QUEEN'S UNIVERSITY BELFAST

MASTER OF PHILOSOPHY

Towards induction of charge-transfer complexation in ionic liquid systems

Sun, Jiajun

Award date:
2023

Awarding institution:
Queen's University Belfast

Link to publication

Terms of use
All those accessing thesis content in Queen's University Belfast Research Portal are subject to the following terms and conditions of use

- Copyright is subject to the Copyright, Designs and Patent Act 1988, or as modified by any successor legislation
- Copyright and moral rights for thesis content are retained by the author and/or other copyright owners
- A copy of a thesis may be downloaded for personal non-commercial research/study without the need for permission or charge
- Distribution or reproduction of thesis content in any format is not permitted without the permission of the copyright holder
- When citing this work, full bibliographic details should be supplied, including the author, title, awarding institution and date of thesis

Take down policy
A thesis can be removed from the Research Portal if there has been a breach of copyright, or a similarly robust reason.
If you believe this document breaches copyright, or there is sufficient cause to take down, please contact us, citing details. Email: openaccess@qub.ac.uk

Supplementary materials
Where possible, we endeavour to provide supplementary materials to theses. This may include video, audio and other types of files. We endeavour to capture all content and upload as part of the Pure record for each thesis.
Note, it may not be possible in all instances to convert analogue formats to usable digital formats for some supplementary materials. We exercise best efforts on our behalf and, in such instances, encourage the individual to consult the physical thesis for further information.

Download date: 12. May. 2024

Towards induction of charge-transfer complexation in ionic liquid systems

Oct. 2019 - Jun.2023

A thesis submitted for the degree of Master of Philosophy

Supervised by Prof. John D. Holbrey

Jiajun Sun

40249857

SCHOOL OF CHEMISTRY AND CHEMICAL ENGINEERING

Queen's University Belfast

David Keir Building, Belfast, Northern Ireland, UK BT9 5AG

Table of Contents

Acknowledgement.....1

Abstract.....2

1 Introduction.....3

1.1 Charge-transfer complex.....5

1.1.1 The Composition of Charge-transfer complexes.....6

1.1.2 The donor-acceptor structure.....8

1.1.3 The charge-transfer complexes with ionic liquids.....10

1.2 Ionic liquid and their mixtures.....13

1.2.1 Synthesis routes of ionic liquids.....14

1.2.2 Aromatic-functionalized imidazolium ionic liquids.....15

1.2.3 Electron-withdrawing pyridinium ionic liquids.....17

1.2.4 Ionic liquid mixtures.....20

1.3 The method for detecting charge-transfer complex.....25

1.4 Projects aims.....27

2 Results and discussion.....29

2.1 Synthesis of ionic liquids.....30

2.1.1 Imidazolium salts with aromatic functions.....32

2.1.2 N-alkyl-cyanopyridinium salts.....34

2.1.3 N-alkyl-cyanopyridinium salts with aromatic functions.....35

2.2 Characterization of ionic liquids.....36

2.2.1 ^{1}H NMR spectra 36

2.2.2 Thermal stability and DSC results 39

2.2.3 IR spectra 43

2.2.4 Single-crystal XRD 46

2.3 The performances of ionic liquid mixtures 51

2.3.1 Melting points of ionic liquid mixtures 52

2.3.2 UV-Vis spectra 53

2.4 Theorical calculation 63

3 Conclusion 68

4 Experimental 71

4.1 Synthesis of ionic liquids 72

4.2 Preparation of ionic liquids-ionic liquids mixtures 77

5 Reference 78

6 Appendix 82

6.1 IR spectra 82

6.2 NMR spectra 84

6.3 TGA 89

6.4 DSC 92

Acknowledgement

First, I would like to thank Prof. John Holbrey for the patient guidance through the project as my supervisor. Under his meticulous supervision, I got abundant knowledge relating to ionic liquids and learned to think in a scientific way, which would make me benefit in the whole life. This must be my most precious memory in my life. I would like to thank for Dr. Jillian Thompson and Dr. Marijana Blesic for the valuable suggestions on my project and writing skills in the mid-term interview. Thanks to QUILL and ASEP for providing analytical service, including DSC, TGA and single-crystal XRD analysis. Thanks also to Anthony Dodd, Quanjun Zhe and everyone in the group for their experimental direction and discussion. Without the help of these people above, I would not complete my project so well.

Abstract

Charge-transfer complexes (short as CT complex) which are composed to two kinds of different aromatic systems are formed by the interactions of electron donor and electron acceptor functions. This type of combination brings new properties like UV, melting points and different colours to the mixtures. In this work, a series of imidazolium-based ionic liquids functionalised with electron-rich aromatic groups have been synthesised and their potential to form binary ionic liquid eutectic mixtures exhibiting charge-transfer complex characteristics when combined with 'electron-withdrawing' cyanopyridinium cations has been investigated. It was determined that CT complex formation is unfavourable due to competing cation-cation coulombic repulsions between pairs of cations and an alternative approach to generate solely ionic liquid CT complexes by including both electron donor and acceptor in a single aromatic-functionalized cyanopyridinium cation was also investigated.

Keywords: ionic liquids, charge-transfer complex, aromatic-functionalized.

1 Introduction

With the continuing developments of society and technology, problems and challenges about the generation and sources of energy are becoming increasingly important issues for everyone. Oil, gas and coal sources are finite and non-renewable (except on a geological timescale). Therefore, new, non-CO_2 producing sources of energy production like solar, tidal and wind for power production are becoming increasingly important with electricity generation as the main use of these clean energy resources. Compared with the conventional fossil fuel, these power generation sources can be intermittent influenced by the environments. Therefore, storage devices for these energy resources are required to complement primary power generation.

Electrochemical energy storage devices like supercapacitors, batteries and electrochemical double-layer capacitors (EDLCs) are under continued investigation. For batteries, electrolytes that act as an intermediate transfer medium allowing charge to transfer between the electrodes, played an important role which influence the performances of the devices including stability, charging circles and energy density.[1] Electrolytes can be divided into several groups based on their composition (organic or inorganic), states of matters (solid and liquids[2]) and also on their application areas. For electrolytes, the properties of ionic liquids which are different from those of a conventional molecular solvent/salt based electrolytes are attractive for research.[3]

Ionic liquids are totally composed of cations and anions and have interest as electrolytes for because ionic liquids have a high ion conductivity, high ionic strength while avoiding the need to include volatile and potentially flammable solvents[4]. Although the prices of ionic liquids are quite high which is the main reason why it cannot be widely used in the energy storage devices. The ionic liquids can be used as the additives which could improve the performances of the electrolytes like thermostability in the electrolytes.[5] It has been projected that, with increased scale of production and the associated economies of

scale, some imidazolium based ionic liquids could be prepared at significantly lower costs,[6] and it should be noted that Hallett and co-workers have reported that the protic ionic liquid, triethylammonium hydrogen sulphate, can be produced at less than £5/kg. Properties and characteristics of ionic liquids, such as the general low vapor-pressure,[7] good thermostability, and high ion conductivity can be designed through changing the structures of the cations and anions. Ionic liquids with 1,3-dialkylimidazolium cations are typical examples and have been considered as the potential electrolytes in the electronic double-layer capacitors (EDLC)[8] and solar cells.[5]

Recently, a new electrolytes paradigm has been envisaged in which energy can be stored within the electrolytes through redox reactions as well as the electrolytes acting purely as a transport medium. Compared with the conventional electrolytes,[9] these new paradigm electrolytes could store the energy which means the energy density will be improved without changing the existing devices' structure and the electrodes' materials.[10] The biredox ionic liquids in supercapacitors have a larger capacitance than normal ionic liquids with the porous carbon electrodes and the leakage current of biredox ionic liquids was decreased by almost a factor of 3.[11] This new kind of electrolyte may create a new kind of storage mechanism which is shown in the Figure. 1-1.

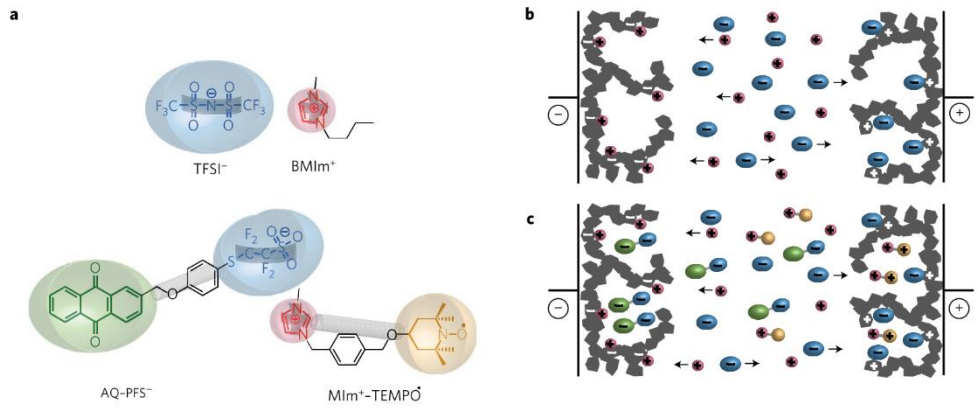


Figure 1-1: comparison of charge storage in EDLC with IL electrolyte and biredox IL-enhanced pseudo capacitor. (a) structure of BMImNTf$_2$ IL and the redox IL (b) comprising a perfluorosulfonate anion bearing anthraquinone (AQ-PFS$^-$) and a methyl imidazolium cation bearing TEMPO (MIm$^+$-TEMPO$^-$). Charge storage in a

purely capacitive EDLC comprising porous carbon electrodes and an IL electrolyte (b) and the herein developed concept of capacitors with additional Faradaic process at the redox active ions of the biredox IL electrolytes (c).[10]

To achieve this aim, the cooperation of the materials should form cavities or domains for holding either electrons or cationic charge carriers. The formation of the charge-transfer complexes leads to structures that can trap charge and so have the potential to support these new paradigm electrolytes. Using an ionic liquid system that can take part in charge-transfer complex formation could enable the advantages of ionic liquids electrolytes (including high charge density and non-volatility) combined with the opportunity to storage additional energy. The advantage which could change their functions through changing the structure of particle of the ionic liquids is the main reason why ionic liquids could be used as one of the potential selections.

In this research project, a series of aromatic ionic liquids and their mixtures were explored to investigate the potential to form purely ionic liquid/polyaromatic hydrocarbon mixtures that contain volatile and hazardous aromatic components.

1.1 Charge-transfer complex

Charge-transfer complexes were first discussed fully in a review by Karsha in 1950.[9] Charge-transfer complexes are identified as materials that result in changes in their optical emission properties under suitable situations on forming the charge-transfer complex compared to the emission spectra of the components. Except to changes in the optical characteristics, the conductivity and ferroelectric properties can also be modified. However, some intermolecular interactions among different kinds of molecules can also perform the similar properties like single kinds of organic molecules.

Ionic liquids that exhibit charge-transfer complex formation, resulting in a colour change, in the presence of electron-rich aromatic electron donors were reported by Hardacre and co-workers[12] for pyridinium ionic liquids containing electron-withdrawing nitrile groups on the cation ring. On mixing the ionic

liquid at 1:1 molar ratio with 1-methylnaphthalene, the mixture immediately changes from two colourless liquids into an intense yellow for the 1:1 mixture. The formation of this type of charge-transfer complex is based on the intermolecular interactions. The intermolecular interactions are of different kinds like strong interactions (hydrogen bond, halogen bond and Coulomb Force) and weak interactions (Van der Waals force and π-π interactions). Charge-transfer complexes contain components that are electron-rich and π-conjugated, most often electron-rich aromatic materials which can be induced to self-assemble into a supramolecular charge-transfer ensemble. The π-conjugated chromophores are the essential factor and property for the charge-transfer complex.

1.1.1 Composition of Charge-transfer complexes.

With the different energy levels, the charge-transfer complexes renew an electron-jump from bonding orbitals to the antibonding orbitals. From the interactions among the molecules, the coulombic intermolecular interaction is the main reason for the formation of the charge-transfer complexes.[13] The main performance indicator of charge transfer complexes is the photophysical signature. Different composition of the charge-transfer complexes can perform different photophysical signatures due to different aggregates methods.

Therefore, there are two kinds of photophysical performances among different types of charge-transfer complexes which are called red-shift and blue-shift. These shifts correspond to two different aggregates: J-aggregate and H-aggregate[14]. These aggregates explain some reasons of the performances. J-aggregates are based on the interactions between aromatic-functionalized particles which have positive charges and neutral aromatic molecules. Although both combination methods are based on the intermolecular Coulomb coupling, the H-aggregate is positive, and the J-aggregate is negative. The charge-transfer complexes based on the H-aggregate prefer intersystem crossing and phosphorescence because highest energy state (excitons) consumes all of the oscillator strength is focused highest energy state

consumes all the oscillator strength. In contrast, the oscillator strength of J--aggregate is focused on the lowest energy exciton and no suppression of fluorescence. The sign of the Coulomb coupling to the relative orientation between neighbouring chromophores, leading to the often-utilized association of 'side-by-side' transition dipoles with H-aggregates and 'head to tail' transition dipoles with J-aggregates. However, both J-aggregates and H-aggregates from Kasha's theory are focused on the molecules' arrangement and intermolecular interactions among pure organic molecules. The Coulomb-coupled aggregates is the ubiquity of π-stacked aggregate where close nearest-neighbour contacts (<4 Å) enable substantial wave function overlap and intermolecular charge transfer.[15, 16] Conventional charge-transfer complexes are composed by interactions between pairs of molecules, the intermolecular interactions are simple and easy to be analysed. Mixtures' intermolecular interactions are different. Other interactions among different molecules may have a negative influence on the formation of charge-transfer complexes.

The two kinds of Coulomb coupling methods are sorted by the angles of two corresponding molecules. According to the Kasha's theory,[16-18] the magic angle θ_M is 54.7 degrees. Figure 1-2 shows the interactions between molecules '1' and '2'. The J-aggregate is less than the θ_M. And the H-aggregate is between θ_M and π/2.

For this project, the interactions between electron-withdrawing pyridinium ionic liquids and aromatic-functionalized imidazolium ionic liquids were targeted. In conventional charge transfer complexes composed of electron-withdrawing pyridinium and aromatic rings, the UV-Vis absorption of the mixtures have an obvious blue-shift in the crystal structure which means H-aggregation among these series mixtures.

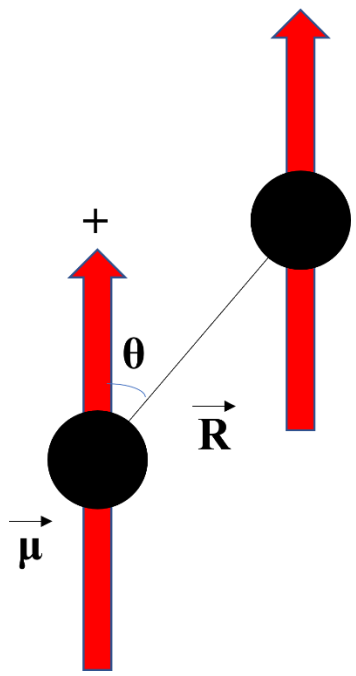


Figure 1-2: Relative orientation of transition dipole moments defining a J-aggregate ($\theta < \theta_M$) and H-aggregate ($\theta_M < \theta < \pi/2$) under the point dipole approximation. The magic angle θ_M is 54.7 degrees.[17]

1.1.2 Donor-acceptor structure

The charge transfer complexes are also called donor-acceptor structures (DA).[19] These organic molecules' combination may lead to the enhanced supramolecular electronic effects, for example bringing the DA metallicity (or even superconductivity), emission and ferroelectricity. Therefore, the DA complexes bring a new potential application in semiconductor and photovoltaic devices. Compared with conventional n-type and p-type semiconductors, the organic DA complexes may have some unique advantages arising from their unique molecular packing and structure-property relationships through formation of organic ionic DA complexes. First, the growth of densely packed DA complex crystals with will reduce the impurities and traps in the mixtures which are not separated from the purification from the self-assembly process. Second, the organic DA complexes could form a supramolecular organic mixture, which can facilitate charge transfer depending on the driving forces during the co-assembly

processes. Third, the performances like operation mode and tuneable band of the organic semiconductors could be systematically controlled through changing the components. Finally, the theorical calculations also play an important role in studying and understanding the structure-property relationships and the results of the calculations help us design the DA complexes' semiconductors.

Generally, the supramolecule nonbonding methods like hydrogen-bonding, π-π stacking, halogen-bonding interactions act as the driving forces of the assembly organic molecules. In the DA complexes, the donors are attached to the bent convex surface which improves the π-π interactions. The formation pathways of the DA complexes are separated by co-sublimation and solution-process. The co-sublimation is based on those small molecules orderly packing under vapor state. The solution-process is similar with the formation of the cocrystals which involves cooling a solution, evaporation of the solvent and diffusion of mixed solvents.[20]

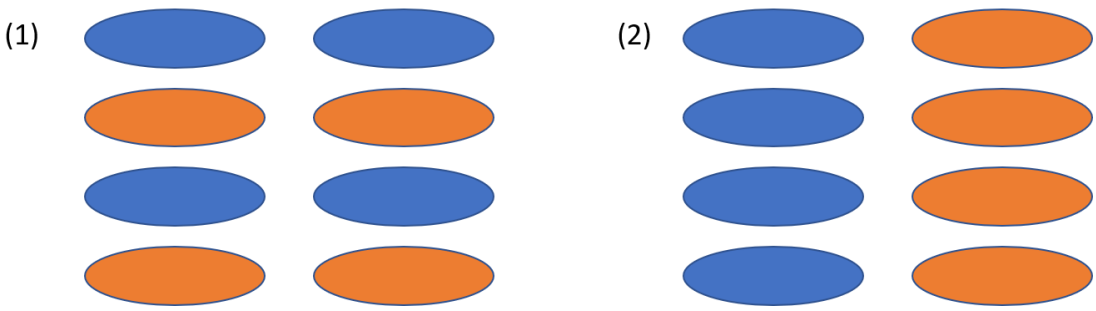


Figure 1-3: the different stacking methods of the DA complexes: (1) the mixed-stack (MS): the donor and acceptor molecules alternately stack altogether; (2) the separated-stack (SS): the donor and acceptor molecules from two different columns.[21]

The stacking of DA complexes could be separated mixed-stacking (MS) and segregated-stacking (SS). In MS systems, the donor and acceptor particles alternate along the stacking directions (-D-A-D-A-D-A-) to form the π-columns like Figure 1-3 (left).[21] Although the nearest neighbour D (or A) molecules in

the MS system are too far to interact with each other directly, the hybridization of the frontier orbitals of the closet donor makes the acceptor act as a 'bridge'. Therefore, the electrons and holes can travel through stacking DA columns. Compared with the MS system, the donor and acceptor molecules in the SS system which further pack alternatingly stacked separately (-D-D-D-D- and -A-A-A-A-)[22] in the same plane to form two-dimensional (2D) layers or form two different layers which belong to donor and acceptor separately. In this case, the holes for positive charges and electrons transport through the network in the cocrystals. Other stoichiometries (like 2:1 or 3:1) of DA compounds also have semiconducting properties. However, these are not widely found among ionic liquids.

However, ionic liquids are also diverse in their structural features and different types of ionic liquids can exhibit different charge-trapping models. In aliphatic cations (such as quaternary ammonium, phosphonium, and pyrrolidinium cations), the electron is localized and trapped as a cavity electron.[23, 24] Compared with the aliphatic ionic liquids, the imidazolium ionic liquids have a better performance in electron trapping because of two potential factors: (1) the formation of the cavity electron and (2) the delocalized electron in aromatic rings which stabilize the radical. From the data,[25-27] the strength of absorption of the 1-alkyl-3-methylimidazolium ionic liquids in diluted (≤5 mM) solutions in polar solvents has a stronger strength than aliphatic ionic liquids.

1.1.3 Charge-transfer complexes with ionic liquids

All forms of electric storage, batteries, capacitors and EDLC have their own drawbacks. Lithium batteries are restricted by the number of charge/discharge cycles that can be applied and capacitors typically have insufficient energy density. The electrolytes in devices for each of these applications play an intermediary of energy or electron transfer. The energy or electrons cannot be stored in the electrolytes, and so a new paradigm of electrolytes which can both store the electrons (charges) as well as functioning as an electrolyte have been brought into the scientists' view.

In order to store electrons in electrolytes, the structures of the electrolytes need to incorporate some unique function that can be cycled from reduced to oxidized states under different conditions to store/release energy as well as allowing conduction of the free electrons. Therefore, the electrolytes should be divided into two parts which is responsible for the oxidation and reduction at the same time.[28]

Rochefort and co-workers have studied the behaviours of inorganic redox active metal salts (Cu^{2+} V^{2+}, and Fe^{2+}) added into electrolytes.[29, 30] The solubility of these salts is the main standard of the addictive. Even some water-based electrolytes which are clean and low toxicity have been considered although the oxidation and reduction window of water is too small and restricts cell voltage to a window between 1.23-1.5 V which makes these salts be further away from being redox addictive. This is the reason why many organic electrolytes and water-based electrolytes are excluded from screening. Therefore, all solid-state supercapacitors are suitable for future applications and the electrolytes are also modified by some addictive. Some imidazolium ionic liquids could be used for enlarging the capacitance and increasing the charge/discharge cycles.[31]

According to the drawbacks of the water-based electrolytes and organic molecules, using ionic liquids as the base electrolyte while enabling storage of energy through charging of redox active sites within the liquid, biredox ionic liquids have been proposed as solutions that can avoid two significant problems: shuffle effect and self-discharge. The properties of ionic liquids can be modified through changing the structure of cations or anions. The choice of anions should be suitable for the environments of the applications. To increase ionic liquids conductivity and enhance the thermal and electrochemical stability, some anions like bromide, are not suitable for ELDC. And the bis{(trifluoromethyl)sulfonyl}imide ($[NTf_2]^-$) is widely used in the lithium batteries and EDLC. Moural et al. [10] have used 1-butyl-4-methylimidazolium ionic liquids as the co-electrolytes with redox-active cations and anions which can be charged/discharged to provide capacitive energy storage (Figure 1-4).

When the redox ionic liquid components were combined with ionic liquid which is used as the electrolyte in the supercapacitor.[29] A significant enhancement in the energy density of the supercapacitor with a capacity of 1000F at the same time the cyclability of a supercapacitor was observed.[32]

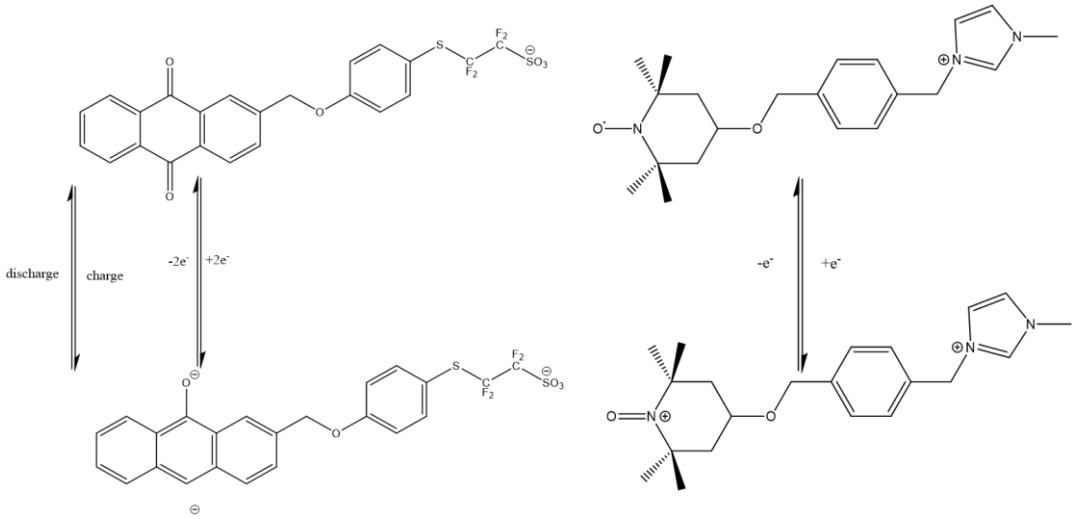


Figure 1-4: the mechanism of the new paradigm electrolyte.[10]

From molecular orbital theory, the formation of charge-transfer complexes is the inter-combination of different molecules orbitals which form a supramolecular structure. When the redox ionic liquid was added into the imidazolium ionic liquids, the cyclic number and specific capacitance are increasing like Figure 1-5 shows. This proves the redox ionic liquids could improve the performance of ionic liquids electrolyte.

In my project, the charge-transfer complexes have the potential to be used as the redox ionic liquid additive because their electrons could also travel through the molecules to improve the performances the capacitors.[33]

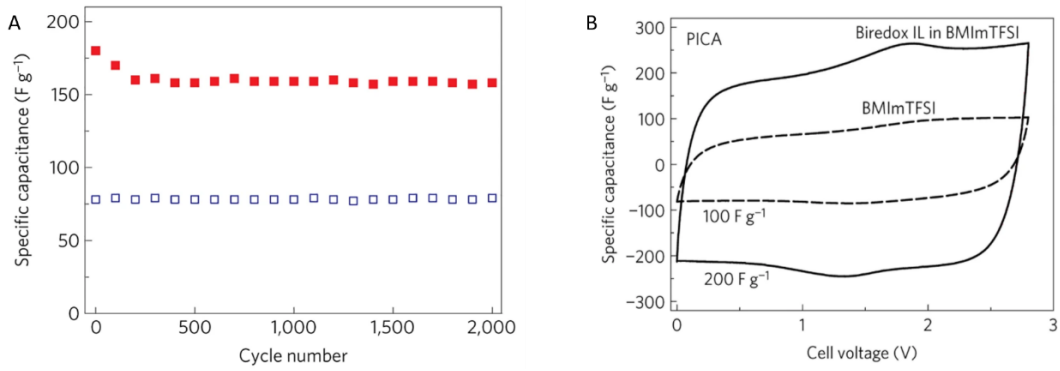


Figure 1-5: the performance of the redox ionic liquids: (A) the red dots are the capacitance of the biredox ionic liquid+BMImTFSI, and the blue dots are the capacitance of the pure BMImTFSI; (B) the cyclic voltammetry of the biredox IL in BMImTFSI.[6]

1.2 Ionic liquids and their mixtures

Ionic liquids are, by definition, liquids composed exclusively of ions. Although, this definition applies to all molten salts (e.g. molten NaCl at 801°C), ionic liquids are commonly treated as room temperature ionic liquids which have melting points much lower than the regular inorganic salts. The definition of RTILs is the melting point below 100 °C. Due to the large range of potential types and functionality that can be incorporated into ionic liquid materials, they are often referred to as 'designer solvents'. The potential of being used as the solvents is widely studied by scientists. Compared with the organic solvents, the low volatility and low flammability are the irreplaceable advantages of ionic liquids. Compared with the water, the solvability of organic molecules is also more attractive.

The first recorded room temperature ionic liquid with an organic cation, ethyl-ammonium nitrate was reported by Paul Walden in 1914. Since these initial reports, the range of organic salt types that can form different kinds of ionic liquids have been expanded by scientists. Nowadays, ionic liquids can be divided into a range of arbitrary classes such as metal-containing ionic liquids[34], ammonium salts, phosphonium salts, aromatic ionic liquid based on the types of cation employed,[35] and by their uses as catalysts, solvents,

electrolytes and so on in green chemistry and biochemistry.[36] Also, the dissolution ability of the ionic liquids is also used in the absorption of carbon dioxide, sulphur dioxide and other gases[37, 38] In addition, the extraction of mercury and desulfurization of the fuels are also potential applications for ionic liquids.

1.2.1 Synthesis routes of ionic liquids

The development of ionic liquids since 1990s has been symbiotic with the growth in importance of Green Chemistry, and while ionic liquids as materials may not be specifically ‘green’ or ‘benign’, their uses are primarily as materials or solvents in green and sustainable chemical applications, especially as alternative to volatile organic compounds (VOCs). In these applications, ionic liquids that are ideally hydrophobic and, at least minimally, not sensitive to air and water are desirable. The hydrophilic or hydrophobic nature of ionic liquids can be controlled through selecting or changing the structures of the cations or anions.

Synthesis of ionic liquids with organic cations is relatively straight-forward and the sequences used can be divided into two parts: (i) one-step, direct syntheses and (ii) multi-step synthesis incorporating an anion metathesis stage.

