(CH_2)_n$, X=Br$^-$ [101];

$\mathbf{R}_3$=$\mathbf{R}_4$=COO$^-$, low yield [102];

$\mathbf{R}_3$=$\mathbf{R}_4$=Me, X=Br$^-$ and $\mathbf{R}_1$=$\mathbf{R}_2$=Me, X=Br$^-$ [103]

It is clearly visible that methods for preparation of electron-poor diquat derivatives are scarce. However, a personal communication with Dr. Benjamin J. Coe revealed that attempts to prepare the desired ester-functionalized diquat are promising and remains to be carried out in further work by employing more reactive alkylating agents – *bis*-mesylate, *bis*-triflate or *bis*-fluorosulfonate esters of ethylene glycol [100].

To be comparable with data of viologen salts later, diquat dibromide was converted into $[NTf_2]^-$ salt reducing the melting point from 322 to 122 ^{o}C.

2.3.4. Solubility of Bipyridinium Salts in Ionic Liquids

A salt dissolves in a solvent if either the ion-pair solvation or the total of anion solvation, cation solvation, and “dissociating or ionizing power” of the solvent, which is usually reflected in its dielectric constant, exceeds the crystal energy of the salt [104]. The solubilities of prepared bipyridinium salts in $[C_4C_1][NTf_2]$ were determined using ^{1}H-NMR measurements of clear, saturated solutions and integrating the corresponding signals of both the solvent and solute. To achieve higher accuracy of integration, the signal/noise ratio in spectra should be increased as high as possible, especially in case if solubility of the salt in IL is low. Ideally, neat solutions should be analysed thus greatly increasing the signal intensity. In that case strong band broadening would be observed due to the viscosity of IL thus again causing integration problems. Detour around this problem is to increase the sample temperature during the measurement what reduces viscosity of the IL and returns the normal appearance of peaks. However, this procedure would require large amounts of the sample and long NMR operation time so in this study just greater mass of the sample than usually was taken up in DMSO-d_6 and a regular ^{1}H-NMR spectra recorded. From the data of integration solubilities were easily calculated (**Fig. 2.9.**).

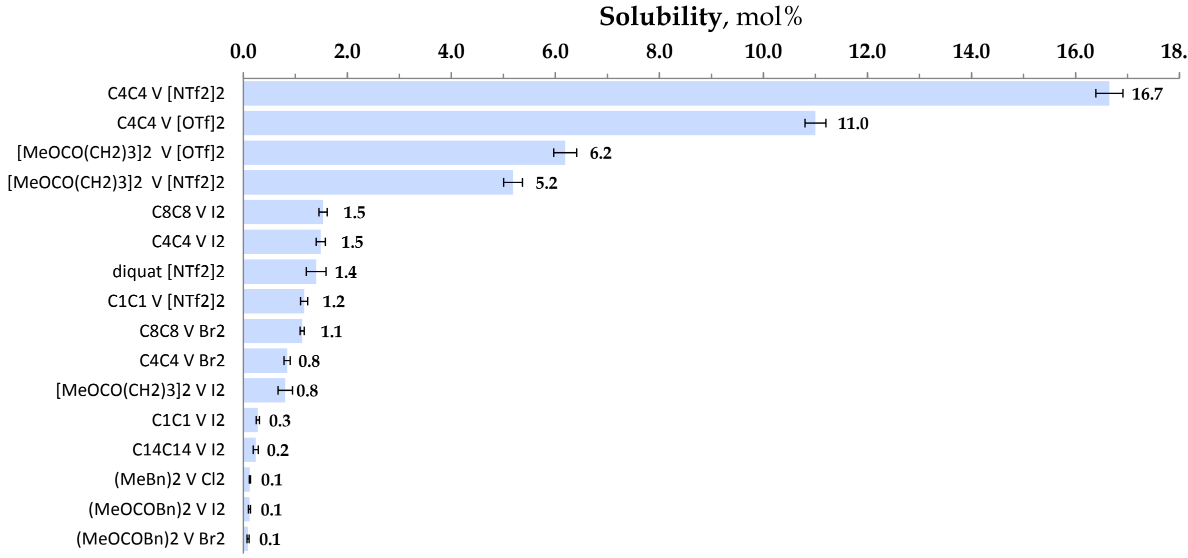


Fig. 2.9. *Solubility of Bipyridinium Salts in IL* $[C_4C_1im][NTf_2]$ *at 22 °C Measured by* ^1H*-NMR*

First thing to mention is that there is clearly distinguishable influence of salt anion on the solubility in $[C_4C_1im][NTf_2]$. Contrary to the expected, bipyridinium salts with bisimide anion $[NTf_2]^-$ show increased solubility up to 16.7 mol% $C_4C_4V[NTf_2]_2$ if the substituent at nitrogen is moderately short, non-functionalized alkyl chain. It might be a sign that there is some contribution of hydrophobic interactions or conformational freedom in reduction of the lattice energy, and that there is no so-called common-ion effect with solvent present. The first assumption is also supported by the low value of 1.2 mol% for the solubility of $C_1C_1V[NTf_2]_2$, and the fact that Kosower has also observed the ethyl-substituted pyridinium dye **1** possessing greater solubility in non-polar media compared to that of methyl-substituted dye [68].

Although $[(MeOCO)(CH_2)_3]_2V[NTf_2]_2$ has comparable number of carbon atoms in the linear part of the substituent, the presence of ester functionality shows reduced salt solubility of 5.2 mol% in comparison with $C_4C_4V[NTf_2]_2$. It ruins the expectations of its positive effect on the solubility coming from the hydrogen-bonding capable moieties. Also, solubility of hydroxyl- and amide-functionalized salts of group **C** (**Table 2.1.**) turned to be around the limit of detection so was not evaluated.

Despite the fact that bipyridinium salts containing halide anions wouldn't be suitable for the objective of this work anyway due to their strong CT donor properties, it is clearly visible from the solubility measurements that they form essentially low-soluble and thus highly stable crystal lattices; probably because of their good conformational compatibility with the bipyridinium core. Besides, the structure of substituent has very minor effect on the halide salt solubility in IL $[C_4C_1im][NTf_2]$.

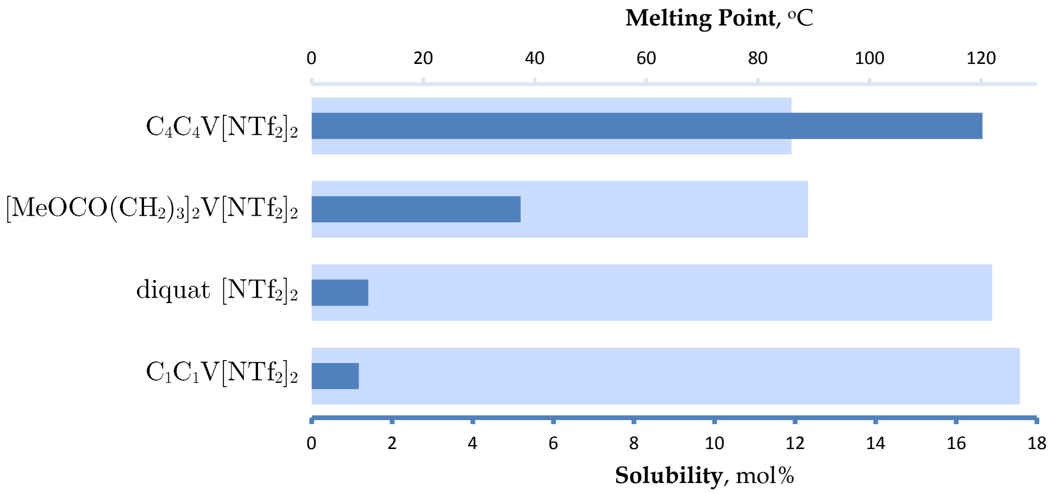


Fig. 2.10. *Solubility of Various Bipyridinium Bisimide Salts in IL $[C_4C_1im][NTf_2]$ Compared with their Melting Point*

Among the melting experiments performed, only bisimide salts underwent the proper melting at elevated temperature – no signs of decomposition were observed. If one compares solubilities of these salts in $[C_4C_1im][NTf_2]$ with their melting points, the obvious correlation can be noticed, namely – the solubility is inversely proportional to the melting point regardless any specific structural features (**Fig. 2.10.**). This leads to the conclusion that the solubility behaviour of $[NTf_2]^-$ salts in IL $[C_4C_1im][NTf_2]$ is not related to any specific solvent – solute interactions, or are related to them negligibly; the solubility is mainly dictated by the energy of crystal lattice what is in strong contrast to the common solubility rules observed in molecular solvent – solute systems.

One serious concern must be kept in mind: almost never melting points are used as variables in thermodynamics. This may be related to the fact that the temperature of melting describes the current experimental conditions rather than flow of the heat or its amount. Certainly, the use of melting points is perfectly suitable for qualitative evaluation of the purity of the sample investigated or trivially evidencing its identity.

By knowing that the salt does not undergo any chemical changes upon melting, apart from losing its crystalline structure, the enthalpy of fusion, $\Delta_{fus}H$, can be experimentally determined employing differential scanning calorimetry. As a result, the reliable thermodynamic parameter acquired can be conveniently correlated with other properties of the substance. However, several processes of structural changes in solids, possessing their own heat, may occur with heating. Modifications in crystalline form, known as polymorphism, are among them. Therefore $\Delta_{fus}H$ measured would characterize the melting of the most stable crystalline form, finally present before the melting, and not of that the measurement was started with. Viologen bisimide salts also exhibit this phenomenon of structural transitions with heating [105]. Nonetheless, use of $\Delta_{fus}H$ values of bipyridinium bisimides so far remains to be explored.

2.4. Design of the Dianions and their Charge Transfer Donor Properties

The main precondition for good CT donor, as mentioned before, is high electron density in the highest occupied molecular orbital. It may be provided by several structural features, and here (1) the presence of easily polarizable atoms with large atomic radius, (2) possessing a number of unshared electron pairs and, of course, (2) double unit charge was utilized. Suitability of a single carbo-dianion was also evaluated.

2.4.1. Sulfur-containing Dianions

For the introduction of sulphur dianion in solution, the corresponding imidazolium salts were prepared. Anions meeting the abovementioned requirements were considered to be thiosulfate $S_2O_3^{2-}$ and sulphite SO_3^{2-}. Regarding the non-diffused and suitable unity charges, and the fact that atoms formally bearing the charge are oxygen, it was doubtful that pure ILs could be obtained via regular alkali salt metathesis. Indeed, due to this or any other reason metathesis between anhydrous $Na_2S_2O_3$ and $[C_4C_1im]Cl$ failed yielding product of ambiguous quality.

The method very successfully applied in preparation of literally any-ion-based ILs (under condition if they are hydrophilic) [106] is ion exchanging with ion exchange resins. Thoroughly following the protocol, products of very high quality may be prepared. In this case, the choice in favour to the exchanger of anion was benefited, as the source of thiosulfate anion is readily available in comparison to that of cation $[C_4C_1im]^+$.

