People's Democratic Republic of Algeria

Ministry of Higher Education and Scientific Research

Dr Moulay Tahar University of Saida

Faculty of Sciences

Department of Chemistry

Dissertation

Presented by:

Sara Taibi and **Warda Yazid**

Presented to obtain the Master's degree of the 2nd Cycle

Specialty: **Organic chemistry**

Theme:

Synthesis, vibrational and thermal properties of new dicationic ionic liquids DILs

Defended on: 13/07/2021 in front of the jury composed of

Miss	MOSTEFAI Asmâa	Prof. at Dr Moulay Tahar University of Saida	President
Mr	HADDAD Boumediene	Prof. at Dr Moulay Tahar University of Saida	Supervisor
Mr	BRAHIM Houari	Prof. at Dr Moulay Tahar University of Saida	Examiner
Mr	BOUMEDIENE Mostefa	Dr.at Dr Moulay Tahar University of Saida	Co-supervisor

Academic year 2020/2021

Acknowledgment

First of all, I thank God for giving us the strength to get here,

This work was carried out at the “Dr Moulay Tahar” University of Saida in university chemistry department.

We thank **Professor Boumediene Haddad**, thesis director, for giving us the opportunity to work on this wonderful topic, for his many tips to guide us.

We extend our sincere thanks and gratitude to **Dr. Mustafa Boumediene** for standing with us at all times of our work.

I would like to extend our sincere thanks to **Prof. MOSTEFAI Asmâa** for her participation before she became the head of the jury.

Without forgetting **Prof. BRAHIM Houari** for his participation as a member of examiners on this jury.

I would also like to thank everyone who helped us from far and near.

Dedication

This research is lovingly dedicated to my ***respective parents****, who continually provide moral, spiritual, emotional and financial support.*

To my beloved sisters: Hanane, Selamet, Aya and Chaimaa;

To my loving brothers: Zakaria, Yacine and little one Mohammed;

To my ***sweet beloved grandparents****;*

To my uncls: Yahya, Mohammed, Farid and Morad; and thier wives;

To my other mothers "aunties": Bouh and Nour;

This is my large extensive family who have been my constant source of inspiration, they have given me the drive and discipline to tackle a task with enthusiast and determination.

To my only two friends ever: Assma and Warda without their support the dissertation would not have been made possible.

-SARA TAIBI

Dedication

I dedicate this modest work:

To the two dearest beings, my father and my mother, for their love, their support and their sacrifices, as a testimony of my great esteem.

To my very dear brothers "Anes, salim, mosaab and yousef" who give me the courage, and all the possibilities to succeed and finish my studies.

To my very dear sisters "Assia, asma, Khadija and chaimaa" for their benevolent attention, their encouragement, their help and their love.

To my uncle and his wife.

To my faithful friends "Sara and Assma" and their families.

To all the promotion of organic chemistry 2020/2021

To all who love me and who I love too.

-WARDA YAZID

List of figures:

Chapter 1

Chapter 2

Chapter 3

List of schemas:

Chapter 1

Chapter 2

Chapter 3

List of tables:

Chapter 1

Chapter 2

Chapter 3

Abbreviations list

ILs: Ionic Liquids

DILs: Dicationic Ionic Liquids

TGA: Thermal gravimetric analysis

DTA: Differential thermal analysis

M_p: Melting point

T_d: Thermal decomposition temperature

FTIR / ATR: Fourier transform infrared spectroscopy / Attenuated total reflectance

NMR: Nuclear Magnetic Resonance

NTf_2^- : $(CF_3SO_2)_2N^-$:(trifluoromethylsulfonyl) imide

Contents

part 2: Materials and experimental techniques

Chapter 3: Results and discussions

General Introduction

General Introduction

In the last century, a lot of awareness has been spread about environmental pollution and the development of its danger to the planet and to human health alike, and the main accused is the chemical industrial sector as a major cause of air pollution caused by volatile gases from organic solvents, therefore, the scientific community of researchers worked on discovering and developing of new organic solvents as alternatives to the old, toxic and flammable ones, with a new ones that were less harmful and volatile.

This new class was known as "ionic liquids" (ILs) and was also known that it is environmentally friendly thanks to its convenient physical and chemical properties, such as its high thermal stability, extremely low vapor pressure and non-flammability. For that reason, they were considered as "green" alternatives to common solvents. In the last two decades, researchers have intensified work on this class of solvents and its physical and chemical properties what controls it is in general is the structure of these liquids, such as the size of the ion, the length of the side chain, or the functional group.

Because of their potential application in green chemistry and as a group of new electrochemical materials. Ionic liquids (ILs) have already become "design solvents" with many of them designed for a specific application, for example as potential electrolytes for various electrochemical devices, including rechargeable lithium batteries. The number of potential cation-anion combinations available corresponds to one trillion of different ILs, so by modifying the chemical structure of the cation-anion combination, it is possible to adjust their properties. For this, a detailed research of the structure-property relationship of ionic liquids is essential. In this context, the target of this research is centered.

Our dissertation entitled “Synthesis, vibrational and thermal properties of new dicationic ionic liquids (DILs)”. On this subject, the understanding of the relation between structure, spectroscopic and thermal properties of an ionic liquids and its presents a paramount parameter to target a precise application.

For this reason, our strategy is to synthesis a new DILs and to modify the structures of these ionic liquids. In this regard, we vary the nature and size of dicationic ionic liquids and its side chain, with incorporating an aromatic group as a bonding spacer between the two 1-butyllimidazolium units gives a new class of materials called dicationic ionic liquids (DILs), to determine the origin of significant effects on structural, vibrational spectroscopic and thermal properties. Para-xylyl linked synthesized DILs combined with three anions respectively bromide, hexafluorophosphate and bis (trifluoromethylsulfonyl) imide.

The information related to the theory, as well as to the cation / anion interactions that enter into the composition of ionic liquids, have been the subject of several studies by vibrational spectroscopies, as well as the analysis of these ionic liquids by Infrared spectroscopy (IR), Raman and thermal analysis, so do ours, which allowed us to estimate the interactions that exist in these ILs and in order to give an interaction in these DILs, the combination between experimental parts and theory of these compounds at the molecular scale.

Our manuscript consists of four chapters, in addition to the general introduction, in the first chapter, we present a bibliographic analysis on ionic liquids, discussing their different properties as well as the different methods used to access them. In the second one and in order to better understand the different vibrational spectroscopic properties, we will present similar works, also the third chapter is devoted to the experimental study including the material and the methodology of preparation of our materials (synthesis of dicationic ionic liquids 'DILs'), followed in the last chapter by an interpretation of the results obtained following characterizations of these synthesized DILs and the study of their structural, thermal and vibrational spectroscopic properties. Finally, a conclusion contain our important results.

Chapter 1

Basic knowledge about ionic liquids

1.1 Introduction :

Ionic Liquids (ILs) with their unique structure that can be variable , this variability lead to produce vast range of physical, chemical, and even electrochemical, thermal properties (1). ILs often called molten salts because they have a melting point below 100 °C, as they called, they are a liquids that completely made of many coupled ions (2), the amount of research in ILs area has increased over the past two decades because they have shown an interesting industrial applications (3), nowadays research on chemistry of ILs could be almost both necessary and needed seeing that ILs enter in so many branches of modern industry such as:

- Energy storage (71)
- Material science (72)
- Pharmacy (73)

They even considered green solvents and good substitute to volatile organic solvents (4).

1.2 History of ionic liquids:

In 1877, french scientific journal published friedel-crafts reaction, they observe and separate red-colored phase during the reaction of toluene formation by the mix of benzene and chloromethane catalyzes by $AlCl_3$, they called the phase “red oil”, and when NMR spectroscopy could be available in chemistry one century later, japanese chemists discovered that this phase is an ionic liquid (5).

In 1914, during Paul Walden's reaction which is the neutralization of ethylamine by concentrated nitric acid, he observes the physical properties of ethyl ammonium nitrate ($[EtNH_3][NO_3]$) like his molting point (m_p: 13–14 °C) and considered as the first ionic liquid and the beginning of this interesting filed (6).

The progress was very slow and there's no other ionic liquid reported until 1951 by Hurley and Weir (7). In 1980 John Wilke (7) discovered " imidazolium-based ILs" family, and the amount of research started to increase and this new class of compounds started to be interesting in the late 1990's, precisely in years 1998-2000 ..(7)

1.3 Definition:

Ionic liquids are a new class of compounds that have an interesting properties such as:

- High conductivity
- Low melting point
- Low viscosity (8)
- Very low vaporization voltage
- Thermal and chemical stabilities
- High solubilities (9)

Depending on the number of cation paired with anion, there are two type on ILs:

- monocationic (10)
- dicationic (10)

According to its properties and different types, ILs have been widely used, its applications are:

- Electrolytes in lithium batteries (74)
- Solvents in high temperature organic synthesis (75)
- Additive in dye-sensitized solar cells (76)
- In extraction liquids (77)
- In mass spectroscopy (78)

1.4 Nomenclature:

Ionic liquids are liquid organic salts differing from all molten salts by a melting point of less than 100 °C (arbitrarily fixed with reference to the boiling point of water) but a large number of them are liquid at room temperature, called RTIL's (room temperature ionic liquids)[11]. These solvents are formed by the combination of organic cations and anions, with almost infinity variations of structures both at the level of anions and cations. Among the most studied cations, mention may be made of quaternary ammoniums and polycyclic aromatic compounds such as imidazolium and pyrrolidinium rings, while alkylpyridinium, alkylphosphonium or alkylsulfonium cations are less frequently encountered.

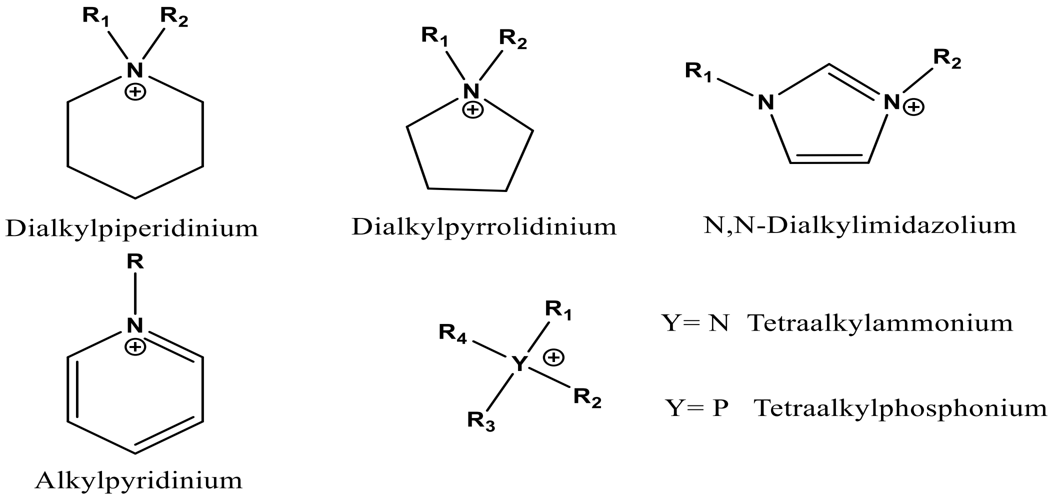
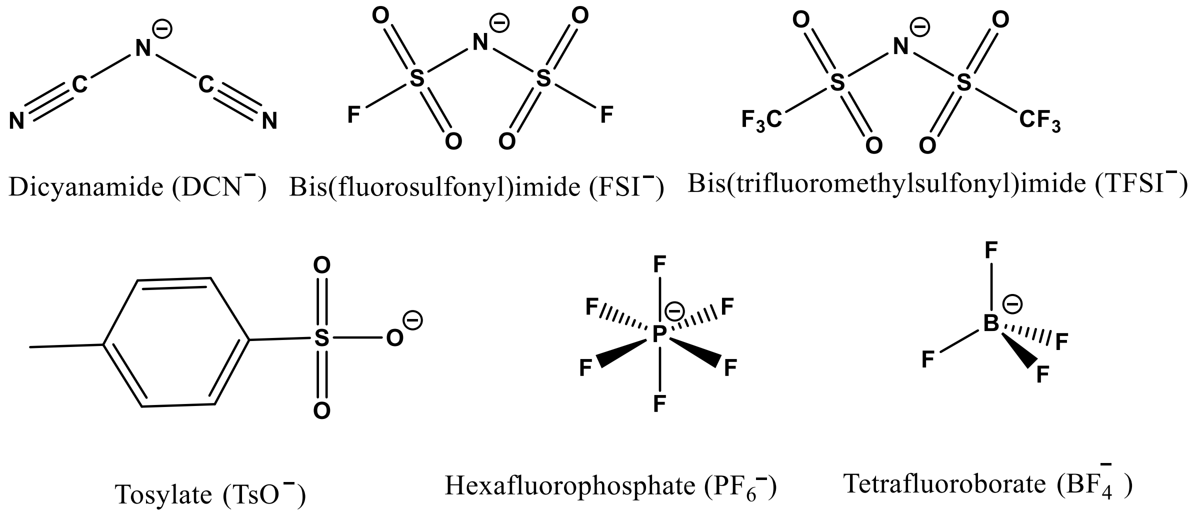


Figure 1.1: Examples of cations that can be paired with anions to produce ionic liquids.

The most widely used counterions are either inorganic anions such as: BF_4^-, PF_6^-, Cl^-, NO_3^-, $AlCl_4^-$, SbF_6^- etc… or organic anions ($CF_3SO_3^-$, $(CF_3SO_2)_2N^-$, $CF_3CO_2^-$ and $CH_3CO_2^-$ etc…). The tetrafluoroborate (BF_4^-) and hexafluorophosphate (PF_6^-) anions are widely used in organic or organometallic chemistry because they confer a desired solubility to the ionic species which are the basis of a large number of liquid salts.



Dicyanamide (DCN$^-$) Bis(fluorosulfonyl)imide (FSI$^-$) Bis(trifluoromethylsulfonyl)imide (TFSI$^-$)

Tosylate (TsO$^-$) Hexafluorophosphate (PF_6^-) Tetrafluoroborate (BF_4^-)

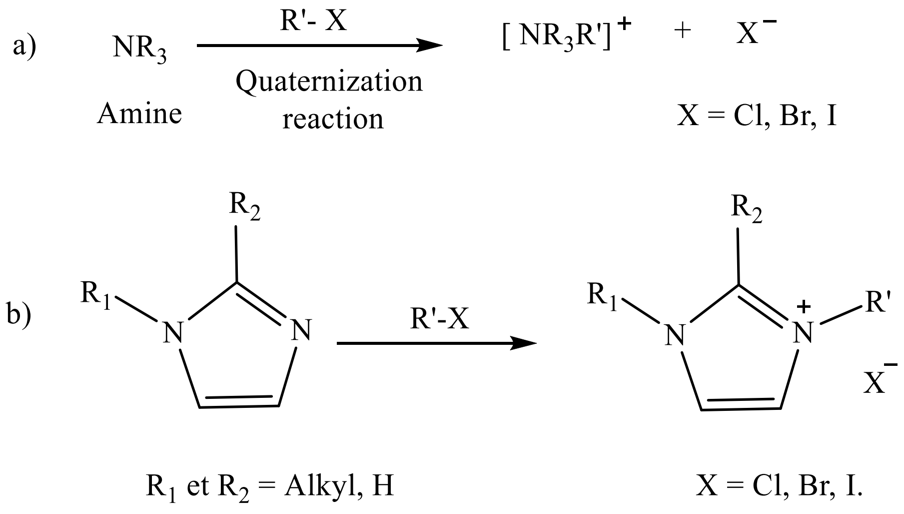
Figure 1.2: Examples of anions that can be paired with cations to produce ionic liquids.