The one-step synthesis is widely used in the quaternation and acid-base neutralization reactions to form ammonium salts and phosphonium salts. The main advantage of this routes that there are no by-products, and so this is atom efficient. The first published ionic liquid $[EtNH_3][NO_3]$ was prepared by neutralisation of nitric acid and ethylamine forming a low melting point stable liquid. With the development of technology, new types of synthesis methods like ultrasonic and microwave heating have been used in the synthesis which can shorten reaction times and increase conversion.

The two-step synthesis is used for ionic liquids which cannot be directly or conveniently synthesized by the one-step method. Firstly, halo-alkanes and

organic esters are used to alkylate starting materials to prepare intermediates salts of the form s[cation][X] where X^- is the anion generated from the leaving group of the initial alkylating agent. Reacting with metal salts (MY) or Lewis acids (MX_Y) to make the product [cation][Y] and [cation][MX_{Y+1}][39] can be used to obtain more desirable ionic liquids materials.

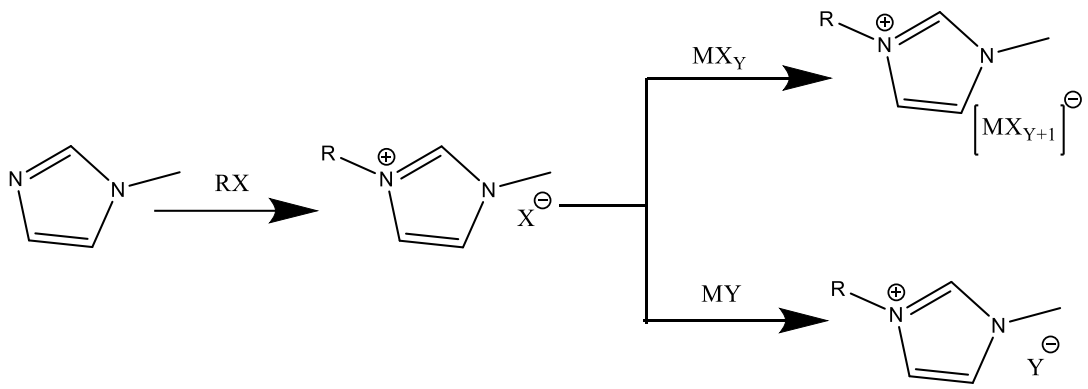


Figure 1-6: The synthesis routes of two-step method.

1.2.2 Aromatic-functionalized imidazolium ionic liquids

Imidazolium ionic liquids are widely used in many fields as catalysts, solvents and electrolytes. The normal structures of the imidazolium ionic liquids are show in the Figure 1-7. The properties of the imidazolium ionic liquids like solubility, Lewis's acidity which is potential for catalysis, melting points and viscosity could be adjusted through changing the functional groups and the anions. And the other functional groups which are connected with imidazolium rings bring new properties which are based on different types interactions like These interactions bring these fluids some different rheological behaviours like viscosities.[40]

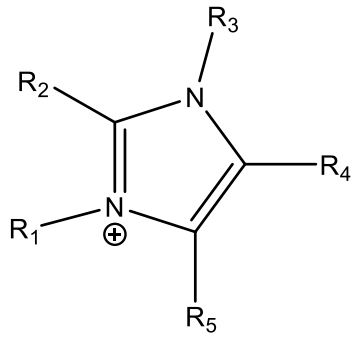


Figure 1-7: The structure of imidazolium cations

In this work, a series of ionic liquids containing cations that have been functionalised by appending electron-rich aromatic rings such as naphthalene or pyrene have been investigated. The cation structures of a representative 1-alkyl-3-(2-naphthalenemethyl)imidazolium ionic liquid is shown in Figure 1-8. Ionic liquids from this series have previously been widely explored as structuring agents in supramolecular chemistry[41] and as templating agents to controlling the size of zeolites.[42]

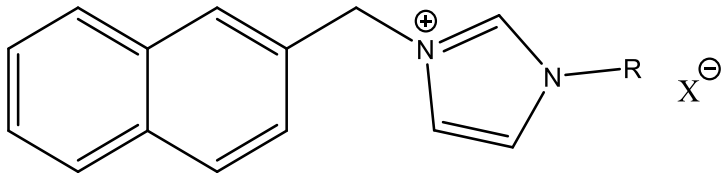


Figure 1-8: the cation structure of 1-alkyl-3-(2-naphthalenemethyl) imidazolium ionic liquids

Compared with the alkyl-functionalized imidazolium ionic liquids, the naphthalene group brings some different properties like the exfoliation of grapheme.[43] The aromatic rings like naphthalene can interact with graphene layers through π-π overlapping. The overlapping of the naphthalene rings brings it a stable crystal structure in solid state and high viscosity in liquid

state.

Strong π-π interactions between the electron-rich polyaromatic functional groups in the cations lead to self-assembly of the ionic liquids into aggregates in solution. In *Firth's* article, the pore sizes of zeolites templated from 1-methyl-3-naphthylmethylimidazolium bromide solution was controlled by the degree of self-aggregation of the ionic liquid components producing supramolecular porogens.[42]

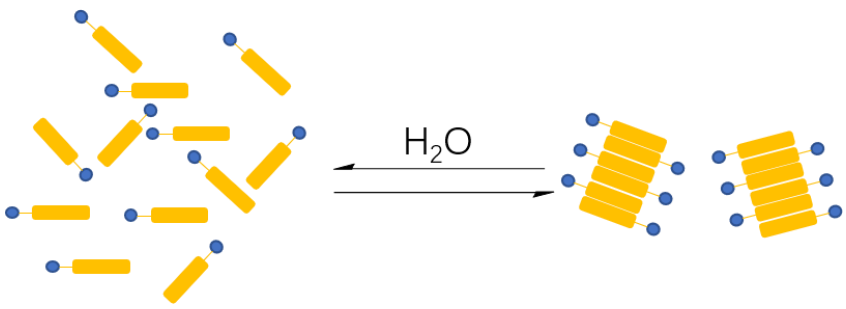


Figure 1-9: the indications of self-assemble effect

The XRD results shows that π-π interaction causes the naphthalene rings to overlap with each other.[44] Supramolecular association with hosts such as cucurbit[8]uril are also well established enabling a number of dynamic supramolecular architectures to be formed This type of the structure does increase the viscosity of ionic liquids and current study focuses on controlling the scale of the polymerization.[45, 46]

1.2.3 Electron-withdrawing pyridinium ionic liquids

By definition, the cations used to form ionic liquids have a high electron affinity due to their positive charge. However, ionic liquid design principles, particularly that of ensuring good charge delocalisation and disruption on packing efficiency by using asymmetric aromatic cations when possible, lead to poor and non-directional cation-electron (anion) associations in general.

Using pyridinium cations containing electron-withdrawing functional groups sited on the pyridinium rings (Figure 1-10), Hardacre et *al.*, reported the formation of a series of ionic liquids that displayed an increased association with aromatic solutes. These characteristics were used to enhance the extraction of aromatic components from oil[47], of use for dearomatisation of fuels for example. Moreover, when combined with electron-rich polyaromatics the functionalized pyridinium ionic liquids formed liquid charge-transfer complexes with aromatics such as 1-methylnaphthalene and pyrene. There are kinds of ionic liquid which is also used in separating sulphur compounds from alkanes because of association with unipolar compounds.[38]

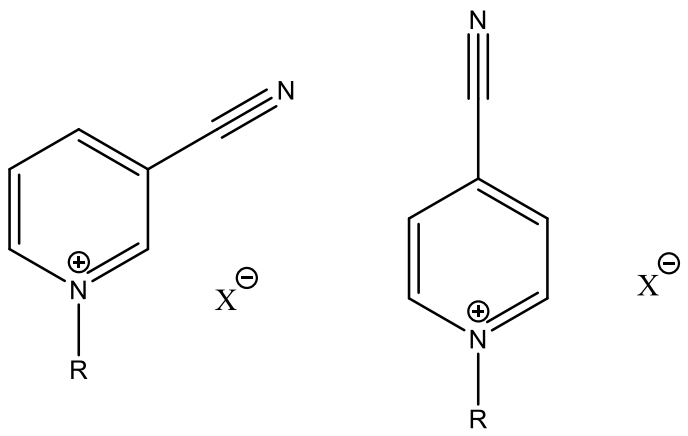


Figure 1-10: the structures of the n-electron-withdrawing pyridinium ionic liquids. X^- means the different types of anions.

These ionic liquids have strongly electron-withdrawing properties which lead to strong cation-π associations with the naphthalene rings generating highly coloured charge-transfer complexes. The formation of the CT-complex formed between 1-methylnaphthalene and N-ethyl-4-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide is shown Figure 1-11[12]. This kind of complex has a different UV-Vis absorption spectra and higher melting points than the two components, indicating constructive association between the components. This type of mixture is called as charge-transfer complex. The

most obvious appearance of the formation of a charge-transfer complex is the colour change of the mixtures.

Interestingly, comparing the CT-complex formation between 1-methylnaphthalene with the ionic liquids with isomeric N-ethyl-4-cyanopyridinium and N-ethyl-3-cyanopyridinium cations, in the liquid state both ionic liquids generated coloured CT complexes. However, on cooling, the ionic liquid with the N-ethyl-3-cyanopyridinium cation selectively crystallised as 1:1 co-crystals with 1-methylnaphthalene forming π-cation alternating stacks because of the different lattice energy of pyridinium ionic liquids. N-ethyl-3-cyanopyridinium bistriflimide is more favourable than that for crystallisation of the charge-transfer complex. Therefore, the pure ionic liquids crystalised in preference from mixtures.

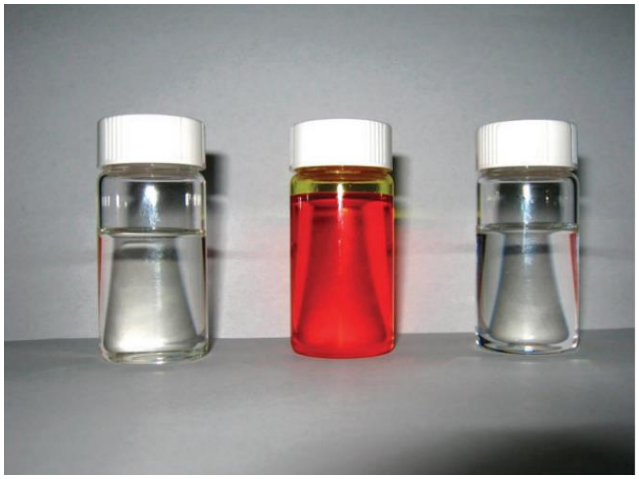


Figure 1-11: the colour change following the addition of 1-methylnaphthalene (right) to liquid 1-ethyl-4-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide to form liquid charge-transfer complex (centre) at 293K.[12]

Due to *Hardacre*'s work, the mechanism of the formation of the charge-transfer complex has been indicated clearly. The differences of the HOMO energy levels are the main reason of the formation of the charge-transfer complex. The LUMO energy level of the acceptors (pyridinium) is lower than

the donors' (aromatic rings such as: 1-methylnaphthalene and pyrene). The electrons in the donor's HOMO jump into the acceptor's LUMO. The absorption wavelength of the charge-transfer complex may be different from either compound.

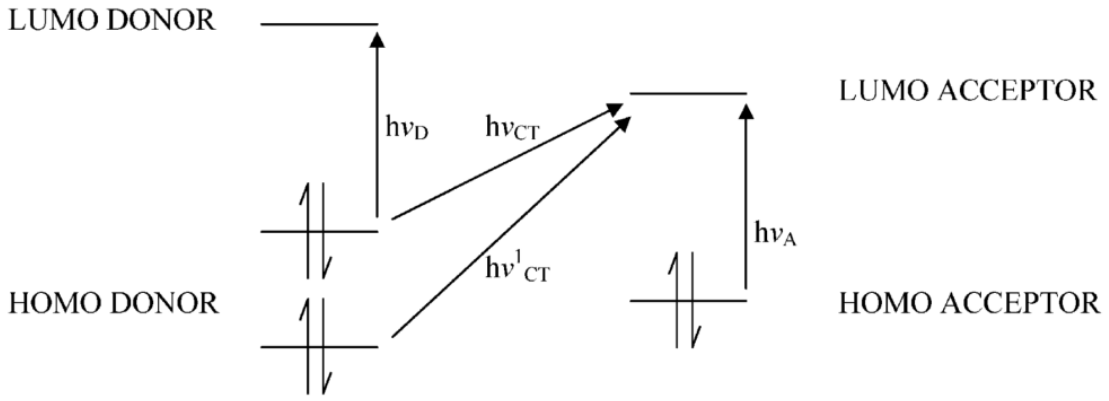


Figure 1-12: charge transfer transitions for HOMOs of the donors and LUMOs[12]

In these studies, the aromatic electron donors for the CT-complex formation are polyaromatic hydrocarbons. However, the smaller electron-rich aromatic donors (for example naphthalene and methylnaphthalene) have high vapour pressures and can readily evaporate. Both parts are also possible to be synthesized in one cation. New ionic liquids containing polyaromatic functional substituents and electron-withdrawing groups on the cation rings will be investigated with aromatic functional groups acting as a donor and the electron-withdrawing pyridinium cations as the CT-acceptors. Both donor and acceptor components in this planned system are incorporated within the cations of ionic liquids, which means that Coulombic repulsive force is a non-negligible factor for forming charge-transfer complexes.

1.2.4 Ionic liquid mixtures

Although the ionic liquids are nominated as 'designer solvents', the creation of new type ionic liquids is still time-consuming and expensive work, and the

synthesized ionic liquids may still be far away from the properties we need. Therefore, mixing the existing ionic liquids to replace an unknown ionic liquid is a more adaptive method for the solvents' development[48]. Ionic liquid mixtures have some advantages: (1) the ionic liquids can be well-characterised, (2) the cost and time of making ionic liquids are lower than developing new ionic liquids, (3) the safety of the existing ionic liquids is more certain and the safety tests than new ionic liquids. However, there are some disadvantages in ionic liquid mixtures such as there is no certain direction or regulation for making ionic liquid mixtures and the physical and chemical properties of the ionic liquid mixtures may not match the anticipated properties like viscosities, conductivities, vapor pressure and melting point. There are few theories about the formation of ionic liquid mixtures. Basically, the formation of ionic liquid mixtures is a kind of engineering theory which lacks scientific theory to direct.[48]

The two simplest sets of ionic liquid mixtures that can be considered are those with (i) a single cation or anion remains constant in the mixture with variations in the speciation of counter ions (i.e. a constant cation with mixtures of two different anions) and (ii) mixtures of two different ionic liquids (i.e. containing two different cations and two different anions).[49] In the both systems of nomenclatures, the [A][X] + [B][X] is abbreviated as $[A]_a[B]_b[X]$(a and b are the mole fractions of [A] and [B] in the mixtures.). And the [A][X] +[A][Y] is also called as $[A][X]_x[Y]_y$(x and y are the mole fractions of [X] and [Y] in the mixture.). These types of mixtures which are composed of three ions are called binary ionic liquid mixtures. On the other hand, the ionic liquids are which are composed to totally different cations and anions like $[A]_a[B]_b[X]_x[Y]_y$are called as ternary reciprocal ionic liquid mixtures[48]. Besides, there might be some reactions happening when the ionic liquids mixed with each other like Eq (1). In this system, we cannot treat it as a kind of mixture. It is more likely to the new ionic liquid when they mix together in 1:1.

$$AX + MX_n \rightarrow A[MX_{n+1}] \quad \text{Eq (1)}$$

According to the physical properties' literature,[50] the basic cations and anions

in the references are 1-methyl-3-butylimidazolium and 1-methyl-4-butylpyridinium bis{(trifluoromethyl)sulfonyl}imide ($[NTf_2]^-$) and 1,1,1-trifluoromethanesulfonate ($[OTf]^-$).

An ideal ionic liquid mixture should have a linear relationship between T_g (glass transition temperature) and χ (mole fraction). However, from the literature, in many cases, there is deviation from the ideal mixing state. For mixtures of $[C_2C_1im]$-$[PF_6]$ (mp. 61.1 °C) and $[C_2C_1pz]$-$[PF_6]$ (mp. 79.1 °C; $[C_2C_1pz]^+$ = 1-ethyl-2-methylpyrazolium) a eutectic composition was found at $\chi\{[C_2C_1im]^+\}$= 0.47 with a melting point of 23.1 °C.[51] Eutectic compositions have also been found in the system for $[C_3C_1pyrr][FSI][NTf_2]$($\chi\{[FSI]^-\}$=0.67, mp.= 247 K, $[FSI]^-$= bis(fluorosulfonyl)imide)[52]. Many ionic liquids are glass-transforming materials[35], and therefore don't have a clear freezing point. The recent example of a binary ionic liquid mixture shows the glass transition temperature of the mixture may raise in the range of the simple component. In the most mixtures of ionic liquid, the eutectic points are associated with severe melting point depression and the formation of glasses, rather than distinct crystallisations.

Ionic liquids are ion conductive fluids. Although the ionic liquids are composed of pure ions, the ion conductivities are not fast because the ions are large. The batteries and supercapacitors always focus on different electrochemical properties of electrolytes. The conductivity, measured by impedance spectroscopy, is referred to as $\Lambda_{m,Imp}$. The Nernst-Einstein equation is also used in the calculation of the conductivity with the self-diffusion constants and the outcome of the calculation is presented as $\Lambda_{m,NMR}$. The 'Haven', R_H, is defined as the ratio of the measured conductivity and the diffusion coefficients' conductivities, and R_H should be equal to one in a system of fully dissociated and independent ions.

$$R_H = \Lambda_{m,Imp}/\Lambda_{m,NMR} \quad \text{Eq (2)}$$

The conductivity doesn't have a linear relationship with mole fraction, χ. Instead, a logarithmic relationship between the conductivity and χ has

previously been identified as a likely outcome for ionic liquids. Therefore, each of the two conductivity curves ($\Lambda_{m,Imp}$ and $\Lambda_{m,NMR}$) are fitted by a logarithmic eqn:

$$\log\Lambda = \chi\log\Lambda_1 + (1-\chi)\log\Lambda_2 + \chi(1-\chi)(f/RT) \quad \text{Eq (3)}$$

With the inclusion of the f parameter, the conductivity data can be modelled for the majority of ionic liquid mixtures that have been investigated with all data falling within, or close to, the error. The reciprocal binary mixture [C_4C_1im] [C_4C_1pyrr] [OTf][NTf_2], exhibits the worst fit for the conductivity measured from diffusion coefficients, $\Lambda_{m,Imp}$. However, the differences in measured conductivities of the two ionic liquids [C_4C_1im] [OTf] and [C_4C_1pyrr] [NTf_2], are relatively small. Therefore, even the largest deviations from a logarithmic curve are quite small deviations from the expected conductivities for all ionic liquid mixtures with pyridinium and imidazolium rings. Compared with the molar volume, glass transition temperature and viscosity studies, the anions $[NTf_2]^-$ and $[MePO_4]^-$ demonstrate a reasonable logarithmic relationship between conductivity and mole fraction. A lower viscosity of ionic mixtures may cause a higher conductivity. Therefore, the non-ideality parameters 'f', for the two conductivities are expected to always be opposite sign relative to the viscosity parameter. However, there is a general tendency for the bulk conductivities from impedance spectroscopy, $\Lambda_{m,Imp}$, to be higher than ideal. And the self-diffusion constants, $\Lambda_{m,NMR}$ is lower than ideal.

The overall deviations of conductivity are quite small and the anticipated linear relationship between log Λ_m and logη^{-1} corresponds well. Ionic liquid mixtures can be expected to behave related with conductivity; data points are fitted well by a logarithmic curve.

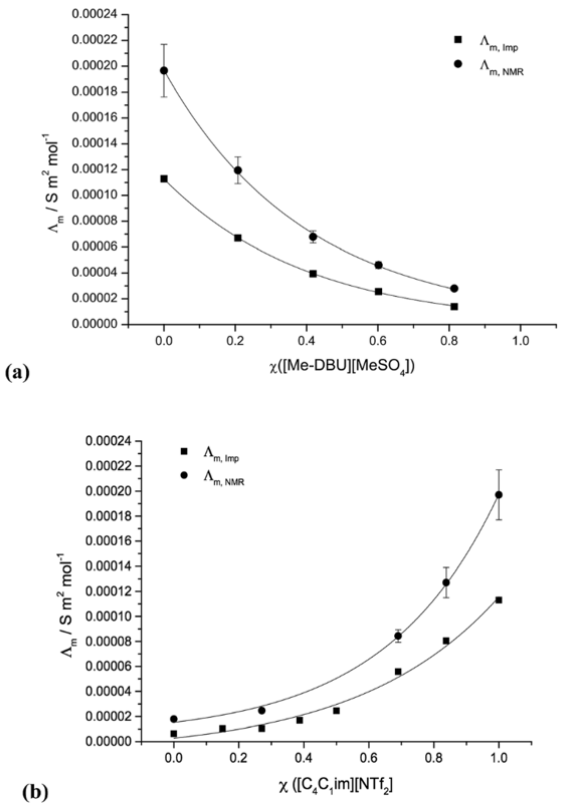


Figure 1-13: Conductivity of binary ionic liquid mixtures [C_4C_1im][Me-DBU][$MeSO_4$][NTf_2], obtained from impedance spectroscopy, $\Lambda_{m,Imp}$, and from the self-diffusion coefficients, $\Lambda_{m,NMR}$: [C_4C_1im][Me-DBU][$MeSO_4$][NTf_2].[50]

The binary mixtures are quite close to the ideal situation because when the cations or anions mixed are of similar sizes for example mixing [C_4C_1im][OTf] and [C_4C_1im][NTf_2], the interactions between ions are quite close to ideal situation. In contrary, when mixing containing the disparately sized [C_4mim]$^+$ and [P_{66614}]$^+$ cations which have same anions, the mixtures' appearance is different from ideal situation because the sizes of cations has an influence on intermolecular interactions. Ionic liquids have many useful characteristics as materials, including conductivity and their properties can be modified both by changes to their chemical structures and functions, and also by forming mixtures. Interest in ionic liquids as electrolytes primary focusses on ionic conductivity. From the earlier work in the group, described above, forming charge-transfer complexes between certain ionic liquids and polyaromatic

quest molecules, it was proposed that these self-associated charge-transfer structures could provide pathways for rapid electron transfer within ionic liquids. However, as previous work has shown, the CT-complexes formed between 1-alkyl-4-cyanopyridinium salts and polyaromatic such as 2-methylnaphthalene lead to more stable, higher melting congruent complexes, therefore an investigation of alternative aromatic components and their behaviour in mixtures is needed. In this work, the effect of combining mixtures of ionic liquids/salts where one contains electron-deficient acceptor cations and a second incorporates polyaromatic donor functions, is investigated to determine (i) whether associated mixtures can be formed and (ii) how the phase behaviour of mixtures is modulated, and whether low temperature glass-forming eutectic, or congruent melting stable complexes are generated.

Basically, the conventional electrolytes should have high conductivity and ion conductivity for many applications like batteries and supercapacitors which are suitable for ionic liquids and their mixtures. Although there are some methods improving the performances of ionic liquids and their mixtures,[31, 53] ionic liquids still have some unavoidable drawbacks under conventional energy transfer or storage methods like high viscosity, and low ion conductivity. To improve the performances of ionic liquids, the new kinds of electron-transfer methods are essential for the ionic liquids. There is a new migrating method for the electrons among the electrons instead of moving with the particles. The π-electron is a suitable electron for these kinds of applications. Therefore, the aromatic-functionalized ionic liquids have the potential to achieve the electron-transfer methods electrolytes and avoid the ionic liquids' drawbacks of conventional electrolytes.

1.3 The method for detecting charge-transfer complex

The formation of the charge-transfer complex is a spontaneous intermolecular interaction. The LUMO energy differences between the donor and acceptor are the main impetus of the interaction. The existence of a charge-transfer complex should be proved through the below methods. Firstly, the most

obvious and convincing proof is the formation of new absorption bands in the UV-Vis of the mixtures. Charge-transfer complexes have a different absorption wavelength from the single compound i.e. colour formation is observed. The differences of the LUMO energy between donor and acceptor bring the unique UV absorption of charge-transfer complex in the Figure 1-14.

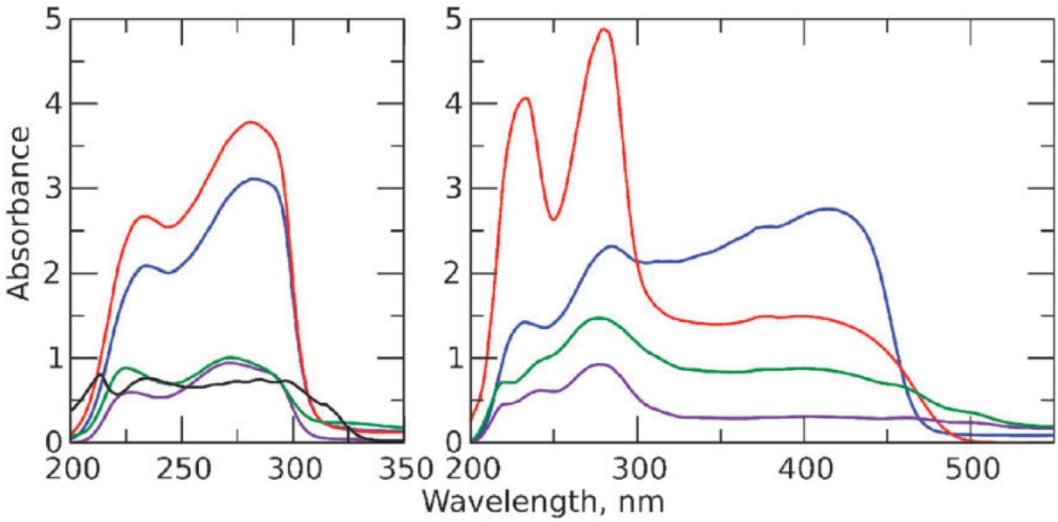


Figure 1-14: UV-Vis absorption spectra of pure ionic liquids and aromatic hydrocarbon (left) and complexes (right) of 1-methylnaphthalene with 1-methyl-4-cyanopyridinium $[NTf_2]^-$ (blue), 1-ethyl-4-cyanopyridinium $[NTf_2]^-$ (red), 1-butyl-4-cyanopyridinium $[NTf_2]^-$ (purple) and 1-hexyl-4-cyanopyridnium $[NTf_2]^-$ (green).[12]

Another convincible proof of the existence of charge-transfer complexes in the solid state is from single crystal X-ray diffraction. The packing diagrams of crystallographic unit cell are shown in the Figure 1-15. In this structure, the cations and 1-methylnaphthalene molecules form an alternative π-stack (with the MS DA configuration). The separation distance between cations and naphthalene aromatic planes of 3.5 Å is consistent with two aromatic stacking.[12, 54]

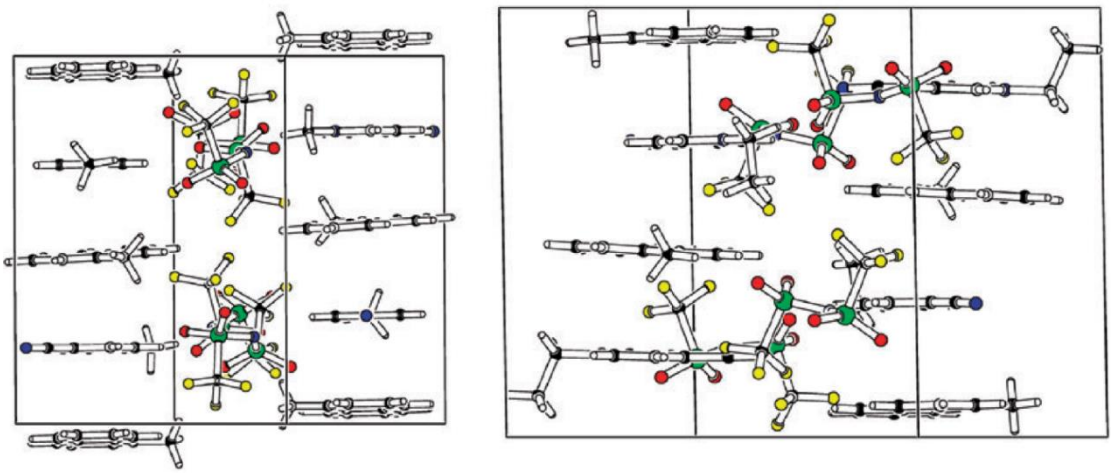


Figure 1-15: Packing diagrams for the 1:1 1-methylnaphthalene combines with 1-methyl-4-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide (left) and 1-ethyl-4-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide (right) showing p–p stacks of cation and aromatic along the c-axis.[12]

The single crystal X-ray diffraction and UV-vis absorption spectra are two kinds of methods which can be tested to inner structures of the charge-transfer complexes. As they are mixtures of two compounds, some thermal properties like melting point can also be used as proof of charge-transfer complex maker. The melting point of the 1:1 1-ethyl-4-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide/1-methylnaphthalene charge-transfer complex is higher than that of either component, indicative of a positive contribution to the overall lattice energy of the solid crystalline state, although in contrast, the molten liquid CT complex formed between 1-methylnaphthalene and the isomeric 1:1 1-ethyl-3-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide does not persist to the solid state, and the pure pyridinium salt crystallises preferentially from the melt.[12]

1.4 Projects aims

The previous publications show that the charge-transfer transitions between 1-ethyl-4-cyanopyridinium cations and 1-methylnaphthalene change the mixtures' colours like Figure 1-11.[12] This transition has the potential for changing the electronic properties. The conductivities of conventional

electrolytes are based on the diffusion speed of cations and anions under a charge gradient from the applied voltage. If this transfer method could also happen for electrons, the mobility of the bulky ions wouldn't be the limiting factor restricting conductivity of electrolyte, which could become an electronic conductive fluid. The objective of this work was to investigate the potential formation of new charge-transfer forming ionic liquid complexes which are totally composed by pure ions as electronic conductors by synthesising and mixing ionic liquids containing polyaromatic electron-donor substituents and electron-defficient (acceptor) groups to determine whether (i) CT-complex forming ionic liquid mixtures can be generated and (ii) whether mixtures result in (undesirable) enhancement of melting points through complex formation or (desirable) suppression of freezing through eutectic formation.