Unfortunetely $[C_4C_1im]_2S_2O_3$ turned to be unstable and decomposed yielding elemental sulphur while $[C_4C_1im]_2SO_3$ – hardly soluble in $[C_4C_1im][NTf_2]$.

2.4.2. Tetracyanoquinodimethanide Dianion

Well known CT donors since the 1960s are derivatives of tetracyanoquinodimethanide $TCNQ^0$ [107]. $TCNQ^0$ is characterized by extremely wide red-ox chemistry (**Fig. 2.11.**) what must be beard in mind when dealing with it [108, 109]. Imidazolium salts containing the radical anion $[TCNQ]^{\cdot-}$ are also known [110]. The molecule of TCNQ's reduced form, H_2TCNQ, bears two moderately acidic non-aromatic protons ($pK_{a1}=7.1$, $pK_{a2}=10.3$), each being under influence of three electron withdrawing functionalities – two nitrile groups and the aromatic ring.

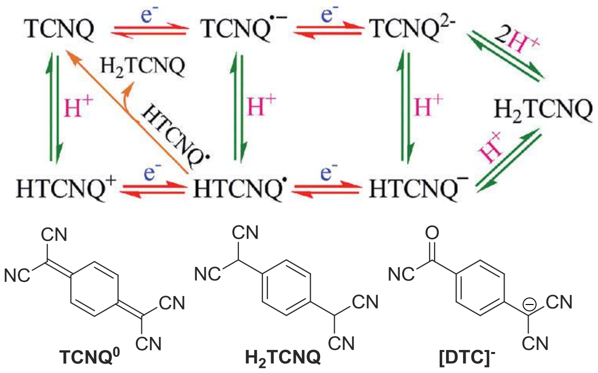
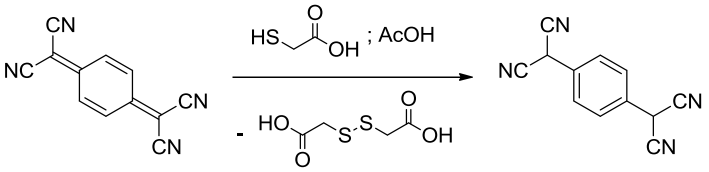


Fig. 2.11. *The Redox Chemistry of TCNQ Derivatives* [108]

So far CT complexes of $[TCNQ]^{2-}$ are known only in solid form, in vast majority of cases prepared for crystallographic studies and not employed further. Also synthetic methods for obtaining these complexes are based on techniques utilized in crystal growth rather than in preparative chemistry. As a rule of thumb, the presence of some transition metal cation is a mandatory requisite (Zn^{2+}, Cd^{2+}, Mn^{2+}) to ensure the air-stability of the final $[TCNQ]^{2-}$ complex [111–115].

The first step here was to prepare the reduced H_2TCNQ which is an air-stable solid. Several methods are known for reduction of $TCNQ^0$ – employing thiophenol, hydroiodic acid or either thioglycolic acid [116]. The latter was preferred due to its less hazardous properties. Under reflux in glacial acetic acid, the reaction was complete in 15 min yielding the precious $TCNQH_2$ with yield of 50%:



Despite that the introduction of anion in solution also had to be achieved indirectly, the preparation of the corresponding imidazolium salt $[C_4C_1im]_2[TCNQ]$ was not attempted due to the many evidences in literature about the extreme oxidative sensitivity of $[TCNQ]^{2-}$ against O_2 [117, 118]. Here, the neat ionic liquid was attempted to use for the deprotonation of H_2TCNQ *in situ* regarding that five-fold molar excess of Li[OAc] has proved to completely ionize H_2TCNQ [108]. In neat acetate IL this ratio surely would be even greater. However, addition of H_2TCNQ to $[C_4C_1im][OAc]$ caused immediate development of bright orange colour (**Fig. 2.12.**), what is not characteristic to $[TCNQ]^{2-}$, and was identified as α,α-dicyano-*p*-toluoylcyanamide anion $[DTC]^-$ after its UV-Vis absorbtion maxima of 484 nm [119].

Fig. 2.12. *IL* $[C_4C_1im][OAc]$ *Before* (**A**) *and after* (**B**) *Addition of* H_2TCNQ *and Mixing* (**C**)

This observation proves that the double deprotonation by ionic liquid had occurred, but in presence of oxygen immediate oxidation of the dianion had also proceeded leading to the formation of the undesired $[DTC]^-$. The UV-Vis spectrum (**Fig. 2.13.**) also evidenced the presence of the radical anion $[TCNQ]^{\bullet -}$ produced by disproportination [119].

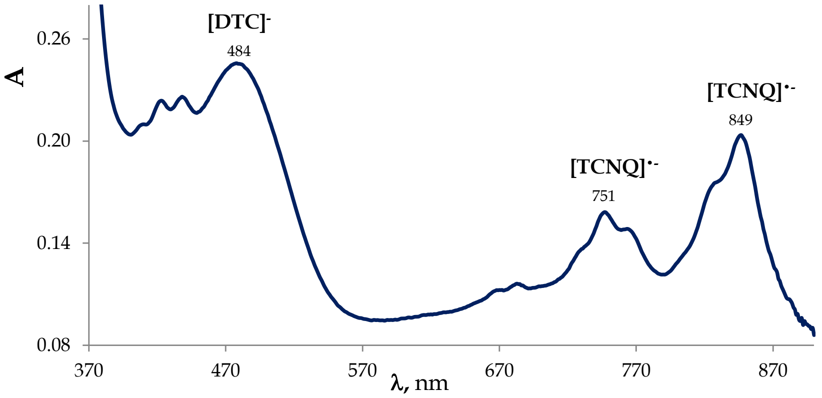


Fig. 2.13. UV-Vis Spectrum of H_2TCNQ Solution in IL $[C_4C_1im][OAc]$

In order yet to observe $[TCNQ]^{2-}$ spectroscopically, similar experiment was repeated in $[C_4C_1][NTf_2]$ by dissolving the neutral $TCNQ^0$ and adding of excess Li[OAc] to a solution that has been pre-dried in vacuo. Serious difficulties were then met to obtain a clear solution for UV-Vis examination due to insolubility of the remaining Li[OAc]. However, the solution finally obtained through extensive microfiltration displayed a single absorption band at 322 nm and was attributed to the desired $[TCNQ]^{2-}$ (**Fig. 2.14.**). This anion has been electrogenerated before after rigorous exclusion of oxygen from the MeCN solution, and is described with the absorption maxima of 330 nm [117]. The negative shift of wavelength in this experiment could be explained by solvatochromic effect caused by the IL $[C_4C_1im][NTf_2]$.

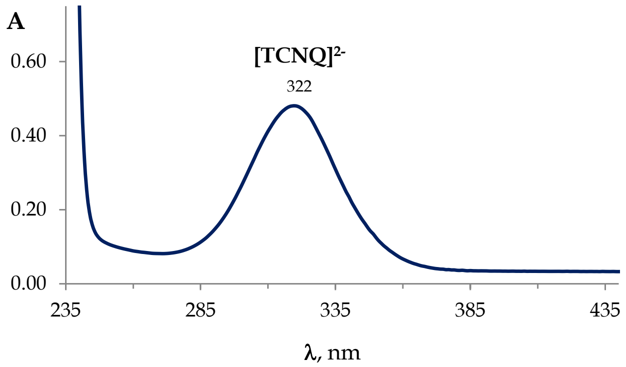


Fig. 2.14. UV-Vis Spectrum of $[TCNQ]^{2-}$ Generated *in situ* in IL $[C_4C_1im][NTf_2]$

However, the chemistry of TCNQ derivatives has appeared to be far more complex than expected limiting its use as a simple CT tool, but, still maintaining an outstanding potential, remains to be explored more thoroughly.

2.5. Evaluation of Dication – Dianion Charge Transfer in Ionic liquids

The results obtained so far do not allow drawing any fundamental conclusions on ion A^{2+} and B^{2-} pairing in ILs as the main experiment cannot yet be carried out. Be that as it may, these experiments serve as valuable information about suitability of CT partners to be employed further and clarify practical details that sooner or later would be faced in study like this. Important data have been deduced about how to introduce the dication in solution, and it surely will be used in future.

3. EXPERIMENTAL DETAILS

Apparatus and equipment. All the NMR spectra were acquired using Bruker AV400 instrument running at 400 MHz for ^{1}H and 100 MHz for ^{13}C experiments. The chemical shifts in spectra were referenced to the NMR solvent peak or that of MeOH for ^{13}C spectra run in D_2O. The melting points of solids were determined using automated Optimelt MPA100 system, and followed manually. The drying of ILs and other substances was maintained by membrane-pump supplied *Schlenk* line ensuring the pressure below 10^{-2} mbar. Mass spectra were registered using Waters Micromass AutoSpec Premier. UV-Vis spectra were recorded with *Perkin Elmer Lambda 25* spectrophotometer and quartz cuvettes with path lengths of 1 mm to 5 cm.

All the starting materials and solvents were obtained from chemical suppliers (*VWR, Sigma-Aldrich, Alfa-Aesar, TCI Chemicals, Apollo Scientific*). The starting materials for synthesis of the ILs were dried with appropriate drying agents and distilled prior to use, all other chemicals were used as received.

Syntheses were carried out under an inert atmosphere of pre-dried nitrogen using the *Schlenk* techniques in glassware previously dried at 120 °C. Dichloromethane and toluene were obtained from the dry solvent column (activated alumina), ethylacetate and acetonitrile was pre-dried with 4 Å molecular sieves and distilled from CaH_2 prior to use.

3.1. Synthesis of the Ionic Liquids

1-Butyl-3-methylimidazolium Chloride [C_4C_1im]Cl

In a 3 L round-bottomed flash to 1—methylimidazole (243 g, 3.05 mol) in ethyl acetate (500 mL) 1-chlorobutane (427 g, 4.61 mol) was added dropwise with stirring. The mixture was heated in 50 °C bath under nitrogen atmosphere for 122 h, and then cooled at +5 °C for 10 h. Two colourless layers formed, the topper was discarded and the remaining washed with ethyl acetate (3×100 mL) with vigorous stirring. The resulting ionic liquid was recrystallized from the mixture of EtOAc and MeCN using a seed crystal to promote the crystallization. The resulting slurry was washed with EtOAc (3×100 mL), the solvent removed via canula and dried in *vacuo* at 50 °C for 24 h yielding small, white crystals (311 g, 58%) with m.p. 70 °C (lit. 66-68 °C [120]).

^{1}H-NMR (400 MHz, DMSO-d_6, δ): 0.90 (t, 3H, J=7.2 Hz), 1.25 (m, 2H), 1.76 (m, 2H), 3.85 (s, 3H), 4.17 (t, 2H, J=7.0 Hz), 7.72 (t, 1H, J=1.7 Hz), 7.79 (t, 1H, J=1.7 Hz), 9.23 (s, 1H) ppm. The spectroscopic data is consistent with the literature [121].