1.5 Synthesis:

The very large diversity of possible cation and anion pairings allows access to unlimited preparation of ILs, generally the synthesis of the ionic liquid distributed in two stages, the formation of cation required then the exchange of anions to have the ionic liquid targeted, in some cases, a second step is not needed, as an example the formation of ethylammonium nitrate, in other cases the cation does exist, all what's needed is the second step which is anion exchange, such as halide salt (12).

1.5.1 Quaternization/Alkylation reaction:

A so-called quaternary compound if its cation consists of a central pnictogen atom (nitrogen, phosphorus, etc.), carries a positive charge, with an environment of four substituents, in particular organic groups (alkyl, aryl, etc.), without counting hydrogen atoms. There are two mechanisms for preparing the cation, either by carrying out protonation in an acidic medium or quaternization of an amine with a haloalkane. Quaternary ammoniums [13] (nitrogen is the central atom) and phosphoniums [14] (phosphorus is the central atom) are the most common quaternary compounds in this field. Quaternization reactions can proceed without the use of a solvent, a relatively polar solvent such as acetonitrile or methanol is generally required for a cleaner synthesis.



Scheme 1.1 General mechanism of quaternization of an amine (a) and an N-alkylimidazolium (b).

Among the structural parameters that directly influence the thermophysical properties of ionic liquids, we can mention:

- The length of alkyl chain.
- The choice of the halide determines the solubility of the product.
- The size of the coupled cation-anion.
- The reaction conditions, such as temperature and/or pressure.
- The presence of impurities can affect their physicochemical properties.

Usually, the longer the alkyl chain, the longer the time required for a complete reaction. Often, the reaction is refluxed to reduce reaction time [15].

1.5.2 Anion exchange reaction:

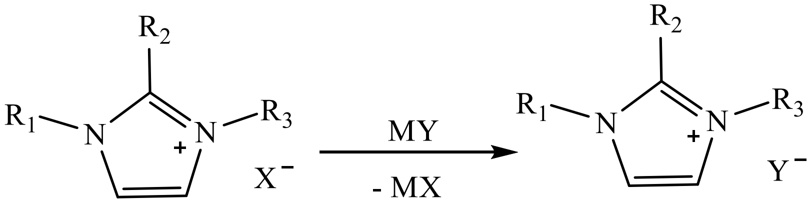
Most of the time, the counterion obtained from the quaternization process is not the desirable ion, so it is necessary to carry out an anion exchange reaction. The anion exchange reactions of ionic liquids can be divided into two reactions:

- Metathesis of anions.
- The direct reaction of halide salts with Lewis acids to form ionic liquids.

1.5.2.1 Metathesis:

The reaction where the halide of the quaternary salt is exchanged with another anion of choice is a metathesis reaction which can be carried out by one of two methods depending on the water solubility of the ionic liquid. If the target IL is hydrophilic, then the reaction is generally carried out in polar solvents (water, acetonitrile, DMSO, acetone, etc.).

In this case, a range of water soluble silver salts such as silver nitrate Ag [NO_3], silver tetrafluoroborate Ag [BF_4] or silver dicyanamide Ag [$N(CN)_2$] can be used as the source of the desired anion. In such reactions, in addition to the water soluble product, a water insoluble silver halide is generated as a precipitate. If the desired IL is immiscible in water, then other synthetic methods should be used. An example of such a case is the synthesis of [C_2mim] [$(CF_3SO_2)_2N$], and this synthetic method is in fact generally useful for most salts of Bistriflimide (NTf_2) (16-20).



R_1, R_2 et R_3 = Alkyl X= Cl, Br, I MY=$LiNTf_2$, KPF_6, NH_4BF_4 .....

Scheme 1.2: General mechanism of the protonation of an N-alkylimidazolium.

1.5.2.2 Lewis acid-based ionic liquids:

The formation of ionic liquids by the reaction of halide salts with Lewis acids is usually very exothermic, which requires us to be careful when adding one reagent to another. The syntheses of ionic liquids are carried out either by conventional traditional methods (reflux, etc.) or by modern methods (microwave irradiation, ultrasound irradiation, etc.) (21).

$$[\mathrm{RMIM}]^+\ \mathrm{Cl}^- \quad + \ \mathrm{AlCl_3} \quad = \quad [\mathrm{RMIM}]^+\ [\mathrm{AlCl_4}]^- \qquad \text{(a)}$$

$$[\mathrm{RMIM}]^+ \quad [\mathrm{AlCl_4}]^- + \ \mathrm{AlCl_3} \quad = \quad [\mathrm{Al_2Cl_7}]^- \qquad \text{(b)}$$

$$[\mathrm{RMIM}]^+\ [\mathrm{Al_2Cl_7}]^- + \ \mathrm{AlCl_3} \quad = \quad [\mathrm{Al_3Cl_{10}}]^- \qquad \text{(c)}$$

Scheme 1.3: reaction of a quaternary halide salt with a Lewis acid.

1.5.3 Purification of ionic liquids

The purity of ILs is an important parameter, because the presence of impurities can affect their physicochemical properties as well as their reactivity (23).

The non-volatility of the ILs can be advantageous in the case where the other chemical species present in the medium are volatile, because in this case it is easily possible to carry out a distillation to recover the IL (24). However, in the case where one or more other species present in the medium are not volatile, purification by distillation becomes not used anymore. Noted that the purification by chromatography is also difficult to envisage, because the strong polarity of the ILs prevents them from migrating correctly (25).

Although some recent progress has brought solutions to a good number IL's problems of purification, in particular in industrial processes (26), the fact remains that these methods remain very dependent on the specificity of the species used in these processes, and obviously cannot be generalized (27). Particular care must therefore be taken during the synthesis to minimize the presence of impurities, in particular the starting substrates and traces of water.

Regarding the anion exchange step, it’s relatively difficult to set up purification methods given the proximity of the properties of the ILs before and after the exchange (solubility in solvents as well as physical state often similar). It is therefore essential to ensure that the exchange is as complete as possible, in particular by introducing an excess of the exchange reagent to promote balance in the desired direction (22).

1.6 Properties:

There are a range of thermal properties that are important for ILs applications. Their thermal stability is the most important and the most widely cited, this latter information can be obtained by thermogravimetric analysis (TGA) coupled to a mass spectrometer or by pyrolysis mass spectrometry. There is therefore growing interest in the ability to predict the thermophysical properties and behavior of ionic liquids from simple structural information. Given the importance of these properties, recent advances in our understanding, prediction and correlation of some physical properties of these ionic liquids (28).

The properties of ILs are mainly related to their ability to act as a hydrogen bond donor or acceptor. Van Der Walls interactions are one of the important parameters which strongly depend on the type of anion involved, it can thus be noted that the ionic liquids having a tetrafluoroborate anion (BF_4^-) have a lower viscosity than those having a counterion: hexafluorophophate (PF_6^-).

1.6.1 Melting point:

A molten salt is defined as an ionic liquid when generally its melting point is less than 100 ˚C. The melting temperature is influenced by the charge distribution on the ions, the capacities of hydrogen bonds, the symmetry of the ions and the Van der Waals interactions. There is great uncertainty about the value of many melting points of ionic liquids from the literature (30), because some ILs have the property of being supercooled, that is to say, they have a temperature range in which they pass through a glassy crystalline phase. Indeed, Ngo et al (30) have shown that the melting point of some ILs can vary greatly depending on whether they are heated or cooled (30). Supercooled state is a characteristic associated with many ionic liquids based on imidazolium cations (29–31). For example, the literature indicates that the imidazolium cations combined with the Tf_2N anions are generally liquid above -30 to - 50˚C, but they become very viscous to the glassy state without our being able to observe their melting point (29).

The influence of the symmetry of the 1,3-dialkylimidazolium cation on the value of the melting point of ILs has also been studied by Ngo et al. (30). The results of their studies indicate a notable decrease in the melting point of ILs when there is a strong asymmetry of the substituents of the imidazolium cation, the length of the alkyl chain grafted to the cation has a great influence on their melting point (32–35). As a rule, the value of the melting point decreases as the length of the alkyl chain increases. It should be noted that some conclusions reported by awad that can be criticized due to the supercooled state of some ionic liquids (79).

The effect of the anion on the melting point is more difficult to explain. In the case of ILs based on imidazolium cations combined with triflate (TfO^-) or bistriflimide ($(CF_3SO_2)_2N^-$) anions, the low values of the melting points are attributed to a significant delocalization of the charge on the anion, and low hydrogen bond interaction (36).

1.6.2 Thermal stability:

Generally, imidazolium cations have higher decomposition temperatures than ammonium cations, allowing their use at temperatures above 250 ˚C superior and in some cases above 400˚C (29). Thermal stability for an ionic liquid consisting of an imidazolium cation depends primarily on the structure of the anion. Thus, the anions generating the weakest intermolecular interactions induce the highest decomposition temperatures, with the order: $(CF_3SO_2)_2N^- > PF_6^- > BF_4^- > I^- > Br^- > Cl^-$ (30).

1.6.3 Density:

The relationship between density as a function of temperature has been studied for ionic liquids based on imidazolium, pyridinium, ammonium, phosphonium and pyrrolidinium. For pure ILs, the values vary depending on the choice of anion and cation. The majority of ILs are denser than water, their typical values range from 1.05 to 1.64 $g.cm^{-3}$ at 20 °C and decrease between 1.01 and 1.57 $g.cm^{-3}$ at temperature of 90 °C. The densities are related to the molar mass of the liquid. The density measured for each ionic liquid as a function of the temperature (from 20 to 120 °C) and at 0.1 MPa, the density decreases with the increase in the length of the alkyl chain for the same common anion. For a common cation (37), Shukla indicate that the density increases with an increase in the molar mass of the anion, in the order: $Cl^- < BF_4^- < CF_3SO_3^- < PF_6^- < (CF_3SO_2)_2N^- <$ [methide] -or $[(CF_3 SO_2)_3C^-]$ (37- 39), all these effects seem to be related to the steric hindrance of the cation and / or anion of the ionic liquid, impact of impurities also tends to decrease density (40).

1.6.4 Viscosity:

The viscosity of an IL increases with the lengthening of the alkyl chain and this for the same anion. While traditional solvents have viscosities around 1 cP, the ILs have values ranging from 20 to more than 600 cP. It has been found that, just as with melting temperatures, the viscosity of the IL is strongly dependent on the nature of the two ions. The high viscosities are attributed to the small size of the anion, for which electrostatic interactions and hydrogen bonds are stronger (41, 42). In addition, the symmetry of the in/organic anion was considered as an additional parameters (43). The viscosity decreases in the order $Cl^- > [PF_6^-] > [BF_4^-] > [(CF_3SO_2)_2N^-]$ for the anions and pyrrolidinium > imidazolium for the cations (31). On the other hand, the increase in Van Der Waals interactions leads to the decrease in Coulomb interactions thus causing the decrease in fluidity (the inverse of viscosity)(44).

Table 1.1: Physical properties of some ionic liquids, at room temperature.

Ionic liquid	Melting point (°C)	Density ($g \cdot ml^{-1}$)	Viscosity (cP)	decomposition temperature (°C)
1-butyl-3-methylimidazolium				
Hexafluorophosphate	10	1,373	450	349
Tetrafluoroborate	-81	1,208	219	403
Trifluoroacetate	--	1,209	73(20°C)	--
trifluoromethanesulfonate	16	1,290	90(20°C)	--
bis(trifluoromethylsulfonyl) imide	--	1,429	52	--
octyl sulfate	--	1,064	34	--
1-ethyl-3-methylimidazolium				
Trifluoroacetate	-14	1,285	35(20°C)	--
bis(trifluoromethylsulfonyl) imide	-39	1,470	37	--
trifluoromethanesulfonate	-9	1,390	45(20°C)	--
tetrafluoroborate	6	1,248(20°C)	67(20°C)	--
ethyl sulfate	--	1,238	98	--
1-hexyl-3-methylimidazolium				
bis(trifluoromethylsulfonyl)imide	--	1,377	71	--
hexafluorophosphate	-61	1,304	585	376
tetrafluoroborate	-82	1,208	314	--
1-octyl-3-methylimidazolium	--			
bis(trifluoromethylsulfonyl)imide	-86	1,310	87	>300
tetrafluoroborate	-79	1,110	439	--
hexafluorophosphate	-70	1,238	682	--

-Not reported in literature.

1.6.5 Solubility :

Ionic liquids have a great solvating power, which allows them to solubilize a wide range of organic, inorganic and also organometallic compounds, and are liquid over a wide temperature range. These last two properties make it easy to consider them as reaction solvents (80).

1.6.5.1 Solubility in water:

The hydrophilic or hydrophobic nature of ionic liquids is an important parameter in the study of their solvation properties, most of the results relating to the miscibility of ionic liquids in water concern dialkylimidazolium ILs. Their solubilities in water are mainly governed by the nature of the anion and the length of the alkyl chain grafted by the cation. Ionic liquids have the property of being hygroscopic, which means, they can absorb water from the atmosphere (45). Cammarata et al have established that water molecules absorbed in ionic liquids are in the "free" state interacting by hydrogen bonds with anions at concentrations between 0.2 and 1.10^{-3} $mol.L^{-1}$ (46). The strength of the hydrogen bonds between the anion and water increases in the order of: $PF6^- < BF_4^- < Tf_2N^- < TfO^- < NO_3^-$.

Table I.2: qualitatively gives the solubility of some ionic liquids in water and some organic solvents. (M: Miscible; I: Immiscible).

ionic liquid		**Solvent**				
		water	**methanol**	**acetonitrile**	**acetone**	**n-hexane**
EMIM	PF^-_6	M	M	-	M	I
	$CH_3SO_3^-$	M	-	M	M	-
	$CF_3SO_3^-$	I	-	-	-	-
	$(CF_3SO_3^-)_2N^-$	I	M	M	-	-
BMIM	Cl^-	M	-	-	-	-
	I^-	M	-	-	-	-
	PF^-_6	I	M	-	M	I
	BF^-_4	M	M	M	I	I
	$CH_3SO_3^-$	M	-	M	M	-
	$CF_3SO_3^-$	I	M	M	-	-
	$CF_3SO_3^-)_2N^-$	I	M	M	-	-

-Not reported in literature.