In my project, a series of charge-transfer complexes will be made through mixing two kinds of different ionic liquids which are aromatic-functionalized imidazolium ionic liquids and electro-withdrawing pyridinium ionic liquids. For decreasing the influence of Coulomb Force, the aromatic-functionalized electro-withdrawing pyridinium ionic liquids are also made. Otherwise, to prove the existence of the charge-transfer complexes, the energy levels of the HOMO and LUMO are calculated through the Spartan. The structures and existence of charge-transfer complexes will be proved through UV-vis absorption and single-crystal X-ray diffraction. The thermal properties of these ionic liquids and their mixtures will also be measured.

2 Results and discussion

To achieve the charge-transfer complexes in ionic liquids, the electron donor and acceptor are essential for this structure. These two parts could be in different particles or in same particles.

From the previous work,[12] ionic liquids containing 1-methyl-cyanopyridinium cations as electron-acceptors which could form charge-transfer complexes with polyaromatic electron-donors have been reported. If there is a kind of adaptable ionic liquid which could be electron-rich, the charge-transfer complexes could be formed among these ionic liquids. Three kinds of 1-alkyl-3-(2-naphthalenylmethyl)imidazolium ionic liquids have been synthesised and are characterized through NMR spectroscopy, TGA and DSC. These ionic liquids were mixed with 1-methyl-4-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide in order to study potential formation of charge-transfer complexes, determined by UV-Vis absorption. The data from UV shows that there is no convincible proof of the existence of CT complexes, which is ascribed to the repulsive Coulomb forces between two different cations.

To decrease the influence of the Coulomb force, two kinds of imidazolium bis{(trifluoromethyl)sulfonyl}imide which are 1-methyl-3-(1-pyrenylmethyl)imidazolium bis{(trifluoromethyl)sulfonyl}imide, 1-methyl-3-(2-naphthyl-2-ethyl)imidazolium bis{(trifluoromethyl)sulfonyl}imide were investigated. These salts were synthesized, initially as halide salts in a microwave reactor to improve the yield and shorten the reaction time followed by anion metathesis. There is no unique or new absorption peak forming in these mixtures.

According to the data from ionic liquid mixtures, the separated donors and acceptors find it difficult to form the charge-transfer complexes due to the influence of cation-cation Coulomb repulsions. Therefore, there is another potential structure which could combine the electron-donor and acceptor in

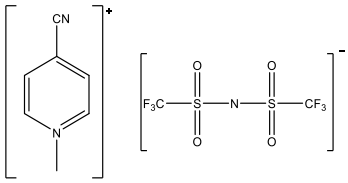
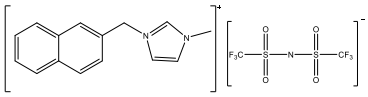
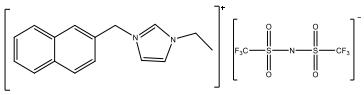
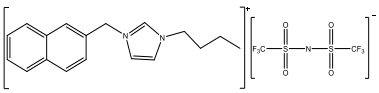
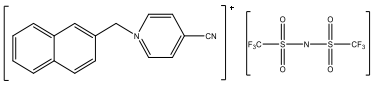
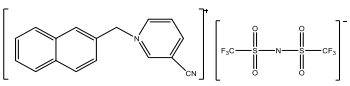
the same particle to decrease the influence of Coulomb Force. The aromatic-functionalized electron-withdrawing pyridinium ionic liquids which are N-[(2-naphthyl)methyl]-4-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide and N-[(2-naphthyl)methyl]-3-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide were synthesized. However, it is hard to prove the existence of charge-transfer complexes because the absorption in visible light range is not convincing enough for proving the existence of charge-transfer complexes. The inner interaction between aromatic rings and electron-withdrawing pyridinium rings is also possible to cause the change of UV-vis absorption. To identify whether the absorption in visible light range is based on charge-transfer complexes, the N-(2-naphthyl-2-ethyl)-4-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide is made. If they have same UV-Vis absorption spectra appearance as N-(naphthylmethyl)-4-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide or the previous charge-transfer complexes which are composed by 1-methyl-naphthalene and 1-methy-4-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide, the UV-Vis spectra in visible light range is caused by the formation of charge-transfer complexes. The same UV-Vis absorption wavelength as previous charge-transfer complex which are made by the 2-methylnaphthalene and 1-methyl-4-cyanopyridinium ionic liquid shows this interaction is from the intermolecular interaction not the molecular itself.

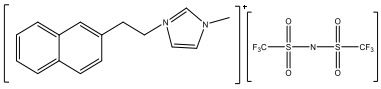
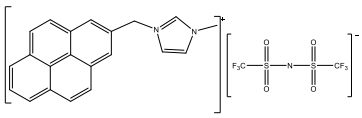
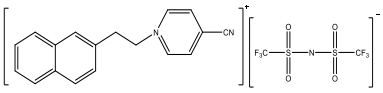
2.1 Synthesis of ionic liquids

To find the adaptable electron-donors which have the potential to form charge-transfer complexes with 1-methyl-4-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide, there were five kinds of aromatic-functionalized imidazolium ionic liquids synthesized in this project. This series of ionic liquids could provide π-electron through the aromatic rings which could combine 1-methyl-4-cyanopyridnium without any positive charges. From the current data, there is no charge-transfer complex among these mixtures.

Therefore, there are three kinds of aromatic-functionalized electron-withdrawing pyridinium ionic liquids which are combining both donors and acceptors in the same particle. All these eight kinds of ionic liquids and 1-methyl-4-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide are listed in Table 2-1. All these ionic liquids were prepared from the bromide salts to bis{(trifluoromethyl)sulfonyl}imide salts.

Table 2-1: Structures, appearance, and their names of nine ionic liquids as their $[NTf_2]^-$ salts.

Structure of compounds	Appearance	Name
	White powder	1-methyl-4-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide
	Brown powder	1-methyl-3-(2-methylnaphthalene)imidazolium bis{(trifluoromethyl)sulfonyl}imide
	Brown liquid	1-ethyl-3-(2-methylnaphthalene)imidazolium bis{(trifluoromethyl)sulfonyl}imide
	Brown liquid	1-butyl-3-(2-methylnaphthalene)imidazolium bis{(trifluoromethyl)sulfonyl}imide
	Bright yellow powder	N-[(2-naphthyl)methyl]-4-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide
	Pale yellow powder	N-[(2-naphthyl)methyl]-3-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide

	Brown powder	1-methyl-3-(2-naphthyl-2-ethyl)imidazolium bis{(trifluoromethyl)sulfonyl}imide
	Black liquid	1-methyl-3-(1-pyrenylmethyl)imidazolium bis{(trifluoromethyl)sulfonyl}imide
	Bright yellow powder	N-(2-naphthyl-2-ethyl)-4-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide

2.1.1 Imidazolium salts with aromatic functions

1-methyl-3-(2-methylnaphthalene)imidazolium bis{(trifluoromethyl)sulfonyl}imide, 1-ethyl-3-(2-methylnaphthalene) imidazolium bis{(trifluoromethyl)sulfonyl}imide, and 1-butyl-3-(2-methylnaphthalene)imidazolium bis{(trifluoromethyl)sulfonyl}imide were prepared by alkylation of N-substituted imidazole with 2-bromomethylnaphthalene, followed by metathesis with Li[NTf$_2$] in water as shown below.

This type of imidazolium cation could be potential by used as the electron donor where the naphthalene rings provide the aromatic-electrons which could cooperate with the electron-withdrawing pyridinium ionic liquid.

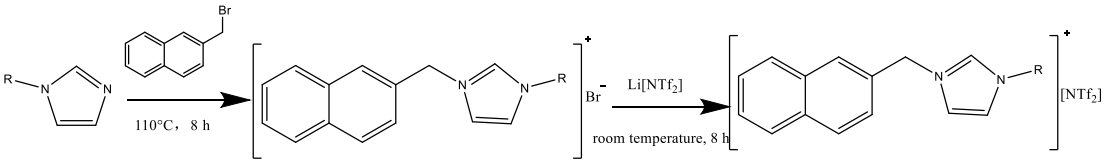


Figure 2-1: General preparative route to 1-alkyl-3-(2-naphthyl) methylimidazolium salt, R represents methyl, ethyl and butyl substituents on imidazole.

Toluene was chosen as the solvent for these reactions because it not only could dissolve both the N-alkylimidazole and 2-methylnaphthalene, but also

act as a diluent and heat sink to control and moderate the reactivity as alkylation reactions with 2-bromomethylnaphthalene were very exothermic. In addition, the products were insoluble in the toluene and so were readily isolated in high purity from the reaction mixtures with good yield as all the N-alkylimidazole is alkylated by 2-methylnaphthalene under reflux over 8 h.[55]

Anion metathesis with Li[NTf_2] from the bromide salts to yield the corresponding [NTf_2]$^-$ based hydrophobic salts, was done with aqueous Li[NTf_2]. The hydrophobic salts were isolated from aqueous solution, 1-methyl-3-methylnaphthalenylimidazolium bis{(trifluoromethyl)sulfonyl}imide is solid which could be separated by filtration and the other ionic liquids are liquids which are separated through dropping. All these ionic liquids are dried under high vacuum.

The 1-ethyl-3-(2-naphthylmethyl)imidazolium bis{(trifluoromethyl)sulfonyl}imide and 1-butyl-3-(2-naphthylmethyl)imidazolium bis{(trifluoromethyl)sulfonyl}imide were liquids in the room temperature.

The three other ionic liquids, 1-methyl-3-(1-pyrenylmethyl)imidazolium bis{(trifluoromethyl)sulfonyl}imide and 1-methyl-3-(2-naphthyl-2-ethyl)imidazolium bis{(trifluoromethyl)sulfonyl}imide were all prepared through the alkylation of substituted imidazole with naphthalene and pyrene reagents under microwave, followed by metathesis with Li[NTf_2] in water. The reason for using microwave reactor is that the conventional heating methods needs more solvent to solve the reagents and the products are not dissolved in the toluene which means the separation would be difficult under this small amounts of reagents. Otherwise, the microwave reaction could shorten the reactions time and hold higher vapour pressure which could accelerate the reaction speed and improve the yield of products. All three were isolated as solids.

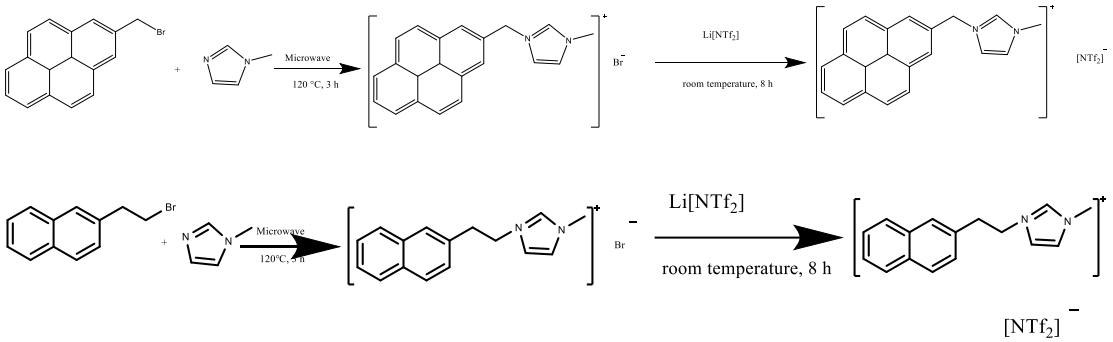


Figure 2-2: synthesis routes for some aromatic-functionalized imidazolium ionic liquids.

The two alkylating agents, bromomethylpyrene and bromoethylnaphthalene are much less reactive than bromomethylnaphthalene or dimethylsulfate and gave poorer conversion to the imidazolium products under conventional heating. To improve the reaction conversion, heating under microwave conditions was used heating for 3 hours at 120 °C (AntonPaar Monowave 300 Microwave) which gave some conversion, although the overall product yields in each case remained low. Otherwise, the products are not dissolved in the solvent.

2.1.2 N-alkyl-cyanopyridinium salts

1-methyl-4-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide ($[C_1{}^4CNpy][NTf_2]$) was synthesized from the 4-cyanopyridine and dimethyl-sulphate, followed by metathesis with $Li[NTf_2]$ in water.

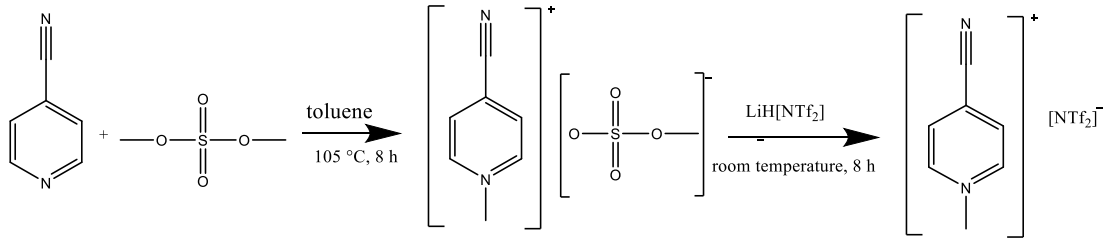


Figure 2-3: Synthesis route to 1-methyl-4-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide

The conditions of this reaction are similar to the imidazolium ionic liquids. The solvent is also toluene and the temperature was 105 °C. The reaction time is only 3 hours which is shorter than imidazolium series.[12]

2.1.3 N-alkyl-cyanopyridinium salts with aromatic functions

All pyridinium ionic liquids that had been synthesized in this project were solid in the room temperature and the aromatic-functionalized pyridinium ionic liquids are yellow.

The two isomeric N-[(2-naphthyl)methyl]-n-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide systems with nitrile groups position *meta* and *para* to (n=3 and 4) were synthesized by alkylation of 3- and 4-cyanopyridine with 2-bromomethylnaphthalene, followed by metathesis with Li[NTf_2] in water.

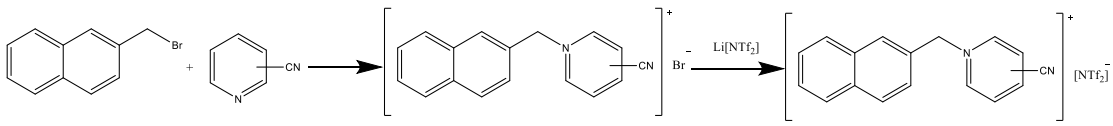


Figure 2-4: General preparative route to N-[(2-naphthyl)methyl]-n-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide through alkylation of cyanopyridine by 2-bromomethylnaphthalene

The alkylation reaction was performed in CH_3CN as both N-[(2-naphthyl)methyl]-4-cyano-pyridinium bis{(trifluoromethyl)sulfonyl}imide and N-[(2-naphthyl)methyl]-3-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide could be separated from the solutions as yellow solid. Both reactions gave low yields because 2-bromomethylnaphthalene was not reactive as the dimethyl sulphate.

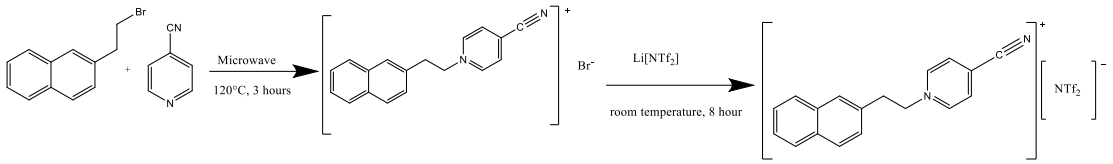


Figure 2-5: synthesis route of N-(2-naphthyl-2-ethyl)-4-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide.

This synthesis route of N-(2-naphthyl-2-ethyl)-4-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide has the same conditions as the 1-methyl-3-(1-pyrenylmethyl)imidazolium bis{(trifluoromethyl)sulfonyl}imide and 1-methyl-3-(2-naphthyl-2-ethyl)imidazolium bis{(trifluoromethyl)sulfonyl}imide which have been described above.

2.2 Characterization of the ionic liquids synthesised

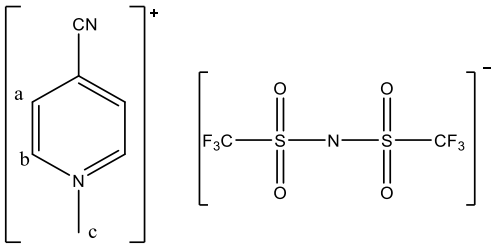
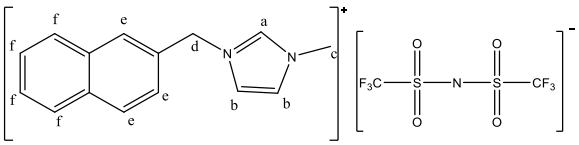
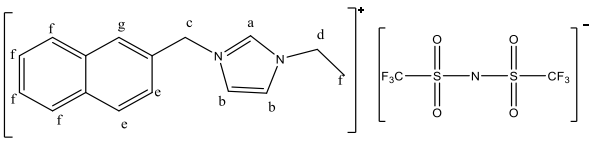
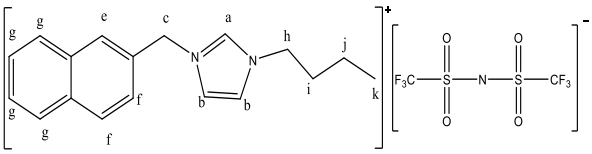
Although the charge-transfer complexes are the main purpose of this project, the ionic liquids' properties are also important. The ^{1}H NMR, IR, TGA and DSC are shown as below.

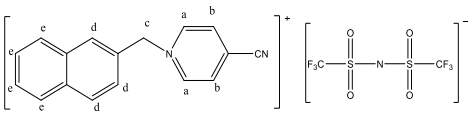
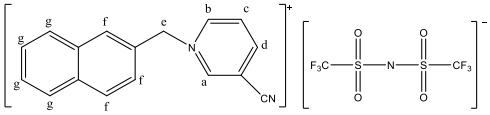
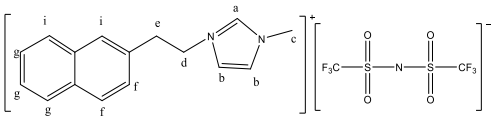
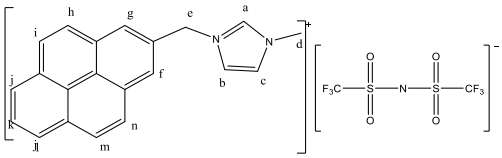
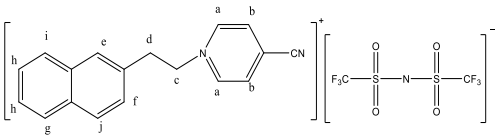
2.2.1 ^{1}H NMR spectra

All the H-NMR data for these compounds are found in Table 2-4. The NMR data was used for identifying the structures of the ionic liquids. As shown in Table 2-2. The chemical shifts of hydrogen atom which was connected to the carbon atom which was located between the nitrogen atoms of the imidazolium ring was in 8.0-10.0 ppm. And the hydrogen atoms which were connected to the carbon atoms in the pyridinium rings which were next to the pyridine's nitrogen atom were located over 8.0 ppm. The hydrogens on the naphthalene ring were concentrated in 7-8ppm, and the hydrogens on the alkyl groups which related to the N atoms of imidazole or pyridine ring have a

significant downfield shift. The methyl group which was far away from the imidazole ring had nearly no influence from the imidazolium cations. The other chemical shifts are from the impurities of solvents.

Table 2-2: chemical shifts of nine different compounds in 300 MHz and 400 MHz 1H NMR spectra, solvents are CD_3Cl, DMSO or MeOD-d_4. ^{1}H NMR spectra can be found in the appendix Fig.6-5, 6, 7, 8, 9, 10, 11, 12, 13.

Structure of compounds	Chemical shifts of different hydrogens
 Solvent: $CDCl_3$	9.34 (2H, d, Hb), 8.62 (2H, s, Ha), 4.65 (3H, s, Hc)
 Solvent: $CDCl_3$	10.41 (1H,s, Ha), 7.42 (2H, d, Hb), 7.86 (4H, dd, Hf), 7.49 (3H, m, He), 5.72 (2H, s, Hd), 4.01 (3H, s, Hc)
 Solvent: $CDCl_3$	8.82 (1H, s, Ha), 7.87 (4H, dd, Hf), 7.50 (2H, m, He), 7.37 (1H, d, Hg), 7.24 (2H, m, Hb), 5.35 (2H, m, Hc), 4.17 (2H, m, Hd), 1.47 (3H, dt, Hf)
 Solvent: $CDCl_3$	8.93 (1H, s, Ha), 7.86 (2H, d, Hb), 7.52 (2H, m, Hf), 7.39 (1H, m, He), 7.22 (4H, p, Hg), 5.45 (2H, s, Hc), 4.14 (2H, t, Hh), 1.81 (2H, m, Hi), 1.33 (2H, dq, Hj), 0.92 (3H, t, Hk)

 Solvent: MeOD-d4	9.53 (2H, d, Ha), 8.73 (2H, d, Hb), 8.02 (4H, dd, He), 7.61 (3H, dd, Hd), 6.09 (2H, s, Hc),
 Solvent: MeOD-d_4	9.82 (1H, s, Ha), 9.34 (1H, d, Hb), 9.02 (1H, d, Hd), 8.33 (1H, m, Hc), 8.01 (4H, m, Hg), 7.60 (3H, dd, Hf), 6.08 (2H, s, He)
 Solvent: $CDCl_3$	8.98 (1H, s, Ha), 8.24 (2H, dd, Hb), 8.20 (2H,dd, Hf), 8.12 (2H, dd, Hi), 8.05 (3H, m, Hg), 7.06 (2H, m, Hd), 6.06 (2H, s, He), 3.93 (3H, s, Hc)
 Solvent: DMSO	10.58 (1H, s, Ha), 7.98 (1H, d, Hb), 7.88 (1H, d, Hc), 7.78 (1H, d, Hg), 7.53 (3H, m, Hf,m,n), 7.36 (1H, m, Hh), 7.17 (1H, m, Hi), 6.90 (3H, m, Hj,l,k), 4.74 (2H, t, He), 4.01 (3H, s, Hd)
 Solvent: MeOD-d_4	8.88 (2H, d, Ha), 8.31 (2H, d, Hb), 7.52 (7H, m, He, f, j, h, g, i), 4.99 (2H, t, Hc), 3.75 (2H, t, Hd)

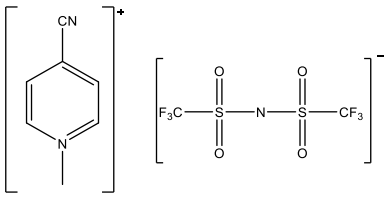
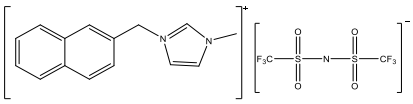
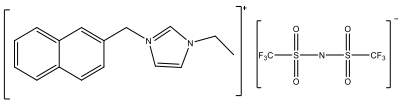
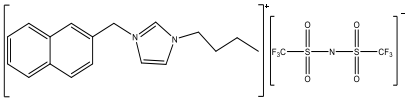
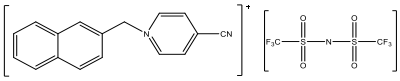
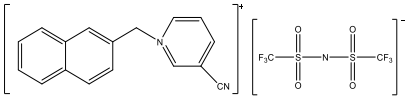
Most imidazolium ionic liquids like 1-alkyl-3-(2-naphthylmethyl) imidazolium ionic liquids could be dissolved in d-chloroform. The other imidazolium ionic liquids are dissolved in the DMSO-d_6. Besides, some aromatic-functionalized pyridinium ionic liquids could not be solved in the d-chloroform. Therefore, the MeOD-d_4 is used as the solvent for NMR.

2.2.2 Thermal stability and DSC results

The decomposition temperature (T_{dec}) of these salts were investigated by dynamic TGA, the results in the Table 2-3 were recorded when the mass of the salts reduced to 95%. T_{dec} of ionic liquids mainly depends on the property of anions, with little variation between cations, as presented in Table 2-3. The salts with $[NTf_2]^-$ (T_{dec} > 290 °C) have a better stability than the salts with bromide (T_{dec} < 200 °C). And this conclusion is corresponding with the stability of bis{(trifluoromethyl)sulfonyl}imide and bromide.[56] The specific TGA profiles are shown in the appendix. The data of 1-methyl-4-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imides is different from the others where there is a 3.23% mass loss from room temperature to 348 °C which might from the impurities.

Melting points were determined by DSC from the second heating cycle. The charge-transfer complexes ought to be formed by mixing the aromatic-functionalized imidazolium ionic liquids with electron-withdrawing pyridinium ionic liquids. These mixtures melting points were also measured through the DSC. And the specific data and figures are shown in the Table 2-3.

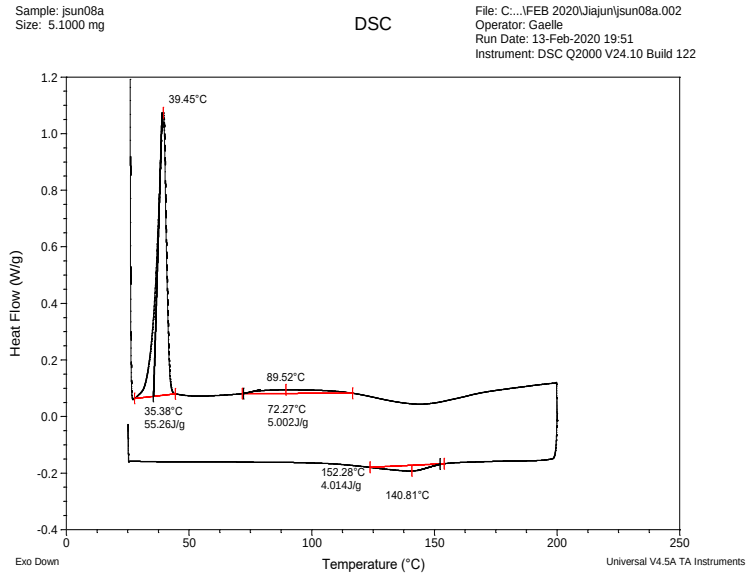
Table 2-3: Melting points and decomposition temperatures of six ionic liquids.[57]

Structure of compounds	Melting point/°C	Decomposition temperature/℃
	65.17	348
	39.45	375
	23.06	387
	19.23	388
	/	223
	/	210

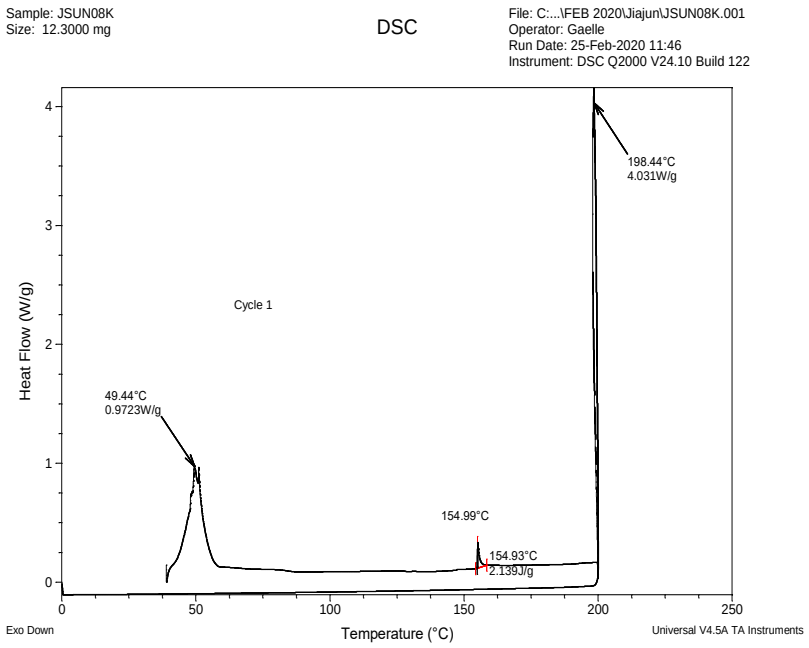
The melting points of aromatic-functionalized electron-withdrawing pyridinium bis{(trifluoromethyl)sulfonyl}imides are not shown in the table because the salts decomposition prior to, or during, melting.