1-Butyl-3-methylimidazolium *bis*-(Trifluoromethanesulfonyl)-imide $[C_4C_1im][NTf_2]$

In a 0.5 L round-bottomed flask solution of 1-butyl-3-methylimidazolium chloride (57.8 g, 0.331 mol) in dichloromethane (160 mL) was vigorously stirred with solution of $LiNTf_2$ (83.5 g, 0.349 mol) in water (80 mL) at room temperature under nitrogen atmosphere for 24 h. Dichloromethane phase was then thoroughly washed with water (6×50 mL) until chloride-free ($AgNO_3$ test). Dichloromethane was then removed under vacuum and the obtained liquid stirred with activated charcoal for 24 h at 50 °C. The mixture was filtered through a short pad of acidic and basic alumina an 40 µm PTFE filter, resulting product was dried in *vacuo* at 60 °C for 12 h yielding the title compound as colourless, viscous liquid (100.25 g, 72%).

^{1}H-NMR (400 MHz, DMSO-d_6, δ): 0.90 (t, 3H, J=7.4 Hz), 1.26 (m, 2H), 1.76 (m, 2H), 3.84 (s, 3H), 4.16 (t, 2H, J=7.2 Hz), 7.69 (t, 1H, J=1.8 Hz), 7.75 (t, 1H, J=1.8 Hz), 9.10 (s, 1H) ppm.

^{13}C-NMR (100 MHz, DMSO-d_6, δ): 13.2, 18.8, 31.4, 35.7, 48.5, 119.5 (q, $J_{13C-19F} =$ 321 Hz), 122.3, 123.6, 136.5 ppm. The spectroscopic data is consistent with the literature [122].

m/z (FAB$^+$): 139 (100%) $[C_4C_1im]^+$.

m/z (FAB$^-$): 281 (100%) $[NTf_2]^- + H^+$.

1-Butyl-1-methylpyrrolidinium Chloride [C_4C_1pyrr]Cl

In a 2 L round-bottomed flash to *N*-methylpyrrolidine (300 g, 3.52 mol) in ethyl acetate (265 mL) 1-chlorobutane (395 g, 4.27 mol) was added dropwise with stirring. The mixture was heated in 75 °C bath under nitrogen atmosphere for 93 h during what white crystals appeared. After cooling to room temperature, the solvent was removed via canula, and several washes with ethyl acetate performed (5×100 mL). The resulting product was dried in *vacuo* at 85 °C for 12 h yielding white microcrystalline powder (370 g, 59%) with m.p. 110 °C.

^{1}H-NMR (400 MHz, DMSO-*d*$_6$, δ): 0.93 (t, 3H, *J*=7.3 Hz), 1.30 (m, 2H), 1.67 (m, 2H), 2.07 (bs, 4H), 3.00 (s, 3H), 3.30-3.38 (m, 2H), 3.39-3.56 (m, 4H) ppm.

^{13}C-NMR (100 MHz, DMSO-*d*$_6$, δ): 13.5, 19.3, 21.0, 24.9, 47.4, 62.8, 63.3 ppm. The spectroscopic data is consistent with literature [123].

1-Butyl-1-methylpyrrolidinium *bis*-(Trifluoromethanesulfonyl)-imide [C_4C_1pyrr][NTf_2]

In a 0.25 L round-bottomed flask solution of 1-butyl-1-methylpyrrolidinium chloride (29.6 g, 0.167 mol) in dichloromethane (80 mL) was vigorously stirred with solution of $LiNTf_2$ (52.2 g, 0.182 mol) in water (40 mL) at room temperature under nitrogen atmosphere for 24 h. Dichloromethane phase was then worked up similarly as for [C_4C_1im][NTf_2] yielding the title compound as colourless, viscous liquid (56.7 g, 81%).

^{1}H-NMR (400 MHz, DMSO-*d*$_6$, δ): 0.94 (t, 3H, *J*=7.5 Hz), 1.33 (m, 2H), 1.64-1.75 (m, 2H), 2.10 (bs, 4H), 2.99 (s, 3H), 3.26-3.34 (m, 2H), 3.38-3.52 (m, 4H) ppm.

^{13}C-NMR (100 MHz, DMSO-*d*$_6$, δ): 13.2, 19.3, 21.0, 25.0, 47.5, 63.1, 63.5, 119.6 (q, $J_{13C-19F}$ = 320 Hz) ppm. The spectroscopic data is consistent with the literature [123].

m/*z* (FAB$^+$): 142 (100%) [C_4C_1py]$^+$.

m/z (FAB$^-$): 281 (100%) $[NTf_2]^- + H^+$.

1-Butyl-3-methylimidazolium Methylsulfate $[C_4C_1im][MeSO_4]$

In a 1 L round-bottomed flask to the solution of *N*-butylimidazole (144 g, 1.16 mol) in toluene (150 mL) dimethyl sulfate (152 g, 1.21 mol) was added dropwise over the course of 1 h with vigorous stirring. During addition, the reaction mixture was kept at 0...+5 °C by means of cooling with ice – water bath. Afterwards, the mixing was continued for 24 hours at room temperature. The formed ionic liquid phase was separated and thoroughly washed with toluene (10×50 mL), the residual solvent removed under vacuum, and remaining ionic liquid stirred with activated charcoal at 40 °C overnight. The charcoal was then removed by passing the mixture through a short pad of basic and acidic alumina and 40 µm PTFE filter. After drying at 50 °C in *vacuo* for 12 h, the title compound was obtained as colourless, viscous liquid (219 g, 75%).

^{1}H-NMR (400 MHz, DMSO-d_6, δ): 0.90 (t, 3H, J=7.3 Hz), 1.25 (m, 2H), 1.76 (m, 2H), 3.37 (s, 3H), 3.85 (s, 3H), 4.16 (t, 2H, J=7.2 Hz), 7.70 (t, 1H, J=1.7 Hz), 7.77 (t, 1H, J=1.7 Hz), 9.11 (s, 1H) ppm. The spectroscopic data is consistent with the literature [121].

1-Butyl-3-methylimidazolium Hydrogensulfate $[C_4C_1im][HSO_4]$ [124]

In an open-topped three-necked round-bottomed flask, equipped with a thermometer and dropping funnel, to 1-butyl-3-methylimidazolium methylsulfate (219 g, 0.875 mol) 25 mL of water and 5 drops of conc. H_2SO_4 were added. The mixture was heated using the Drysyn heating mantle allowing the water and formed methanol to boil off. The water was dispensed dropwise from the dropping funnel at slow rate in order to maintain the temperature in the flask of about 175 °C. The addition of water and heating was continued for at least 3 hours. The progress of the reaction was monitored by the disappearance of the methyl peak from the methylsulfate anion in ^{1}H-NMR.

The yellowish ionic liquid was dried in *vacuo* at 60 °C until the bubbling ceased. The activated charcoal was then added and evacuation with stirring continued for 24 h at 60 °C. The black mixture was then diluted with 40 mL of dichloromethane and purified by means of vacuum filtration at 60 °C employing the plastic syringe, equipped with plastic tube – heating coil, short pad of basic alumina and 40 µm PTFE filter. The syringe was connected to a two-necked round-bottomed flask with the rubber cushion and the receiving flash – to the vacuum from the Schlenk-line. After the slow filtration was done (ca. 8 h), colourless, white solid was obtained in the receiving flask. Drying at 60 °C for 12 h yielded colourless liquid what easily crystallized upon cooling to room temperature (103 g, 50%).

^{1}H-NMR (400 MHz, DMSO-d_6, δ): 0.89 (t, 3H, *J*=7.3 Hz), 1.25 (m, 2H), 1.76 (m, 2H), 3.85 (s, 3H), 5.16 (t, 2H, *J*=7.31 Hz), 7.71 (m, 1H), 7.78 (m, 1H), 9.70 (bs, 1H) ppm.

^{13}C-NMR (100 MHz, DMSO-d_6, δ): 13.3, 18.8, 31.4, 35.8, 48.5, 122.3, 123.6, 136.6. The spectroscopic data is consistent with the literature [125].

m/z (FAB$^+$): 139 (100%) $[C_4C_1im]^+$, 83 (18%) $[C_1Him]^+$.

m/z (FAB$^-$): 97 (100%) $[HSO_4]^-$.

1-Butyl-3-methylimidazolium Hydroxide $[C_4C_1im]OH$

Freshly recrystallized barium hydroxide is standardized by means of potentiometric titration with HCl to find the exact amount of crystallization water. Strictly stoichiometric amount of $Ba(OH)_2$ hydrate to that of the latter $[C_4C_1im]HSO_4$ is dissolved with heating and stirring in 200 mL of freshly boiled deionized water. The clear, hot solution is then added to a stirred aqueous solution of $[C_4C_1im]HSO_4$ (61.27 g, 259.3 mmol, ca. 300 mL) in three-necked 1 L round-bottomed flask. The solution is allowed to cool with stirring under nitrogen atmosphere, and then filtered without delay under vacuum through the glass-fibre filter paper yielding ca. 500 mL of ~10% (w/w) aqueous [C_4C_1im]OH solution. It solution should be kept in an air-tight container and used further as soon as possible; it can be acidimetrically standardized to find the exact concentration if required for the intended purpose.

1-Butyl-3-methylimidazolium Acetate [C_4C_1im][OAc]

To the titrated aqueous solution of [C_4C_1im]OH (1 eq) glacial acetic (1.05 eq) was added dropwise with stirring and cooling. The solution was stirred for 1 h and then subjected to evaporation at reduced pressure at 60 °C. After drying with rotary evaporator 2 more h, the IL was treated with charcoal as described before. Drying in *vacuo* at 60 °C for 24 h yielded colourless, viscous liquid.

^{1}H-NMR (400 MHz, DMSO-d_6, δ): 0.87 (t, 3H, J=7.3 Hz), 1.22 (m, 2H), 1.57 (s, 3H), 1.75 (m, 2H), 3.87 (s, 3H), 4.19 (t, 2H, J=7.2 Hz), 7.81 (s, 1H), 7.88 (s, 1H), 10.0 (s, 1H) ppm. The spectroscopic data is consistent with the literature [121].

1-Butyl-3-methylimidazolium Thiosulfate [C_4C_1im]$_2S_2O_3$

C.a. 160 mL of dry anion-exchange resin Amberlite IRA400-Cl (1.4 meq/mL, 0.224 eq in bed volume) was swelled under deionized water for 4 h and loaded in a column with diameter of 8 cm. The column was then flushed with ~1.5 L of deionized water till pH of the eluting water reached 3-4. C.a. 1 kg of 10% (*w/w*) sodium thiosulfate solution (0.632 eq) was passed through the resin in the time of 5 h and the column was then left under the solution overnight. After flushing the column with ~1 L of water (~1 h), 1 L of [C_4C_1im]Cl solution (1 L, 43 mmol/L, 5.2 eq) was slowly passed through with a constant flowrate (~2.8 mL/min, 6 h). Approx. 730 mL of solution was collected and subjected to lyophilisation. The final ionic liquid was then dried in *vacuo* at 25 °C.