1.6.5.2 Solubility in organic solvents:

On one hand, organic solvents are all the more miscible with ILs as they are polar. ILs are therefore miscible with short chain alcohols and ketones, dichloromethane and acetonitrile. On the other hand, by a choice of the nature of the cation and / or of the anion, the ILs can be immiscible with alkanes, dioxane, toluene and ether (29, 47).

1.6.6 Toxicity and dangerousness:

These two parameters are still poorly understood because relatively few studies have been carried out on the subject, although often described as being “green” species, it nevertheless emerges in the light of some toxicological studies, in particular that of THUY PHAM et al (48), that this supposed non-toxicity is not applicable to the 'set of ILs. Research carried out by various teams since the early 2000s has shown that the nature of the cation seems to have a significant influence on the toxicity of LIs much more than that of the anion (49). Imidazolium salts appear to exhibit greater Eco toxicity as the alkyl chain is long (50). However, we have recently seen the development of new so-called "bio / eco-compatible" ILs, more in line with environmental constraints. We find in particular examples of LIs based on amino acids (51), terpenes (52), sugars (53) or even natural aromatic aldehydes (54).

1.7 Application of ionic liquids:

Ionic liquids are new compounds in green chemistry, their important proprieties make them a good candidates in many applications.

1.7.1 Electrochemical applications:

IONMET (New ionic Liquids solvent Technology to Transform Metal Finishing Products and Process) is a network of 33 companies created in 2005, whose objective is to promote the applications of ionic liquids in surface coating processes with metals.

One of these projects involves the electroplating of aluminum on a steel surface in an ionic liquid such as imidazolium. This project, currently under development, provides adherent, uniform and corrosion-resistant aluminum coatings (55). IONMET wants to extend the application of ionic liquids to other surface coating processes.

Much research work described in the literature deals with the electrodeposition of many metals in ionic liquids including the electrodeposition of reactive heavy metals like aluminum, tantalum, silicon, selenium, lithium …. etc (56-58).

1.7.2 Applications in organic synthesis and catalysis:

Organic synthesis and catalysis are certainly the two growing areas in the use of ionic liquids (59). There are many applications of ionic liquids in these fields (59, 60). From a chemical point of view, the main potential of ionic liquids is to increase the yield and the kinetics of the reaction. From a practical and economical point of view, the great variety of ionic liquids allows to improve the reactions according to the specific properties of each liquid. In addition, all experts in organic synthesis and catalysis indicated that's possible to more easily separate the reaction product and the catalyst used, thus allowing possible recycling of the ionic liquids.

1.7.3 Liquid-liquid extraction:

The evaluation of ionic liquids as an alternative to conventional organic solvents, initially focused on the study of the extraction of ionic inorganic compounds. Dai et al were the first to report the very high efficiency of the use of [BMIM, PF_6] and [BMIM, $(CF_3SO_2)_2N$] in the extraction of Sr^{2+} with the use of 18-crown ether6-dicyclohexano as an extractant (61). Many similar studies were then carried out depending on the nature of the ionic liquid (length of the chain alkyl, nature of the anion ...) (62-64). Wei et al extracted the compounds Ag^+, Hg^{2+} , Cu^{2+} , Pb^{2+}, Cd^{2+} and Zn^{2+} in [BMIM, PF_6] with dithizone as a chelating agent (65). Mehdi et al (66), studied the reaction at the interface between [C_4min] [hfac] and a solution of cobalt. They observed two phases and a color change for the ionic liquid instantly after the addition of the cobalt complex (Figure 1.3).

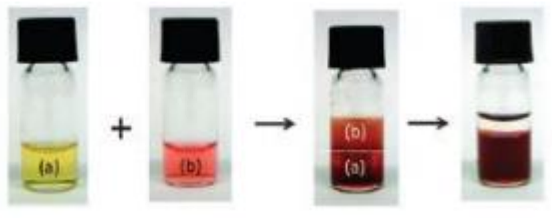


Figure 1.3: Reaction with [C_4min] [hfac] (a) in contact with a cobalt solution (b)

[hfac] :1,1,1,5,5,5-Hexafluoroacétylacétone

A crystal structure was formed, showing that the cobalt (II) ion is octahedral surrounded by three hexafluoroacetylacetonate anions: (Figure 1.4)

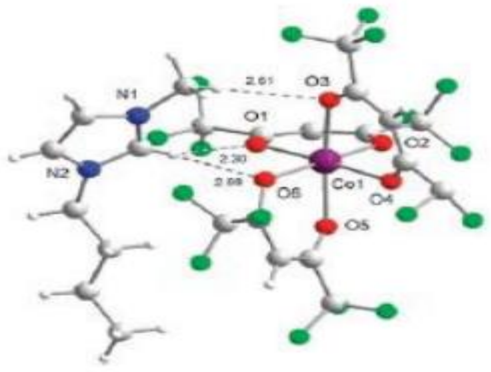


Figure 1.4: Crystal structure of [C_4min] [Co (hfac) 3]

Better quality results were found with the extraction of heavy metals by trioctylmethylammonium thiosalicylate (TOMATS) (Figure 1.5).

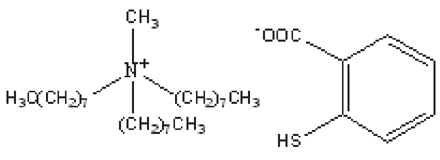


Figure 1.5 TOMATS

The first application is the extraction of copper from an aqueous phase of Cu_2^+ tetramine (67). After the addition of TOMATS, two phases are considered (Figure 1.6): with formation of two phases, one without copper and the other upper containing dark copper, after stirring and phase separation, all copper is extracted in the upper phase (third test tube)

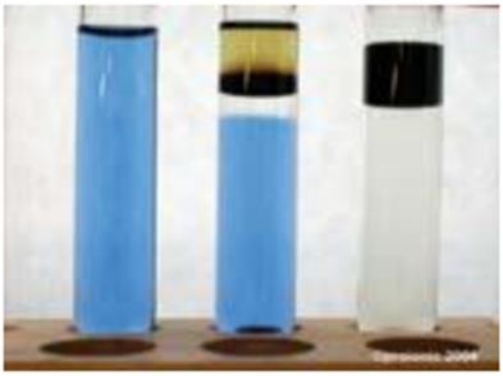


Figure 1.6 Copper extraction by TOMATS

Ionic liquids have also been applied to numerous extractions of organic compounds such as substituted benzene derivatives (68) or polyaromatic hydrocarbons (PAHs) (69). Carda-Broch et al from aveiro university evaluated in detail the properties of [BMIM, PF_6] and determined the distribution coefficient [BMIM, PF_6] / water and [BMIM, PF_6] / heptane of forty compounds at different pH (70). A comparison made with the octanol / water partition coefficient showed a better affinity of basic aromatic compounds (aromatic amines) for the ionic liquid phase and a poorer affinity of acid compounds (derivatives of aromatic acids and phenols) for the ionic liquid phase.

References

1. Singh, S. K., & Savoy, A. W. (2020). Ionic liquids synthesis and applications: An overview. *Journal of Molecular Liquids*, *297*, 112038.
2. Freemantle, M. (2010). *An introduction to ionic liquids*. Royal Society of chemistry.
3. Haddad, B., Paolone, A., Villemin, D., Lohier, J. F., Drai, M., Bresson, S., ... & Belarbi, E. H. (2018). para-Xylyl bis-1-methylimidazolium bis (trifluoromethanesulfonyl) imide: Synthesis, crystal structure, thermal stability, vibrational studies. *Journal of Molecular Liquids*, *260*, 391-402.
4. Sanchora, P., Pandey, D. K., Rana, D., Materny, A., & Singh, D. K. (2019). Impact of size and electronegativity of halide anions on hydrogen bonds and properties of 1-Ethyl-3-methylimidazolium-based ionic liquids. *The Journal of Physical Chemistry A*, *123*(23), 4948-4963...
5. Freemantle, M. (2010). *An introduction to ionic liquids*. Royal Society of chemistry.
6. Walden, P. (1914). Molecular weights and electrical conductivity of several fused salts. *Bull. Acad. Imper. Sci.(St. Petersburg)*, *1800*.
7. Hurley, F.H. and Wier, T.P. (1951) The Electrodeposition of Aluminum from Nonaqueous Solutions at Room Temperature. Journal of Electrochemical Society, 98, 207-212.
8. Drai, M., Mostefai, A., Paolone, A., Haddad, B., Belarbi, E., Villemin, D., ... & Rahmouni, M. (2017). Synthesis, experimental and theoretical vibrational studies of 1-methyl and 1, 2-dimethyl, 3-propyl imidazolium bis (trifluoromethanesulfonyl) imide. *Journal of Chemical Sciences*, *129*(6), 707-719.
9. Moumene, T., Belarbi, E. H., Haddad, B., Villemin, D., Abbas, O., Khelifa, B., & Bresson, S. (2016). Vibrational spectroscopic study of imidazolium dicationic ionic liquids: effect of cation alkyl chain length. *Journal of Applied Spectroscopy*, *83*(2), 165-171.
10. Boumediene, M., Haddad, B., Paolone, A., Drai, M., Villemin, D., Rahmouni, M., ... & Abbas, O. (2019). Synthesis, thermal stability, vibrational spectra and conformational studies of novel dicationic meta-xylyl linked bis-1-methylimidazolium ionic liquids. *Journal of Molecular Structure*, *1186*, 68-79.
11. Chowdhury, S., Mohan, R. S., & Scott, J. L. (2007). Reactivity of ionic liquids. *Tetrahedron*, *63*(11), 2363-2389.
12. Fareghi-Alamdari, R., & Hatefipour, R. (2015). Synthesis and thermophysical characterization of novel azide functionalized imidazolium based ionic liquids. *Thermochimica Acta*, *617*, 172-178.
13. Sun, J., Forsyth, M., & Macfarlane, D. R. (1998). Room-temperature molten salts based on the quaternary ammonium ion. *The Journal of Physical Chemistry B*, *102*(44), 8858-8864.
14. Bradaric, C. J., Downard, A., Kennedy, C., Robertson, A. J., & Zhou, Y. (2003). Industrial preparation of phosphonium ionic liquids. *Green Chemistry*, *5*(2), 143-152.
15. Rogers, R. D., & Seddon, K. R. (2003). Ionic liquids--solvents of the future?. *Science*, *302*(5646), 792-793.
16. Rogers, R. D., Seddon, K. R., & Volkov, S. (Eds.). (2012). Green industrial applications of ionic liquids (Vol. 92). Springer Science & Business
17. Helfferich, F. (1962). Ion-exchange kinetics. 1 III. Experimental test of the theory of particle-diffusion controlled ion exchange. *The Journal of Physical Chemistry*, *66*(1), 39-44.

18. Alcalde, E., Mesquida, N., Ibáñez, A., & Dinarès, I. (2012). A Halide-for-Anion Swap Using an Anion-Exchange Resin (A–Form) Method: Revisiting Imidazolium-Based Anion Receptors and Sensors.

19. Hurley, F. H., & Wier Jr, T. P. (1951). Electrodeposition of metals from fused quaternary ammonium salts. *Journal of The Electrochemical Society*, *98*(5), 203.

20. Shiddiky, M. J., & Torriero, A. A. (2011). Application of ionic liquids in electrochemical sensing systems. *Biosensors and Bioelectronics*, *26*(5), 1775-1787.

21. Wilkes, J. S., Levisky, J. A., Wilson, R. A., & Hussey, C. L. (1982). Dialkylimidazolium chloroaluminate melts: a new class of room-temperature ionic liquids for electrochemistry, spectroscopy and synthesis. *Inorganic Chemistry*, *21*(3), 1263-1264.

22. Cai, D. N., Huang, K., Chen, Y. L., Hu, X. B., & Wu, Y. T. (2014). Systematic study on the general preparation of ionic liquids with high purity via hydroxide intermediates. *Industrial & Engineering Chemistry Research*, *53*(17), 6871-6880.

23. Karimi, B., Tavakolian, M., Akbari, M., & Mansouri, F. (2018). Ionic liquids in asymmetric synthesis: an overall view from reaction media to supported ionic liquid catalysis. *ChemCatChem*, *10*(15), 3173-3205.

24. Zhou, J., Sui, H., Jia, Z., Yang, Z., He, L., & Li, X. (2018). Recovery and purification of ionic liquids from solutions: a review. *Rsc Advances*, *8*(57), 32832-32864.

25. Nockemann, P., Binnemans, K., & Driesen, K. (2005). Purification of imidazolium ionic liquids for spectroscopic applications. *Chemical physics letters*, *415*(1-3), 131-136.

26. Weerachanchai, P., & Lee, J. M. (2014). Recyclability of an ionic liquid for biomass pretreatment. *Bioresource technology*, *169*, 336-343.

27. Mukesh, C., Mondal, D., Sharma, M., & Prasad, K. (2013). Rapid dissolution of DNA in a novel bio-based ionic liquid with long-term structural and chemical stability: successful recycling of the ionic liquid for reuse in the process. *Chemical Communications*, *49*(61), 6849-6851.

28. Alloin, F., Hirankumar, G., & Pagnier, T. (2009). Temperature-Dependent Raman Spectroscopy of Lithium Triflate− PEO Complexes: Phase Equilibrium and Component Interactions. *The Journal of Physical Chemistry B*, *113*(52), 16465-16471.

29. Bonhote, P., Dias, A. P., Papageorgiou, N., Kalyanasundaram, K., & Grätzel, M. (1996). Hydrophobic, highly conductive ambient-temperature molten salts. *Inorganic chemistry*, *35*(5), 1168-1178.

30. Ngo, H. L., LeCompte, K., Hargens, L., & McEwen, A. B. (2000). Thermal properties of imidazolium ionic liquids. *Thermochimica Acta*, *357*, 97-102.

31. Huddleston, J. G., Visser, A. E., Reichert, W. M., Willauer, H. D., Broker, G. A., & Rogers, R. D. (2001). Characterization and comparison of hydrophilic and hydrophobic room temperature ionic liquids incorporating the imidazolium cation. *Green chemistry*, *3*(4), 156-164.

32. Holbrey, J. D., & Seddon, K. R. (1999). The phase behaviour of 1-alkyl-3-methylimidazolium tetrafluoroborates; ionic liquids and ionic liquid crystals. *Journal of the Chemical Society, Dalton Transactions*, (13), 2133-2140.

33. Visser, A. E., Holbrey, J. D., & Rogers, R. D. (2001). Hydrophobic ionic liquids incorporating N-alkylisoquinolinium cations and their utilization in liquid–liquid separations. *Chemical Communications*, (23), 2484-2485.

34. Dzyuba, S. V., & Bartsch, R. A. (2001). New room-temperature ionic liquids with C2-symmetrical imidazolium cationsElectronic supplementary information (ESI) available: 1H NMR and IR spectra and elemental analysis results consistent with the indicated structures for all of the [(Cn) 2-Im] Br and [(Cn) 2-Im] PF6 compounds. See http://www. rsc. org/suppdata/cc/b1/b104512c. *Chemical Communications*, (16), 1466-1467.