During the heating cycle, the glass transition points of ionic liquids play an important role on the phase transition. All the DSC data is in the appendix from Fig. 6-14 to Fig. 6-25. In this section, the pure ionic liquids' performances will be shown and discussed. Fig 2-6 shows the 1-methyl-3-(2-naphthyl)methyl)imidazolium bis{(trifluoromethyl)sulfonyl}imides and 1-methyl-

4-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imides’ DSC results.



(a)



(b)

Figure 2-6: the two heating cycles of 1-methyl-3-(2-naphthanylmethyl)imidazolium bis{(trifluoromethyl)sulfonyl}imide (a) and the 1-methyl-4-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide (b)

It seems there are some unexplainable absorption peaks during the heating cycle. The 1-methyl-3-(2-naphthyl)methyl)imidazolium bis{(trifluoromethyl)sulfonyl}imides has three small peaks at 89 °C,152 °C and 140 °C which might from the impurities. And the absorption peak at 199 °C of 1-methyl-4-cyanopyridinium is unexplainable.

2.2.3 IR spectra

All the IR data are recorded in the appendix. The stretching frequency of different bonds of different molecules are given in Table 2-3. The stretching of alkyl C-H bond on aromatic or heterocyclic rings was around 3100 cm^{-1} and the alkyl C-H bond was in range 3000-2850 cm^{-1}. The nitrile vibration was observed at around 2247 cm^{-1} and there is no observation of nitrile peaks in 1-(2-naphthanylmethyl)-4-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide and N-(2-naphthyl-2-ethyl)-4-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide which might be influenced by the crystal structures of these ionic liquids.

According to the previous work, the nitrile peaks of 1-methyl-4-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide was also not observed. The N-CH_3 group of one cation overlays a nitrile group of the adjacent cation to form a herringbone pattern like Figure 2-7, which weakens the bond order of nitrile group, so that no apparent C≡N stretching can be observed. These pyridinium ionic liquids which the C≡N peaks are not observed may mean that the aromatic rings may also weaken the bond order of nitrile group.

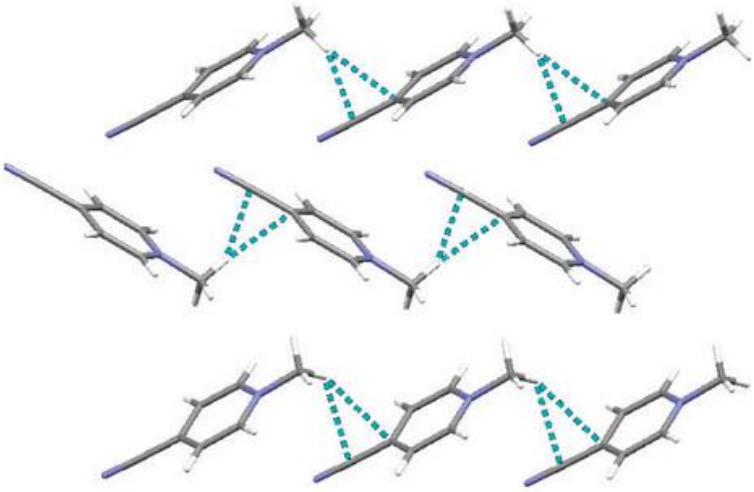


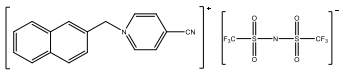
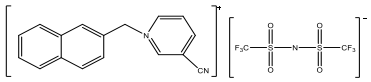
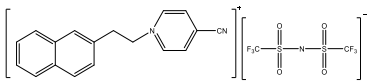
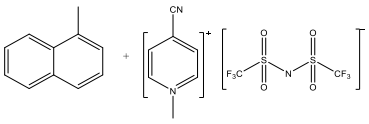
Figure 2-7: cation-cation packing in the crystal structure of [C_1^4CNpy][NTf_2], showing the formation of alternating herringbone packing of cations, the crystal structure of [C_1^4Cnpy][NTf_2] is from Hardacre's work.[58]

The bond vibrations in $[NTf_2]^-$, 1339.3 cm^{-1}, 1174.9 cm^{-1} and 1052.1 cm^{-1} belong to S=O, C-S and C-F vibrations respectively. The bond vibration in the cations is shown in the Table 2-4.

Otherwise, the previous charge-transfer complex which are composed by the 2-methylnaphthalene and 1-methyl-4-cyanopyridinium ionic liquids had similar C≡N and aromatic C-H absorption with the N-(2-naphthyl-2-ethyl)-4-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide's IR. The IR spectra is influenced by molecules' structure and the interactions among the ions. The influence from cyano group and other functional groups is similar, However, the intermolecular interactions in a charge-transfer complexes have a different influence on the C≡N and aromatic C-H absorption. If the N-(2-naphthyl-2-ethyl)-4-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide can't form the charge-transfer complexes through intermolecular interactions. The IR absorption of N-(2-naphthyl-2-ethyl)-4-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide shall have no overlap with charge-transfer complexes. The interactions between the naphthalene rings and pyridinium rings in N-(2-naphthyl-2-ethyl)-4-cyanopyridinium

bis{(trifluoromethyl)sulfonyl}imide and 2-methylnaphthalene with pyridinium are very similar. Therefore, the N-(2-naphthyl-2-ethyl)-4-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide shows a high possibility of having formed a charge-transfer complex.

Table 2-4: IR spectra data of three ionic liquids were recorded in the range 4000-550 cm^{-1}. IR spectra can be found in the appendix from Fig. 6-1 to Fig. 6-4.

Structure of compounds	Stretching frequency of different bonds/cm^{-1}				
	C—H (aromatic)	C—H (alkane)	C≡N	C=N	C—N
	3114.6, 3060.5	2849.9	/	1634.4	1174.9
	3085.7	2961.4	2251.9	1637.2	1186.9
	3056.3 3126.6	2948.7 2851.4	/	1640.4	1185.1
	3126.5 3056.3	2949	/	1640.4	1185.3

Although the same wavelength and similar absorption strength are not direct proof of the existence of charge-transfer complexes among the aromatic-functionalized pyridinium ionic liquids, the intermolecular interactions among these pyridinium cations are existing and strong enough to influence the physical properties of these ionic liquids.

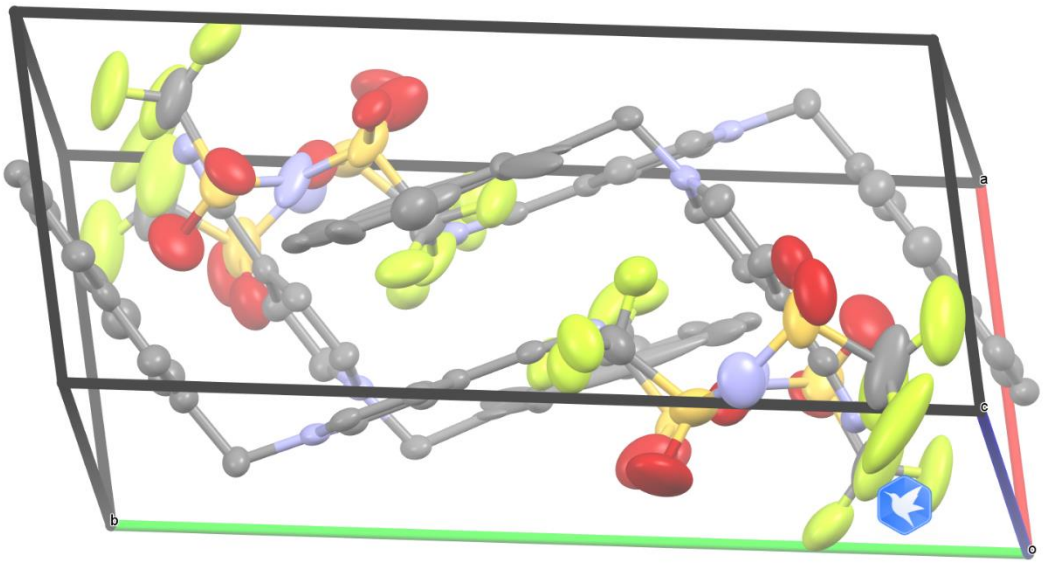
2.2.4 Single-crystal XRD

Single crystal X-ray diffraction (XRD) was used to determine the crystal structure of one aromatic-functionalized cyano-pyridinium salt that was obtained in diffractal crystalline form. The structure and solid-state packing are compared to that of the previously characterized CT-complexes of 4-cyanopyridinium/methylnaphthalene crystal structures in which alternating stacks of co-planar pyridinium/naphthalene rings are found. The single-crystal XRD give us the direct figure of the specific crystal structure of the aromatic-functionalized pyridinium ionic liquids. 1-(2-Naphthylmethyl)-4-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide was the only combined donor/acceptor pyridinium salt for which crystals suitable for XRD were isolated and the structure successfully refined. Packing in the unit cell of 1-(2-naphthylmethyl)-4-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide and its brief packing method are shown in Figure 2-8. See 2D-sheets of cations forming, through naphthalene-π to cation stacking, with a number of different packing motifs found to grow the sheets. Each sheet is separated from the next by a layer of anions that are interconnected through F-F contacts, with cation-anion contacts at the Van der Waals separation distances.

The crystal information is shown in the Table 2-5. It is a kind of typical triclinic crystal.

Table 2-5: crystal information of N-(2-naphthylmethyl)-4-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide

Formula	$[C_{17}H_{11}N_2][C_2F_6NO_4S_2]$
Crystal System	triclinic
Space group	P-1 (No. 2)
a, b, c [Å]	6.7472(4) 16.5952(9) 19.4245(6)
α, β, γ [deg]	85.385(4) 81.337(4) 80.836(5)
V [Å^3]	2119.17(19)
Z	24
D(*calc*) [g/cm^3]	1.644



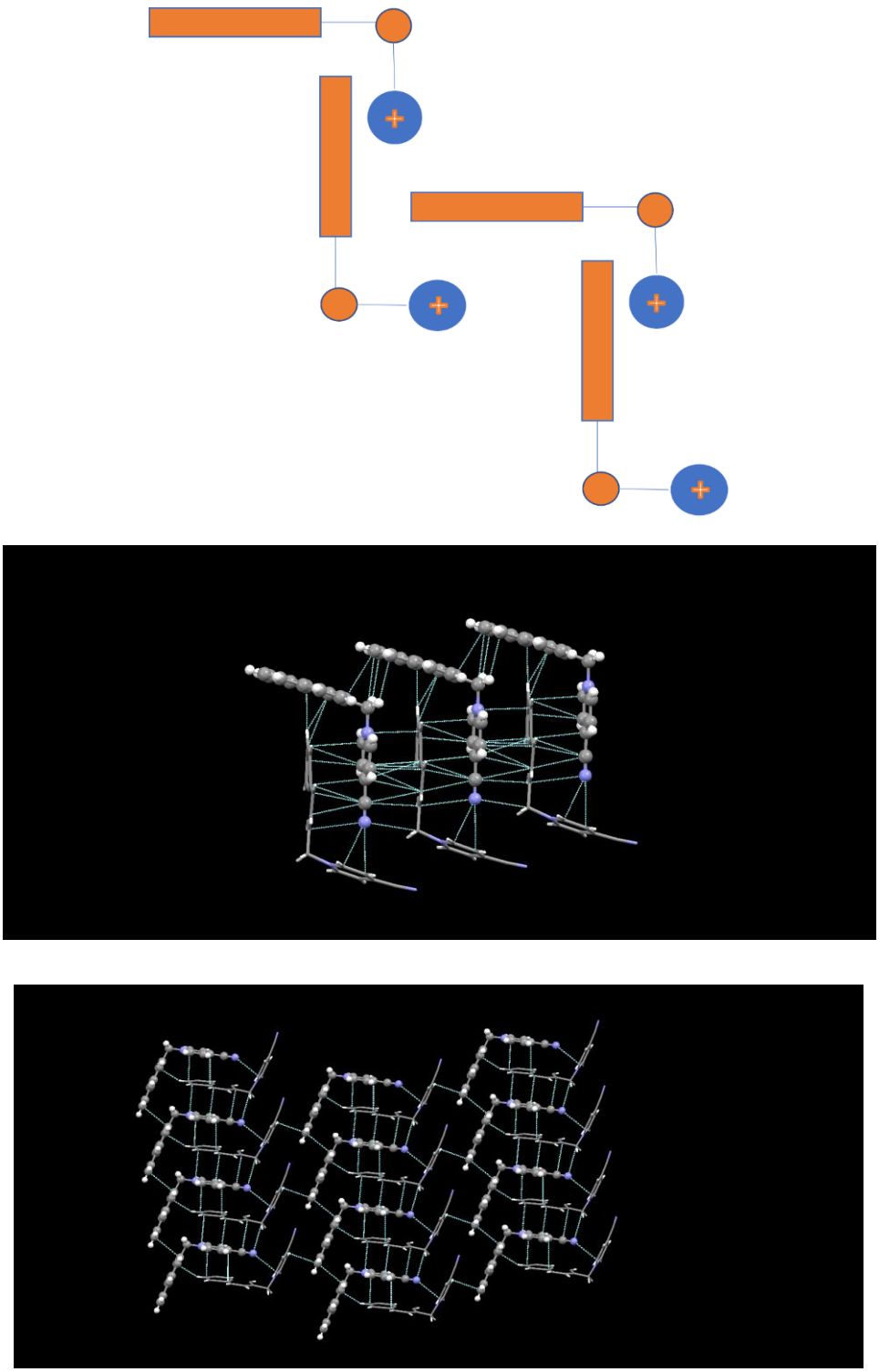


Figure 2-8: the single crystal of 1-(2-naphthylmethyl)-4-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide and its cation's brief overlapping figure.

There is one alternating pyridinium-naphthalene stack, and like the previous

structures also has the aromatic group in a site-disordered form. Due to packing constraints and symmetry, the aromatic group of the non-disordered pyridinium cations participating in the alternating stack sit out at approximately 108 degrees from the direction of the column and participate in an offset series of π-π staggered interactions with alternate naphthyl groups from the naphthyl-disordered cations of the next adjacent column linking these columns into a 2D sheet.

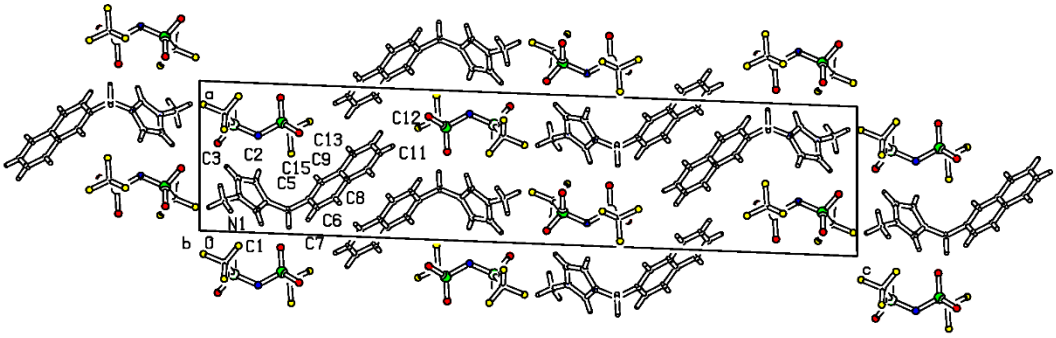
There are three *π*-stacking motifs: disordered naphthalene-cation π-stack, plane-plane separation and the π-stacking between ribbons. Disordered naphthalene-cation π-stack in a head-to-tail fashion providing extension of columns of π-cation stacks. The ordered naphthalene of cations where the cyano-pyridinium core is the acceptor of the columnar stacks are placed over the end of each disordered naphthyl unit, providing edge-π-face capping (C-H ring at 2.72 Å) and also close contact across to the next available pyridinium cation at the N-CH_2 methylene group (CN-H_2C, 3.24 Å). At the opposite side of the ribbon, the nitrile group of the non-disordered cations sits directly over, and orthogonal to the pyridinium ring of the naphthyl disordered cations (3.2 Å). Plane-plane separation of naphthalene and pyridinium rings is 3.3 Å. Between ribbons, the non-disordered naphthyl groups show a second layer of π to cation stacking with the cyanopyridinium groups of the disordered cations, generating a link between ribbons and forming an extended 2D sheet. The 2D sheets are separated by layers of anions, which are connected through two CF_3-CF_3 fluoric interactions between pairs of anions, one linear and one offset, at 2.82/2.87 Å. Typical anion-cation close contact separations are at 2.5 Å, typical of Van der Waals contacts.

The pyridinium cations and naphthalene are co-planar with an interlayer spacing of 3.335 Å. Compared with the previous work, the distance is shorter than the charge-transfer complex's two parts' distance which is composed of the 1-methylnaphthalene and 1-methyl-4-cyanopyridinium.[12] The crystal structure of this ionic liquid is not similar to the previous charge-transfer complex. Compared with the previous charge-transfer complex, the planar

extension of the crystal structure is the main distinction of the aromatic-functionalized pyridiniums' crystal structure. And the colour of pyridinium ionic liquid is the same as it in acetonitrile solution. The UV-Vis absorption in the visible light range is from the change of the overlap between naphthalene and pyridinium rings not the self-assemble effect. If it is from the self-assemble effect, the naphthyl rings should overlap with each other which is different from the pictures mentioned above.

Compared with the crystal structure of 1-methyl-3-(2-naphthylmethyl)imidazolium (shown in Figure 2-9), the overlap between naphthyl rings and pyridinium rings is the main difference. The imidazolium cation has a different packing structure in the crystal with edge-on stacking of the naphthalene rings, and then alternating imidazolium-cation and NTf_2 anions. There is no charge-transfer complexes formed in the crystal structure.

This structure is the main proof of the existence of charge-transfer complexes in the aromatic-functionalized pyridinium ionic liquids. The formation of CT complexes is hard to be established within the crystalline structure of this crystalline of this single pair ionic liquid salt.



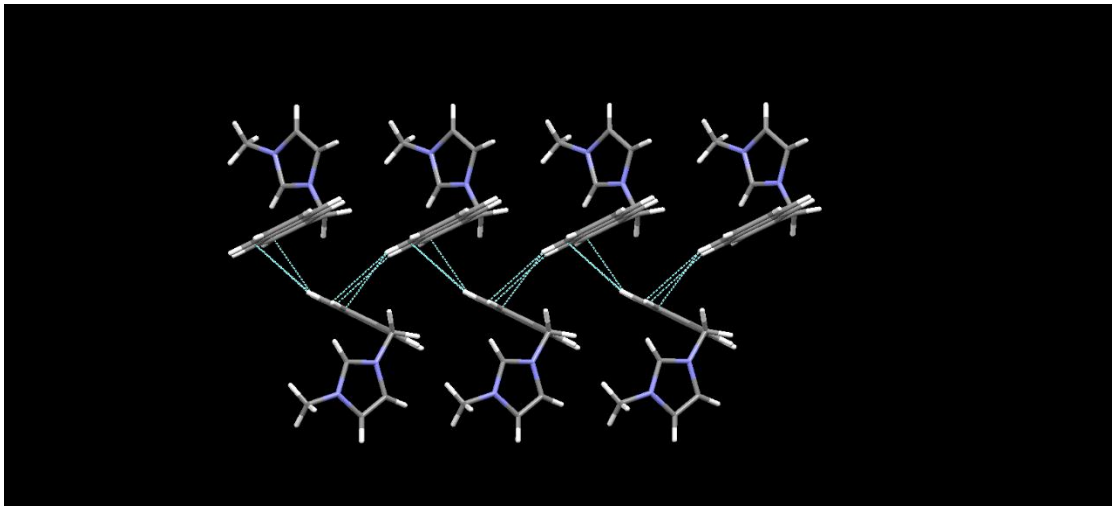


Figure 2-9: The crystal structure of 1-methyl-3-(2-naphthylmethyl)imidazolium cation crystal structure.

2.3 The performances of ionic liquid mixtures

In order to form the charge-transfer complexes, the electron-donor and electron-acceptor are prepared through these pure ionic liquids. however, the existence of charge-transfer complexes among these mixtures should be detected through different methods like DSC and UV-Vis. Although the data from the analysis of these ionic liquid mixtures is not condensable enough for detecting the existence of charge-transfer complexes because of the repulsive Coulomb Force, they are still worthy for the future development of charge-transfer complex.

2.3.1 Melting points of ionic liquid mixtures

When dissolving the imidazolium ionic liquids and pyridinium ionic liquids 1:1 in the ethyl acetate altogether, the theoretical appearance is forming a new kind of stable and uniform solution. When they are dissolved in ethyl acetate, the solution is still brown and there is no different colour appearing in liquid. However, the deposit is forming two layers which means the mixtures are not stable and uniform. The aromatic-functionalized electron-withdrawing pyridinium ionic liquids were different. Although they were not as stable as the imidazolium series, the melting points cannot be used as the proof of the existence of charge-transfer complexes because the charge-transfer complexes are not formed by two different kinds of materials which means there is no comparison among these materials. This is the reason why the melting points of these ionic liquids were not measured.

Although the charge-transfer complexes should have higher melting points than the compounds, these ionic liquids mixtures cannot prove the existence of charge-transfer complexes through measuring the melting points. Most solid-state charge-transfer complexes have higher melting points than their ingredients. However, some charge-transfer complexes can't form a stable solid -state which the charge-transfer complexes are not stable enough in solid-state like the charge-transfer complex which are composed by the 1-methyl-3-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide and 2-methylnaphthalene. This complex can only exist during the melting state. When it cooled down, the naphthalene would separate from the 1-methyl-3-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide. The microscope is also used for observing the melting process of donors and acceptors under heating. From the mixtures' observation, compared with the ingredients, the colours of the ionic liquids have no change whether they are melted or not.

And the mixtures' melting points or glass transition points were also measured through the DSC which are shown in the appendix, which were not clear enough to be read as a precise data. There is no specific melting point for the

mixtures like the normal mixtures. Although the charge-transfer complexes might be formed in the mixtures, the combinations of these ionic liquids just took a small proportion in these mixtures. therefore, there is no unique and special absorption phase transition points from the others. And the charge-transfer complex can't be found in these mixtures through UV-Vis absorption.

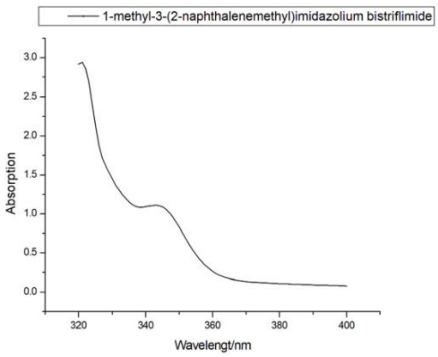
2.3.2 UV-Vis spectra

UV-Vis absorption spectra of the single ionic liquids and their mixtures are shown in Figure 2-10. The data was recorded from 300 nm^{-1} because the high absorption levels arising from aromatic π-π* transitions in the UV region masked lower intensity features in the visible region. The absorption from 200 to 300 nm is overlapped by different functional groups. Otherwise, the proof of the existence of charge-transfer complexes from UV-Vis absorption is based on the new absorption peaks which are in the visible light range because the previous charge-transfer complexes show that the unique absorption peaks of charge-transfer complexes always happened in the visible light ranges from these H-aggregate CT complexes.[59] The change of absorption would change from ultraviolet light range to visible light range.

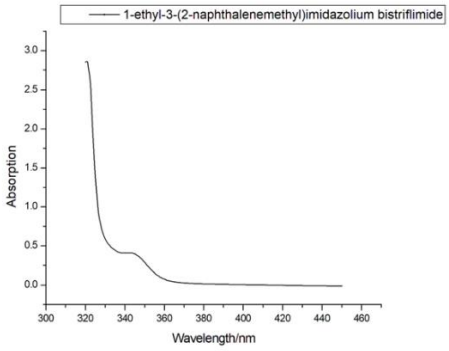
All these aromatic-functionalized imidazolium ionic liquids have the obvious weak absorption from 340 nm^{-1} to 360 nm^{-1}. The strength of this type of ionic liquids' absorption is different from the absorption from the chemical bond. Therefore, this absorption is based on the self-assemble effect.

The mixtures which are composed of the aromatic-functionalized imidazolium and 1-methyl-4-cyanopyridinium ionic liquids have a different UV-Vis from the aromatic-functionalized pyridinium ionic liquids. As the colours of ionic liquids and their mixtures show, both aromatic-functionalised imidazolium ionic liquids are the same as their mixtures. The mixtures' UV-Vis absorptions are shown in the Figure 2-7. The intermolar interactions cannot bring a weak absorption in the UV-Vis. The absorption of the intermolecular interactions among the mixtures is from 340 nm^{-1} to 360 nm^{-1}. To detect whether this type of interaction is from the interaction between aromatic-functionalized

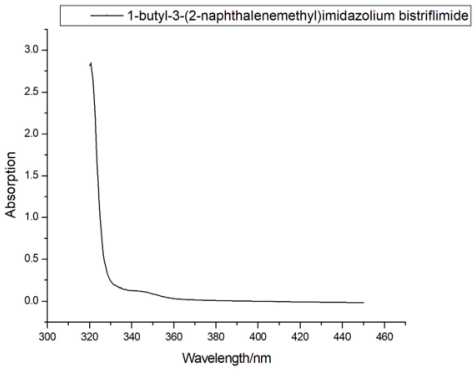
imidazolium and electron-withdrawing pyridinium cations or *π*-*π* interactions from aromatic-functionalised imidazolium cations, the change of the strength of the absorption is recorded and shown in the Figure 2-11.