^{1}H-NMR (400 MHz, D_2O, δ): 0.88 (t, 2H, J=7.4 Hz), 1.28 (m, 2H), 1.81 (m, 2H), 3.86 (s, 3H), 4.16 (t, 2H, 7.2 Hz) ppm.

^{13}C-NMR (100 MHz, D_2O, δ): 12.8, 18.9, 31.4, 35.8, 49.4, 122.4, 123.6, 135.9 ppm.

m/z (FAB$^+$): 139 (100%) $[C_4C_1im]^+$, 83 (18%) $[C_1Him]^+$.

m/z (FAB$^-$): 97 (100%) $[HSO_4]^-$, 80 (10%) $[SO_3]^{2-}$.

3.2. Synthesis of the Bipyridinium Salts

Boronium Viologen Diiodide BVI_2 [87]

To a stirred solution of borane—trimethylamine adduct (1.00 g, 14 mmol) in toluene (50 mL), elemental iodine (1.70 g, 7 mmol) was added in small portions over the period of 30 min. As hydrogen was evolved, nitrogen was slowly flushed through the system to reduce the safety risks. After stirring for 30 min 4,4'-bipyridyl (1.09 g, 7 mmol) was added to the pale amber-coloured solution and the resulting mixture was refluxed for 72 h. After cooling the mixture, the product was collected by filtration, washed with ether and dried in *vacuo* yielding bright orange microcrystalline solid (3.07 g, 81%). The crude product was then recrystallized from acetone – water (9:1) reducing the dried product yield to 61%.

^{1}H-NMR (400 MHz, DMSO-d_6, δ): 2.71 (s, 18H), 8.61 (d, 4H, J=6.9 Hz), 9.16 (d, 4H, J=6.9 Hz) ppm. The spectroscopic data is consistent with the literature [87].

Boronium Viologen *bis*-(Trifluoromethane-sulfonyl)-imide $BV[NTf_2]_2$

To a solution of boronium viologen diiodide (3.24 g, 5.8 mmol) in water (180 mL) concentrated aqueous $LiNTf_2$ (3.40 g, 12 mmol) was added with stirring. Pale precipitate formed immediately, and was continuously stirred for 30 minutes. The mixture was filtered on a Buchner funnel and washed with plenty of water till iodide-free ($AgNO_3$ test). After washing with ether and drying in *vacuo* the title compound was obtained as white solid (4.53 g, 90%) with m.p. 159-160 °C.

^{1}H-NMR (400 MHz, DMSO-d_6, δ): 2.70 (s, 18H), 8.61 (d, 4H, J=6.8 Hz), 9.15 (d, 4H, J=6.8 Hz) ppm.

^{13}C-NMR (100 MHz, DMSO-d_6, δ): 49.9, 117.9, 125.9, 148.8, 150.7 ppm.

1,1'-*bis*-(4-Methylbenzyl)-4,4'-bipyridinium Dichloride (MeBn)$_2$VCl$_2$

To a stirred solution of 4,4'-bipyridyl (5.00 g, 32 mmol) in 100 mL of acetonitrile 4-methylbenzylchloride (14.0 mL, 150 mmol) was added with stirring, and the mixture was then refluxed for 24 h. After cooling down, the product was collected by vacuum filtration, and purified by suspending in ~150 mL of boiling acetone and adding water dropwise till full dissolution. After cooling, filtration, washing with ether and drying in air, the desired compound was obtained as tiny, almost colourless needles (4.48 g, 41%) with m.p. 283-288 °C (dec.).

^{1}H-NMR (400 MHz, D$_2$O, δ): 2.36 (s, 6H), 5.87 (s, 4H), 7.35 (d, 4H, *J*=8.0 Hz), 7.42 (d, 4H, *J*=8.0 Hz), 8.50 (d, 4H, *J*=7.0 Hz), 9.12 (d, 4H, *J*=7.0 Hz) ppm.

^{13}C-NMR (100 MHz, D$_2$O, δ): 20.4, 64.8, 127.2, 129.3, 129.5, 130.4, 141.0, 145.5, 150.3 ppm.

1,1'-Dibutyl-4,4'-bipyridinium Diiodide C$_4$C$_4$VI$_2$

To a solution of 4,4'-bipyridyl (5.00 g, 32 mmol) in 90 mL of acetonitrile was added 1-iodobutane (8.4 mL, 70 mmol) with mixing, and the mixture was then refluxed for 24 h. After cooling down, the product was collected by vacuum filtration, and washed with several portions of acetonitrile and diethyl ether. Drying in *vacuo* yielded dark brown crystals (16.8 g, 71%) with m.p. 335-335.5 °C (dec.).

^{1}H-NMR (400 MHz, DMSO-d_6, δ): 0.94 (t, 6H, *J*=7.6 Hz), 1.34 (m, 4H), 1.97 (m, 4H), 8.80 (d, 4H, *J*=6.8 Hz), 9.40 (d, 4H, *J*=6.8 Hz) ppm.

^{13}C-NMR (100 MHz, DMSO-d_6, δ): 13.3, 18.8, 32.7, 60.7, 126.6, 145.7, 148.6 ppm.

1,1'-Dimethyl-4,4'-bipyridinium Diiodide C$_1$C$_1$VI$_2$

To a stirred solution of 4,4'-bipyridyl (5.00 g, 32 mmol) in 50 mL of acetonitrile methyliodide (4.4 mL, 48 mmol) was added with stirring. In 30 min after the solution has been brought to reflux the reaction was stopped because of solidification. The mixture was cooled, filtered and washed with MeCN. Recrystallization from ca. 0.5 L of methanol, drying in *vacuo* yielded dark red crystals (14.1 g, 22%) with m.p. 320 °C (dec.) (lit. 325 °C [126]).

^{1}H-NMR (400 MHz, DMSO, δ): 4.44 (s, 6H), 8.77 (d, 4H, *J*=6.9 Hz), 9.30 (d, 4H, *J*=6.9 Hz) ppm.

^{13}C-NMR (100 MHz, D_2O, δ): 48.0, 126.0, 146.6, 148.1 ppm. The spectroscopic data is consistent with the literature [126].

1,1'-*bis*-(2-Ethoxy-2-oxoethyl)- 4,4'-bipyridinium Dibromide $(EtOCOCH_2)_2VBr_2$

The title compound was prepared similarly to $C_4C_4VI_2$ starting from ethyl bromoacetate (4.4 mL, 40 mmol) and 4,4-bipyridyl (1.56 g, 10 mmol) yielding the title compound as yellow crystals (3.09 g, 62%) with m.p. 200-202 °C (lit. 185 °C [127]) after recrystallization from aqueous ethanol.

^{1}H-NMR (400 MHz, DMSO-d_6, δ): 1.28 (t, 6H, *J*=7.2 Hz), 4.27 (m, 4H), 5.81 (s, 4H), 8.93 (d, 4H, *J*=7.1 Hz), 9.39 (d, 4H, *J*=7.1 Hz) ppm.

^{13}C-NMR (100 MHz, DMSO-d_6, δ): 14.0, 60.4, 62.5, 126.6, 147.2, 149.7, 166.2 ppm. The spectroscopic data is consistent with the literature [127].

1,1'-*bis*-(4-Methoxy-4-oxobutyl)-4,4'-bipyridinium Diiodide $[(MeOCO(CH_2)_3]_2VI_2$

The title compound was prepared similarly to $C_4C_4VI_2$ starting from methyl 4-iodobutyrate (10.96 g, 48 mmol) and 4,4-bipyridyl (3.00 g, 19 mmol) yielding the title compound as orange crystals (6.85 g, 58%) with m.p. 204-206 °C (dec.) after recrystallization from methanol - acetone.

^{1}H-NMR (400 MHz, DMSO-d_6, δ): 2.30 (m, 4H, *J*=7.2 Hz), 2.48-2.56 (m, 4H), 3.61 (s, 6H), 4.77 (t, 4H, *J*=7.0 Hz), 8.84 (d, 4H, *J*=6.9 Hz), 9.44 (d, 4H, *J*=6.9 Hz) ppm.

^{13}C-NMR (100 MHz, DMSO-d_6, δ): 25.9, 29.9, 51.6, 60.1, 126.6, 145.9, 148.6, 172.3 ppm.

1,1'-*bis*-(4-Methoxy-4-oxobutyl)-4,4'-bipyridinium Ditriflate [(MeOCO(CH$_2$)$_3$]$_2$V(OTf)$_2$

To an aqueous solution of **[(MeOCO(CH$_2$)$_3$]$_2$VI$_2$** (3.6229 g, 5.918 mmol in 200 mL) silver triflate was added with stirring (3.0420 g, 11.839 mmol). The resulting precipitate was removed by filtration, and remaining solution evaporated to dryness yielding a white solid.

^{1}H-NMR (400 MHz, DMSO-d_6, δ): 2.29 (m, 4H), 2.45-2.55 (m, 4H), 3.60 (s, 6H), 4.74 (t, 4H, *J*=7.0 Hz), 8.81 (bs, 4H), 9.38 (bs, 4H) ppm.

^{13}C-NMR (100 MHz, DMSO-d_6, δ): 25.9, 29.9, 51.6, 60.2, 122.3, 126.6, 146.0, 148.7, 172.3 ppm.

m/z (ESI$^+$): 257 (100%) MeOCO(CH$_2$)$_3$V$^+$, 180 (40%) [(MeOCO(CH$_2$)$_3$]$_2$V^{2+}, 358 (55%) [(MeOCO(CH$_2$)$_3$]$_2$V^{2+}-H$^+$.

m/z (ESI$^-$): 148 (100%) [OTf]$^-$.

1,1'-*bis*-(4-Methoxy-4-oxobutyl)-4,4'-bipyridinium Di-(*bis*-(trifluoromethanesulfonyl)imide) [(MeOCO(CH$_2$)$_3$]$_2$V(NTf$_2$)$_2$

To a solution of [(MeOCO(CH$_2$)$_3$]$_2$VI$_2$ (0.49 g, 0.80 mmol) in water (9 mL), solution of LiNTf$_2$ (0.49 g, 1.7 mmol) in water (9 mL) was added with stirring. The precipitate formed was filtered, washed with water, ether and dried to yield white solid (0.66 g, 89%) with m.p. 89.5-91.5 °C.

^{1}H-NMR (400 MHz, DMSO-d_6, δ): 2.29 (m, 4H), 2.51-2.55 (m, 4H), 3.60 (s, 6H), 4.74 (t, 4H, *J*=6.6 Hz), 8.81 (d, 4H, *J*=6.7 Hz), 9.39 (d, 4H, *J*=6.7 Hz) ppm.

^{13}C-NMR (100 MHz, DMSO-d_6, δ): 25.9, 29.9, 51.6, 60.2, 119.5 (q, $J_{13C-19F} =$ 320 Hz), 126.6, 146.0, 148.7, 172.3 ppm.

m/z (ESI$^+$): 257 (100%) $MeOCO(CH_2)_3V^+$, 180 (30%) $[(MeOCO(CH_2)_3]_2V^{2+}$, 358 (55%) $[(MeOCO(CH_2)_3]_2V^{2+}$-H^+.

m/z (ESI$^-$): 279 (100%) $[NTf_2]^-$.