35. Chun, S., Dzyuba, S. V., & Bartsch, R. A. (2001). Influence of structural variation in room-temperature ionic liquids on the selectivity and efficiency of competitive alkali metal salt extraction by a crown ether. *Analytical Chemistry*, *73*(15), 3737-3741.

36. Pringle, J. M., Golding, J., Baranyai, K., Forsyth, C. M., Deacon, G. B., Scott, J. L., & MacFarlane, D. R. (2003). The effect of anion fluorination in ionic liquids—physical properties of a range of bis (methanesulfonyl) amide salts. *New journal of chemistry*, *27*(10), 1504-1510.

37. Shukla, M., Srivastava, N., & Saha, S. (2010). Theoretical and spectroscopic studies of 1-butyl-3-methylimidazolium iodide room temperature ionic liquid: Its differences with chloride and bromide derivatives. *Journal of Molecular Structure*, *975*(1-3), 349-356.

38. Jeon, Y., Sung, J., Seo, C., Lim, H., Cheong, H., Kang, M., ... & Kim, D. (2008). Structures of ionic liquids with different anions studied by infrared vibration spectroscopy. *The Journal of Physical Chemistry B*, *112*(15), 4735-4740.

39. Lassègues, J. C., Grondin, J., Cavagnat, D., & Johansson, P. (2009). New interpretation of the CH stretching vibrations in imidazolium-based ionic liquids. *The Journal of Physical Chemistry A*, *113*(23), 6419-6421.

40. Lassègues, J. C., Grondin, J., Cavagnat, D., & Johansson, P. (2009). New interpretation of the CH stretching vibrations in imidazolium-based ionic liquids. *The Journal of Physical Chemistry A*, *113*(23), 6419-6421.

41. Chiappe, C., & Pieraccini, D. (2005). Ionic liquids: solvent properties and organic reactivity. *Journal of Physical Organic Chemistry*, *18*(4), 275-297.

42. Branco, L. C., Rosa, J. N., Moura Ramos, J. J., & Afonso, C. A. (2002). Preparation and characterization of new room temperature ionic liquids. *Chemistry–A European Journal*, *8*(16), 3671-3677.

43. Huddleston, J. G., Visser, A. E., Reichert, W. M., Willauer, H. D., Broker, G. A., & Rogers, R. D. (2001). Characterization and comparison of hydrophilic and hydrophobic room temperature ionic liquids incorporating the imidazolium cation. *Green chemistry*, *3*(4), 156-164.

44. Angell, C. A., Byrne, N., & Belieres, J. P. (2007). Parallel developments in aprotic and protic ionic liquids: physical chemistry and applications. *Accounts of chemical research*, *40*(11), 1228-1236.

45. Seddon, K. R., Stark, A., & Torres, M. J. (2000). Influence of chloride, water, and organic solvents on the physical properties of ionic liquids. *Pure and applied chemistry*, *72*(12), 2275-2287..

46. Cammarata, L., Kazarian, S. G., Salter, P. A., & Welton, T. (2001). Molecular states of water in room temperature ionic liquids. *Physical Chemistry Chemical Physics*, *3*(23), 5192-5200.

47. Welton, T. (1999). Room-temperature ionic liquids. Solvents for synthesis and catalysis. *Chemical reviews*, *99*(8), 2071-2084.

48. Pham, T. P. T., Cho, C. W., & Yun, Y. S. (2010). Environmental fate and toxicity of ionic liquids: a review. *Water research*, *44*(2), 352-372.

49. Montalbán, M. G., Hidalgo, J. M., Collado-González, M., Baños, F. G. D., & Víllora, G. (2016). Assessing chemical toxicity of ionic liquids on Vibrio fischeri: Correlation with structure and composition. *Chemosphere*, *155*, 405-414.

50. Bubalo, M. C., Radošević, K., Redovniković, I. R., Slivac, I., & Srček, V. G. (2017). Toxicity mechanisms of ionic liquids. *Arhiv za higijenu rada i toksikologiju*, *68*(3), 171-179.

51. Hulsbosch, J., De Vos, D. E., Binnemans, K., & Ameloot, R. (2016). Biobased ionic liquids: solvents for a green processing industry?. *ACS Sustainable Chemistry & Engineering*, *4*(6), 2917-2931.

52. Luo, X. Y., Lv, X. Y., Shi, G. L., Meng, Q., Li, H. R., & Wang, C. M. (2019). Designing amino-based ionic liquids for improved carbon capture: One amine binds two CO2. *AIChE Journal*, *65*(1), 230-238.

53. Nageshwar, D., Rao, D. M., & Acharyulu, P. V. (2009). Terpenes to ionic liquids: synthesis and characterization of citronellal-based chiral ionic liquids. *Synthetic Communications®*, *39*(18), 3357-3368..

54. Sahiner, N., & Sagbas, S. (2018). Sucrose based ionic liquid colloidal microgels in separation of biomacromolecules. *Separation and Purification Technology*, *196*, 191-199.

55. Abbott, A. P., Ryder, K. S., & König, U. (2008). Electrofinishing of metals using eutectic based ionic liquids. *Transactions of the IMF*, *86*(4), 196-204.

56. Legeai, S., Diliberto, S., Stein, N., Boulanger, C., Estager, J., Papaiconomou, N., & Draye, M. (2008). Room-temperature ionic liquid for lanthanum electrodeposition. *Electrochemistry Communications*, *10*(11), 1661-1664

57. Abbott, A. P., & McKenzie, K. J. (2006). Application of ionic liquids to the electrodeposition of metals. *Physical Chemistry Chemical Physics*, *8*(37), 4265-4279.

58. Zein El Abedin, S., Moustafa, E. M., Hempelmann, R., Natter, H., & Endres, F. (2006). Electrodeposition of nano-and microcrystalline aluminium in three different air and water stable ionic liquids. *Chemphyschem: a European journal of chemical physics and physical chemistry*, *7*(7), 1535-1543.

59. Olivier-Bourbigou, H., & Magna, L. (2002). Ionic liquids: perspectives for organic and catalytic reactions. *Journal of Molecular Catalysis A: Chemical*, *182*, 419-437.

60. Baudequin, C., Baudoux, J., Levillain, J., Cahard, D., Gaumont, A. C., & Plaquevent, J. C. (2003). Ionic liquids and chirality: opportunities and challenges. *Tetrahedron: Asymmetry*, *14*(20), 3081-3093..

61. Dai, S., Ju, Y. H., & Barnes, C. E. (1999). Solvent extraction of strontium nitrate by a crown ether using room-temperature ionic liquids. *Journal of the Chemical Society, Dalton Transactions*, (8), 1201-1202.

62. Visser, A. E., Swatloski, R. P., Reichert, W. M., Griffin, S. T., & Rogers, R. D. (2000). Traditional extractants in nontraditional solvents: Groups 1 and 2 extraction by crown ethers in room-temperature ionic liquids. *Industrial & Engineering Chemistry Research*, *39*(10), 3596-3604.

63. Chun, S., Dzyuba, S. V., & Bartsch, R. A. (2001). Influence of structural variation in room-temperature ionic liquids on the selectivity and efficiency of competitive alkali metal salt extraction by a crown ether. *Analytical Chemistry*, *73*(15), 3737-3741.

64. Villemin, D., & Didi, M. A. (2013). Extraction of rare earth and heavy metals, using ionic solvents as extraction medium (A Review). *Oriental Journal of chemistry*, *29*(4), 1267.

65. Wei, G. T., Yang, Z., & Chen, C. J. (2003). Room temperature ionic liquid as a novel medium for liquid/liquid extraction of metal ions. *Analytica Chimica Acta*, *488*(2), 183-192.

66. Mehdi, H., Binnemans, K., Van Hecke, K., Van Meervelt, L., & Nockemann, P. (2010). Hydrophobic ionic liquids with strongly coordinating anions. *Chemical communications*, *46*(2), 234-236..

67. Ionic Liquids ChemFiles, (2006), vol 6, number 9.

68. Huddleston, J. G., Willauer, H. D., Swatloski, R. P., Visser, A. E., & Rogers, R. D. (1998). Room temperature ionic liquids as novel media for 'clean'liquid–liquid extraction. *Chemical Communications*, (16), 1765-1766.

69. Liu, J. F., Chi, Y. G., Peng, J. F., Jiang, G. B., & Jönsson, J. Å. (2004). Ionic liquids/water distribution ratios of some polycyclic aromatic hydrocarbons. *Journal of Chemical & Engineering Data*, *49*(5), 1422-1424..

70. Carda–Broch, S., Berthod, A., & Armstrong, D. W. (2003). Solvent properties of the 1-butyl-3-methylimidazolium hexafluorophosphate ionic liquid. *Analytical and bioanalytical chemistry*, *375*(2), 191-199.

71. Watanabe, M., Thomas, M. L., Zhang, S., Ueno, K., Yasuda, T., & Dokko, K. (2017). Application of ionic liquids to energy storage and conversion materials and devices. *Chemical reviews*, *117*(10), 7190-7239.

72. Torimoto, T., Tsuda, T., Okazaki, K. I., & Kuwabata, S. (2010). New frontiers in materials science opened by ionic liquids. *Advanced Materials*, *22*(11), 1196-1221.

73. Egorova, K. S., & Ananikov, V. P. (2018). Fundamental importance of ionic interactions in the liquid phase: A review of recent studies of ionic liquids in biomedical and pharmaceutical applications. *Journal of Molecular Liquids*, *272*, 271-300.

74. Kim, G. T., Jeong, S. S., Xue, M. Z., Balducci, A., Winter, M., Passerini, S., ... & Appetecchi, G. B. (2012). Development of ionic liquid-based lithium battery prototypes. *Journal of Power Sources*, *199*, 239-246.

75. Zhao, H., & Malhotra, S. V. (2002). Applications of ionic liquids in organic synthesis.

76. Ito, S., Zakeeruddin, S. M., Comte, P., Liska, P., Kuang, D., & Grätzel, M. (2008). Bifacial dye-sensitized solar cells based on an ionic liquid electrolyte. *Nature Photonics*, *2*(11), 693-698.

77. Wei, G. T., Yang, Z., & Chen, C. J. (2003). Room temperature ionic liquid as a novel medium for liquid/liquid extraction of metal ions. *Analytica Chimica Acta*, *488*(2), 183-192.

78. Tholey, A., & Heinzle, E. (2006). Ionic (liquid) matrices for matrix-assisted laser desorption/ionization mass spectrometry—applications and perspectives. *Analytical and bioanalytical chemistry*, *386*(1), 24-37.

79. Awad, W. H., Gilman, J. W., Nyden, M., Harris Jr, R. H., Sutto, T. E., Callahan, J., ... & Fox, D. M. (2004). Thermal degradation studies of alkyl-imidazolium salts and their application in nanocomposites. *Thermochimica Acta*, *409*(1), 3-11.

80. Muldoon, M. J., Aki, S. N., Anderson, J. L., Dixon, J. K., & Brennecke, J. F. (2007). Improving carbon dioxide solubility in ionic liquids. *The Journal of Physical Chemistry B*, *111*(30), 9001-9009.

Chapter 2

Similar work and synthesis

Part 1

2.1 Introduction :

In the past few years, a newly discovered type of ILs called dicationic liquid ionic (DILs) has been focused on in recent scientific studies (1), them structures composed of a two main groups are cationic linked by an alkyl chain called spacer, paired with two singly charged anions (2-4). The spacer could be rigid or flexible (5).

Dicationic liquid ionic (DILs) based on imidazolium (6), pyrrolidinium (7), pyridinium (8) and ammonium (9) cations, represent the majority of the research in this area.

DILs typically exhibit better thermal stability: their thermal decomposition temperatures range from (330 - 400°C), compared to their monocationics equivalents they can be as low as (145 - 185°C) for monocationic ILs (10-12); and higher viscosity then the viscosity of monocationics ionic liquids, DILs viscosity can be tuned by varying the length of spacer and the anions (The longer the chain = the higher the viscosity)(12); high density and designability (13).

Vibrational and NMR spectroscopies are fundamental tools to characterize ionic liquids, IR and Raman spectroscopies have provided deep insights on the nature of ionic interactions, the role played by cation-anion hydrogen bonds, molecular conformations, and their modifications as pressure and temperature is varied in the normal liquid phase, during phase transition to crystalline or amorphous (glassy) solid phases, after vaporization (18).

2.2 Similar studies :

Compared with monocationic ionic liquid the research in this field related with dicationic ionic (DILs) liquid is very limited for various reasons but mainly because this field of research is basically in its beginnings, so similar works to ours are very few, here are some details of similar studies.

2.2.1 Procedure for the synthesis of p-xylyl-based DILs

In this study (14,15), the objectives are:

Step 1: synthesis of para-xylyl linked di-imidazolium [p-$C_6H_4(CH_2ImMe)_2^+$] ionic liquid paired with different anions, the method is based on the alkylation reaction of methyl imidazole, the precursor exchange three different fluorinated anions :

- bis(trifluoromethanesulfonyl)imide [$(CF_3SO_2)_2N^-$]
- tetrafluoroborate (BF_4^-)
- hexafluorophosphate (PF_6^-)

Step 2: in order to confirm the appropriate structure, the reported DILs are investigated by using ^{1}H-NMR, ^{13}C-NMR, ^{19}F-NMR , ^{31}P-NMR, and FT-IR spectroscopy.

Step 3: in order to indicate the melting point and the decomposition, the thermal proprieties are investigated by (DTG) and (TGA).

Step 4: To study vibrational spectroscopy by infrared (IR), Raman (FT-Raman) spectroscopy.

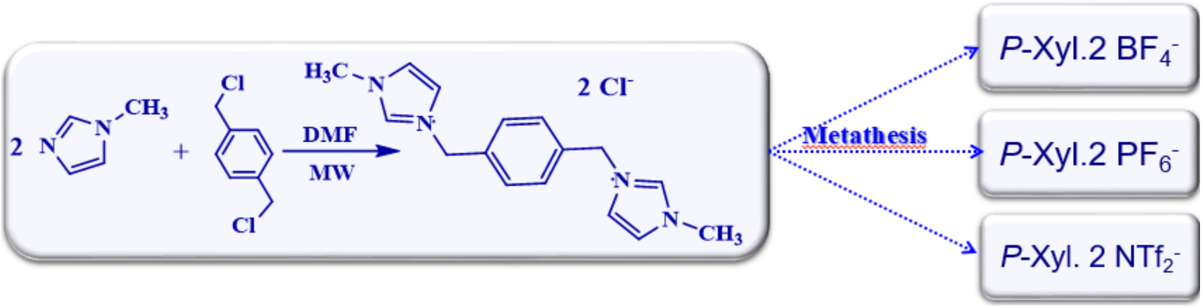


Figure 2.1: General synthesis of [*p*-C_6H_4(CH2ImMe)$_2$]X_2 (with X =[Cl^-], [BF_4^-], [PF_6^-] and [$(CF_3SO_2)_2N^-$].