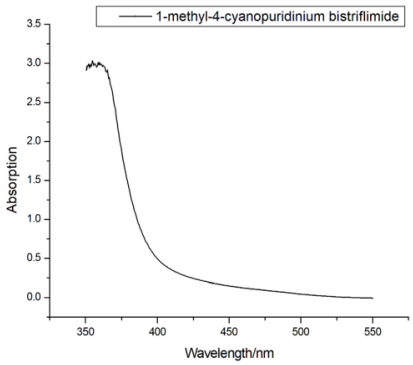
(1)



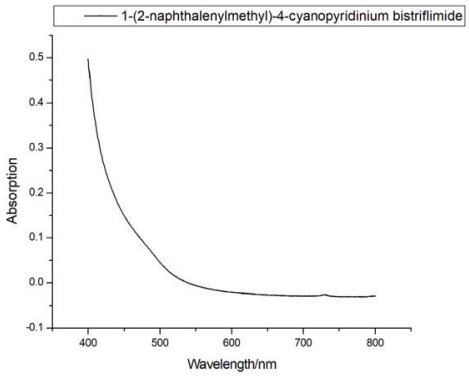
(2)

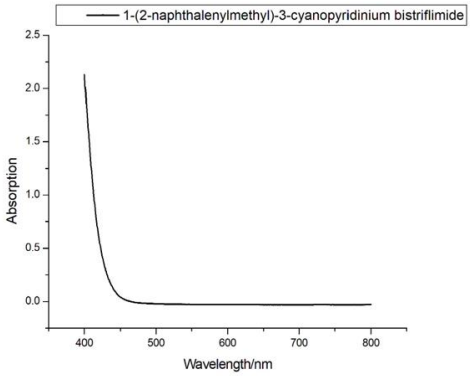


(3)

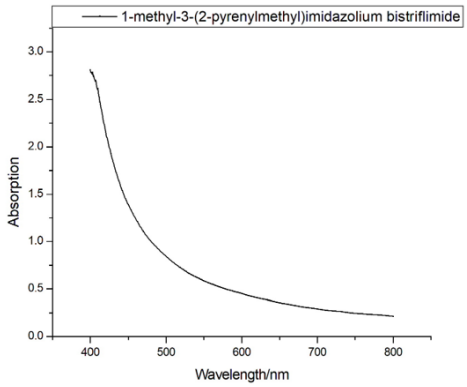


(4)

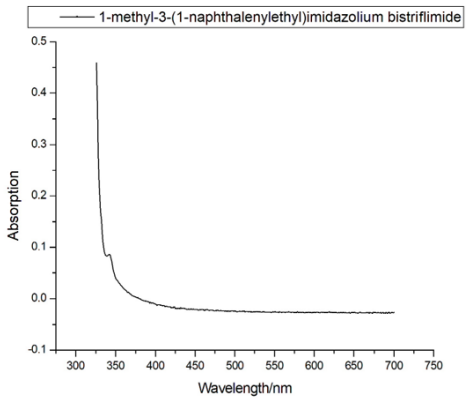




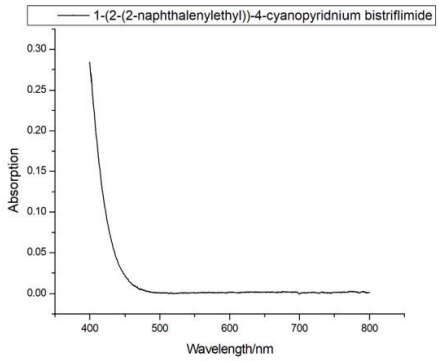
(5)



(6)



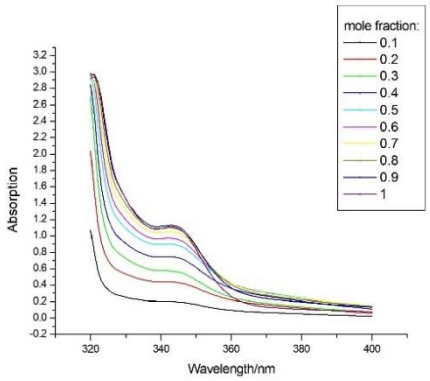
(7)



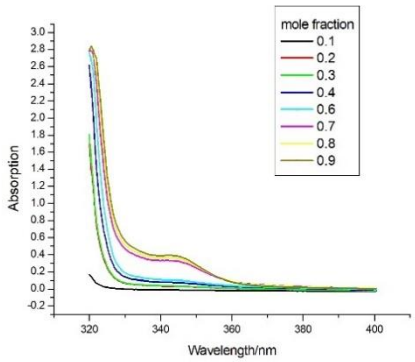
(8)

(9)

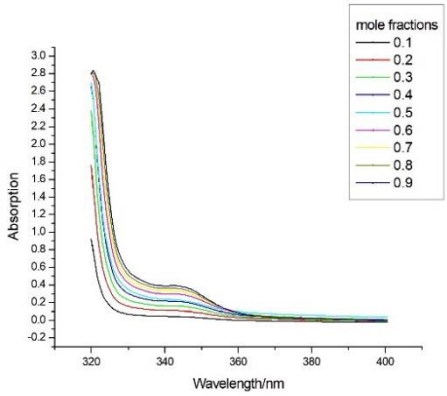
Figure 2-10: UV-Vis absorption spectra all ionic liquid are solved in CH_3CN at 25 mmol/L: (1)1-methyl-3-(2-naphthylmethyl)imidazolium [NTf_2]; (2) 1-ethyl-3-(2-naphthylmethyl)imidazolium [NTf_2]; (3) 1-butyl-3-(2-naphthylmethyl)imidazolium [NTf_2]; (4) 1-methyl-4-cyanopyridinium [NTf_2]; (5)1-(2-naphthylmethyl)-4-cyanopyridinium [NTf_2]; (6) 1-(2-naphthylmethyl)-3-cyanopyridinium [NTf_2]; (7) 1-methyl-3-(1-pyrenylmethyl)imidazolium [NTf_2]; (8) 1-methyl-3-(1-naphthylethyl)imidazolium [NTf_2]; (9) 1-[2-(2-naphthylethyl)]-4-cyanopyridinium [NTf_2].



(1)



(2)

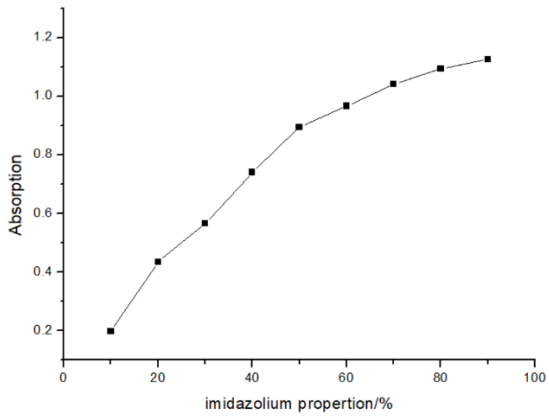


(3)

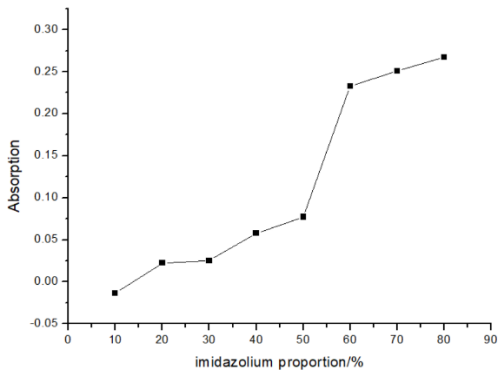
Figure 2-11: UV-Vis absorption spectra of different proportions of aromatic-functionalized imidazolium ionic liquids. The total concentrations of the solutions are 50 mmol/L in CH_3CN at room temperature (1) the change of proportions of 1-methyl-3-(2-naphthylmethyl)imidazolium in the CH_3CN; (2) the change of proportions of 1-ethyl-3-(2-naphthylmethyl)imidazolium in the CH_3CN; (3) the change of proportions of 1-butyl-3-(2-naphthylmethyl)imidazolium in the CH_3CN.

The strength of the absorption might be changed through the change of the proportion of electron-withdrawing pyridinium ionic liquids under the same total concentration. There might be a climax which can be used as the proof of the existence of the charge-transfer complexes and for detecting the stoichiometry of the charge-transfer complexes. For example, there might be a peak appearing when the concentration of pyridinium ionic liquids reached half total concentration which means the charge-transfer complexes are

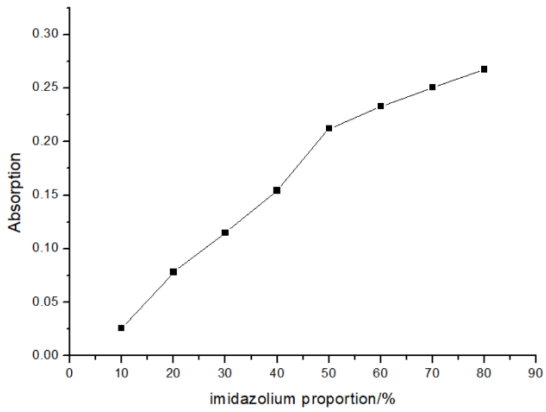
composed by aromatic rings and electron-withdrawing pyridinium ionic liquids under the proportion 1:1 which is the normal proportion of CT complexes which are composed by neutral molecules and electron-withdrawing pyridinium. Therefore, the Job's Plots of these mixtures, plotting the absorption at 350 nm^{-1} which show the change of the strength of the intermolecular interactions are shown in the Figure 2-12.



(1)



(2)



(3)

Figure 2-12: Job's plots of ionic liquid mixtures between [C_1^4CNpy][NTf_2] and aromatic-functionalized imidazolium: (1) 1-methyl-3-(2-naphthylmethyl)imidazolium; (2) 1-ethyl-3-(2-naphthylmethyl)imidazolium; (3) 1-butyl-3-(2-naphthylmethyl)imidazolium, the total concentration of mixture is 50 mmol/L.

Although they are not a straight line which means there might be some interactions among the aromatic-functionalized imidazolium and electron-withdrawing pyridinium ionic liquids, the increase of the concentration also strengthens the absorption. The existence of the charge-transfer complexes is hard to prove through the mixtures UV-Vis absorption and the Job's Plots. The interactions among the cations are influenced by the Coulomb Force. The positive charge is the main reason why two different types of cations cannot combine altogether. To form the charge transfer complexes through combining two kinds of cations, the charge-transfer complexes should overcome the self-assemble effect and Coulomb Force which means the LUMO energy differences should be strong enough to disrupt the components' structures. From the previous work, the influence of the self-assemble effect is less than the combination of the formation of charge-transfer complexes. Therefore, this Coulombic repulsion of cations may be the main reason why the charge-transfer complex cannot be detected through the UV-Vis absorption among these ionic liquid mixtures.

To decrease the repulsive Coulomb Force influence, there are two potential methods for solving this problem. The longer carbon chain which is connected between aromatic rings and imidazolium and larger aromatic systems which could delocalize the positive charge are potential for solving the influence of repulsive Coulomb Force. The UV-Vis absorption spectra of 1-methyl-3-(1-naphthylethyl)imidazolium bis{(trifluoromethyl)sulfonyl}imide and 1-methyl-3-(1-pyrenylmethyl)imidazolium and their respective mixtures with the CT-acceptor [C_1^4CNpy][NTf_2] is shown in Figure. 2-13.

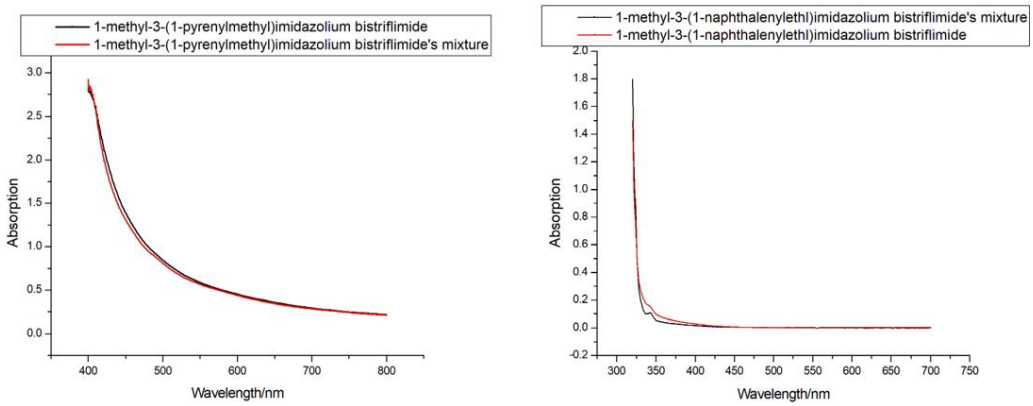


Figure 2-13: the UV-Vis absorption of the 1-methyl-3-(1-naphthylethyl)imidazolium bis{(trifluoromethyl)sulfonyl}imide, 1-methyl-3-(2-pyrenylmethyl)imidazolium and [C_1^4CNpy][NTf_2] mixtures which are composed by[C_1^4CNpy][NTf_2] and these imidazolium ionic liquids mentioned before.

Again, no new unique absorption peaks among these UV-Vis absorption spectra can be observed in the mixtures compared to the two initial imidazolium ionic liquid solutions. These two kinds of imidazolium ionic liquids UV-Vis absorption have different characters because of different aromatic rings. If 1-methyl-3-(1-naphthylethyl)imidazolium bis{(trifluoromethyl)sulfonyl}imide could form charge-transfer complexes with 1-methyl-4-cyanopyridinium ionic liquids, the appearance of charge-transfer complexes could be similar to the charge-transfer complex which is composed to the naphthalene and 1-methyl-4-cyanopyridinium because the naphthalene could be the only choice of the potential electron donor in the 1-methyl-3-(1-naphthylethyl)imidazolium. The combination of the pyrene ring could distract the positive charge to decrease the repulsive force from the Coulomb Force, there are still two kinds of different kinds of aromatic nitrile rings imidazolium and pyridinium with positive charge. As for the 1-methyl-3-(2-pyrenylmethyl)imidazolium, the π-electrons of pyrene are much richer than the naphthalene. The self-assemble effect of pyrene is much stronger than naphthalene. The colour of the ionic liquid is brown which is also different from the other imidazolium ionic liquids. Therefore, the UV-Vis absorption of

1-methyl-3-(2-pyrenylmethyl)imidazolium is quite different from other aromatic-functionalized imidazolium ionic liquids. The self-assemble effect of pyrene hinders the overlap with the pyridinium.

For the current ionic liquid mixtures, there is no convincible proof of existence of charge-transfer complexes. There are no unique absorption peaks in mixtures from their ingredients. Normally, if the absorption from charge-transfer complexes is in the visible light range which there is no absorption from solvent. However, the effect of solvent should not be ignored. Acetonitrile is a kind of polar solvent, which could distract the positive charge of cations which could decrease the influence of Coulomb Force. Otherwise, there is not so much influence on the naphthalene from polar solvent. Therefore, the solvent makes a positive influence on the formation of charge-transfer complexes. There might be a higher possibility of formation of a charge-transfer complexes in the polar solvent than in the non-polar solvent which can't solve the imidazolium ionic liquids.

The charge-transfer complexes are composed of the electron-donors and electron-acceptors, which may bring an extra absorption band in either UV or visible region in the UV-Vis spectra. However, most electron-donors are not cations which are different from my projects. Both acceptors and donors are cations. The coulomb force is the main hinder once to formation of charge-transfer complexes. Compared with the conventional charge-transfer complexes, the extra absorption band from charge-transfer complexes which are composed to pure cations might be not as apparent as the conventional charge-transfer complexes. And the self-assemble effect of aromatic-functionalized imidazolium donors can't also be ignored. The overlap of different aromatic rings also decreases the possibility of overlap with pyridinium rings.

The acceptors are always electron-withdrawing which could provide empty molecular orbitals which are suitable for the donor's electrons. To form the charge-transfer complexes, the electrons in the donor which are from the

aromatic rings like naphthalene and pyrene in imidazolium cations should be cooperated with the pyridinium cations. However, the positive charge of imidazolium makes the electrons in the aromatic rings be attracted to the positive charge which may decrease the electron density of aromatic rings which may also decrease the possibility of formation of a charge-transfer complex with pyridinium cations.

The 4-cyanopyridinium ionic liquids containing a polyaromatic N-substituent: 1-(2-naphthylmethyl)-4-cyanopyridinium and 1-[2-(2-naphthylethyl)]-4-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide have a similar absorption with the charge-transfer complex which is composed of the 2-methylnaphthalene and 1-methyl-4-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide with an intensive absorption in the range 400-450 nm, corresponding to their observable yellow colour in the neat state and in solution. The 1-(2-naphthylmethyl)-4-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide is pale yellow.

As for the aromatic-functionalized pyridinium ionic liquids, the UV-Vis absorption cannot explain the existence of the charge-transfer complexes because of the lack of the comparison. However, if the UV-Vis absorption in the visible light range of these ionic liquids has the similar absorption with the combinations which are composed by electron-withdrawing ionic liquids and 1-methylnaphtahlene, the intermolecular interactions of pyridinium ionic liquids should be also similar to charge-transfer complexes. Figure 2-14 shows UV-Vis absorption of these 1-naphthylalkyl-4-cyanopyridinium ionic liquids and charge-transfer complex in the visible light range. Although the strength and the wavelength of the absorption are different, the previous charge-transfer complex is quite similar with the 1-{2-(2-naphthylethyl)}-4-cyanopyridinium. The absorption is hard to be explained by the intermolecular interactions among the cations or interactions in the cations. Although theoretically the 1-(2-naphthylmethyl)-4-cyanopyridinium and 1-[2-(2-naphthylethyl)]-4-cyanopyridinium should not have the similar UV-Vis absorption from the single function groups. The absorption in the visible light

range should be from the interaction between the cations, not from the inside of cations. However, there is no direct proof that the structures of aromatic-functionalized 4-cyanopyridinium are forming the charge-transfer complexes.

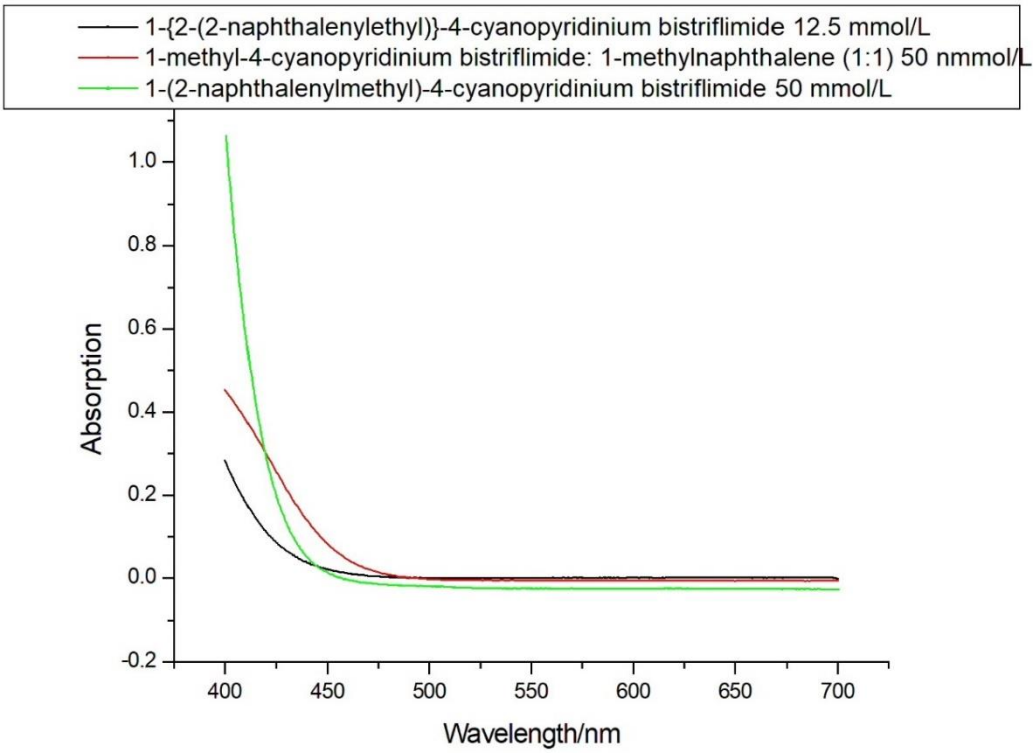


Figure 2-14: the UV-Vis absorption of aromatic-functionalized pyridinium ionic liquids in visible light range in MeCN: 1-(2-naphthylmethyl)-4-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide (green) 50mmol/L; 1-{2-(2-naphthylethyl)}-4-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide (black) 12.5mmol/L; 1-methyl-4-cyanopyridinium:1-methylnaphthalene (1:1) (red) 50mmol/L.

Associated with the IR spectra, the structure of the aromatic-functionalized pyridinium ionic liquids is possible to be the charge-transfer complex's structure. Compared with the imidazolium series ionic liquid mixtures, the influence of the Coulomb Force in aromatic-functionalized pyridinium ionic liquids is much less than the combination of two different kinds of cations. Although the physical linking of donor and acceptor in the cation means that

there is greater opportunity to self-assemble, the appearance of the self-assemble might be different from the charge-transfer complexes. As for the combining methods of the cations, the solid state will be shown in the next chapter.

2.4 Theorical calculation

The LUMO energy for each cation from the ionic liquids studied in this project were calculated by density functional theory (DFT) with the default B3LYP model using Spartan with the cation structure minimised in the nonpolar solvent. The results are shown in table 2-6. The LUMO energy differences are the main driving factors of forming charge-transfer complexes which are shown in Figure 2-15. From the existing charge-transfer complexes, the donors' LUMO energy is lower than the acceptors.

From the data, the LUMO energy of different kinds of cations shows the electron-withdrawing pyridinium ionic liquid has lowest LUMO energy. The 2-methylnaphthalene has the highest LUMO energy among these particles. And from the calculation results, the alkyl groups which connect to the imidazole rings have nearly no influence on the LUMO and HOMO energy. Otherwise, the 1-methyl-3-(1-naphthylethyl)) imidazolium and 1-methyl-3-(1-pyrenylmethyl) imidazolium are different from the other aromatic-functionalized imidazolium cations. Compared with the α-aromatic-functionalized imidazolium, the 1-methyl-3-(1-naphthylethyl)) imidazolium has higher LUMO and HOMO energy which means the possibility of charge-transfer complex formation is higher than the other imidazolium cations. From this data, the longer carbon chain between naphthalene and imidazolium may decrease the influence on the repulsive Coulomb Force. However, the longer chain also makes the naphthalene prefer to combining the imidazolium rather than electron-withdrawing pyridinium rings to form the self-combination which is based on the interactions inside of itself.

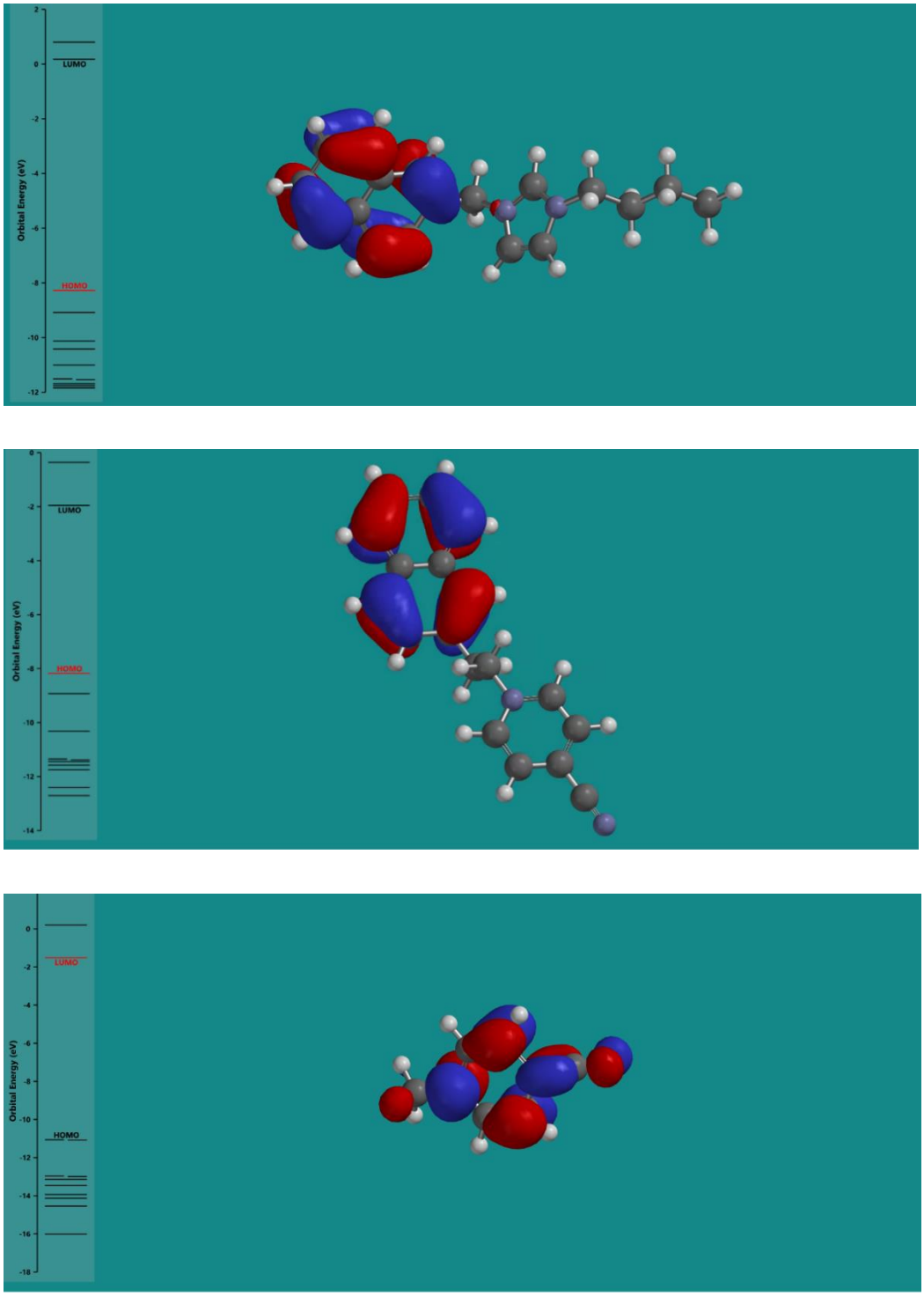


Figure 2-15: the Spartan calculation figures about the three series ionic liquids in polar solvent: (top) aromatic-functionalized imidazolium; (middle) aromatic-functionalized pyridinium; (bottom) 1-methyl-4-cyanopyridinium.

As for the 1-methyl-3-(1-pyrenylmethyl) imidazolium, there is some similarity with naphthalene. They have the same HOMO energy which is higher than the other imidazolium cations. However, the LUMO energy of it is lower than the other imidazolium. The energy difference between pyridinium and 1-methyl-3-(1-pyrenylmethyl) imidazolium is lower than the other aromatic-functionalized imidazolium cations. The self-assemble effect between pyrene rings is much stronger than the naphthalene rings which might be the main reason why the charge-transfer complex is harder to be formed between electron-withdrawing pyridinium and pyrene-functionalized imidazolium. Theoretically, the combination of two kinds of different cations in order form a new kind of stable and uniform material which is based on the intermolecular interactions is possible and achievable. However, the influence of repulsive Coulomb Force and the damages of the π-π interaction cannot be ignored. The energy of destroying π-π interaction is hard to be calculated and Spartan can only calculate the two different cations in the same system at the same time.

Table 2-6: all LUMO and HOMO energy of the cations which are used in the formation of the charge-transfer complex by mixing two different kinds of cations calculated through Spartan in non-polar solvent.

Cations	HOMO/eV	LUMO/eV
1-methyl-3-(2-naphthylmethyl) imidazolium	-8.3	0.2
1-ethyl-3-(2-naphthylmethyl) imidazolium	-8.3	0.2
1-butyl-3-(2-naphthylmethyl) imidazolium	-8.3	0.2
1-methyl-4-cyanopyridinium	-11.5	-2.0
1-methyl-3-(1-naphthylethyl)) imidazolium	-8.1	0.4
1-methyl-3-(1-pyrenylmethyl) imidazolium	-7.7	-0.5
2-methylnaphthalene	-7.7	0.9

To decrease the influence of the repulsive Coulomb Force, there is a kind of new aromatic-functionalized imidazolium cation which the aromatic rings connect with both imidazole's nitrogen atom designed and calculated in the Figure 2-16 through Spartan. This cation shows the type of the π-π interaction is highly possible to form in the cations. The HOMO and LUMO energies of this cation are -8.0 eV and 0.4 eV. The HOMO and LUMO energy of 1,3-(2-naphthalnyl-methyl) imidazolium are similar with 1-methyl-3-(1-naphthylethyl)) imidazolium. If it could be mixed with N-methyl-4-cyanopyridinium ionic liquids, the repulsive force between these two kinds of cations might not be decreased. However, the possibility of charge-transfer complex formation is much higher than the 1-methyl-3-(2-naphthyl-methyl) imidazolium because these two naphthyl rings have more possibility of combining with the pyridinium rings.

The calculation results of aromatic-functionalized electron-withdrawing pyridinium ionic liquids are not shown because the donor and acceptor are in the same cation which the Spartan can't calculate the energy of different parts of the same cation..