1,1'-Dimethyl-4,4'-bipyridinium Di-*bis*-(trifluoromethanesulfonyl)imide $C_1C_1V(NTf_2)_2$

The title compound was prepared similarly to $[(MeOCO(CH_2)_3]_2V(NTf_2)_2$ from $LiNTf_2$ (1.85 g, 6.44 mmol) and $C_1C_1VI_2$ (1.35 g, 3.10 mmol) yielding a white solid (1.98 g, 86%) with m.p. 126.9-129.5 °C (lit. 132.2 °C [128]).

^{1}H-NMR (400 MHz, DMSO-d_6, δ): 4.43 (s, 6H), 8.75 (d, 4H, J=6.8 Hz), 9.28 (d, 4H, J=6.8 Hz) ppm.

^{13}C-NMR (100 MHz, DMSO-d_6, δ): 48.0, 119.5 (q, $J_{13C-19F} =$ 320 Hz), 126.1, 146.7, 148.2 ppm. The spectroscopic data is consistent with the literature [128].

m/z (ESI$^+$): 171 (80%) MeV^+.

m/z (ESI$^-$): 279 (100%) $[NTf_2]^-$.

1,1'-*bis*-(3,3-Dimethyl-2-oxobutyl)-4,4'-bipyridinium Diiodide $(^tBuOCOCH_2)_2VI_2$

To a stirred solution of 4,4'-bipyridyl (1.51 g, 10 mmol) in 25 mL of acetonitrile iodomethylpivalate (5.5 g, 23 mmol) was added with stirring. Dark brown precipitate formed immediately. The mixture was then refluxed for 17 h and worked up similarly as before. After drying, dark orange crystals were obtained (5.00 g, 81%) with m.p. 252-254 °C (dec.).

^{1}H-NMR (400 MHz, DMSO-d_6, δ): 1.19 (s, 18H), 6.54 (s, 4H), 8.87 (d, 4H, J=6.9 Hz), 9.55 (d, 4H, J=6.9 Hz) ppm.

^{13}C-NMR (100 MHz, DMSO-d_6, δ): 26.4, 38.3, 79.7, 117.9, 127.1, 145.9, 150.8, 176.4 ppm.

m/z (ESI$^+$): 356 (18%) $(tBuOCOCH_2)_2V^{2+} + H^+$

1,1'-*bis*-(3,3-Dimethyl-2-oxobutyl)-4,4'-bipyridinium *bis*-(Trifluoromethanesulfonyl)-imide $(^tBuOCOCH_2)_2V[NTf_2]_2$

To a stirred solution of 1,1'-*bis*-(3,3-dimethyl-2-oxobutyl)-4,4'-bipyridinium diiodide (0.27 g, 0.42 mmol) saturated aqueous solution of $LiNTf_2$ (0.32 g, 1.1 mmol) was added with. The resulting white crystals were collected by filtration after stirring for 20 min, and washed with water. After drying, yellowish-white crystals were obtained (0.32 g, 80%) with m.p 130.9-132.1 °C.

^{1}H-NMR (400 MHz, DMSO-d_6, δ): 1.19 (s, 18H), 6.52 (s, 4H), 8.81 (d, 4H, *J*=7.0 Hz), 9.53 (d, 4H, *J*=7.0 Hz) ppm.

^{13}C-NMR (100 MHz, DMSO-d_6, δ): 26.4, 38.3, 79.7, 127.1, 145.8, 150.7, 176.4 ppm.

2,2'-(1,4-Phenylene)dimalononitrile H_2TCNQ

To a suspension of $TCNQ^0$ (1.00 g, 5.0 mmol) in glacial acetic acid (24 mL) thioglycolic acid (2 mL, 28 mmol) was added. With heating up the solid fully dissolved and solid again started to form. After refluxing for 15 min, solution was cooled, filtered and precipitate washed with DCM, ether and recrystallized from MeCN. After drying, slight yellow needles were obtained (0.50 g, 50%) with m.p. 236-238 °C (lit. 241-243 °C [116]).

^{1}H-NMR (400 MHz, DMSO-d_6, δ): 5.60 (s, 2H), 7.68 (s, 4H) ppm.

^{13}C-NMR (100 MHz, DMSO-d_6, δ): 113.5, 129.9, 130.6 ppm.

Diquat Dibromide

2,2’-Bipyridyl (3.00 g, 19 mmol) was refluxed in neat 1,2-dibromoethane (30 mL, 348 mmol) for 18 h. After cooling, the product was filtered off, washed with small amount of acetonitrile and ether. The dry product (1.89 g, 29%) was yellow powder with m.p. 322-330 °C (lit. 340 °C [94]).

^{1}H-NMR (400 MHz, DMSO-d_6, δ): 5.36 (s, 4H), 8.47 (t, 2H, J=8.5 Hz), 8.96 (t, 2H, J=8.9 Hz), 9.19 (d, 2H, J=9.2 Hz), 9.41 (d, 2H, J=9.4 Hz) ppm.

^{13}C-NMR (100 MHz, DMSO-d_6, δ): 52.1, 127.8, 130.0, 140.0, 147.1, 147.4 ppm. The spectroscopic data is consistent with the literature [129].

m/z (FAB$^+$): 346 (100%).

m/z (FAB$^-$): 79 (100%) Br$^-$.

Diquat Di-(*bis*-(trifluoromethanesulfonyl)imide)

The title compound was prepared similarly to $[(MeOCO(CH_2)_3]_2V(NTf_2)_2$ from $LiNTf_2$ (1.78 g, 6.20 mmol) and diquat dibromide (1.01 g, 2.94 mmol) yielding a white solid (1.77 g, 81%) with m.p. 122.5-124.1 °C.

^{1}H-NMR (400 MHz, DMSO-d_6, δ):) 5.25 (s, 4H), 8.45 (t, 2H, J=8.4 Hz), 8.95 (t, 2H, J=8.93 Hz), 9.11 (d, 2H, J=9.1 Hz), 9.33 (d, 2H, J=9.3 Hz) ppm.

^{13}C-NMR (100 MHz, DMSO-d_6, δ): 52.2, 119.5 (q, $J_{13C-19F}$ = 320 Hz), 127.8, 130.1, 139.9, 147.2, 147.5 ppm.

m/z (ESI$^+$): 183 (100%).

m/z (ESI$^-$): 279 (100%) $[NTf_2]^-$.

2,2’-Bipyridine-4,4’-dicarboxylic Acid [97]

To 125 mL of conc. H_2SO_4, 2,2’-bipyridyl (5.00 g, 27 mmol) was added with stirring, and also $K_2Cr_2O_7$ (24 g, 82 mmol) at such rate so the temperature did not rise over 70-80 °C. After slowly cooling down to 40 °C the mixture was poured in ice water, the precipitate filtered off and after drying, refluxed with aqueous HNO_3

(170 mL, 50% w/w) for 4 h. After that, the contents of the mixture are diluted with ice water to c.a. 1 L, and the title compound filtered off.

2,2'-Bipyridine-4,4'-dicarboxylic Acid Dimethyl Ester [98]

To a boiling suspension of 2,2'-bipyridine-4,4'-dicarboxylic acid (3.01 g, 12 mmol) in methanol (150 mL), thionyl chloride (25 mL) was added dropwise during c.a. 10 min. After refluxing for 1 h, 10 more mL of $SOCl_2$ was added, and the solution left refluxing overnight. The solution was then cooled down during when white solid precipitated. The solid was filtrated, washed with methanol, while the mother liquor was quenched with $NaHCO_3$, extracted with $CHCl_3$ (3×50 mL), dried over $MgSO_4$, evaporated to dryness and, together with the previous precipitate, recrystallized from propanol-2/chloroform. Cooling of the saturated solution at -20 °C overnight yielded shiny, snow-white flakes (3.28 g, 77% in 2 steps) with m.p. 209.3-210.7 °C (lit. 207-209 °C [97]).

^{1}H-NMR (400 MHz, $CDCl_3$, δ):) 4.02 (s, 6H), 7.93 (dd, 2H, *J*=4.9, 1.6 Hz), 8.90 (d, 2H, *J*=5.0 Hz), 8.98 (bs, 2H) ppm.

^{13}C-NMR (100 MHz, DMSO-*d*$_6$, δ): 15.3, 83.1, 85.8, 101.1, 112.7, 119.0, 128.1 ppm. The spectroscopic data is consistent with the literature [98].

m/z (ESI$^+$): 273 (100%) $[M+H]^+$.

3.3. Solubility Measurements of Bipyridinium Salts

Chromatography vial, equipped with the magnetic fleas, was charged with c.a. 0.5 mL of IL $[C_4C_1im][NTf_2]$, and the salt of interest added ensuring that its amount is greater than solubilisation ability of the solvent. The vial were then sealed and heated at 40 °C with stirring. If dissolution was observed, more salt was added till oversaturation was reached. After stirring on these conditions for 24 h, it was made certain that undissolved salt is still present, and the stirring was continued at 22 °C for 5 more hours.

The solution was then filtered directly in NMR tubes employing 1 mL syringe fitted with 40 μm PTFE microfilter, diluted with DMSO-d_6 and analysed.

CONCLUSIONS

1. The considered boronium viologen dication exhibits charge transfer from iodide in solution similarly to Kosower's dye.
2. Solubility of the proposed charge transfer acceptors – dicationic bipyridinium *bis*-(trifluoromethanesulfonyl)imides – in ionic liquid is mainly dictated by the lattice energies rather than favourable solvent – solute interactions.
3. Ionic liquid 1-butyl-3-methylimidazolium acetate is enough basic media to generate dianion from neutral 2,2'-(1,4-phenylene)dimalononitrile H_2TCNQ.

REFERENCES

1. Pasteur, L. Mémoire sur la relation qui peut exister entre la forme cristalline et la composition chimique, et sur la cause de la polarisation rotatoire. *C. R. Hebd. Seances Acad. Sci.* **1848**, *26*, 538.

2. Tswett, M. Physikalisch-chemische Studien über das Chlorophyll. Die Adsorptionen. *Ber. Dtsch. Bot. Ges.* **1906**, *24*, 316–323.

3. Lui, M. Y.; Crowhurst, L.; Hallett, J. P.; Hunt, P. a.; Niedermeyer, H.; Welton, T. Salts dissolved in salts: ionic liquid mixtures. *Chem. Sci.* **2011**, *2*, 1491.

4. Plechkova, N. V; Seddon, K. R. Applications of ionic liquids in the chemical industry. *Chem. Soc. Rev.* **2008**, *37*, 123–50.

5. Patel, D. D.; Lee, J.-M. Applications of ionic liquids. *Chem. Rec.* **2012**, *12*, 329–55.

6. Freudenmann, D.; Wolf, S.; Wolff, M.; Feldmann, C. Inorganic Synthesis Ionic Liquids: New Perspectives for Inorganic Synthesis? *Angew. Chem. Int. Ed.* **2011**, *50*, 11050–11060.