2.2.1.1 Structural study :

Study the forms of DILs obtained by :

^{1}H NMR

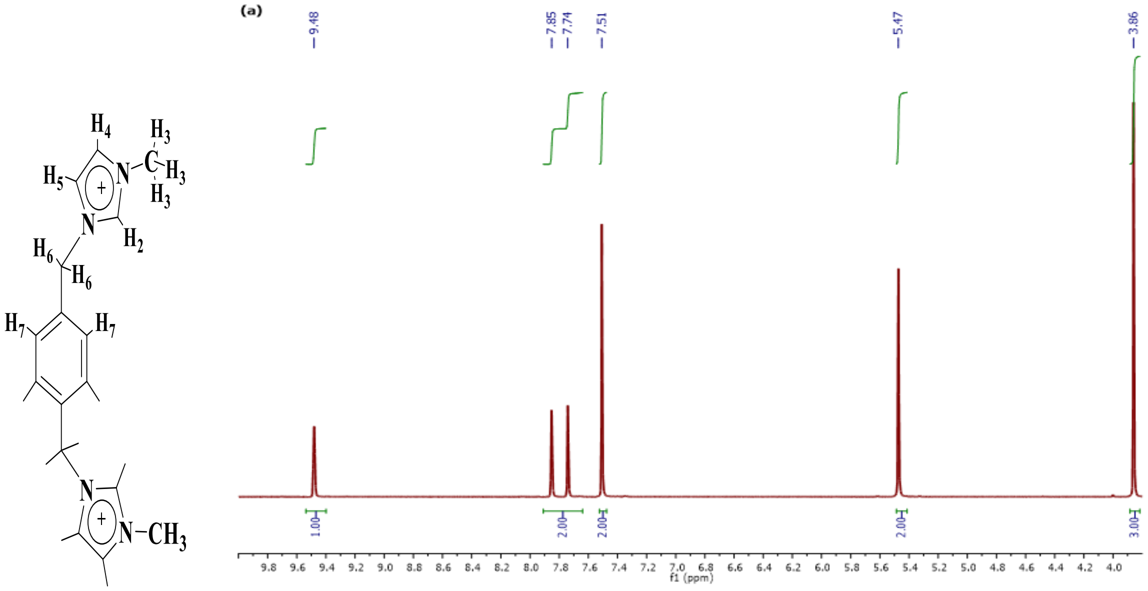


Figure2.2: ^{1}H NMR (500 MHz) spectra of $[p\text{-}C_6H_4(CH_2ImMe)_2{}^{+}][Cl^{-}]_2$.

Then by : **^{13}C NMR**

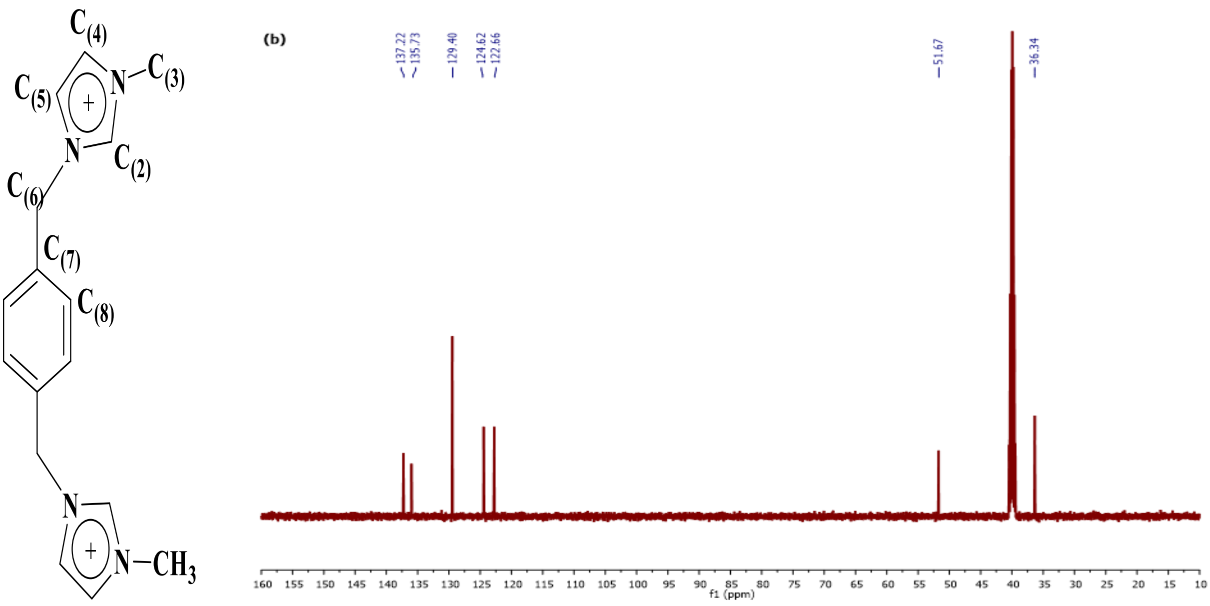
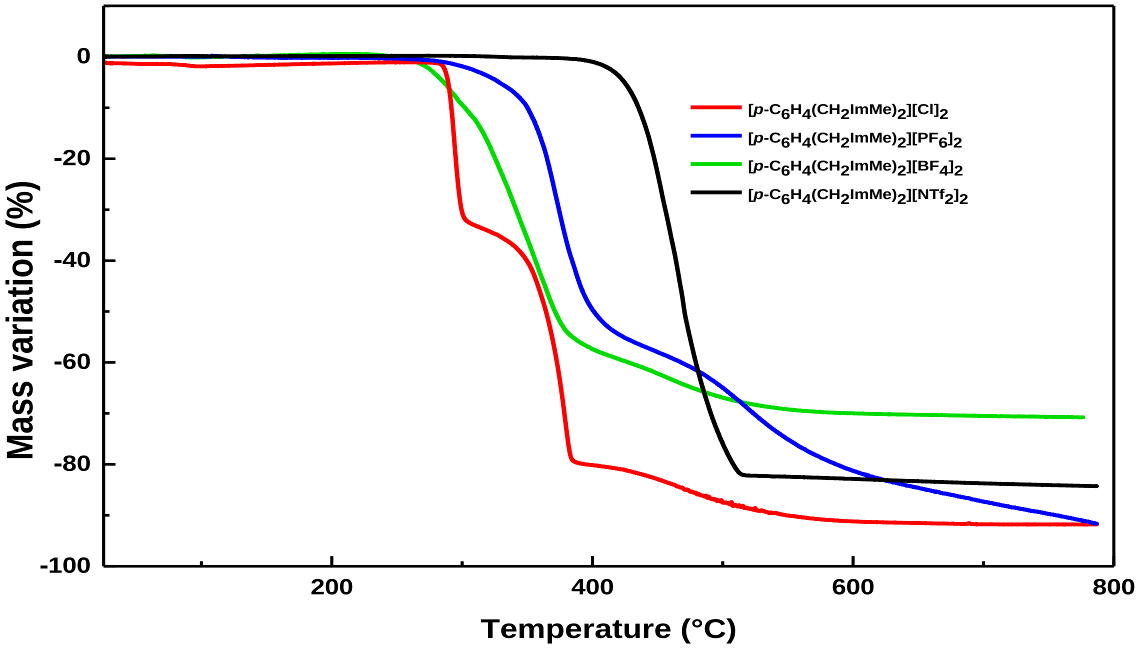


Figure 2.3: ^{13}C NMR (125.75 MHz) spectra of $[p\text{-}C_6H_4(CH_2ImMe)_2{}^{+}][Cl^{-}]_2$.

In this work, boumediene and al clearly showed that the chloride anion is close to the H – $C_{(2)}$ site of the cation to form a specific hydrogen bond, which is much stronger than that of other DILs. However, the chemical shift of $C_{(2)}$ –H increased significantly with anionic basicity, which follows the following order: halide> BF_4^-> PF_6^-> $(CF_3SO_2)_2N^-$. In summary, the chemical shifts of the 1H NMR of our DILs follow the order: $C_{(2)}$ –H> H – $C_{(5)}$ / $C_{(4)}$ –H> (–C_6H_4–)> (–CH_2-) > –CH_3

2.2.1.2 Thermal analysis

In the same work,the author study the thermal properties by using thermographs by: thermogravimetric analysis (TGA) and by differential thermal analysis (DTA), for synthesized dicationic ionic liquids (DILs).



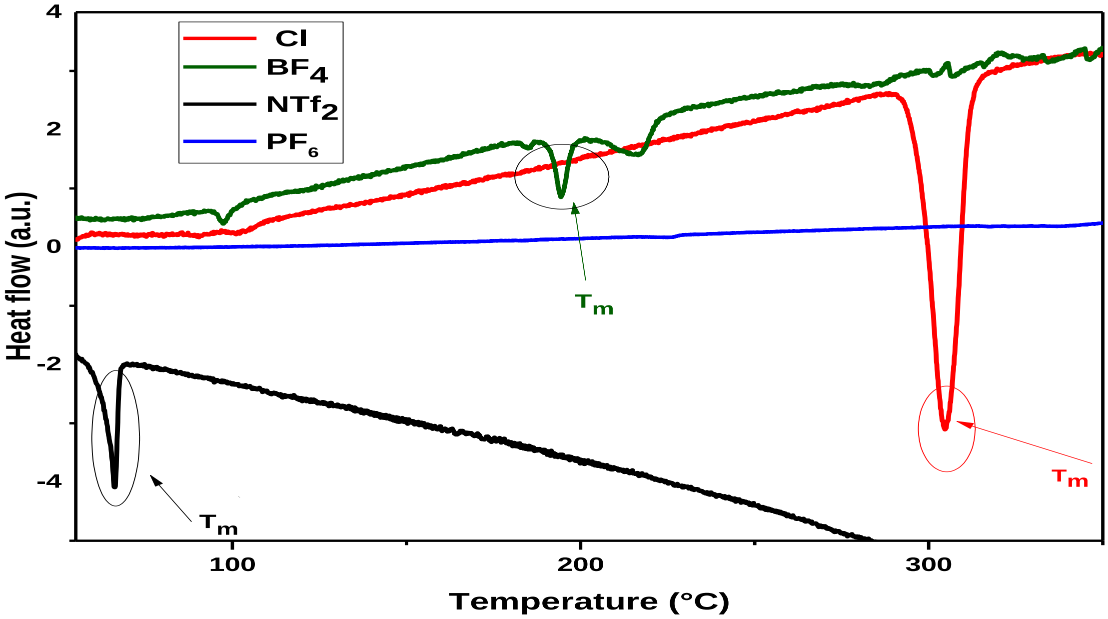


Figure 2.4: Mass variation (TGA) and heat flow (DTA) for the four investigated DILs as a function of temperature.

They concluded that the type of anion plays an important role in these degradation reactions and that the thermal stability increases in the following order: $[Cl]^{-}$ <$[BF_4]^{-}$ <$[PF_6]^{-}$ <$[NTf_2]^{-}$.

Table 2.1: melting temperature and decomposition for DILs.

DILs	Physical state at 25 ° C	M_P	T_d
$[p\text{-}C_6H_4(CH_2ImMe)][CL]_2$	Solid	305° C	294° C
$[p\text{-}C_6H_4(CH_2ImMe)][PF_6]_2$	Solid	---	338° C
$[p\text{-}C_6H_4(CH_2ImMe)][BF_4]_2$	solid	194° C	307° C
$[p\text{-}C_6H_4(CH_2ImMe)][(CF_3SO_2)_2N]_2$	liquid	65° C	485° C

In addition, it can be deduced that the values in the tables indicate that the melting points are considerably reduced when the symmetry of the molecules is lowered in the order given below:

$M_P\ [Cl]^{-} > M_P\ [PF_6]^{-} > M_P\ [BF_4]^{-} > M_P\ [(CF_3SO_2)_2N]^{-}$.

2.2.1.3 Vibrational Spectroscopy Study:

The FT-Raman [45-3300 cm^{-1}] and the IR absorbance [400-3300 cm^{-1}] spectra of the investigated DILs, namely [p-$C_6H_4(CH_2ImMe)_2^+$] X2 (with X =[Cl-], [BF4-] and [$(CF_3SO_2)_2N^-$]), measured at room temperature are reported in following figures:

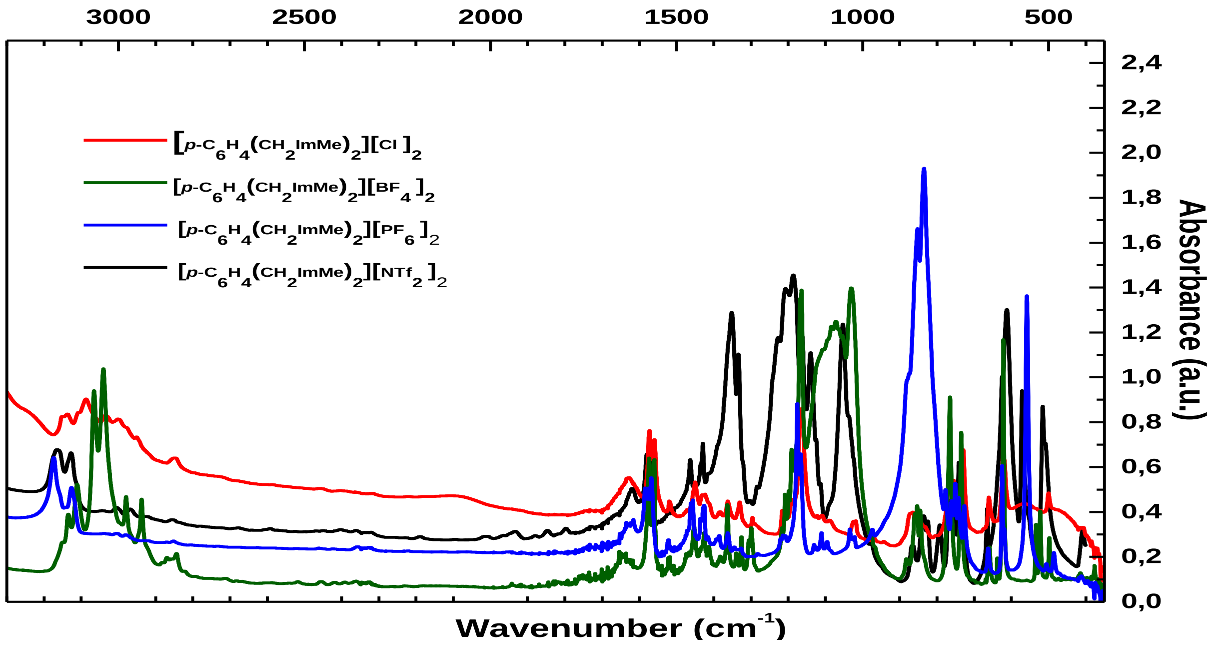


Figure 2.5: Infrared absorption spectra of the four DILs.