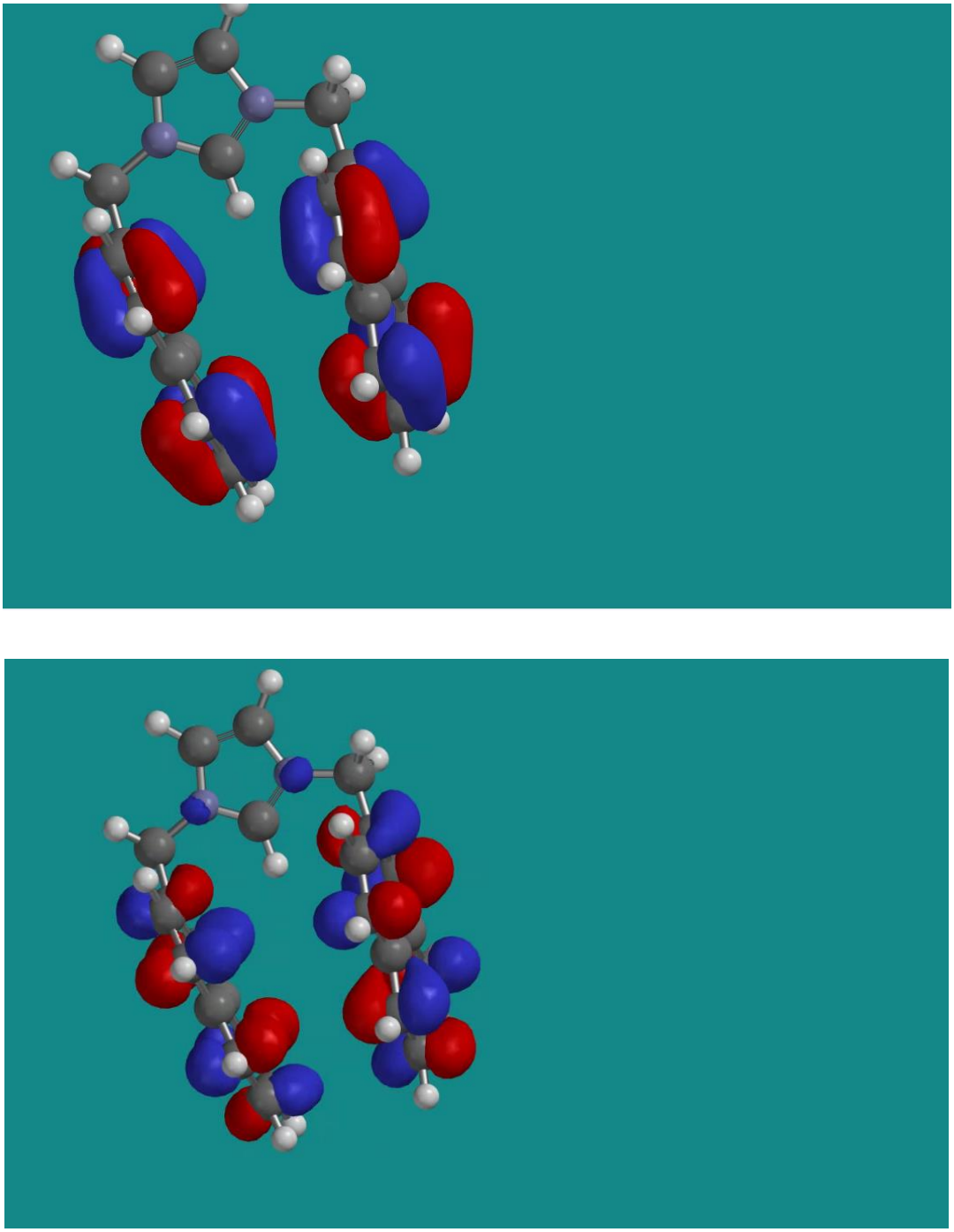


Figure 2-16: the HOMO and LUMO of the 1,3-(2-naphthalnylmethyl) imidazolium

As for the aromatic-functionalized pyridinium cation, the LUMO and HOMO energies' differences are not the main driving factor of forming the charge-

3 Conclusion

Five kinds of imidazolium ionic liquids: 1-methyl-3-(2-naphthylmethyl)-imidazolium bis{(trifluoromethyl)sulfonyl}imide, 1-ethyl-3-(2-naphthylmethyl)-imidazolium bis{(trifluoromethyl)sulfonyl}imide, 1-butyl-3-(2-naphthylmethyl)-imidazolium bis{(trifluoromethyl)sulfonyl}imide, 1-methyl-3-{2-(2-naphthylethyl)}imidazolium bis{(trifluoromethyl)sulfonyl}imide and 1-methyl-3-(2-pyrenylmethyl)imidazolium bis{(trifluoromethyl)sulfonyl}imide and another four kinds of pyridinium ionic liquids: 1-methyl-4-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide, 1-(2-naphthylmethyl)-4-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide, 1-(2-naphthylmethyl)-3-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide and 1-{2-(2-naphthylethyl)}-3-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide are synthesized and characterized in this project. And five series ionic liquid mixtures which are composed of the aromatic-functionalized imidazolium and electron-withdrawing pyridinium were prepared and the properties of these mixtures measured by UV-Vis, DSC and TGA. Compared with the previous charge-transfer complexes which are composed by the aromatic rings and electron-withdrawing pyridinium ionic liquids, there is no new absorption peaks and stable and uniform materials appearing among these new mixtures. The Coulomb Force is the main reason of this appearance. To decrease the influence of Coulomb Force, the longer carbon chain and larger aromatic rings were synthesized and characterized. The new series of ionic liquid mixtures also have no unique absorption peaks in the UV-Vis. There is no convincing proof of the existence of charge-transfer complexes. Theoretically, the charge-transfer complexes could be formed by mixing these two series ionic liquids because of the LUMO energy differences which are calculated through Spartan between them. The 1-methyl-4-cyanopyridinium cation has the lowest LUMO energy among these cations. If the electron-donors which are aromatic-functionalized imidazolium ionic liquids could decrease the repulsive Coulomb Force into an acceptable level, the charge-transfer complexes could be formed between these cations.

As for the aromatic-functionalized pyridinium ionic liquids, the UV-Vis absorption of these 1-(2-naphthylakyl)-4-cyanpopyridinioum ionic liquids is similar to the charge-transfer complex which is composed by [C_1^4CNpy][NTf_2] and 1-methylnaphthalene. The charge-transfer complex's UV-Vis absorption in visible light range is from the interactions between the aromatic rings and electron-withdrawing pyridinium rings. If the similar UV-Vis absorption of 1-(2-naphthylakyl)-4-cyanpopyridinioum ionic liquids is not from the intermolecular interactions and from the aromatic rings, the different carbon chains play an important role on the appearance and UV-Vis absorption of ionic liquids. Theoretically, the different lengths of carbon chains should have completely different UV-Vis absorption spectra in the visible light range. However, the 1-(2-naphthylakyl)-4-cyanopyridinium series ionic liquids have nearly the same UV-Vis absorption in the visible light range. Therefore, the UV-Vis absorption of 1-(2-naphthylakyl)-4-cyanopyridinium in visible light range is from the intermolecular interactions and not from the cations themselves. And from the IR data of these ionic liquids and charge-transfer complexes, the 1-(2-naphthyethyl)-4-cyanopyridinium ionic liquid has the same IR data as charge-transfer complex in many aromatic bonds which mean these bonds may have similar influence from the other chemical groups. This is also the reason why the 1-(2-naphthylmethyl))-4-cyanopyridinium's data is not as similar as the charge-transfer complex. The distance between the naphthalene group and pyridinium rings is shorter than the 1-(2-naphthyethyl)-4-cyanopyridinium which the pyridinium ring may have more influence on the appearance of 1-(2-naphthylmethyl))-4-cyanopyridinium from the inner of cation. Besides, the 1-(2-naphthylmethyl)-4-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide's crystal structure is detected through single-crystal XRD. The naphthalene ring is overlapped with the pyridine ring and the distance between naphthalene and pyridine is shorter than the previous charge-transfer complex which is composed by the 1-methyl-4-cyanopyridinium and 1-methylnaphthalene. Compared with the 1-methyl-3-(2-naphthylmethyl)imidazolium bis{(trifluoromethyl)sulfonyl}imide, the crystal structure of 1-(2-naphthylmethyl)-4-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide is a kind

of ‘L’ shape which is different from the imidazolium ionic liquid. The self-assemble effect of 1-methyl-3-(2-naphthylmethyl)imidazolium bis{(trifluoromethyl)sulfonyl}imide makes imidazolium rings be far away from each other. The 1-(2-naphthylmethyl)-4-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide could form the charge-transfer complex in the crystal.

In the future work, new kinds of imidazolium ionic liquids should be designed and synthesized in order to decrease the influence of the Coulomb Force to form the charge-transfer complexes with electron-withdrawing pyridinium ionic liquids. And if the ionic liquids mixtures form the charge-transfer, the stoichiometry and the solid-state structure of charge-transfer complexes should also be detected. As for the aromatic-functionalized pyridinium ionic liquids, the electrochemical properties should be measured and only 1-(2-naphthylmethyl)-4-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide has single-crystal XRD data. The packing characteristics of the other two aromatic-functionalized pyridinium ionic liquids should also be examined in the solid state through single-crystal XRD. The possibility of storing electrons and energy in the charge-transfer complex should also be tested. The aromatic-functionalized ionic liquids could have two kinds of different spatial arrangements which can be self-assemble or charge-transfer complexes. The main differences between these two kinds of cations are heterocycles and cyano-group. Although the 4-cyanopyridinium cation has more electron-withdrawing, the other cations are also electron-withdrawing. Therefore, there might be some other intermolecular interactions among these cations.

4 Experimental

Solvents:

Toluene (99.7%, Sigma-Aldrich), acetonitrile (99.8%, Fisher Chemical), ethyl acetate (99.7%, Sigma-Aldrich), methanol (99.9%, Sigma-Aldrich), and ethyl acetate (99.9%, Sigma-Aldrich) were used as obtained from the supplier.

Chemicals

Dimethylsulfate (99%, Aldrich), 1-methylimidazole (99%, Aldrich), 1-ethylimidazole (99.9%, Fluorochem), 1-butylimidazole (99.9%, Fluorochem), 4-cyanopyridine (99%, Aldrich), 3-cyanopyridine (99%, Aldrich), 2-bromomethylnaphthalene (97%, Aldrich), 2-(2-bromoethyl)naphthalene (99%, Aldrich), 1-bromomethylpyrene (99%, Aldrich) and lithium bis{(trifluoromethyl)sulfonyl}imide (99%, 3M) were used as received.

Analytical

UV-Vis scan spectra were recorded in air at room temperature using a Perkin Elmer UV/Vis spectrometer. The ionic liquids were dissolved in CH_3CN and spectra collected in 1 cm path length quartz cells from 800 nm^{-1} to 200 nm^{-1}.

^1H NMR spectra were recorded in solutions on a Bruker Advance DPX 300 spectrometer in either D-chloroform, CD_3OD-d4 or DMSO-d6.

Infrared spectra were recorded on a Perkin Elmer spectrum 100 AT-IR spectrometer as powders.

Thermal decomposition temperature profiles were collected by thermogravimetric analysis (TGA Q5000). Upper limits for thermal stability of the liquids were measured in the dynamic heating regime using a TA Instruments Q5000 TGA instrument under nitrogen atmosphere.

Differential scanning calorimetry (DSC) measurements were performed using a TA Instruments DSC Q2000 instrument fitted with RCS 90 cooling system. Samples were loaded into Tzero aluminium pans, and the accurate mass was recorded (±0.0002 g) then sealed using Tzero hermetic lids and transferred to the DSC. Measurements were taken over three heating/cooling cycles across

the temperature range from +20 to +70 °C, with a cooling rate of 5 °C min^{-1} and a heating rate of 1 °C min^{-1}.

4.1 Synthesis of ionic liquids

(1) 1-methyl-3-(2-naphthylmethyl) imidazolium bis{(trifluoromethyl)-sulfonyl}imide

1-methylimidazole (1.42 g, 2 mmol) was dissolved in toluene (100 mL) that was heated to 110 °C in an oil bath with stirring (300 rpm), 2-bromomethylnaphthalene (4.42 g, 2 mmol) was added dropwise to the solution resulting in formation of product as a sticky yellow powder after 8 hours. The reaction mixture was cooled to room temperature and the crude 1-methyl-3-(2-naphthylmethyl) imidazolium bromide was dried by rotary evaporation to remove toluene and then in vacuo to give a brown powder (5.54g, 94.86%).

1-methyl-3-(2-naphthylmethyl) imidazolium bromide (3.08 g, 1 mmol) was then dissolved in water (25 mL) at room temperature and a solution of lithium bis{(trifluoromethyl)-sulfonyl}imide (3.49 g, 1 mmol) in water (25 mL) was added and the mixtures stirred forming two layers. The dense ionic liquid layer was collected using a separating funnel and washed with water several times, then dried under reduced pressure to give a brown liquid that solidified on cooling evaporation (6.30g, 96.1%). δ_H (300 MHz, $CDCl_3$) 10.41 (1H, s), 7.42 (2H, d), 7.86 (4H, dd), 7.49 (3H, m), 5.72 (2H, s), 4.01 (3H, s).

(2) 1-ethyl-3-(2-naphthylmethyl)imidazolium bis{(trifluoromethyl)-sulfonyl}imide

1-ethylimidazole (1.69 g, 2 mmol) was dissolved in toluene (100 mL) that was heated to 110 °C in an oil bath with stirring (300 rpm), 2-bromomethylnaphthalene (4.42 g, 2 mmol) was added dropwise to the solution resulting in formation of product as a sticky yellow powder after 8

hours. The reaction mixture was cooled to room temperature and the crude 1-methyl-3-(2-naphthylmethyl) imidazolium bromide was dried by rotary evaporation to remove toluene and then in vacuo to give a brown powder (5.71g, 93.45%).

1-methyl-3-(2-naphthylmethyl) imidazolium bromide (3.17 g, 1 mmol) was then dissolved in water (25 mL) at room temperature and a solution of lithium bis{(trifluoromethyl)-sulfonyl}imide (3.49 g, 1 mmol) in water (25 mL) was added and the mixtures stirred forming two layers. The dense ionic liquid layer was collected using a separating funnel and washed with water several times, then dried under reduced pressure to give a brown liquid that solidified on cooling evaporation (6.15g, 92.45%) δ_H (300 MHz, CCl_3D) 8.82 (1H, s), 7.84 (4H, m), 7.50 (2H, m), 7.34 (1H, d), 7.24 (2H, m), 5.35 (2H, m), 4.17 (2H, m), 1.47 (3H, dt).

(3) 1-butyl-3-(2-naphthylmethyl)imidazolium bis{(trifluoromethyl)-sulfonyl}imide

1-butylimidazole (2.51 g, 20 mmol) was dissolved in toluene (100 mL) that was heated to 110 °C in an oil bath with stirring (300 rpm), 2-bromomethylnaphthalene (4.42 g, 20 mmol) was added dropwise to the solution, sticky yellow powders has observed in the bottom of the flask after 8 hours heating and then cooled to room temperature. The 1-methyl-3-(2-naphthylmethyl) imidazolium bromide was a brown powder, which was dried by rotary evaporation and reduced pressure for 5 minutes.

Weigh some 1-buthyl-3-(2-naphthylmethyl) imidazolium bromide (3.44 g, 10 mmol) and dissolve it in water (25 mL) at room temperature. Weigh lithium bis{(trifluoromethyl)-sulfonyl}imide (3.49 g, 10 mmol) and dissolve it in the water (25 mL). Mix both solutions altogether and rotate under 300 rpm. overnight. Separate the water and ionic liquid through a separating funnel. Wash the ionic liquid with water several times and dry it under reduced pressure evaporation (6.53g, 94.33%). δ_H (300 MHz, CCl_3D) 8.93 (1H, s), 7.86 (2H, d), 7.52 (2H, m), 7.39 (1H, m), 7.22 (4H, p), 5.45 (2H, s), 4.14 (2H,

t), 1.81 (2H, m), 1.33 (2H, dq), 0.92 (3H, t)

(4) 1-methyl-4-cyanopyridinium bis{(trifluoromethyl)-sulfonyl}imide

4-Cyanopyridine (10.1 g, 0.1 mol) was dissolved in toluene (40 mL) that was heated to 45 °C in a water bath with stirring (450 rpm), dimethyl sulphate (15.3 g, 0.12 mol) was added dropwise to the solution, then the reaction mixture was heated for a further 24 h and cooled to room temperature. 1-Methyl-4-cyanopyridinium methyl sulphate was precipitated as colourless crystals (19.49 g, 87.24%).

1-Methyl-4-cyanopyridinium methyl sulphate (10.0 g, 0.043 mol) was dissolved in water (40 ml), then mixed with a solution of $Li[NTf_2]$ (13.0 g, 0.045 mol) in water (20 ml). The product formed as a white crystalline precipitate, which was collected by filtration and washed by water, then dried in high vacuum (16.09 g, 92.77%). δ_H (400 MHz, MeOD-d_4), 8.84 (2H, d), 8.35 (2H, d), 4.38 (3H, s).

(5) N-[(2-naphthyl)methyl]-4-cyanopyridinium bis{(trifluoromethyl)-sulfonyl}imide

2-Bromomethylnaphthalene (5.53 g, 25 mmol) was dissolved in toluene (50 ml) that was heated to 110 °C in a water bath with stirring (450 rpm), then 4-cyanopyridine (2.51 g, 2.31 mmol) was dissolved in toluene (50 ml) and added dropwise to the solution, which turned to yellow from colourless after several minutes. The reaction mixture was heated for a further 8 h and cooled to room temperature, bright yellow solid was precipitated and collected by filtration and washed by toluene (5 ml x 3), then dried under reduced pressure (5.41 g, 67.29%).

N-[(2-naphthyl)methyl]-4-cyanopyridinium bromide (8.04 g, 0.025 mol) was dissolved in water (40 ml), then mixed with a solution of $Li[NTf_2]$ (7.18 g, 0.025 mol) in water (20 ml). The product formed as a bright-yellow crystalline precipitate, which was collected by filtration and washed by water, then dried under high vacuum (9.82 g, 64.51%). δ_H (400 MHz, MeOD-d_4) 9.30 (2H, d),

8.43 (2H, d), 8.02 (1H, s), 7.86 (3H, m), 7.48 (3H, m), 6.01 (2H, s).

(6) N-[(2-naphthyl)methyl]-3-cyanopyridinium bis{(trifluoromethyl)-sulfonyl}imide

2-Bromomethylnaphthalene (5.53 g, 25 mmol) was dissolved in toluene (50 ml) that was heated to 110 °C in a water bath with stirring (450 rpm), then 3-cyanopyridine (2.51 g, 2.31 mmol) was dissolved in toluene (50 ml) and added dropwise to the solution, which turned to yellow from colourless after several minutes. The reaction mixture was heated for a further 8 h and cooled to room temperature, bright yellow solid was precipitated and collected by filtration and washed by toluene (5 ml x 3), then dried under reduced pressure (4.28g, 53.26%).

N-[(2-naphthyl)methyl]-3-cyanopyridinium bromide (8.04 g, 0.025 mol) was dissolved in water (40 ml), then mixed with a solution of Li[NTf_2] (7.18 g, 0.025 mol) in water (20 ml). The product formed as an orange crystalline precipitate, which was collected by filtration and washed by water, then dried in high vacuum (9.82 g, 64.50%). δ_H (400 MHz, MeOD-d_4) 9.30 (2H, d), 8.43 (2H, d), 8.02 (1H, s), 7.86 (3H, m), 7.48 (3H, m), 6.01 (2H, s).

(7) N-[(2-naphthyl)-2-ethyl]-4-cyanopyridinium bis{(trifluoromethyl)-sulfonyl}imide

2-Bromo-2-ethylnaphthalene (0.9408 g, 4 mmol) and 4-Cyanopyridine (0.416 g, 4 mmol) were dissolved in toluene (10 mL). The reaction mixture was heated at 70 °C in an AntonPaar Monowave 300 microwave reactor for 4 h and then cooled to room temperature. A pale-yellow solid was precipitated and collected by filtration and washed by toluene (3x 5 ml), then dried under reduced pressure (0.4008 g, 40.87%).

N-[(2-naphthyl)-2-ethyl]-4-cyanopyridinium bromide (0.4 g, 0.021 mol) was dissolved in water (5 ml), then mixed with a solution of Li[NTf_2] (0.6 g, 0.021 mol) in water (5 ml). The product formed as a light-yellow crystalline precipitate, which was collected by filtration and washed by water, then dried

in high vacuum. δ_H (400 MHz, MeOD-*d*$_4$) 8.98 (1H, s), 8.24 (2H, dd), 8.20 (2H, dd), 8.12 (2H, dd), 8.05 (3H, m), 7.06 (2H, m), 6.06 (2H, s), 3.93 (3H, s)

(8) 1-methyl-3-(2-naphthyl-2-ethyl)imidazolium bis{(trifluoromethyl)-sulfonyl}imide

2-Bromo-2-ethylnaphthalene (0.9405 g, 4 mmol) and 1-methylimidazole (0.363 g, 4 mmol) were dissolved in toluene (10 ml). The reaction mixture was heated at 70 °C in an AntonPaar Monowave 300 microwave reactor for 4 h and then cooled to room temperature. A brown solid was precipitated and collected by filtration and washed by toluene (3x 5 ml) (0.4008 g, 40.87%).

1-methyl-3-(2-naphthyl-2-ethyl)imidazolium bromide (0.4 g, 0.021 mol) was dissolved in water (5 ml), then mixed with a solution of Li[NTf$_2$] (0.6 g, 0.021 mol) in water (5 ml). The product formed as a brown crystalline precipitate, which was collected by filtration and washed by water, then dried in high vacuum (0.37g, 58.45%). δ_H (400 MHz, *d*$_4$-DMSO) 8.88 (2H, d), 8.31 (2H, d), 7.98 (1H, d), 7.84 (1H, m), 7.76 (1H, d), 7.48 (2H, dtd), 7.27 (1H, dd), 7.07 (1H, d), 4.99 (2H, t), 3.75 (2H, t).

(9) 1-methyl-3-(1-pyrenylmethyl)imidazolium bis{(trifluoromethyl)-sulfonyl}imide

2-Bromomethylpyrene (1.05 g, 3.4 mmol) and 1-methylimidazole (0.35 g, 7.31 mmol) were dissolved in toluene (10 ml). The reaction mixture was heated at 70 °C in an AntonPaar Monowave 300 microwave reactor for 4 h and then cooled to room temperature. A pale yellow solid was precipitated and collected by filtration and washed by toluene (3 x 5 ml) (0.74 g, 52.86%).

The 1-methyl-3-(1-pyrenylmethyl)imidazolium bromide (0.74 g, 0.00198 mol) was dissolved in water (5 ml), then mixed with a solution of Li[NTf$_2$] (0.574 g, 0.002 mol) in water (5 ml). The product formed as a black crystalline precipitate, which was collected by filtration and washed by water, then dried in high vacuum. (0.237g, 20.5%) δ_H (400 MHz, DMSO-*d*$_4$) 10.58 (1H, s), 7.98 (1H, d), 7.88 (1H, d), 7.78 (1H, d), 7.53 (3H, m), 7.36 (1H, m), 7.17 (1H, m),

6.90 (3H, m), 4.74 (2H, t), 4.01 (3H, s).

4.2 Preparation of ionic liquid-ionic liquid mixtures

Electron-withdrawing pyridinium ionic liquids ([C_1^4CNpy][NTf_2]) was mixed with the aromatic-functionalized imidazolium salts: 1-methyl-3-(2-naphthylmethyl)imidazolium bis{(trifluoromethyl)sulfonyl}imide, 1-ethyl-3-(2-naphthylmethyl)imidazolium bis{(trifluoromethyl)sulfonyl}imide, 1-butyl-3-(2-naphthylmethyl)imidazolium bis{(trifluoromethyl)sulfonyl}imide, 1-methyl-3-(2-naphthyl-2-ethyl)imidazolium bis{(trifluoromethyl)sulfonyl}imide and 1-methyl-3-(1-pyrenylmethyl)imidazolium bis{(trifluoromethyl)sulfonyl}imide) in the solvents (CH_3CN or 1:1 CH_3CN: $CHCl_3$ mixture) to form 1:1 charge-transfer complexes solution, which were characterized by UV-Vis spectrophotometer.

Solid charge-transfer complexes were obtained through melting ionic liquids with excess aromatics and cooling down to room temperature.

5 References

1. C. Zhong, Y. Deng, W. Hu, J. Qiao, L. Zhang and J. Zhang, *Chem Soc Rev*, 2015, **44**, 7484-7539.

2. D. P. Dubal, N. R. Chodankar, D. H. Kim and P. Gomez-Romero, *Chem Soc Rev*, 2018, **47**, 2065-2129.

3. M. Susan, A. Noda, N. Ishibashi and M. Watanabe, *Ion-gels prepared by incorporation of ionic liquids in polymer networks and their characterization as new proton-conducting polymer electrolytes*, 2004.

4. I. Osada, H. de Vries, B. Scrosati and S. Passerini, *Angew Chem Int Ed Engl*, 2016, **55**, 500-513.

5. S. Bai, P. Da, C. Li, Z. Wang, Z. Yuan, F. Fu, M. Kawecki, X. Liu, N. Sakai, J. T. Wang, S. Huettner, S. Buecheler, M. Fahlman, F. Gao and H. J. Snaith, *Nature*, 2019, **571**, 245-250.

6. O. Fontaine, *Energy Storage Materials*, 2019, **21**, 240-245.

7. M. J. Earle, J. M. Esperanca, M. A. Gilea, J. N. Lopes, L. P. Rebelo, J. W. Magee, K. R. Seddon and J. A. Widegren, *Nature*, 2006, **439**, 831-834.

8. F. M. Zhang, L. Z. Dong, J. S. Qin, W. Guan, J. Liu, S. L. Li, M. Lu, Y. Q. Lan, Z. M. Su and H. C. Zhou, *J Am Chem Soc*, 2017, **139**, 6183-6189.

9. M. Kasha, *Discussions of the Faraday Society*, 1950, **9**, 14-19.

10. E. Mourad, L. Coustan, P. Lannelongue, D. Zigah, A. Mehdi, A. Vioux, S. A. Freunberger, F. Favier and O. Fontaine, *Nat Mater*, 2017, **16**, 446-453.

11. C. Bodin, E. Mourad, D. Zigah, S. Le Vot, S. A. Freunberger, F. Favier and O. Fontaine, *Faraday Discuss*, 2018, **206**, 393-404.

12. C. Hardacre, J. D. Holbrey, C. L. Mullan, M. Nieuwenhuyzen, T. G. A. Youngs, D. T. Bowron and S. J. Teat, *Physical Chemistry Chemical Physics*, 2010, **12**, 1842-1853.

13. N. Bodappa, Y.-C. Fu, P. Broekmann, J. Furrer, K. Zick, S. Vesztergom, H. Tahara and T. Sagara, *Electrochimica Acta*, 2019, **320**, 134559-134567.

14. L. Wang, T. Shu, S. Guo, S. Chen, Y. Jiang and X. Hu, *Journal of Energy Chemistry*, 2020, **51**, 182-189.

15. M. Kasha, *Review of Modern Physics*, 1959, **31**, 162-169.

16. J. Frenkel, *Physical Review*, 1931, **37**, 1276-1294.

17. A. S. Davydov, Theory of Molecular Excitons, 1971.

18. M. Kasha, *Radiation Research*, 1963, **20**, 55-70.

19. J. Zhang, W. Xu, P. Sheng, G. Zhao and D. Zhu, *Acc Chem Res*, 2017, **50**, 1654-1662.

20. M. Makha, A. Purich, C. L. Raston and A. N. Sobolev, *ChemInform*, 2006, **37**, 507-517.

21. X. Chi, C. Besnard, V. K. Thorsmølle, V. Y. Butko, A. J. Taylor, T. Siegrist and A. P. Ramirez, *Chemistry of Materials*, 2004, **16**, 5751-5755.

22. T. J. Kistenmacher, T. E. Phillips and D. O. Cowan, *Acta Crystallographica Section B*, 1974, **30**, 763-768.

23. W. Hayes and A. M. Stoneham, *Defects and defect processes in nonmetallic solids*, 1985.

24. J. H. Schulman and W. D. Compton, *Color Centers in Solids*, Macmillan, 1962.

25. K. Takahashi, T. Sato, Y. Katsumura, J. Yang, T. Kondoh, Y. Yoshida and R. Katoh, *Radiation Physics and Chemistry*, 2008, **77**, 1239-1243.