7. Yoshizawa, M.; Xu, W.; Angell, C. A. Ionic liquids by proton transfer: vapor pressure, conductivity, and the relevance of DeltapKa from aqueous solutions. *J. Am. Chem. Soc.* **2003**, *125*, 15411–9.

8. Esperanc, M. S. S.; Earle, M. J.; Gilea, M. A.; Magee, J. W.; Seddon, K. R.; Widegren, J. A. The distillation and volatility of ionic liquids. *Nature* **2006**, *439*, 831–834.

9. Fredlake, C. P.; Crosthwaite, J. M.; Hert, D. G.; Aki, S. N. V. K.; Brennecke, J. F. Thermophysical Properties of Imidazolium-Based Ionic Liquids. *J. Chem. Eng. Data* **2004**, *49*, 954–964.

10. Liaw, H.-J.; Chen, C.-C.; Chen, Y.-C.; Chen, J.-R.; Huang, S.-K.; Liu, S.-N. Relationship between flash point of ionic liquids and their thermal decomposition. *Green Chem.* **2012**, *14*, 2001.

11. Zakrzewska, M. E.; Bogel-Łukasik, E.; Bogel-Łukasik, R. Solubility of Carbohydrates in Ionic Liquids. *Energy & Fuels* **2010**, *24*, 737–745.

12. Anderson, J. L.; Dixon, J. K.; Brennecke, J. F. Solubility of CO2, CH4, C2H6, C2H4, O2, and N2 in 1-hexyl-3-methylpyridinium

bis(trifluoromethylsulfonyl)imide: comparison to other ionic liquids. *Acc. Chem. Res.* **2007**, *40*, 1208–16.

13. Scovazzo, P.; Camper, D.; Kieft, J.; Poshusta, J.; Koval, C.; Noble, R. Regular Solution Theory and CO2 Gas Solubility in Room-Temperature Ionic Liquids. **2004**, 6855–6860.

14. Chiappe, C.; Pomelli, C. S.; Rajamani, S. Influence of structural variations in cationic and anionic moieties on the polarity of ionic liquids. *J. Phys. Chem. B* **2011**, *115*, 9653–61.

15. Tiwari, S.; Kumar, A. Diels-Alder reactions are faster in water than in ionic liquids at room temperature. *Angew. Chem. Int. Ed. Engl.* **2006**, *45*, 4824–5.

16. Walden, P. Ueber die Molekulargrösse und elektrische Leitfähigkeit einiger geschmolzenen Salze. *Bull Acad. Imper. Sci. St. Petersbg.* **1914**, *8*, 405–422.

17. Welton, T. Room-Temperature Ionic Liquids. Solvents for Synthesis and Catalysis. *Chem. Rev.* **1999**, *99*, 2071–2084.

18. Gabriel, S.; Weiner, J. Ueber einige Abkömmlinge des Propylamins. *Berichte der Dtsch. Chem. Gesellschaft* **1888**, *21*, 2669–2679.

19. Hallett, J. P.; Welton, T. Room-temperature ionic liquids: solvents for synthesis and catalysis. 2. *Chem. Rev.* **2011**, *111*, 3508–76.

20. Zahn, S.; Bruns, G.; Thar, J.; Kirchner, B. What keeps ionic liquids in flow? *Phys. Chem. Chem. Phys.* **2008**, *10*, 6921–4.

21. Katritzky, A. R.; Jain, R.; Lomaka, A.; Petrukhin, R.; Karelson, M.; Visser, A. E.; Rogers, R. Correlation of the melting points of potential ionic liquids (imidazolium bromides and benzimidazolium bromides) using the CODESSA program. *J. Chem. Inf. Comput. Sci.* **2002**, *42*, 225–31.

22. Eike, D. M.; Brennecke, J. F.; Maginn, E. J. Predicting melting points of quaternary ammonium ionic liquids. *Green Chem.* **2003**, *5*, 323.

23. Niedermeyer, H.; Ashworth, C.; Brandt, A.; Welton, T.; Hunt, P. a. A step towards the a priori design of ionic liquids. *Phys. Chem. Chem. Phys.* **2013**, *15*, 11566–78.

24. Krossing, I.; Slattery, J. M.; Daguenet, C.; Dyson, P. J.; Oleinikova, A.; Weingärtner, H. Why are ionic liquids liquid? A simple explanation based on lattice and solvation energies. *J. Am. Chem. Soc.* **2006**, *128*, 13427–34.

25. Huddleston, J. G.; Visser, A. E.; Reichert, W. M.; Willauer, H. D.; Broker, G. a.; Rogers, R. Characterization and comparison of hydrophilic and hydrophobic room temperature ionic liquids incorporating the imidazolium cation. *Green Chem.* **2001**, *3*, 156–164.

26. Ranke, J.; Müller, A.; Bottin-Weber, U.; Stock, F.; Stolte, S.; Arning, J.; Störmann, R.; Jastorff, B. Lipophilicity parameters for ionic liquid cations and their correlation to in vitro cytotoxicity. *Ecotoxicol. Environ. Saf.* **2007**, *67*, 430–8.

27. Ranke, J.; Othman, A.; Fan, P.; Müller, A. Explaining ionic liquid water solubility in terms of cation and anion hydrophobicity. *Int. J. Mol. Sci.* **2009**, *10*, 1271–89.

28. Stolte, S.; Arning, J.; Bottin-Weber, U.; M?ller, A.; Pitner, W.-R.; Welz-Biermann, U.; Jastorff, B.; Ranke, J. Effects of different head groups and functionalised side chains on the cytotoxicity of ionic liquids. *Green Chem.* **2007**, *9*, 760.

29. Pringle, J. M.; Golding, J.; Baranyai, K.; Forsyth, C. M.; Deacon, G. B.; Scott, J. L.; MacFarlane, D. R. The effect of anion fluorination in ionic liquids - physical properties of a range of bis(methanesulfonyl)amide salts. *New J. Chem.* **2003**, *27*, 1504.

30. Krossing, I.; Raabe, I. Noncoordinating anions - fact or fiction? A survey of likely candidates. *Angew. Chem. Int. Ed. Engl.* **2004**, *43*, 2066–90.

31. Strauss, S. H. The search for larger and more weakly coordinating anions. *Chem. Rev.* **1993**, *93*, 927–942.

32. Pereiro, A. B.; Araújo, J. M. M.; Martinho, S.; Alves, F.; Nunes, S.; Matias, A.; Duarte, C. M. M.; Rebelo, L. P. N.; Marrucho, I. M. Fluorinated Ionic Liquids: Properties and Applications. *ACS Sustain. Chem. Eng.* **2013**, *1*, 427–439.

33. Fujii, K.; Fujimori, T.; Takamuku, T.; Kanzaki, R.; Umebayashi, Y.; Ishiguro, S.-I. Conformational equilibrium of bis(trifluoromethanesulfonyl) imide anion of a room-temperature ionic liquid: Raman spectroscopic study and DFT calculations. *J. Phys. Chem. B* **2006**, *110*, 8179–83.

34. Lopes, J. N. C.; Shimizu, K.; Pádua, A. a H.; Umebayashi, Y.; Fukuda, S.; Fujii, K.; Ishiguro, S. A tale of two ions: the conformational landscapes of bis(trifluoromethanesulfonyl)amide and N,N-dialkylpyrrolidinium. *J. Phys. Chem. B* **2008**, *112*, 1465–72.

35. Cao, Y.; Chen, Y.; Sun, X.; Zhang, Z.; Mu, T. Water sorption in ionic liquids: kinetics, mechanisms and hydrophilicity. *Phys. Chem. Chem. Phys.* **2012**, *14*, 12252–62.

36. Holbrey, J. D.; Seddon, K. R. The phase behaviour of 1-alkyl-3-methylimidazolium tetrafluoroborates; ionic liquids and ionic liquid crystals. *J. Chem. Soc. Dalt. Trans.* **1999**, 2133–2140.

37. Hummel, M.; Laus, G. Non-Halide Ionic Liquids for Solvation, Extraction, and Processing of Cellulosic Materials. In *Cellulose Solvents: For Analysis, Shaping and Chemical Modification*; Liebert, T. F.; Heinze, T. J.; Edgar, K. J., Eds.; ACS Symposium Series; American Chemical Society: Washington, DC, 2010; Vol. 1033, pp. 229–259.

38. Ab Rani, M. a; Brant, A.; Crowhurst, L.; Dolan, A.; Lui, M.; Hassan, N. H.; Hallett, J. P.; Hunt, P. a.; Niedermeyer, H.; Perez-Arlandis, J. M.; Schrems, M.; Welton, T.; Wilding, R. Understanding the polarity of ionic liquids. *Phys. Chem. Chem. Phys.* **2011**, *13*, 16831–40.

39. Welton, T. All solutions have a solvent. *Green Chem.* **2006**, *8*, 13.

40. Capello, C.; Fischer, U.; Hungerbu, K. What is a green solvent ? A comprehensive framework for the environmental assessment of solvents. **2007**, 927–934.

41. Matthias Maase, Klemens Massonne, Klaus Halbritter, Ralf Noe, Michael Bartsch, Wolfgang Siegel, Veit Stegmann, Miguel Flores, Oliver Huttenloch, M. B. Method for the separation of acids from chemical reaction mixtures by means of ionic fluids. WO 2003062171 A3, 2003.

42. Stegmann, V.; Massonne, K. Method For Producing Haloalkanes from Alcohols. EP 1 663 921 B2, 2005.

43. Boethling, R. S.; Sommer, E.; DiFiore, D. Designing small molecules for biodegradability. *Chem. Rev.* **2007**, *107*, 2207–27.

44. Coleman, D.; Gathergood, N. Biodegradation studies of ionic liquids. *Chem. Soc. Rev.* **2010**, *39*, 600–37.

45. Docherty, K. M.; Dixon, J. K.; Kulpa, C. F. Biodegradability of imidazolium and pyridinium ionic liquids by an activated sludge microbial community. *Biodegradation* **2007**, *18*, 481–93.

46. Rorije, E.; Germa, F.; Philipp, B.; Schink, B.; Beimborn, D. B. Prediction of biodegradability from structure: imidazoles. *SAR QSAR Environ. Res.* **2002**, *13*, 199–204.

47. Petkovic, M.; Ferguson, J. L.; Gunaratne, H. Q. N.; Ferreira, R.; Leitão, M. C.; Seddon, K. R.; Rebelo, L. P. N.; Pereira, C. S. Novel biocompatible cholinium-based ionic liquids—toxicity and biodegradability. *Green Chem.* **2010**, *12*, 643.

48. Petkovic, M.; Seddon, K. R.; Rebelo, L. P. N.; Silva Pereira, C. Ionic liquids: a pathway to environmental acceptability. *Chem. Soc. Rev.* **2011**, *40*, 1383–403.

49. Armand, M.; Endres, F.; MacFarlane, D. R.; Ohno, H.; Scrosati, B. Ionic-liquid materials for the electrochemical challenges of the future. *Nat. Mater.* **2009**, *8*, 621–9.