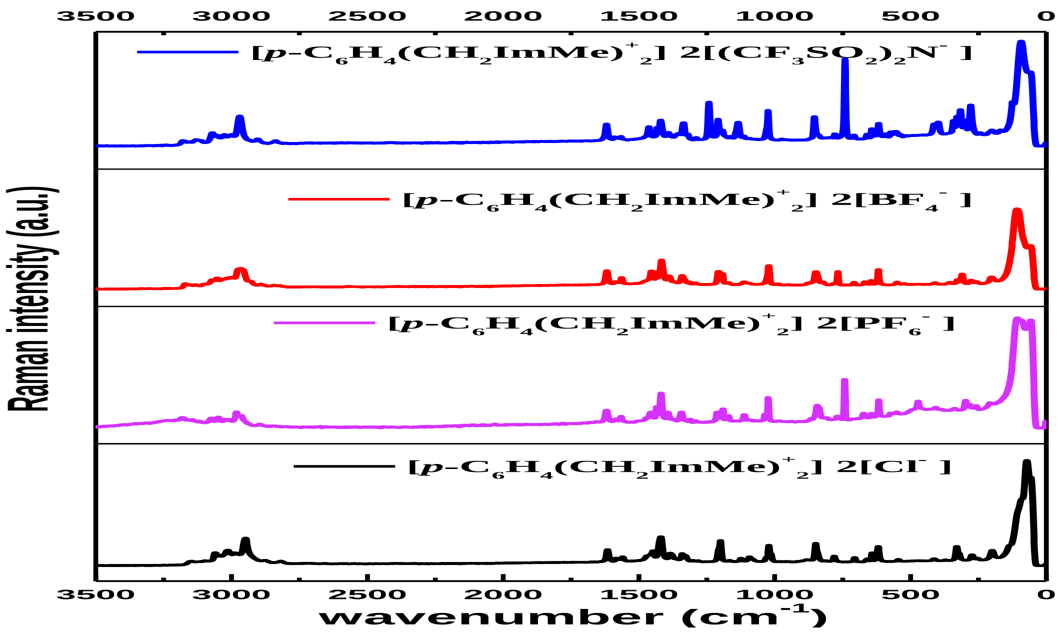


Figure 2.6: Raman absorption spectra of the four DILs.

They concluded the position of H-bonding: $C_{(2)}$ –H> H – $C_{(5)}$ / $C_{(4)}$ –H> (–C_6H_4–)> (–CH_2-) > –CH_3 are important for any interaction with anion , all their values noted in the range of (3000-3500cm-1), but these interaction depends on symmetry of combined anion-cation and specially related to basicity of the anion.

2.2.2 Procedure for the synthesis of biphenyl-based DILs

In this research paper (16), three new substituted dicationic ionic liquids (DILs) based on biphenylenedimethylene linked bis-1-methylimidazolium ionic liquids [Bis-$(PhCH_2MIm)^+$], combined with four anions, namely : dichloride$[Cl]_2$, di(hexafluorophosphate) $[PF_6^-]_2$, bis(tetrafluoroborate) $[BF_4^-]_2$ di(bis(trifluoromethylsulfonyl)Imide) $[(CF_3SO_2)_2N^-]_2$ were synthesized.

The thermal stability of these new DILs was examined by (TGA) and (DTA) measurements, also, they were characterized by (FTIR) and Raman spectroscopy.

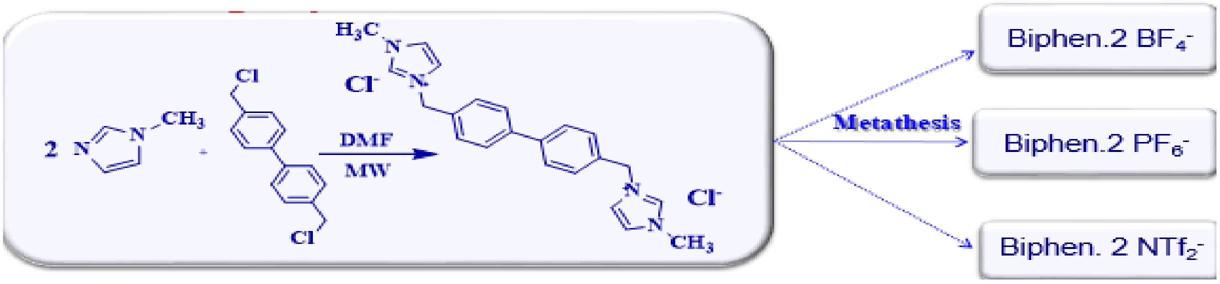


Figure 2.7: General synthesis of [Bis-$(PhCH_2MIm)^+$]X_2 (with X =$[Cl^-]$, $[BF_4^-]$, $[PF_6^-]$ and $[(CF_3SO_2)_2N^-]$.

2.2.2.1 Structural study:

Study the forms of DILs obtained by:

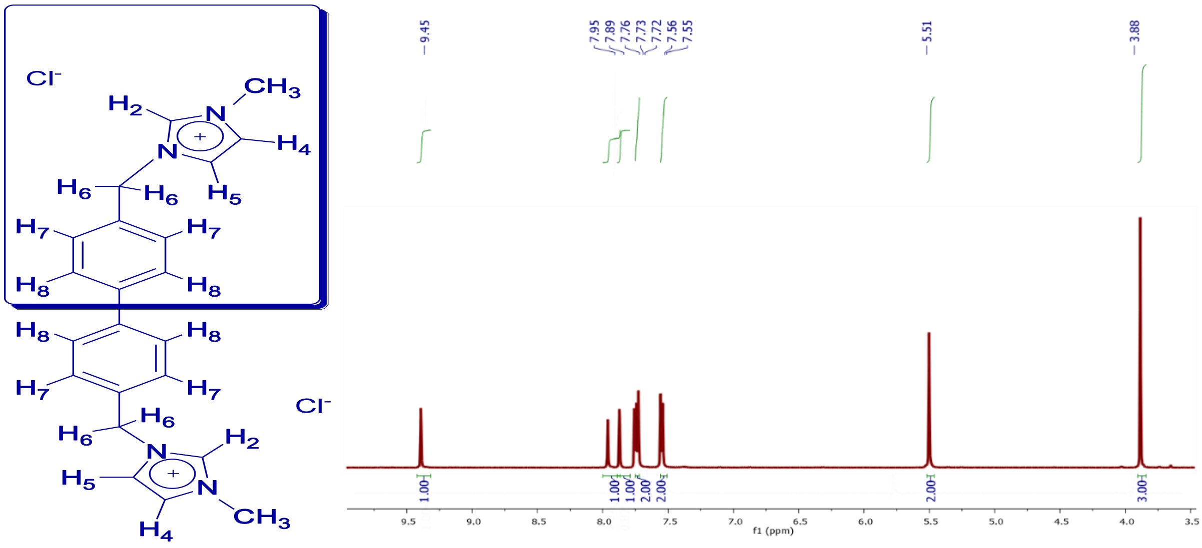


Figure 2.8 ^{1}H NMR (500 MHz) spectra of [Bis-(PhCH$_2$MIm)$^+$][Cl$^-$] 2.

Generally, the presence of electronegative atoms and π-bonds causes downfield chemical shifts. For example, C4, C5, and C2 of the imidazolium rings are deshielded (shifted downfield) due to the presence of the π-electron system in the imidazolium and biphenyl rings, and due to the influence of the electronegative counter-ion.

2.2.2.2 Thermal analysis:

The DILs obtained are also treated by: thermogravimetric analysis (TGA) and by differential thermal analysis (DTA), for synthesized dicationic ionic liquids (DILs).

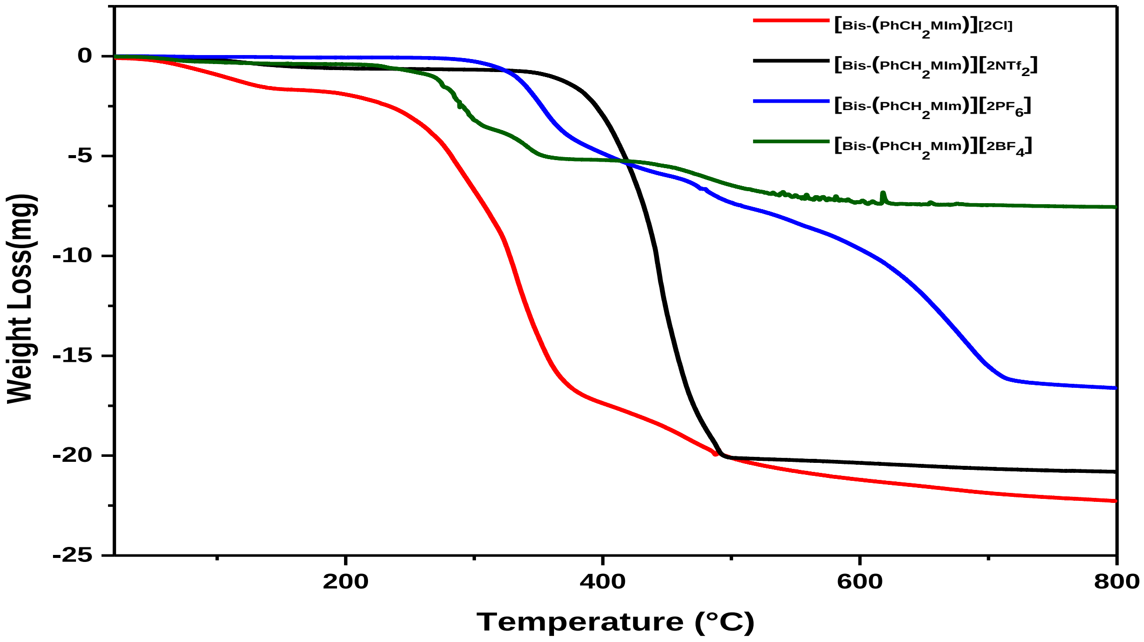


Figure 2.9: TGA thermographs for synthesized dicationic ionic liquids.

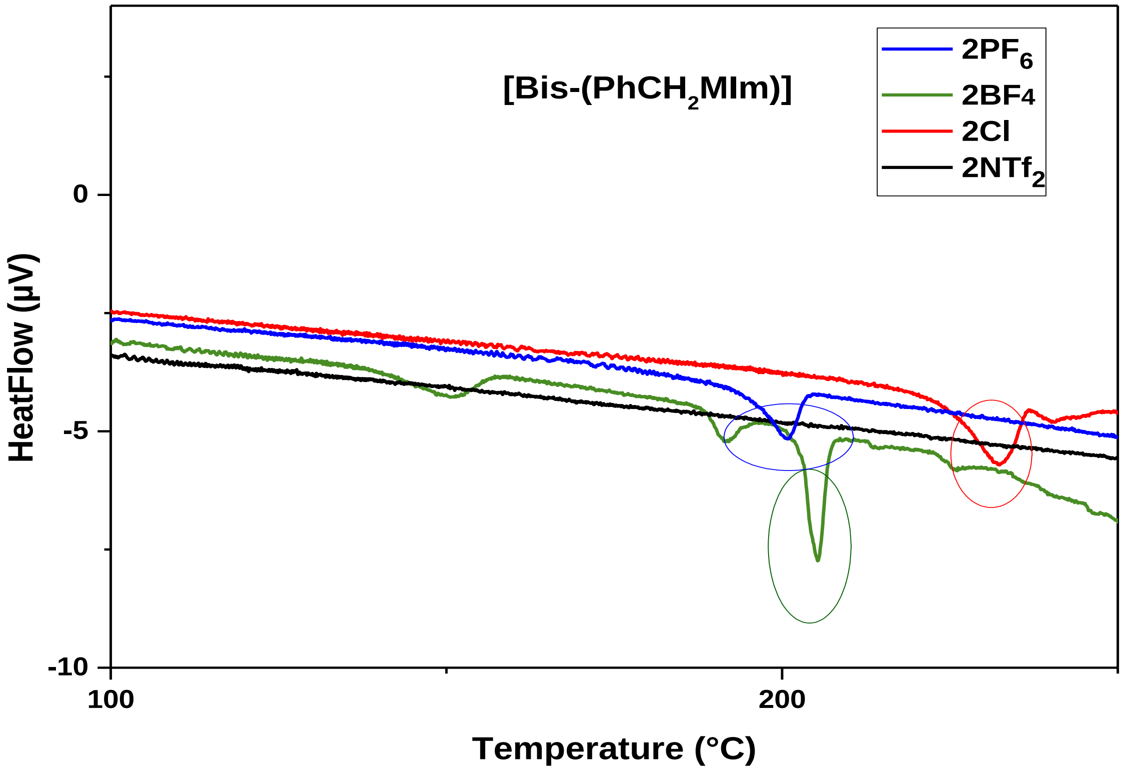


Figure 2.10: DTA thermographs for synthesized dicationic ionic liquids.

They obtained the results shown in the following table:

Table 2.2: DILs and their melting temperature and decomposition temperature.

DILs	Physical state at 25 ° C	M_P	T_d
[(Bis-PhCH_2MIm)][Cl] $_2$	Solid	232° C	252° C
[(Bis-Ph CH_2MIm)][PF_6] $_2$	Solid	200° C	323° C
[(Bis-Ph CH_2MIm)][BF_4] $_2$	solid	150° C	270° C
[(Bis-Ph CH_2MIm)][NTf_2] $_2$	liquid	---	420° C

The values in the tables indicate that the melting points are considerably reduced when the symmetry of the molecules is lowered and vice versa for the thermal stability in the order given below: M_P [Cl]$^-$ > M_P [PF_6]$^-$ > M_P [BF_4]$^-$ > M_P [$(CF_3SO_2)_2N$]$^-$.

2.2.2.3 Vibrational Spectroscopy Study:

The FT-Raman [45-3300 cm^{-1}] and the IR absorbance [400-3300 cm^{-1}] spectra of the investigated DILs, namely [Bis-$(PhCH_2MIm)^+$] X2 (with X =[Cl^-], [BF_4^-] and [$(CF_3SO_2)_2N^-$]), measured at room temperature are reported in following figures:

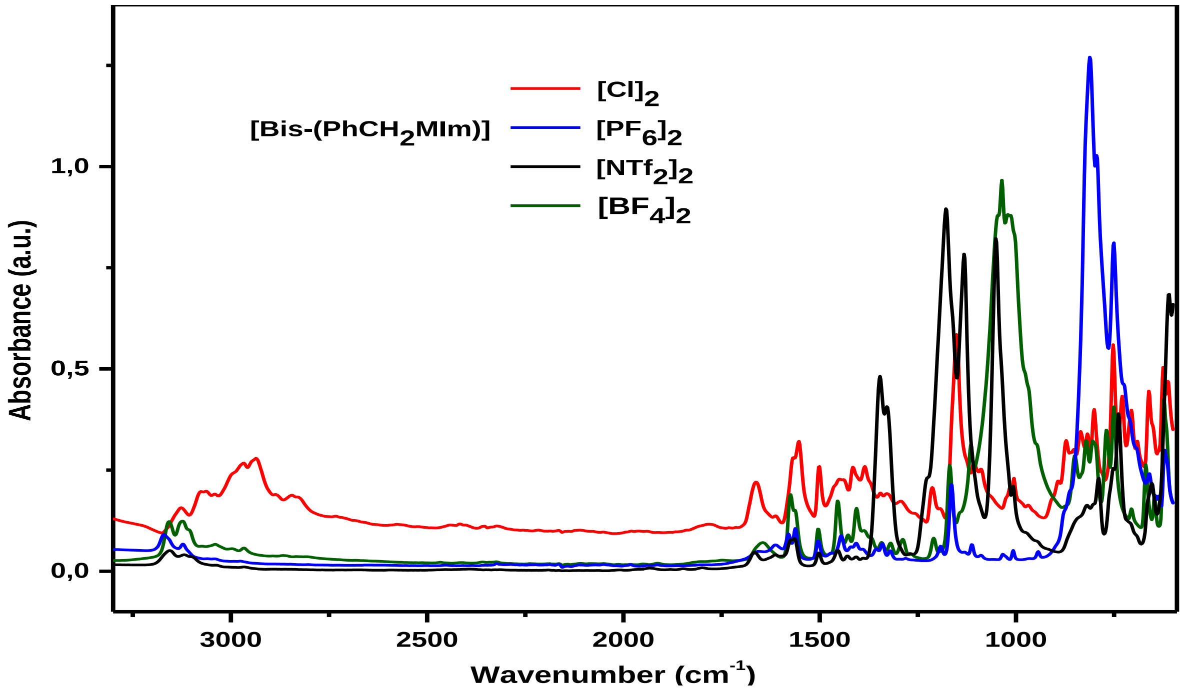


Figure 2.11: Experimental IR vibrational spectra of investigated DILs.