26. A. Marcinek, J. Adamus, J. GęBicki, M. S. Platz and P. Bednarek, *The Journal of Physical Chemistry A*, 2000, **104**, 724-728.

27. D. Behar, C. Gonzalez and P. Neta, *The Journal of Physical Chemistry A*, 2001, **105**, 7607-7614.

28. E. Frackowiak, K. Fic, M. Meller and G. Lota, *ChemSusChem*, 2012, **5**, 1181-1185.

29. B. Gélinas, J. C. Forgie and D. Rochefort, *Journal of The Electrochemical Society*, 2014, **161**, H161-H165.

30. H. J. Xie, B. Gélinas and D. Rochefort, *Electrochemistry Communications*, 2016, **66**, 42-45.

31. L.-Q. Fan, Q.-M. Tu, C.-L. Geng, Y.-L. Wang, S.-J. Sun, Y.-F. Huang and J.-H. Wu, *International Journal of Hydrogen Energy*, 2020, **45**, 17131-17139.

32. E. Mourad, L. Coustan, S. A. Freunberger, A. Mehdi, A. Vioux, F. Favier and O. Fontaine, *Electrochimica Acta*, 2016, **206**, 513-523.

33. N. Yadav, N. Yadav and S. A. Hashmi, *ACS Applied Energy Materials*, 2021, **4**, 6635-6649.

34. T. T. Tran, N. Azra, M. Iqbal and M. S. Lee, *Separation and Purification*

Technology, 2020, **238**, 899-910.

35. T. Welton, *Chemical Reviews*, 1999, **99**, 2071-2084.

36. D. C. Murador, L. M. de Souza Mesquita, N. Vannuchi, A. R. C. Braga and V. V. de Rosso, *Current Opinion in Food Science*, 2019, **26**, 25-34.

37. M. H. Ibrahim, M. Hayyan, M. A. Hashim and A. Hayyan, *Renewable and Sustainable Energy Reviews*, 2017, **76**, 1534-1549.

38. U. Domańska, K. Walczak and M. Zawadzki, *The Journal of Chemical Thermodynamics*, 2014, **69**, 27-35.

39. P. Wasserscheid and W. Keim, *Angewandte Chemie International Edition*, 2000, **39**, 3772-3789.

40. Y. A. Elhamarnah, M. Nasser, H. Qiblawey, A. Benamor, M. Atilhan and S. Aparicio, *Journal of Molecular Liquids*, 2019, **277**, 932-958.

41. J. D. Barrio, J. Liu, R. A. Brady, C. S. Y. Tan, S. Chiodini, M. Ricci, R. Fernandez-Leiro, C. J. Tsai, P. Vasileiadi, L. Di Michele, D. Lairez, C. Toprakcioglu and O. A. Scherman, *J Am Chem Soc*, 2019, **141**, 14021-14025.

42. D. S. Firth, S. A. Morris, P. S. Wheatley, S. E. Russell, A. M. Z. Slawin, D. M. Dawson, A. Mayoral, M. Opanasenko, M. Položij, J. Čejka, P. Nachtigall and R. E. Morris, *Chemistry of Materials*, 2017, **29**, 5605-5611.

43. R. Bari, G. Tamas, F. Irin, A. J. A. Aquino, M. J. Green and E. L. Quitevis, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2014, **463**, 63-69.

44. M. Yao, Q. Li, Y. Xia and Y. Liang, *Russian Journal of Physical Chemistry A*, 2018, **92**, 502-507.

45. J. Yang, L. Shao, J. Yuan and F. Huang, *Chem Commun (Camb)*, 2016, **52**, 12510-12512.

46. D. Jiao and O. A. Scherman, *Green Chemistry*, 2012, **14**, 2445-2454.

47. C. Hardacre, J. D. Holbrey, C. L. Mullan, M. Nieuwenhuyzen, W. M. Reichert, K. R. Seddon and S. J. Teat, *New Journal of Chemistry*, 2008, **32**, 1953–1967.

48. H. Niedermeyer, J. P. Hallett, I. J. Villar-Garcia, P. A. Hunt and T. Welton, *Chem Soc Rev*, 2012, **41**, 7780-7802.

49. P. W. Atkins and J. De Paula, *Atkins' Physical chemistry*, Oxford University Press, Oxford; New York, 2006.

50. M. T. Clough, C. R. Crick, J. Grasvik, P. A. Hunt, H. Niedermeyer, T. Welton and O. P. Whitaker, *Chem Sci*, 2015, **6**, 1101-1114.

51. T. D. J. Dunstan and J. Caja, ECS Proceedings Volumes, 2004, 2004-24(1):312-325.

52. P. M. Bayley, A. S. Best, D. R. MacFarlane and M. Forsyth, *Chemphyschem*, 2011, **12**, 823-827.

53. T. Thomberg, E. Lust and A. Jänes, *Journal of Energy Storage*, 2020, **32**, 101845-101856.

54. H. Adams, C. A. Hunter, K. R. Lawson, J. Perkins, S. E. Spey, C. J. Urch and J. M. Sanderson, *Chemistry – A European Journal*, 2001, **7**, 4863-4877.

55. J. D. Holbrey, W. M. Reichert, R. P. Swatloski, G. A. Broker, W. R. Pitner, K. R. Seddon and R. D. Rogers, *Green Chemistry*, 2002, **4**, 407-413.

56. J. P. Min, J. K. Lee, S. L. Bang, Y. W. Lee and S. G. Lee, *Chemistry of Materials*, 2006, **18**, 1546-1551.

57. R. Tao, G. Tamas, L. Xue, S. L. Simon and E. L. Quitevis, *Journal of Chemical & Engineering Data*, 2014, **59**, 2717-2724.

58. C. Hardacre, J. D. Holbrey, C. L. Mullan, M. Nieuwenhuyzen, T. G. A. Youngs and D. T. Bowron, *The Journal of Physical Chemistry B*, 2008, **112**, 8049-8056.

59. N. J. Hestand and F. C. Spano, *Chemical Reviews*, 2018, **118**, 7069-7163.

6 Appendix

6.1 IR spectra

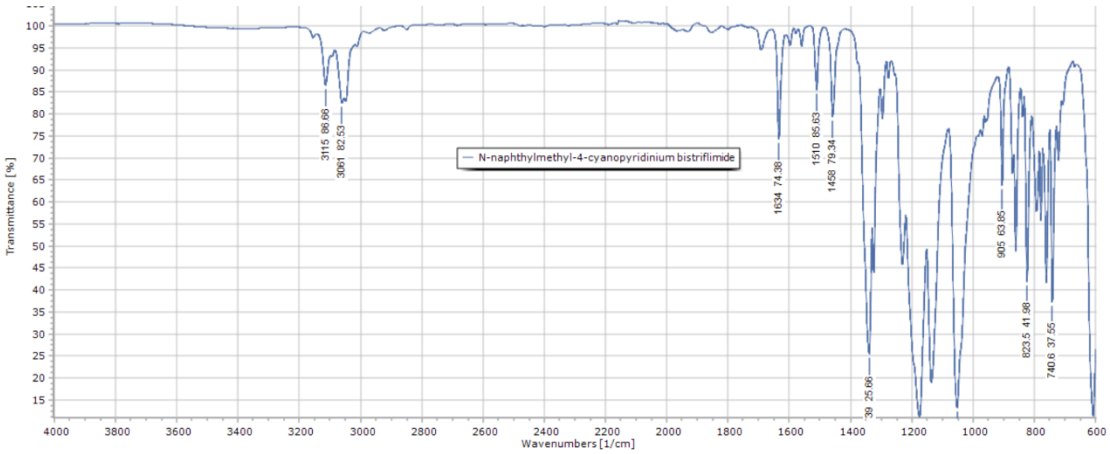


Figure 6-1: N-(2-naphthylmethyl)-4-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide

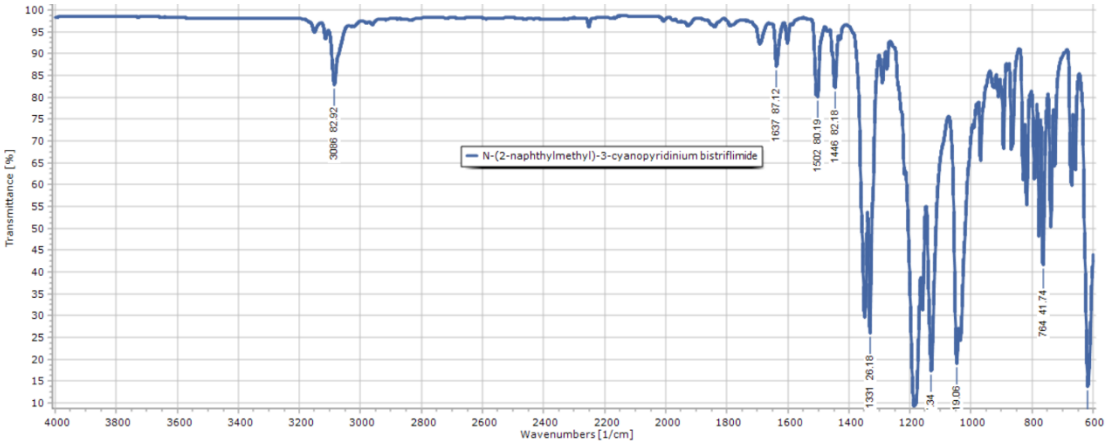


Figure 6-2: N-(2-naphthylmethyl)-3-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide

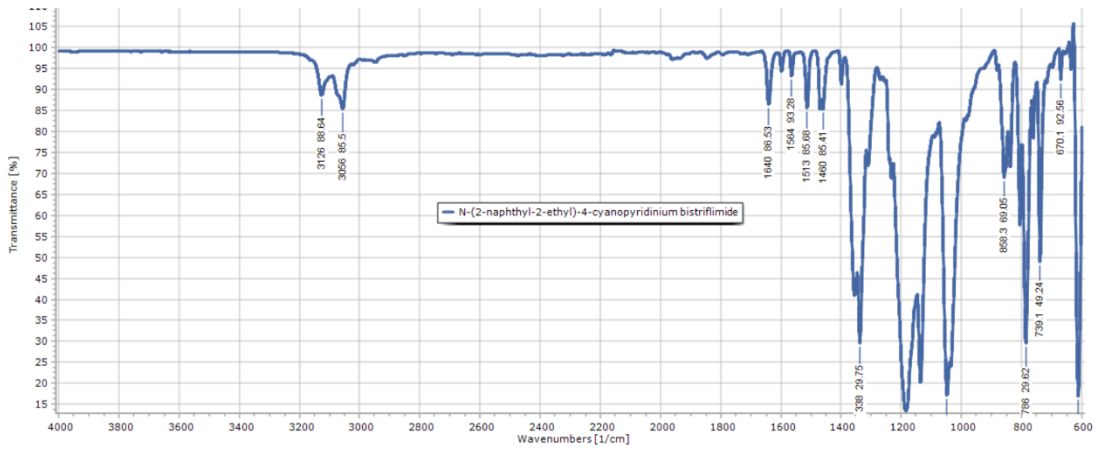


Figure 6-3: N-(2-naphthyl-2-ethyl)-4-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide

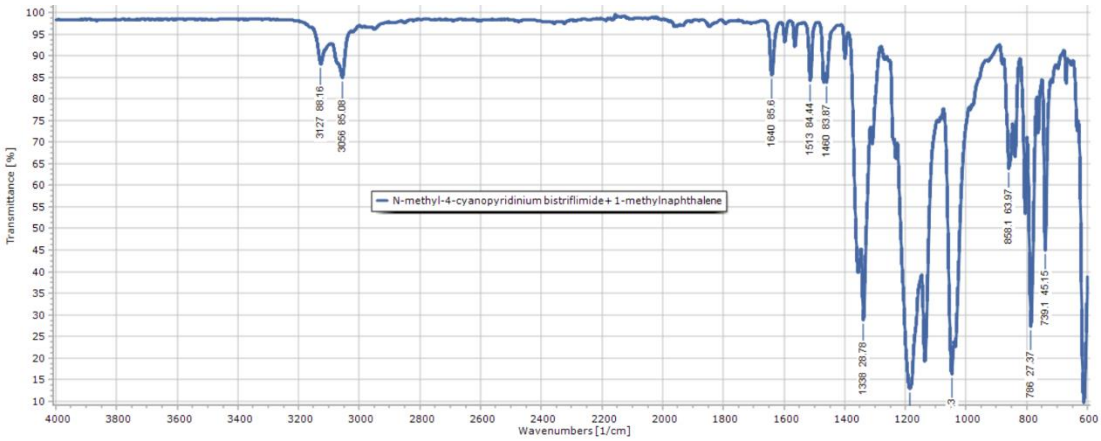


Figure 6-4: charge-transfer complex which are composed by 1-methyl-4-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide and 1-methylnaphthalene 1:1.

6.2 NMR spectra

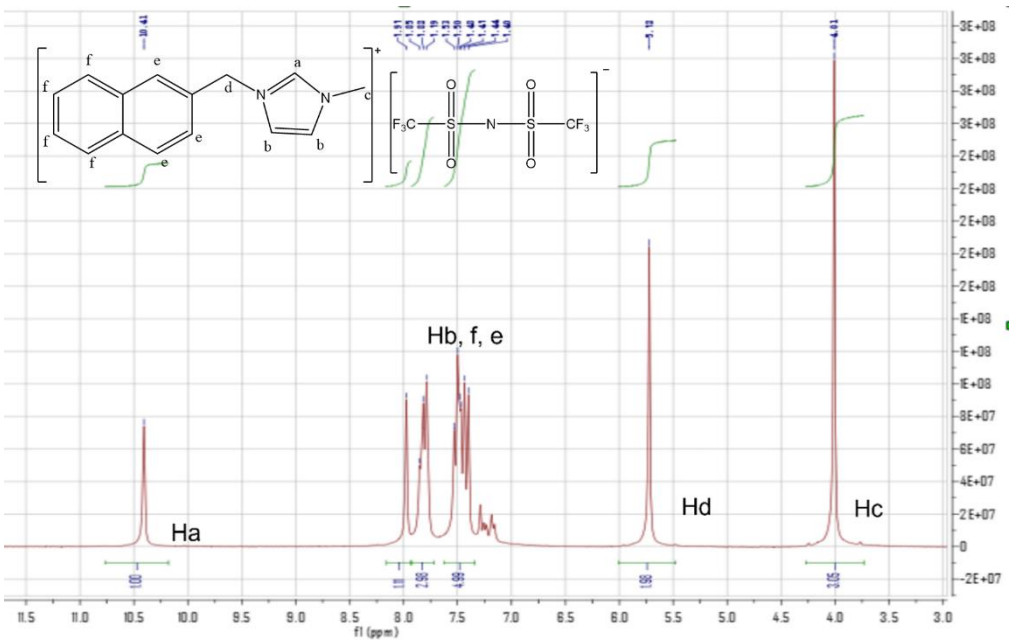


Figure 6-5: 1-methyl-3-(2-naphthylmethyl) imidazolium bis{(trifluoromethyl)sulfonyl}imide (1H NMR, 300 MHz, in $CDCl_3$)

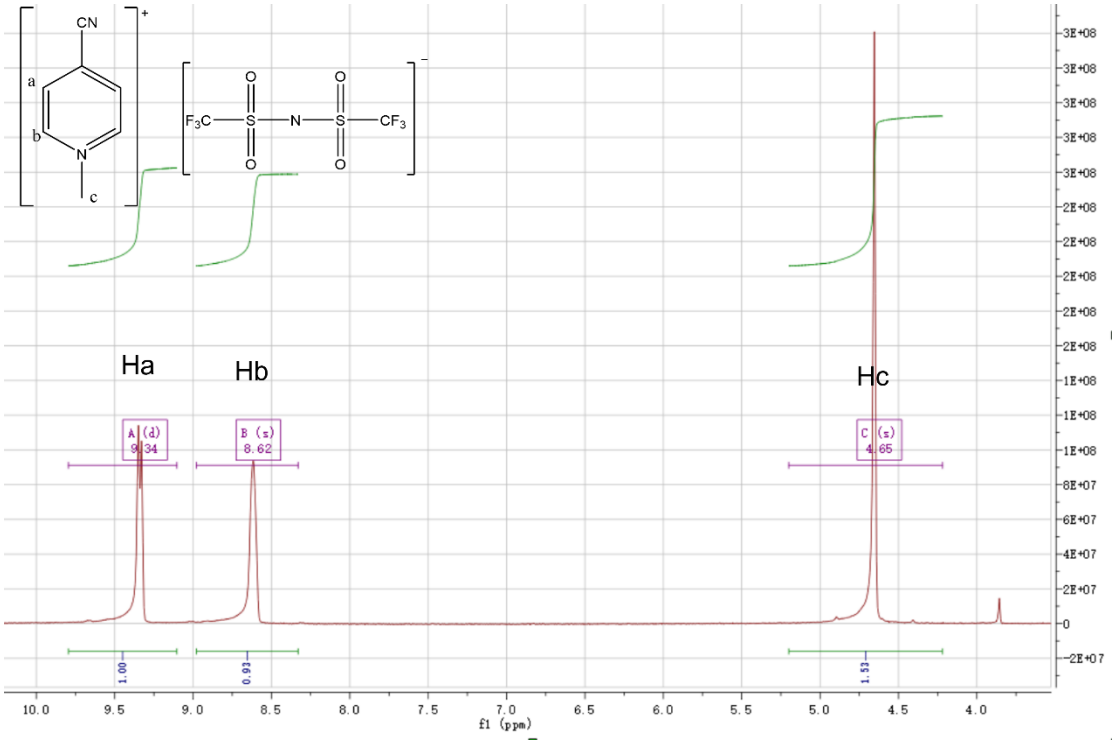


Figure 6-6: 1-methyl-4-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide (1H NMR, 300 MHz, in $CDCl_3$)

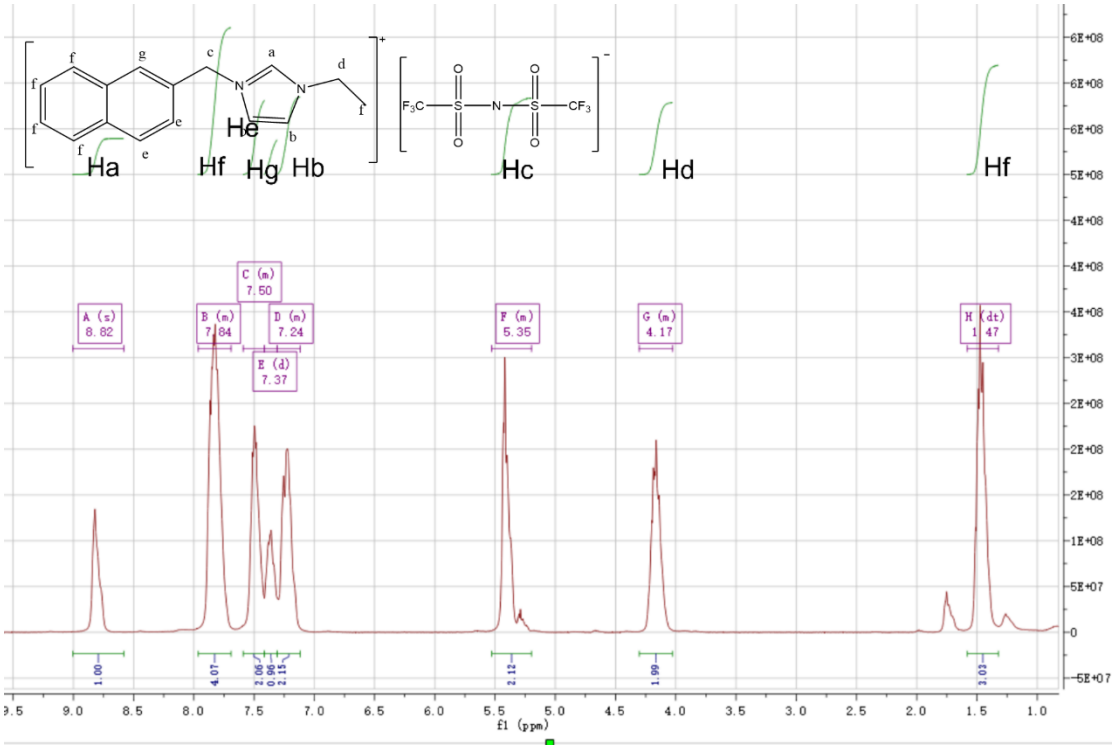


Figure 6-7: 1-ethyl-3-(2-naphthylmethyl)imidazolium bis{(trifluoromethyl)sulfonyl}imide (1H NMR, 300 MHz, in $CDCl_3$)

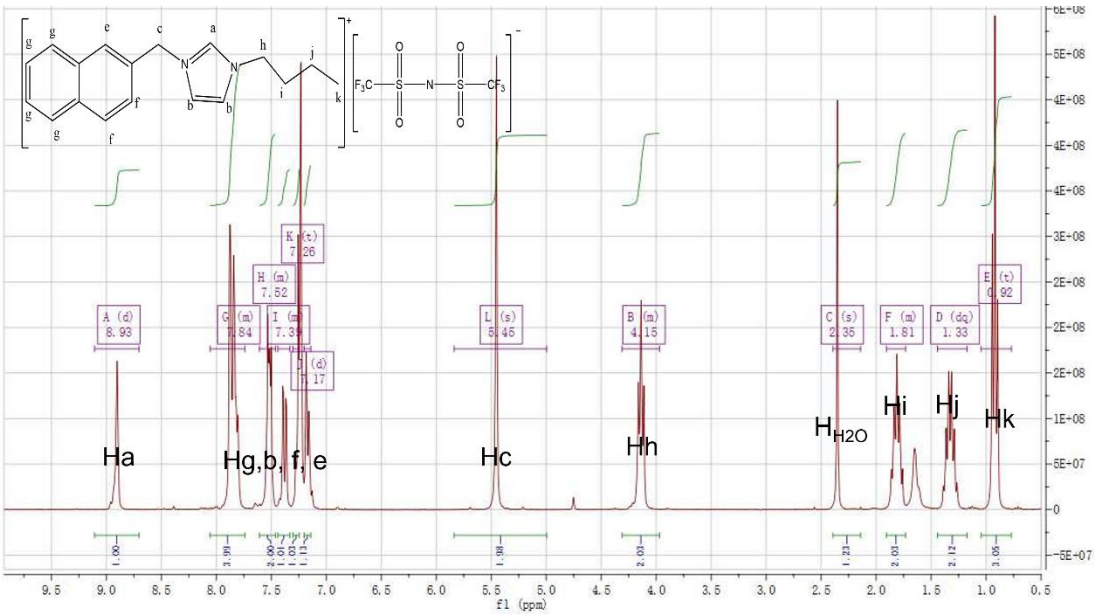


Figure 6-8: 1-butyl-3-(2-naphthylmethyl)imidazolium bis{(trifluoromethyl)sulfonyl}imide (the peak at 2.35 ppm is from the water in the ionic liquid.) (1H NMR, 300 MHz, in $CDCl_3$)

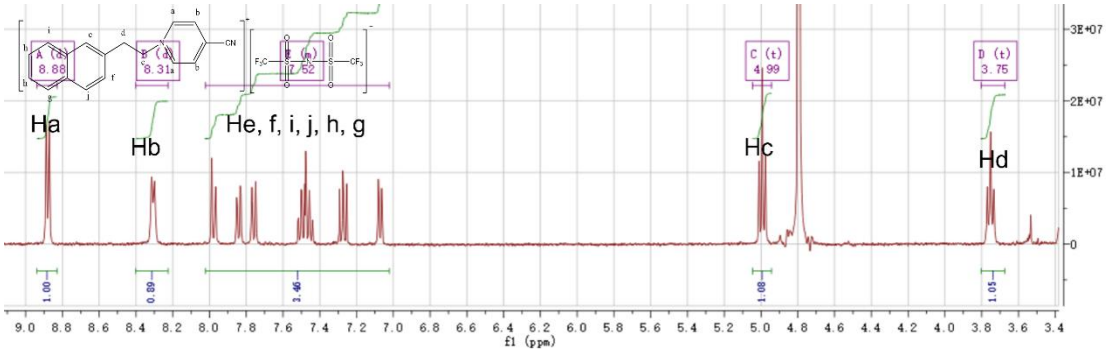


Figure 6-9: N-(2-naphthyl-2-ethyl)-4-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide (1H NMR, 300 MHz, in MeOD-d_4)

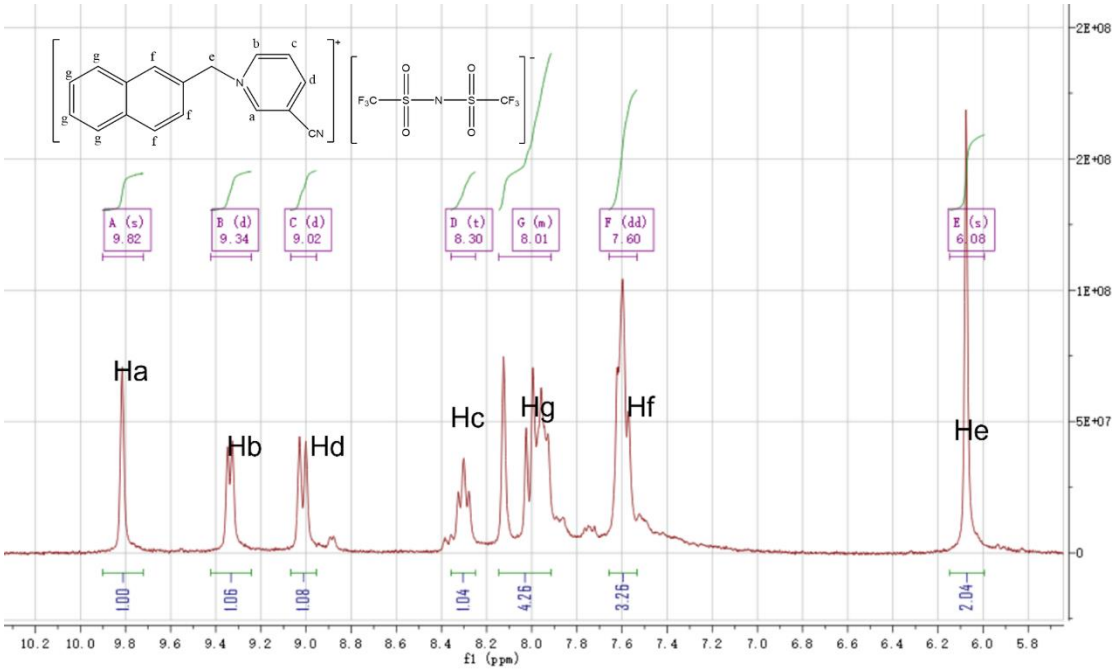


Figure 6-10: N-(2-naphthylmethyl)-3-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide (1H NMR, 300 MHz, in MeOD-d_4)

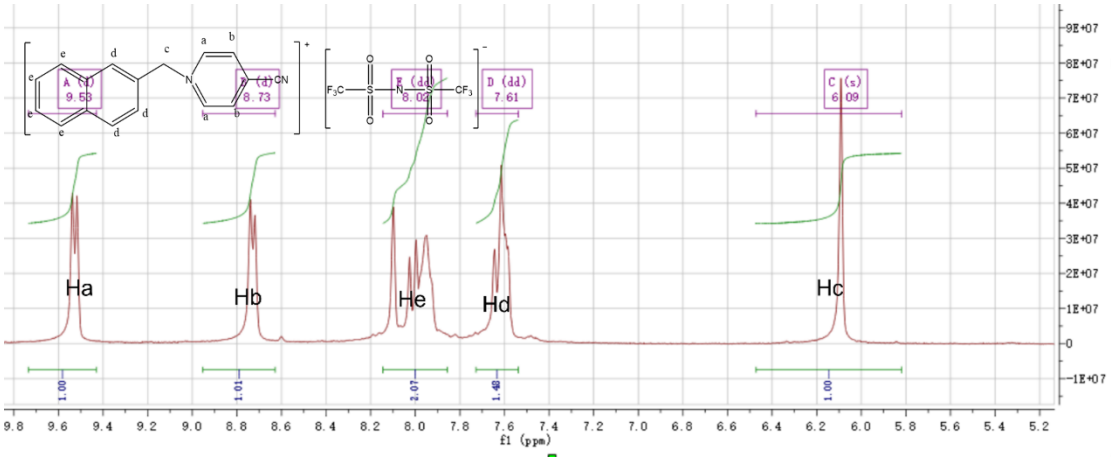


Figure 6-11: N-(2-naphthylmethyl)-4-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide (1H NMR, 300 MHz, in MeOD-d_4)