50. Deetlefs, M.; Seddon, K. R. Assessing the greenness of some typical laboratory ionic liquid preparations. *Green Chem.* **2010**, *12*, 17.

51. Anastas, P. T.; Kirchhoff, M. M. Origins, current status, and future challenges of green chemistry. *Acc. Chem. Res.* **2002**, *35*, 686–94.

52. Wellens, S.; Thijs, B.; Binnemans, K. How safe are protic ionic liquids? Explosion of pyrrolidinium nitrate. *Green Chem.* **2013**, *15*, 3484.

53. Smiglak, M.; Reichert, W. M.; Holbrey, J. D.; Wilkes, J. S.; Sun, L.; Thrasher, J. S.; Kirichenko, K.; Singh, S.; Katritzky, A. R.; Rogers, R. D. Combustible ionic liquids by design: is laboratory safety another ionic liquid myth? *Chem. Commun. (Camb).* **2006**, 2554–6.

54. *IUPAC Compendium of Chemical Terminology*; Nič, M.; Jirát, J.; Košata, B.; Jenkins, A.; McNaught, A., Eds.; IUPAC: Research Triagle Park, NC, 2009.

55. Tubbs, J. D.; Hoffmann, M. M. Ion-Pair Formation of the Ionic Liquid 1-Ethyl-3-methylimidazolium bis(trifyl)imide in Low Dielectric Media. *J. Solution Chem.* **2004**, *33*, 381–394.

56. Armstrong, J. P.; Hurst, C.; Jones, R. G.; Licence, P.; Lovelock, K. R. J.; Satterley, C. J.; Villar-Garcia, I. J. Vapourisation of ionic liquids. *Phys. Chem. Chem. Phys.* **2007**, *9*, 982–90.

57. Hunt, P. a.; Kirchner, B.; Welton, T. Characterising the electronic structure of ionic liquids: an examination of the 1-butyl-3-methylimidazolium chloride ion pair. *Chemistry* **2006**, *12*, 6762–75.

58. Weingärtner, H. Understanding ionic liquids at the molecular level: facts, problems, and controversies. *Angew. Chem. Int. Ed. Engl.* **2008**, *47*, 654–70.

59. Weingärtner, H. The Static Dielectric Constant of Ionic Liquids. *Zeitschrift für Phys. Chemie* **2006**, *220*, 1395–1405.

60. Tokuda, H.; Hayamizu, K.; Ishii, K.; Susan, M. A. B. H.; Watanabe, M. Physicochemical Properties and Structures of Room Temperature Ionic Liquids. 1. Variation of Anionic Species. *J. Phys. Chem. B* **2004**, *108*, 16593–16600.

61. Tokuda, H.; Hayamizu, K.; Ishii, K.; Susan, M. A. B. H.; Watanabe, M. Physicochemical properties and structures of room temperature ionic liquids. 2. Variation of alkyl chain length in imidazolium cation. *J. Phys. Chem. B* **2005**, *109*, 6103–10.

62. Every, H. A.; Bishop, A. G.; MacFarlane, D. R.; Oradd, G.; Forsyth, M. Transport properties in a family of dialkylimidazolium ionic liquids. *Phys. Chem. Chem. Phys.* **2004**, *6*, 1758.

63. Znamenskiy, V.; Kobrak, M. N. Molecular Dynamics Study of Polarity in Room-Temperature Ionic Liquids. *J. Phys. Chem. B* **2004**, *108*, 1072–1079.

64. Kobrak, M. N. Electrostatic interactions of a neutral dipolar solute with a fused salt: a new model for solvation in ionic liquids. *J. Phys. Chem. B* **2007**, *111*, 4755–62.

65. Foster, R. *Organic charge-transfer complexes*; Academic Press, 1969; p. 470.

66. Bender, C. J. Theoretical models of charge-transfer complexes. *Chem. Soc. Rev.* **1986**, *15*, 475.

67. Monk, P. M. S. *The Viologens: Physicochemical Properties, Synthesis and Applications of the Salts of 4,4'-Bipyridine*; John Wiley & Sons, Chichester, 1999; p. 332.

68. Kosower, E. M. The Effect of Solvent on Spectra. I. A New Empirical Measure of Solvent Polarity: Z-Values. *J. Am. Chem. Soc.* **1958**, *80*, 3253–3260.

69. Yuk Yu Lui, M. Special Solvation Behaviour of Salts in Ionic Liquid, Imperial College London, 2012, p. 191.

70. Lui, M. Y.; Crowhurst, L.; Hallett, J. P.; Hunt, P. a.; Niedermeyer, H.; Welton, T. Salts dissolved in salts: ionic liquid mixtures. *Chem. Sci.* **2011**, *2*, 1491.

71. Arce, A.; Earle, M. J.; Katdare, S. P.; Rodríguez, H.; Seddon, K. R. Mutually immiscible ionic liquids. *Chem. Commun. (Camb).* **2006**, *2*, 2548–50.

72. *Ionic Liquids in Synthesis*; Wasserscheid, P.; Welton, T., Eds.; 2nd ed.; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2007; p. 721.

73. Rudra, S.; Talukdar, H.; Kundu, K. K. Ion–ion–solvent interactions in aqueous ionic cosolvent systems. II. Single-ion transfer free energies and entropies using tetraphenylarsonium tetraphenylborate reference electrolyte assumption in aqueous sodium nitrate solvent system. *Can. J. Chem.* **1987**, *65*, 2595–2604.

74. Earle, M. J.; Gordon, C. M.; Plechkova, N. V; Seddon, K. R.; Welton, T. Decolorization of ionic liquids for spectroscopy. *Anal. Chem.* **2007**, *79*, 758–64.

75. Clare, B. R.; Bayley, P. M.; Best, A. S.; Forsyth, M.; MacFarlane, D. R. Purification or contamination? The effect of sorbents on ionic liquids. *Chem. Commun. (Camb).* **2008**, 2689–91.

76. Cammarata, L.; Kazarian, S. G.; Salter, P. a.; Welton, T. Molecular states of water in room temperature ionic liquids. *Phys. Chem. Chem. Phys.* **2001**, *3*, 5192–5200.

77. Freire, M. G.; Neves, C. M. S. S.; Carvalho, P. J.; Gardas, R. L.; Fernandes, A. M.; Marrucho, I. M.; Santos, L. M. N. B. F.; Coutinho, J. a P. Mutual solubilities of water and hydrophobic ionic liquids. *J. Phys. Chem. B* **2007**, *111*, 13082–9.

78. Ebel, K.; Koehler, H. Imidazole and Derivatives. In *... Encyclopedia of Industrial ...*; 2002; pp. 637–645.

79. Hollóczki, O.; Gerhard, D.; Massone, K.; Szarvas, L.; Németh, B.; Veszprémi, T.; Nyulászi, L. Carbenes in ionic liquids. *New J. Chem.* **2010**, *34*, 3004.

80. Song, Z.; Wang, H.; Xing, L. Density Functional Theory Study of the Ionic Liquid [emim]OH and Complexes [emim]OH(H2O) n (n=1,2). *J. Solution Chem.* **2009**, *38*, 1139–1154.

81. Ennis, E.; Handy, S. The Chemistry of the C2 Position of Imidazolium Room Temperature Ionic Liquids. *Curr. Org. Synth.* **2007**, *4*, 381–389.

82. Green, Don W. Perry, R. H. *Perry's Chemical Engineers' Handbook*; 8th ed.; McGraw-Hill Professional, 2007; p. 2400.

83. Denehy, E.; White, J. M.; Williams, S. J. Electronic structure of the sulfonyl and phosphonyl groups: a computational and crystallographic study. *Inorg. Chem.* **2007**, *46*, 8871–86.

84. Guthrie, J. P. Hydrolysis of esters of oxy acids: pKa values for strong acids; Brønsted relationship for attack of water at methyl; free energies of hydrolysis of esters of oxy acids; and a linear relationship between free energy of hydrolysis and pKa holding over a ran. *Can. J. Chem.* **1978**, *56*, 2342–2354.

85. Gardner, L.; Nancollas, H. Crystal Growth in Aqueous Solution at Elevated Temperatures . Barlum Sulfate Growth Kinetics. **1983**, 4699–4703.

86. Russell, J. H.; Wallwork, S. C. The crystal structures of the dichloride and isomorphous dibromide and diiodide of the N,N'-dimethyl-4,4'-bipyridylium ion. *Acta Crystallogr. Sect. B Struct. Crystallogr. Cryst. Chem.* **1972**, *28*, 1527–1533.

87. Dorman, S. C.; O'Brien, R. a; Lewis, A. T.; Salter, E. A.; Wierzbicki, A.; Hixon, P. W.; Sykora, R. E.; Mirjafari, A.; Davis, J. H. A new building block for electroactive organic materials? Synthesis, cyclic voltammetry, single crystal X-ray structure, and DFT treatment of a unique boron-based viologen. *Chem. Commun. (Camb).* **2011**, *47*, 9072–4.

88. Douglass, J. E. Bisamine Complexes of Boronium Ions. The Reaction of Amine Boranes with Iodine. *J. Am. Chem. Soc.* **1964**, *86*, 5431–5433.

89. Cho, C.-W.; Phuong Thuy Pham, T.; Jeon, Y.-C.; Yun, Y.-S. Influence of anions on the toxic effects of ionic liquids to a phytoplankton Selenastrum capricornutum. *Green Chem.* **2008**, *10*, 67.

90. Swinburne, A. N.; Paterson, M. J.; Fischer, K. H.; Dickson, S. J.; Wallace, E. V. B.; Belcher, W. J.; Beeby, A.; Steed, J. W. Colourimetric carboxylate anion sensors derived from viologen-based receptors. *Chemistry* **2010**, *16*, 1480–92.

91. Park, J. J.; Kim, Y.-H.; Rhim, S.; Kang, J. Anion receptors with viologen molecular scaffold. *Tetrahedron Lett.* **2012**, *53*, 247–252.

92. Anderson, T. Ueber die Producte der trocknen Destillation thierischer Materien. *Ann. der Chemie und Pharm.* **1855**, *94*, 358–365.

93. Clough, M. T.; Geyer, K.; Hunt, P. a.; Mertes, J.; Welton, T. Thermal decomposition of carboxylate ionic liquids: trends and mechanisms. *Phys. Chem. Chem. Phys.* **2013**, *15*, 20480–95.

94. Homer, R. F.; Tomlinson, T. E. The stereochemistry of the bridged quaternary salts of 2,2'-bipyridyl. *J. Chem. Soc.* **1960**, 2498.

95. Calder, I.; Sasse, W. Aromatic nitrogen bridgehead compounds. I. The dipyrido[1,2-c:2',1'-e]-imidazolium and related cations. *Aust. J. Chem.* **1965**, *18*, 1819.

96. BRIAN, R. C.; HOMER, R. F.; STUBBS, J.; JONES, R. L. A New Herbicide: 1 : 1′-Ethylene-2 : 2′-Dipyridylium Dibromide. *Nature* **1958**, *181*, 446–447.