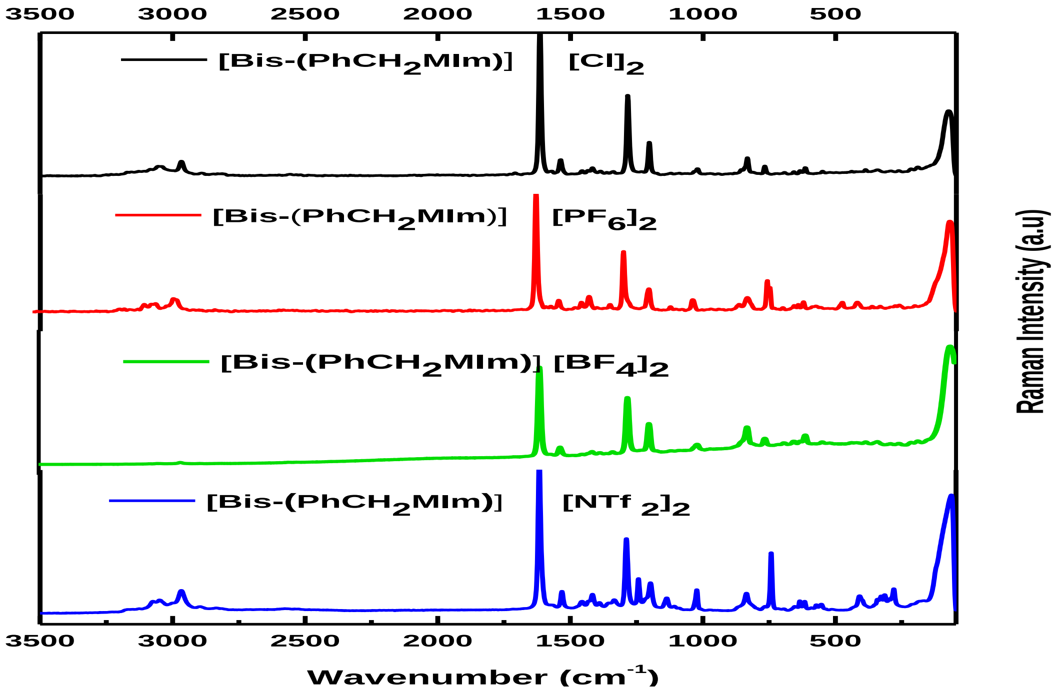


Figure 2.12: Experimental Raman vibrational spectra of investigated DILs.

In summary, the chemical shifts of the 1H NMR of our LIDFs follow the order: $C_{(2)}$ –H> H –$C_{(5)}$ / $C_{(4)}$ –H> (–C_6H_4–)> (–CH_2-) > –CH_3

2.2.3 Procedure for the synthesis m-xylyl-based DILs:

In this paper of investigation (17), four new meta-xylyl linked bis-imidazolium [m-$C_6H_4(CH_2ImMe)_2^+$] ionic liquid (ILs) containing the dichloride $[Cl^-]_2$, di(bis(trifluoromethylsulfonyl)Imide $[(CF_3SO_2)_2N]_2$, bis(tetrafluoroborate) $[BF_4^-]_2$ and bis(hexafluorophosphate) $[PF_6^-]_2$ anions were synthesized.

The obtained dicationic ILs were characterized by ^{1}H NMR, ^{13}C NMR, and FT-IR spectroscopy, also their thermal properties were determined by TGA and DTA.

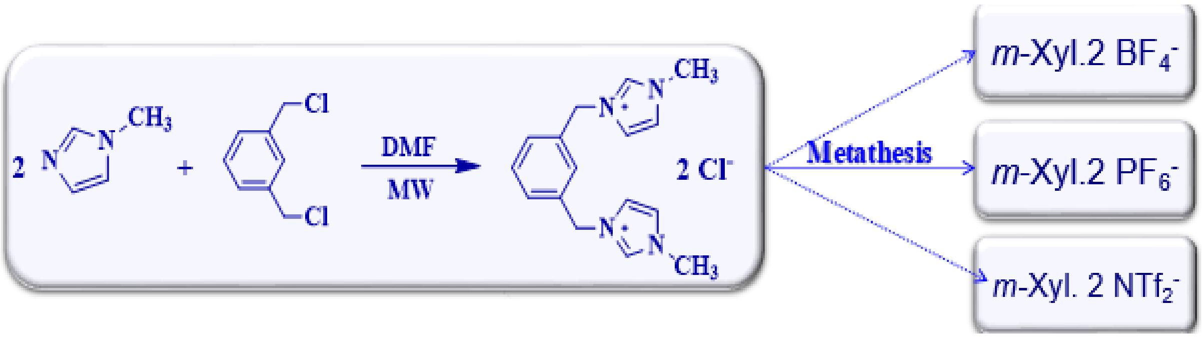


Figure 2.13: General synthesis of [m-$C_6H_4(CH_2ImMe)_2^+$] X2 (with X =[Cl^-], [BF_4^-], [PF_6^-] and [$(CF_3SO_2)_2N^-$]).

2.2.3.1 Structural study:

Study the forms of DILs obtained by:

^{1}H NMR

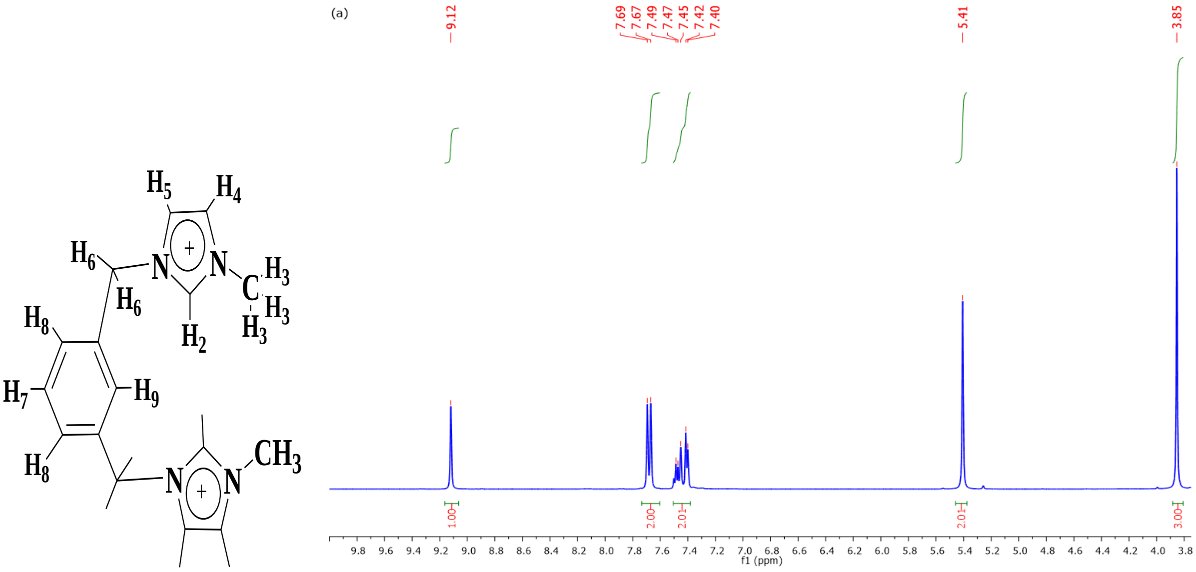


Figure 2.14: ^{1}H NMR (500 MHz) spectra of [*m*- $C_6H_4(CH_2ImMe)\ _2^+$][Cl^-]$_2$.

Then by : **^{13}C NMR**

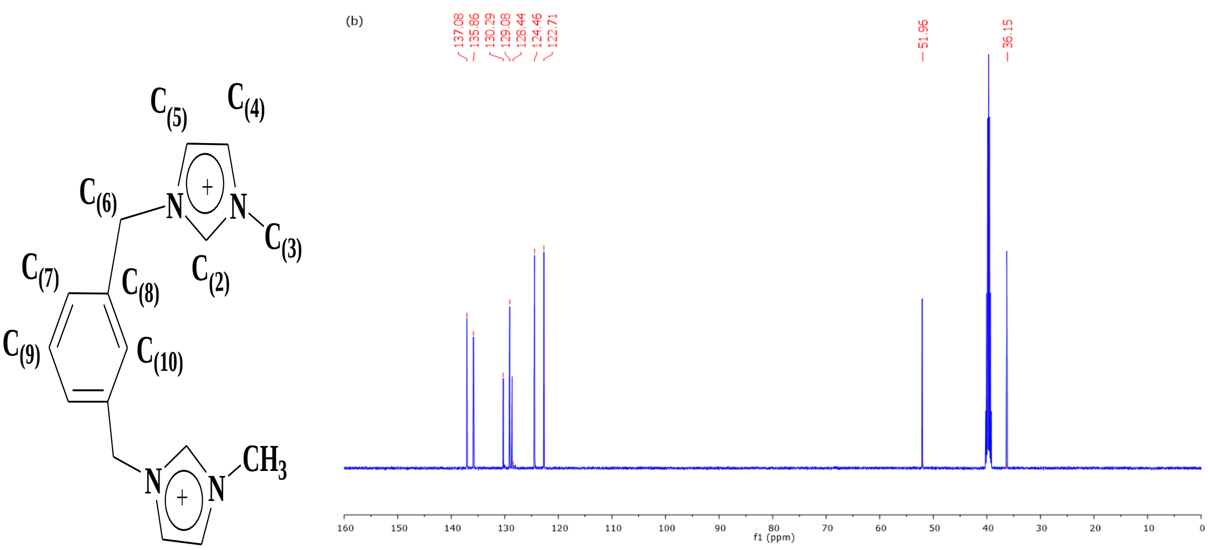


Figure 2.15: ^{13}C NMR (125.75 MHz) spectra of [m-$C_6H_4(CH_2ImMe)_2^+$][Cl^-]2.

The presence of two electron-withdrawing nitrogen atoms in the imidazolium ring makes $C_{(2)}$–H much more acidic than $C_{(4,5)}$–H. Although the charge difference in the C_{Arm}–H phenyl ring is not as large as that in the imidazolium ring, the acidity of all H atoms in 'm-xylene' is low and all $C_{(7, 8, 9)}$ –H and $C_{(6)}$–H can act as donors of H bonds to interact with the anion.

2.2.3.2 Thermal analysis:

The obtained DILs are also processed by: thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of synthetic dicationic ionic liquids (DIL).

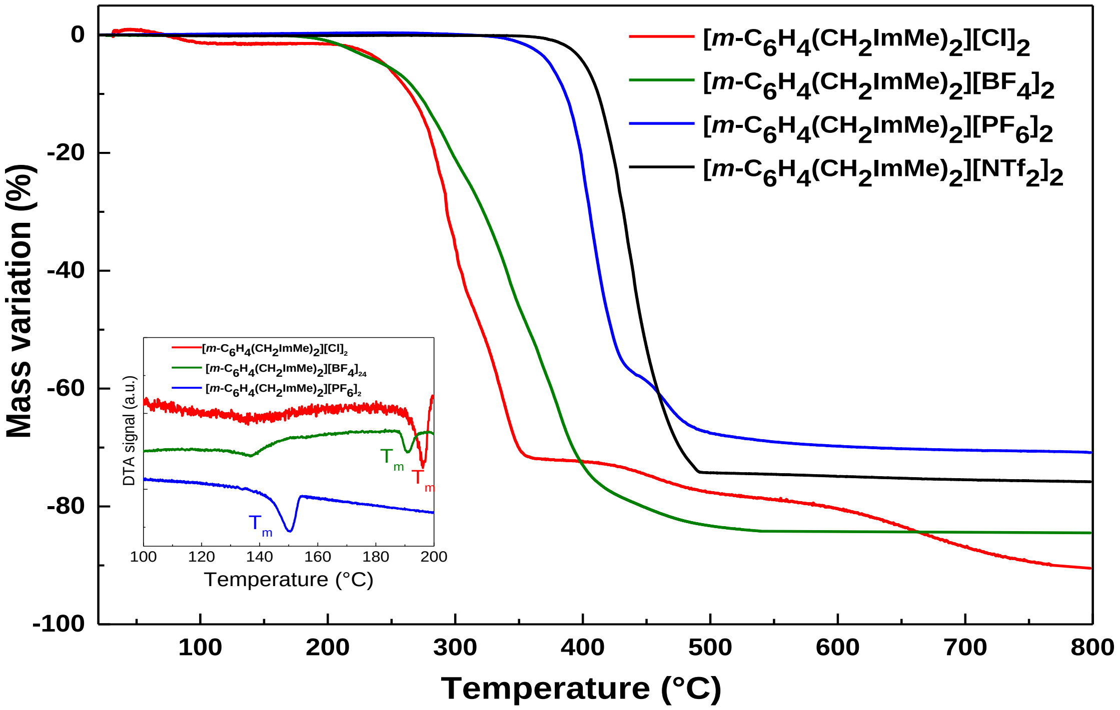


Figure 2.16: TGA and differential thermal analysis (DTA) thermographs for the synthesized dicationic ionic liquids (ILs).

Obtaining the thermal properties for the synthesized dicationic ionic liquids DILs: melting point M_p, and decomposition temperature T_d, from (TGA) and (DTA) thermographs summarized in the table below:

Table 2.3: physical state and melting and decomposition temperatures of DILs.