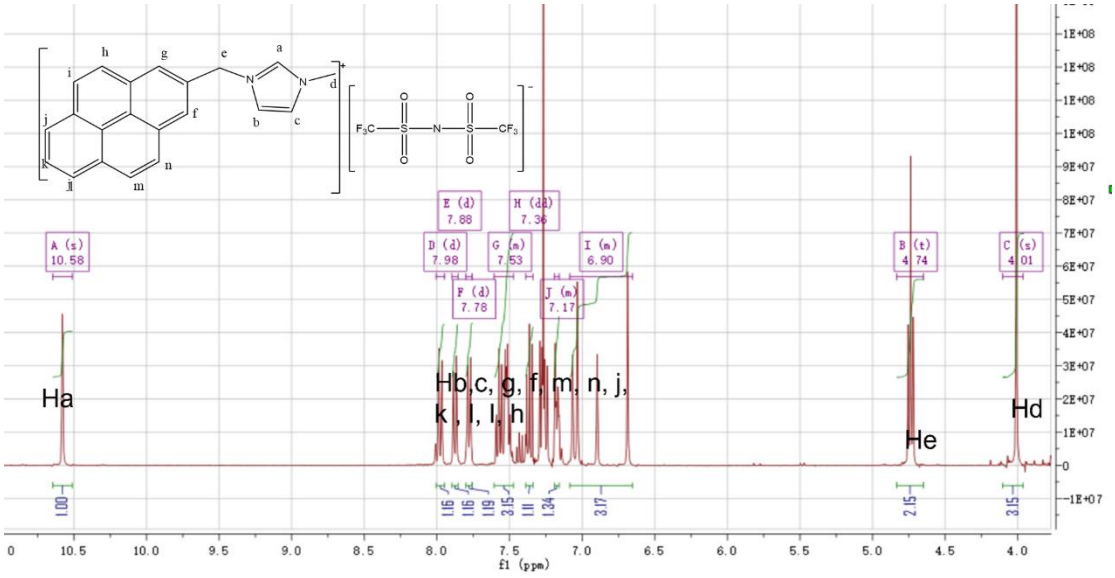


Figure 6-12: 1-methyl-3-(2-pyrenylmethyl)imidazolium bis{(trifluoromethyl)sulfonyl}imide (1H NMR, 300 MHz, in DMSO)

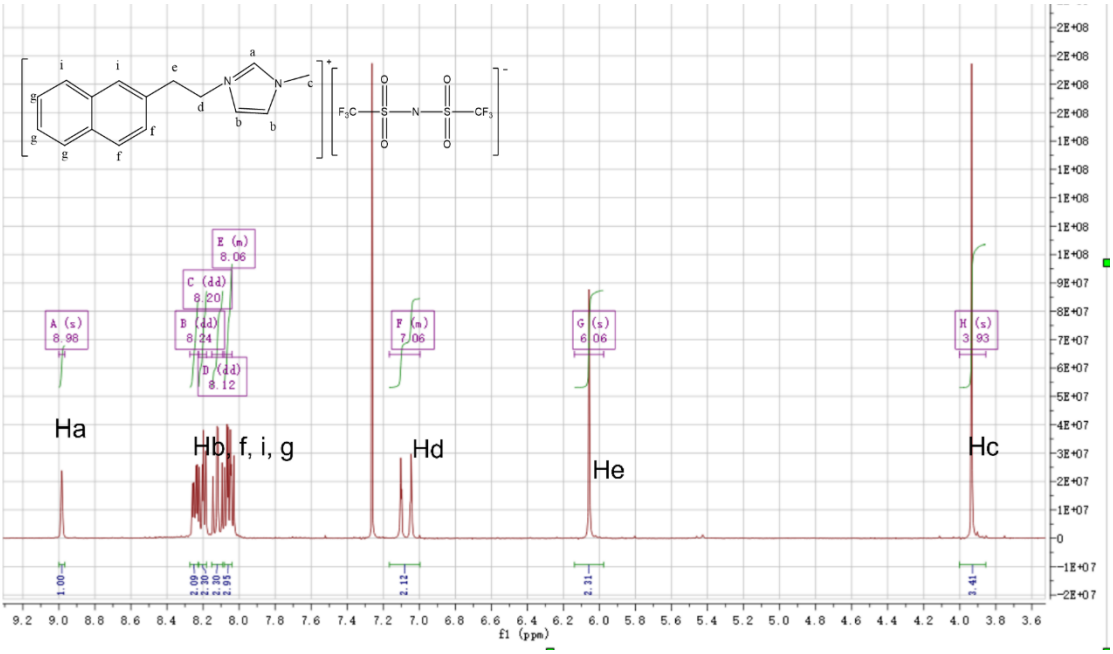


Figure 6-13: 1-methyl-3-(2-2-naphthyl-2-ethyl)imidazolium bis{(trifluoromethyl)sulfonyl}imide (1H NMR, 300 MHz, in $CDCl_3$)

6.3 TGA

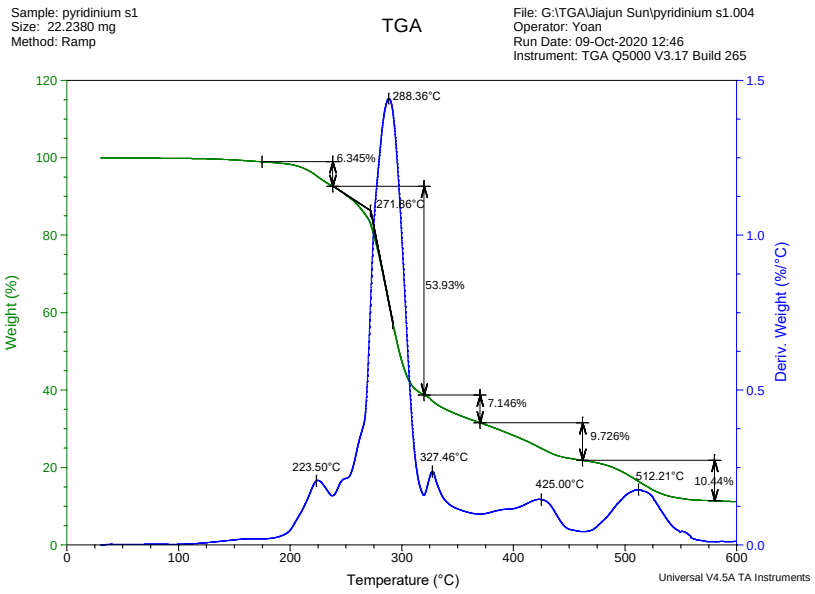


Figure 6-14: TGA mass loss profile for N-(2-naphthyl-2-ethyl)-4-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide

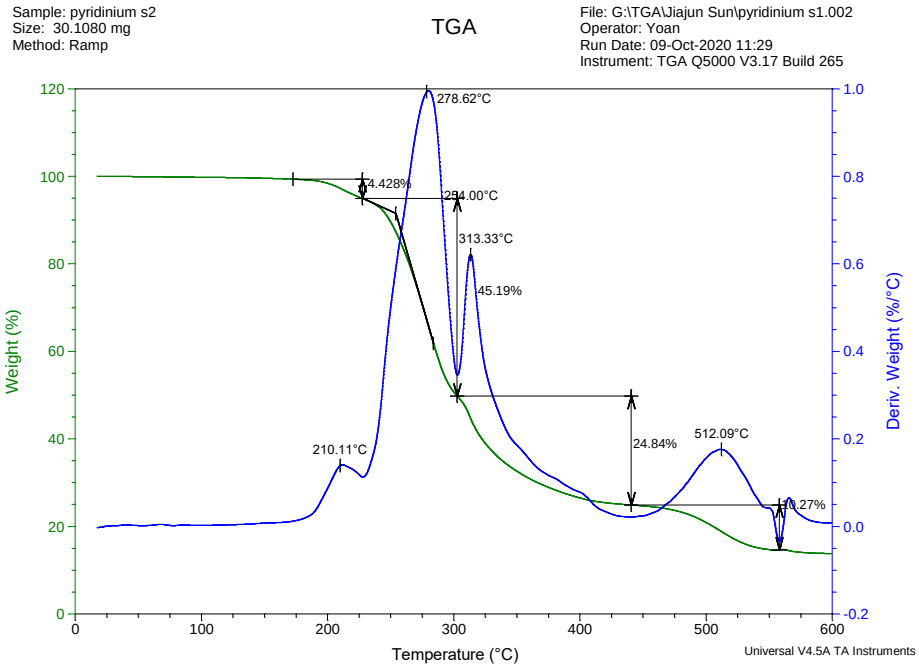


Figure 6-15: TGA mass loss profile for 1-methyl-3-(2-pyrenylmethyl)imidazolium bis{(trifluoromethyl)sulfonyl}imide

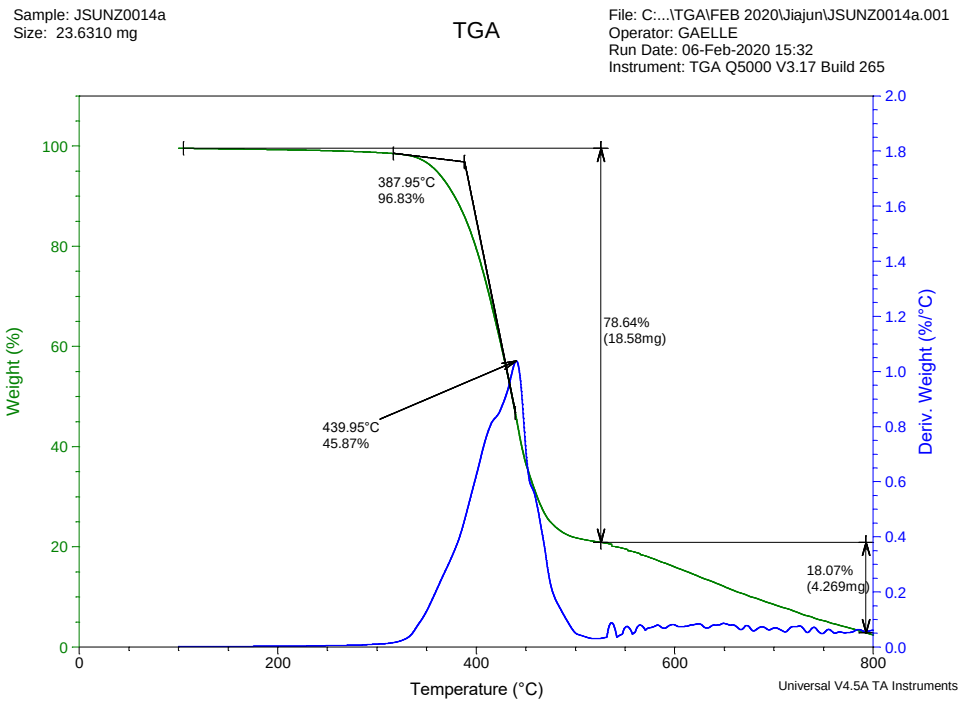


Figure 6-16: TGA mass loss profile for 1-butyl-3-(2-naphthalenylmethyl)imidazolium bis{(trifluoromethyl)sulfonyl}imide

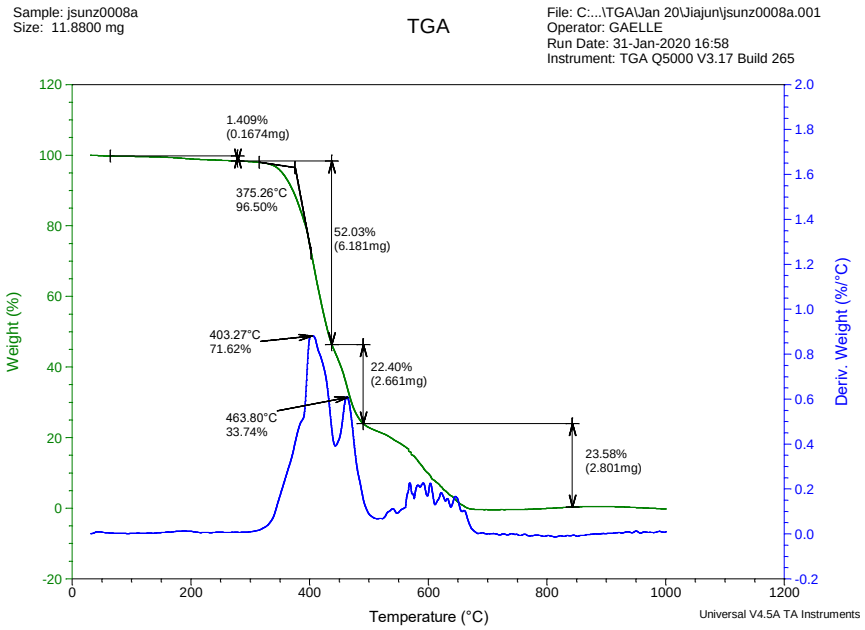


Figure 6-17: TGA mass loss profile for 1-methyl-3-(2-naphthalenylmethyl)imidazolium bis{(trifluoromethyl)sulfonyl}imide.

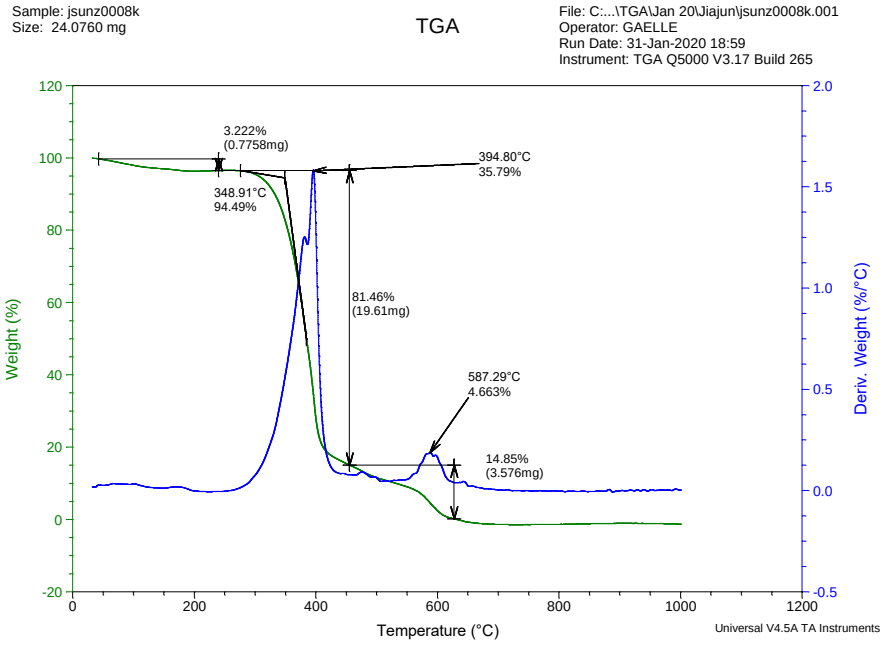


Figure 6-18: TGA mass loss profile for 1-methyl-4-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide

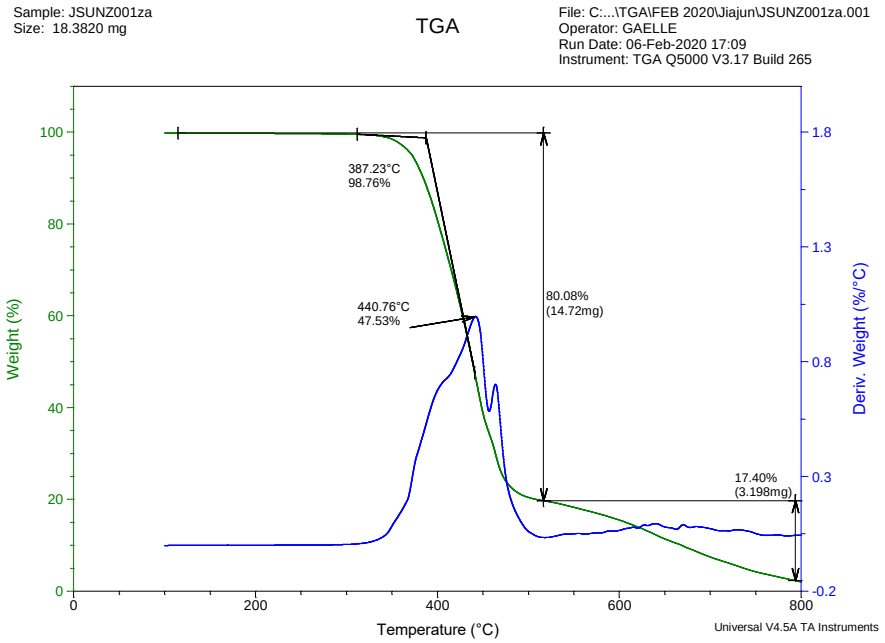


Figure 6-19: TGA mass loss profile for 1-ethyl-3-(2-naphthalenylmethyl)imidazolium bis{(trifluoromethyl)sulfonyl}imide

6.4 DSC

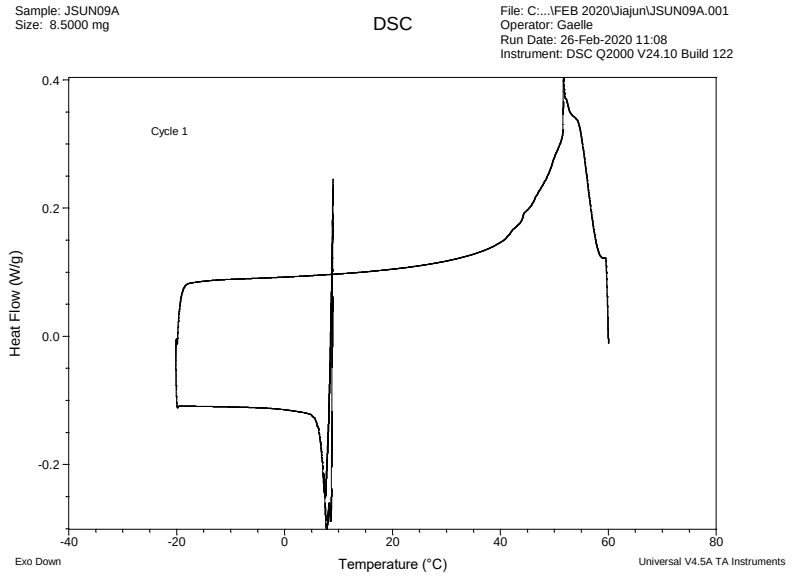


Figure 6-20: The DSC scanning cycle of ionic liquid mixtures which are composed by 1-ethyl-3-(2-naphthalenylmethyl)imidazolium bis{(trifluoromethyl)sulfonyl}imide and 1-methyl-4-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide by 1:3.

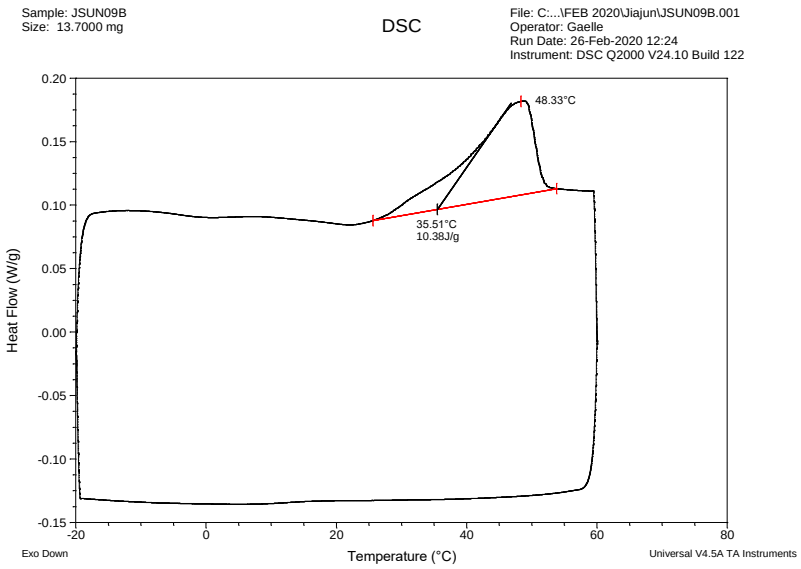


Figure 6-21: The DSC scanning cycle of ionic liquid mixtures which are composed by 1-ethyl-3-(2-naphthalenylmethyl)imidazolium bis{(trifluoromethyl)sulfonyl}imide and 1-methyl-4-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide by 1:1.

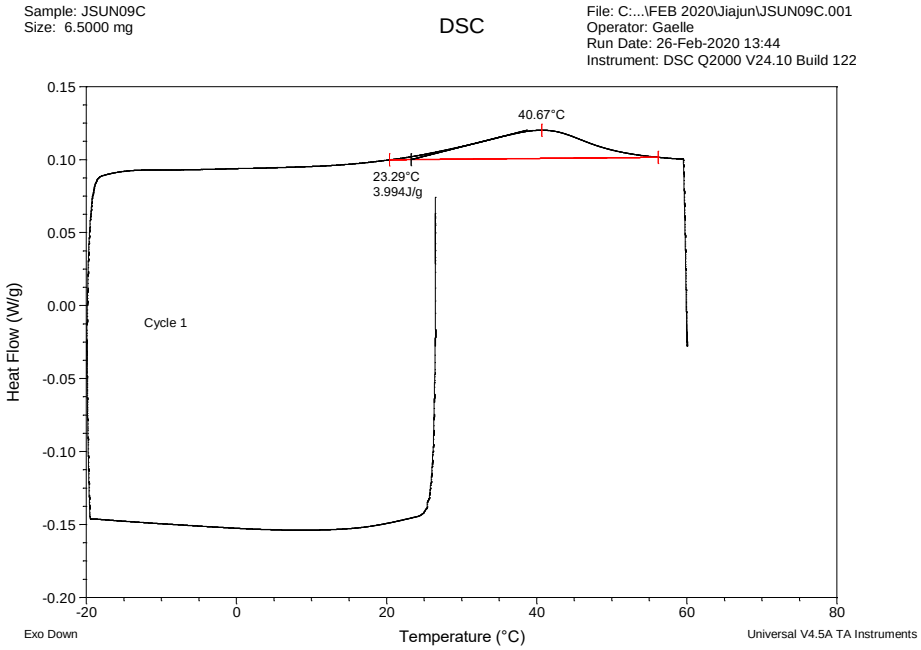


Figure 6-22: The DSC scanning cycle of ionic liquid mixtures which are composed by 1-methyl-3-(2-naphthalenylmethyl)imidazolium bis{(trifluoromethyl)sulfonyl}imide and 1-methyl-4-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide by 3:1.

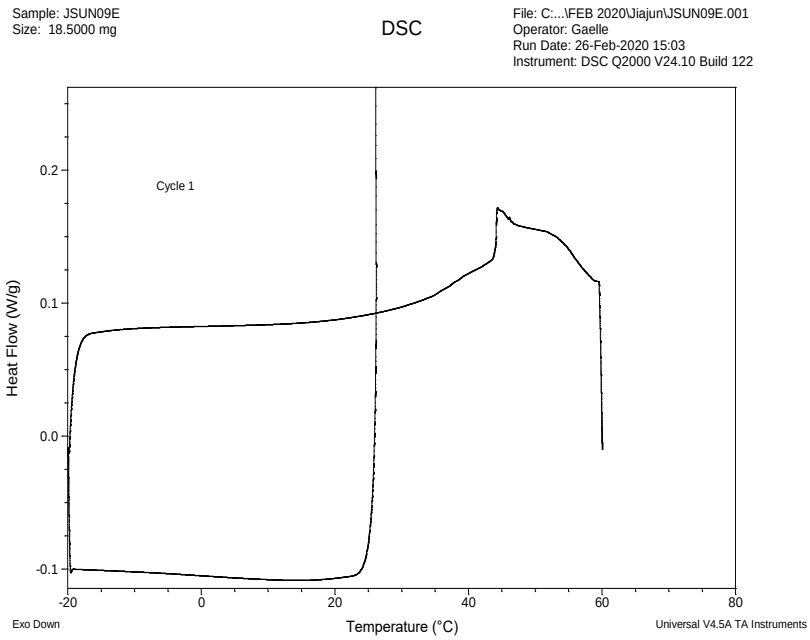


Figure 6-23: The DSC scanning cycle of ionic liquid mixtures which are composed by 1-butyl-3-(2-naphthalenylmethyl)imidazolium bis{(trifluoromethyl)sulfonyl}imide

and 1-methyl-4-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide by 1:3.

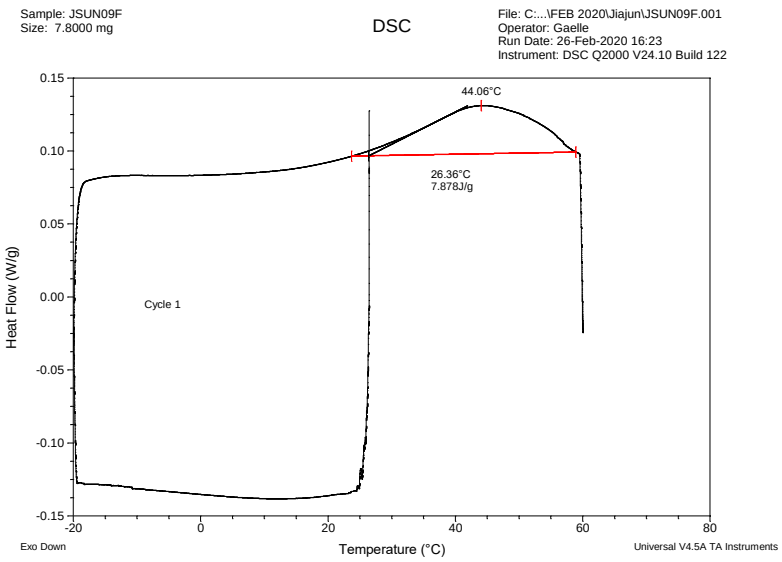


Figure 6-24: The DSC scanning cycle of ionic liquid mixtures which are composed by 1-butyl-3-(2-naphthalenylmethyl)imidazolium bis{(trifluoromethyl)sulfonyl}imide and 1-methyl-4-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide by 1:1.

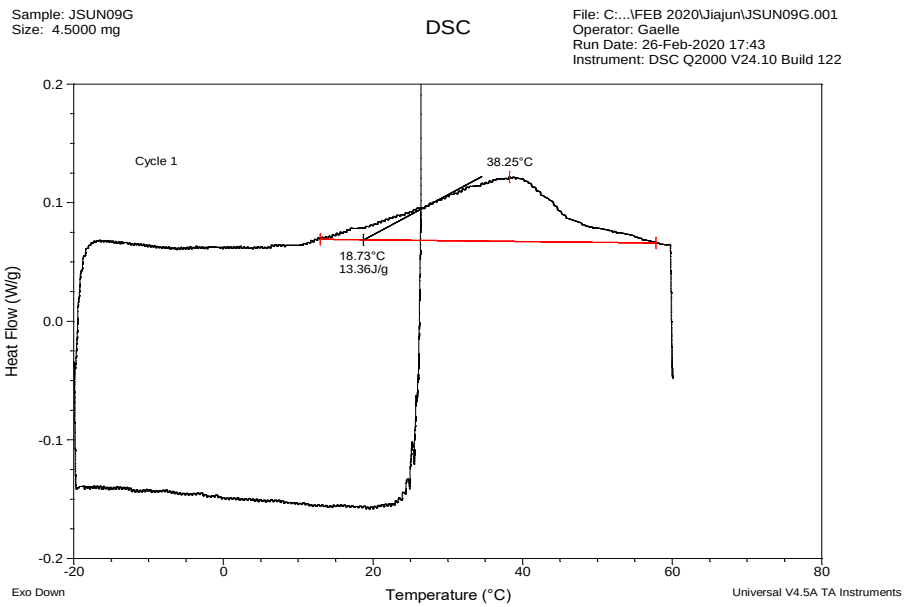


Figure 6-25: The DSC scanning cycle of ionic liquid mixtures which are composed by 1-butyl-3-(2-naphthalenylmethyl)imidazolium bis{(trifluoromethyl)sulfonyl}imide and 1-methyl-4-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide by 3:1.