97. Oki, A.; Morgan, R. An efficient preparation of 4,4′-dicarboxy-2,2′-bipyridine. *Synth. Commun.* **1995**, 37–41.

98. Muldoon, J.; Ashcroft, A. E.; Wilson, A. J. Selective protein-surface sensing using ruthenium(II) tris(bipyridine) complexes. *Chemistry* **2010**, *16*, 100–3.

99. Singh, R. P.; Shreeve, J. M. Syntheses of the first N-mono- and N,N'-dipolyfluoroalkyl-4,4'-bipyridinium compounds. *Chem. Commun. (Camb).* **2003**, 1366–7.

100. Coe, B. J.; Curati, N. R.; Fitzgerald, E. C. Unusually Facile Syntheses of Diquat (6,7-Dihydrodipyrido[1,2- a:2′,1′-c]pyrazinediium) and Related Cations. *Synthesis (Stuttg).* **2006**, 146–150.

101. Thummel, R.; Lefoulon, F. Bisannelated derivatives of 2,2'-bipyridine. *J. Org. Chem.* **1988**, 4745–4747.

102. Chiral, A.; Wdmer, M.; Greiner, G.; Rau, H. Asymmetric Electron Transfer from a Chiral Ruthenium Complex Donor to an Atropisomeric Chiral 2,2'-Bipyridine Acceptor? **1995**, 14161–14166.

103. Xiao, Y.; Chu, L.; Sanakis, Y.; Liu, P. Revisiting the IspH catalytic system in the deoxyxylulose phosphate pathway: achieving high activity. *J. Am. Chem. Soc.* **2009**, *131*, 9931–3.

104. Parker, A. J. The effects of solvation on the properties of anions in dipolar aprotic solvents. *Q. Rev. Chem. Soc.* **1962**, *16*, 163.

105. Bhowmik, P. K.; Han, H.; Cebe, J. J.; Burchett, R. A.; Acharya, B.; Kumar, S. Ambient temperature thermotropic liquid crystalline viologen bis(triflimide) salts. *Liq. Cryst.* **2003**, *30*, 1433–1440.

106. Alcalde, E.; Dinarès, I.; Ibáñez, A.; Mesquida, N. A simple halide-to-anion exchange method for heteroaromatic salts and ionic liquids. *Molecules* **2012**, *17*, 4007–27.

107. Melby, L. R.; Harder, R. J.; Hertler, W. R.; Mahler, W.; Benson, R. E.; Mochel, W. E. Substituted quinodimethans. II. Anion-radical derivatives and complexes of 7, 7, 8, 8-tetracyanoquinodimethan. *J. Am. Chem. Soc.* **1962**, *84*, 3374–3387.

108. Le, T. H.; Nafady, A.; Qu, X.; Bond, A. M.; Martin, L. L. Redox and acid-base chemistry of 7,7,8,8-tetracyanoquinodimethane, 7,7,8,8-tetracyanoquinodimethane radical anion, 7,7,8,8-tetracyanoquinodimethane dianion, and dihydro-7,7,8,8-tetracyanoquinodimethane in acetonitrile. *Anal. Chem.* **2012**, *84*, 2343–50.

109. Grossel, M. C.; Duke, A. J.; Hibbert, D. B.; Lewis, I. K.; Seddon, E. A.; Horton, P. N.; Weston, S. C. An Investigation of the Factors that Influence the Decomposition of 7,7‘,8,8‘-Tetracyanoquinodimethane (TCNQ) and Its Salts to, and Structural Characterization of, the α,α-Dicyano- p -toluoylcyanide Anion. *Chem. Mater.* **2000**, *12*, 2319–2323.

110. Grossel, M. C.; Hitchcock, P. B.; Seddon, K. R.; Welton, T.; Weston, S. C. 1:1 Imidazolium 7,7’,8,8'-Tetracyano-p-quinodimethanide ([TCNQ].bul.-) Salts: Substituent Control of Solid-State Architecture. *Chem. Mater.* **1994**, *6*, 1106–1108.

111. Abrahams, B. F.; Hudson, T. A.; Robson, R. A New Approach to TCNQ-Based Coordination Polymers via TCNQH 2. *Cryst. Growth Des.* **2008**, *8*, 1123–1125.

112. Shimomura, S.; Matsuda, R.; Tsujino, T.; Kawamura, T.; Kitagawa, S. TCNQ Dianion-Based Coordination Polymer Whose Open Framework Shows Charge-Transfer Type Guest Inclusion. *J. Am. Chem. Soc.* **2006**, *128*, 16416–16417.

113. Saber, M. R.; Prosvirin, A. V; Abrahams, B. F.; Elliott, R. W.; Robson, R.; Dunbar, K. R. Magnetic Coupling between Metal Spins through the 7,7,8,8-Tetracyanoquinodimethane (TCNQ) Dianion. *Chemistry* **2014**, 1–6.

114. Abrahams, B. F.; Elliott, R. W.; Hudson, T. a.; Robson, R. A new type of 3D [(MII)2(TCNQ−II)3]2− coordination network with spacious channels of hexagonal cross-section generated from TCNQH2. *CrystEngComm* **2012**, *14*, 351.

115. Hudson, T. A.; Robson, R. A New Class of TCNQ Derivatives Easily Generated from TCNQH 2 Containing Discrete TCNQ 2− Anions and Noncoordinating Cations. *Cryst. Growth Des.* **2009**, *9*, 1658–1662.

116. Hertler, R. Substituted Quinodimethans. I. Preparation and Chemistry of 7,7,8,8-Te trac yanoquinodimethan. **1962**, *81*, 3370–3374.

117. Suchanski, M. R.; Van Duyne, R. P. Resonance Raman spectroelectrochemistry. IV. The oxygen decay chemistry of the tetracyanoquinodimethane dianion. *J. Am. Chem. Soc.* **1976**, *98*, 250–252.

118. Lombardo, A.; Fico, T. R. Mechanism of conversion of 1:1 anion-radical salts of tetracyano-p-quinodimethane to their 1:2 analogs. *J. Org. Chem.* **1979**, *44*, 209–212.

119. Mizoguchi, K.; Tsuji, S.; Tsuchida, E.; Shinohara, I. Chemical stability and electroconductivity of 7,7,8,8-tetracyanoquinodimethane salts containing polycation polymers. *J. Polym. Sci. Polym. Chem. Ed.* **1978**, *16*, 3259–3274.

120. Harjani, J. R.; Nara, S. J.; Salunkhe, M. M.; Sanghvi, Y. S. Transprotection of Silyl Ethers of Nucleosides in FeCl3 Based Ionic Liquids. *Nucleosides, Nucleotides and Nucleic Acids* **2005**, *24*, 819–822.

121. Brandt, A.; Hallett, J. P.; Leak, D. J.; Murphy, R. J.; Welton, T. The effect of the ionic liquid anion in the pretreatment of pine wood chips. *Green Chem.* **2010**, *12*, 672.

122. Correia, I.; Welton, T. An old reaction in new media: kinetic study of a platinum(II) substitution reaction in ionic liquids. *Dalton Trans.* **2009**, 4115–21.

123. Wells, T. P.; Hallett, J. P.; Williams, C. K.; Welton, T. Esterification in ionic liquids: the influence of solvent basicity. *J. Org. Chem.* **2008**, *73*, 5585–8.

124. Clough, M. Hydrolysis of 1-ethyl-3-methylimidazolium methyl sulfate; 1-Ethyl-3-methylimidazolium hydrogen sulfate. *ChemSpider Synth. Pages* **2012**, DOI:10.1039/SP572.

125. Salvi, P. P.; Mandhare, A. M.; Sartape, A. S.; Pawar, D. K.; Han, S. H.; Kolekar, S. S. Brønsted acidic ionic liquids promoted cyclocondensation reaction: Synthesis of 1,8-dioxo-octahydroxanthene. *Comptes Rendus Chim.* **2011**, *14*, 883–886.

126. Ross, J. H.; Krieger, R. I. Synthesis and properties of paraquat (methyl viologen) and other herbicidal alkyl homologs. *J. Agric. Food Chem.* **1980**, *28*, 1026–1031.

127. Depature, L.; Surpateanu, G. Synthesis and Characterisation of Extended p-Bonding Systems in Cycloimmonium Ylides Derived from the 4,4'-Bipyridine. *Heterocycles* **2002**, *57*, 2239.

128. Bhowmik, P.; Han, H.; Nedeltchev, I.; Cebe, J. Room-Temperature Thermotropic Ionic Liquid Crystals: Viologen Bis(Triflimide) Salts. *Mol. Cryst. Liq. Cryst.* **2004**, *419*, 27–46.

129. Rieger, A. L.; Rieger, P. H. Magnetic resonance studies of some bipyridylium dications and cation radicals. *J. Phys. Chem.* **1984**, *88*, 5845–5851.

ACKNOWLEDGEMENTS

The author wishes to thank to all researchers of Welton group for their support during the six month placement at Imperial College, especially to Mr. Alastair J. S. McIntosh for the many fruitful discussions, advices for high-quality IL synthesis and his always knowing and encouraging attitude, to Dr. Lorna Housecroft for teaching the techniques of determination of solvatochromic parameters of ILs, to Mrs. Liyana Ismail Nur and Mr. Gilbert de Gregorio for kindly sharing their workspace and listening to my chemical brainstorming, to Mr. Matthew T. Clough for giving the insight into computational chemistry and as well to Dr. Jason P. Hallett.

Also, gratitude is due to Dr. Igors Klimenkovs and Mr. Agris Berzins (University of Latvia) for sharing their view and proposing promising ideas for further work.

Finally, I owe the greatest acknowledgement to Professor Tom Welton for all he has done in my favour by kindly enrolling me in his research group for these valuable months of my Master studies.

Maģistra darbs „Molekulārās mijiedarbības jonu šķidrumos” izstrādāts LU Ķīmijas fakultātē un Imperial College London Ķīmijas departamentā.

Ar savu parakstu apliecinu, ka pētījums veikts patstāvīgi, izmantoti tikai tajā norādītie informācijas avoti un iesniegtā darba elektroniskā kopija atbilst izdrukai.

Autors: ____
(*personiskais paraksts)* *(paraksta atšifrējums)*

Rekomendēju darbu aizstāvēšanai.
Vadītājs profesors,
Dr. hab. chem. Andris Zicmanis: ____
(*personiskais paraksts)* *(datums)*

Recenzents, asoc. prof.,
Dr. chem. Anda Prikšāne: ____
(*personiskais paraksts)* *(datums)*

Darbs iesniegts Ķīmijas fakultātē: ____________________________________
(*datums*)
Dekāna pilnvarotā persona,
metodiķe Vija Gutāne: ______________________________
(*personiskais paraksts)*

Darbs aizstāvēts bakalaura gala pārbaudījuma komisijas sēdē:

________________ protokols Nr. _______________
(datums) *(protokola Nr.)*

Komisijas sekretāre, lektore: ____
(*personiskais paraksts)* *(paraksta atšifrējums)*