DILs	Physical state at 25 ° C	M_P	T_d
$[m\text{-}C_6H_4(CH_2ImMe)][CL]_2$	Solid	196° C	357° C
$[m\text{-}C_6H_4(CH_2ImMe)][PF_6]_2$	Solid	150° C	476° C
$[m\text{-}C_6H_4(CH_2ImMe)][BF_4]_2$	solid	136° C	407° C
$[m\text{-}C_6H_4(CH_2ImMe)][(CF_3SO_2)_2N]_2$	liquid	---	491° C

Like the two previous studies, it can be concluded that the values in the tables indicate that the thermal stability increases when the symmetry of the molecules is lowered and vice versa for the melting points in the order given below: MP $[Cl]^-$ > MP $[PF_6]^-$ > MP $[BF_4]^-$ > MP $[(CF_3SO_2)_2N]^-$.

2.2.3.3 Vibrational Spectroscopy Study:

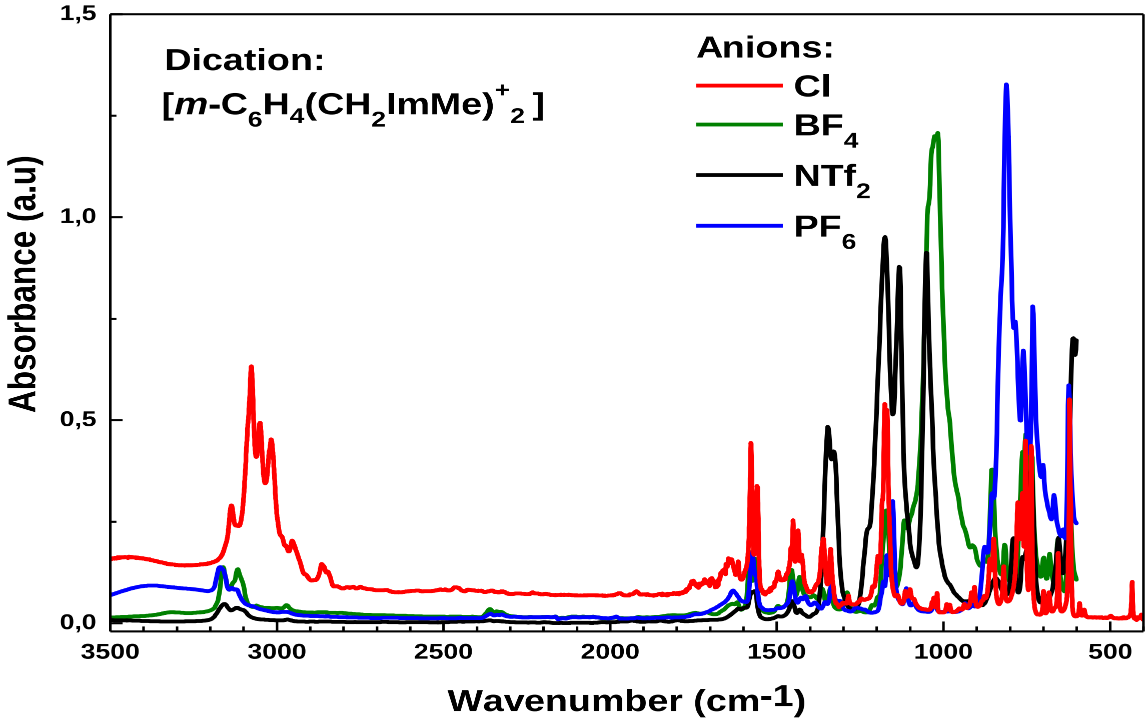


Figure 2.17: Comparison of the infrared absorption spectra of DILs.

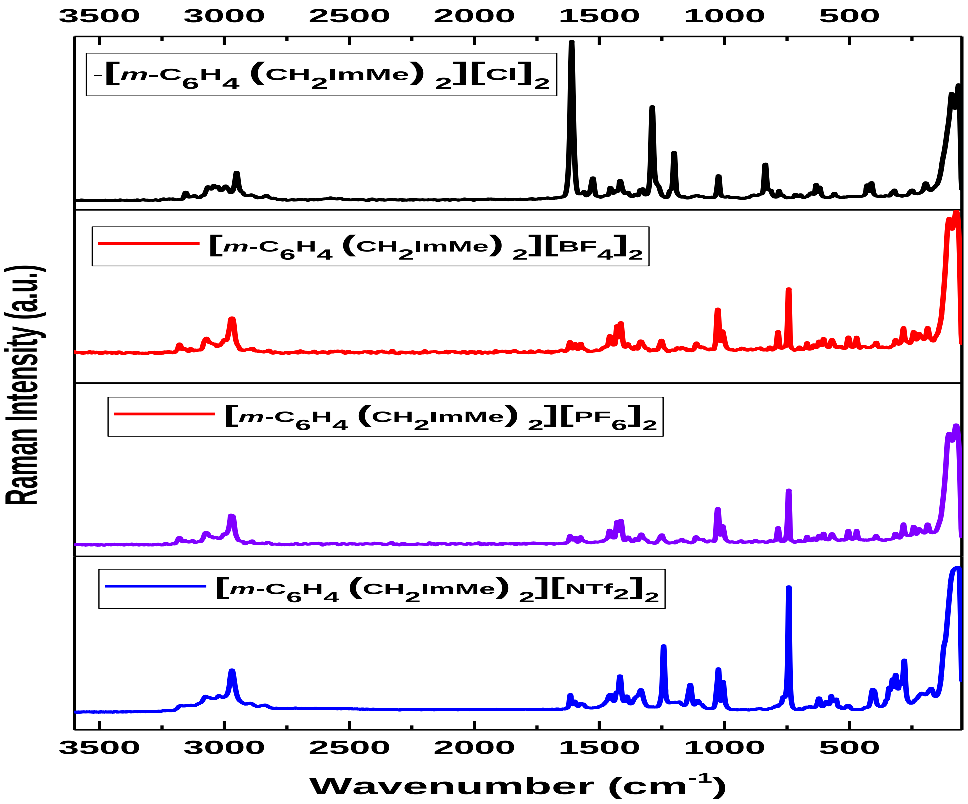


Figure 2.18: Comparison of Raman spectra of the four ionic liquids DILs.

Chapter 2

Similar work and synthesis

Part 2

2.1 Introduction:

The originally of all works in all area , depending on the first step with related to the synthesis steps, published papers related to synthesis of a new compounds and study of their properties, few works have demonstrated the structures and properties salts based on N, N-Alkylene Bis (N'-Alkylimidazolium).

This chapter is devoted to the description of all the experiments carried out as well as the method of characterization of three dicationic ionic liquids DILs.

The thermal properties of imidazolium salts are related not only to the type of anions, but also to the nature of the spacer which connects the imidazolium cations, also the length of the alkyl chain (19).

In this work, new dicationic ILs based on substituted bis-3-butylimidazolium linked to para-xylyl combined with anions, namely: dibromide $[Br^-]_2$, di (hexafluorophosphate) $[PF_6^-]_2$, di (bis (trifluoromethylsulfonyl) Imide) $[(CF_3SO_2)_2N^-]_2$ were studied by structural, vibrational and thermal spectroscopic analysis, the thermal stability of all these dicationic ILs and their decomposition process were studied.

2.1 Materials and method of characterization:

2.2.1 Reagents used:

Table 2.4: Summary of reagents used.

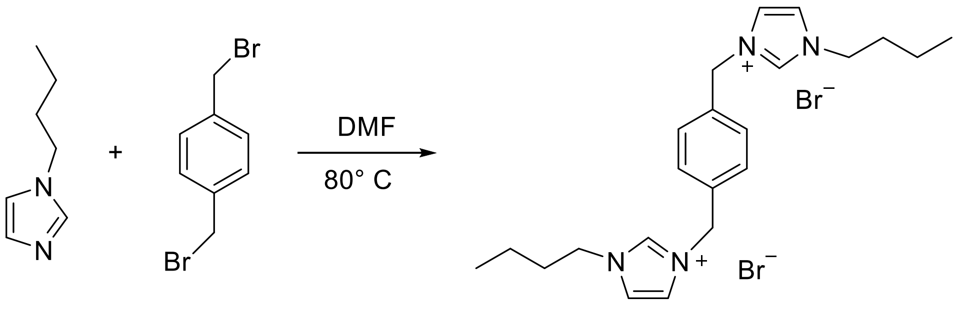
Reagent	**Chemical formula**	**Molar mass**
1-Butylimidazole	$C_7H_{12}N_2$	124
α,α′-Dibromo-p-xylene	$C_8H_8Br_2$	262

Lithium bis(trifluoromethanesulfonyl)imide	$LiC_2F_6NO_4S_2$	229
Potassium hexafluorophosphate	$K[PF_6]$	184
Water, deionized	H_2O	18
Diethyl ether	$(C_2H_5)_2O$	74
Dimethylformamide	C_3H_7NO	73

2.2.2 Preparation of dicationic ionic liquids DILs:

2.2.2.1 Synthesis of halogenated salt DILs:

DIL 3,3' – dibutyl – 1,1 '- (1,4 – phenylenedimethylene) -bis (1H – imidazolium) dibromide was prepared by: a mixture of p-xylene dibromide (2.64 g, 10 mmol) and N-Butylimidazole (2.48 g, 20 mmol) was heated in 3 ml of N, N dimethylformamide (DMF) at 80 ° C for 7 hour at reflux . The resulting mixture was evaporated in rotary evaporator and then washed with diethyl ether (100 mL) to give $[p\text{-}C_6H_4(CH_2ImBu)_2][Br]_2$ as a white hygroscopic solid. Then, the solvent was removed and the product was dried in vacuum for 8 hours to obtain a product of high purity. The yield of this reaction was 93%. The synthesis reaction is shown in scheme3.1



Schema 2.1 Synthesis of the halogenated salt $[p\text{-}C_6H_4(CH_2ImBu)_2]Br_2$.

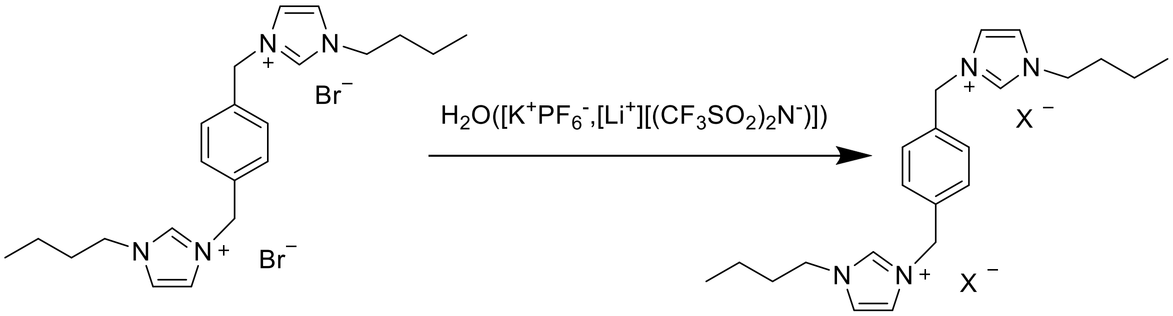
2.2.2.1 Synthesis of fluorinated di-bis (trifluoromethylsulfonyl) imide salt:

The DIL briefly named [*p*-$C_6H_4(CH_2ImBu)_2$] $[NTf_2]_2$ was prepared by an anion exchange reaction from Br^- to $[(CF_3SO_2)_2N]$, which was carried out by mixing the [*p*- C_6H_4 $(CH_2ImBu)_2$] $[Br]_2$ and lithium bis (trifluoromethylsulfonyl) imide (molar ratio = 1: 2) in 20 ml of distilled water at room temperature for 2 hours. Two phases appeared, the lower phase was the ionic liquid, it was washed with water (2x10 ml) and then collected after ten minutes of centrifugation (3000 rpm), the DIL obtained was of a viscous, with a yield of 95%.

2.2.2.2 Synthesis of fluorinated di-hexafluorophosphate salt:

The [*P*-$C_6H_4(CH_2ImBu)_2$] $[PF_6]_2$ was synthesized in the same way as our other DILs. The dibromide salt is dissolved in water, then an aqueous solution of KPF_6 is slowly added to the previous solution with constant stirring for 2-3 hours at room temperature. After that, a white precipitate appears from the resulting solution. After the insulation process, the product is washed with cold water at least 2-3 times. In order to remove the volatile components and the water, the DIL is dried with constant stirring at a temperature of 25 °C for 24 h at a reduced pressure of 2 Pa. Finally, using a Metrohm 831, a test is carried out. Karl Fischer titration to confirm the water content was less than 100 ppm. After drying, the samples were handled under an argon atmosphere.

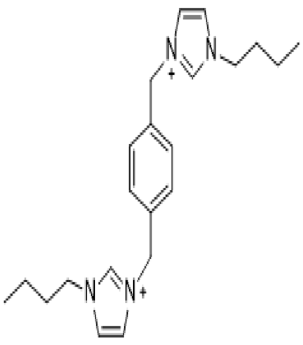
The scheme below summarizes the metathesis reactions to produce the DILs: [*p*-$C_6H_4(CH_2ImBu)_2$] $[NTf_2]_2$ and [*p*-$C_6H_4(CH_2ImBu)_2$] $[PF_6]_2$



Scheme 2.2: Metathesis reactions of [p-$C_6H_4(CH_2ImBu)_2$] $X_{2=}$ (PF_6, NTf_2)from the dibromide salt.

2.3 Structures, nomenclature and abbreviations of synthesized DILs

Table 2.5: Summary of the structures of the prepared DILs and their nomenclature and abbreviations.

Structure of the DIL		**nomenclature**	**Abbreviations**
Dication	**Anion**		
	2 [Br^-]	3,3'–dibutyl–1,1 '-(1,4–phenylenedimethylene) -bis(1H – imidazolium) dibromide	[p-C_6H_4 $(CH_2ImBu)_2$] $[Br]_2$
	2 [PF_6^-]	3,3'–dibutyl–1,1'–(1,4–phenylenedimethylene) –bis(1H–imidazolium) dihexafluorophosphate	[P-$C_6H_4(CH_2ImBu)_2$] [PF6]$_2$

	$2\ [(CF_3SO_2)_2N^-]$	3,3'–dibutyl–1,1'–(1,4–phenylenedimethylene)–bis(1H–imidazolium) dibis(trifluoromethylsulfonyl) imide.	$[p\text{-}C_6H_4(CH_2ImBu)_2][NTf_2]_2$

2.4 Characterization:

2.4.3 NMR measurements

The ^{1}H-NMR (500 MHz), ^{13}C-NMR (125.75 MHz), ^{31}P-NMR (202.47 MHz) and ^{19}F-NMR (470.62 MHz) spectra were recorded on a Bruker DRX 500 MHz spectrometer. The spectra were recorded in dimethyl sulfoxide (DMSO-d6), using the residual peak of DMSO as internal reference 1H ($\delta = 2.50$ and 3.30) and the central peak of DMSO-d6 at $\delta = 39.51$ as reference 13C. The chemical shifts (δ) are given in ppm and refer to the signal of the internal solvent, namely TMS, H3PO4 and CFCl3, respectively. These measurements were performed in university of Caen.

2.4.4 Thermal measurements:

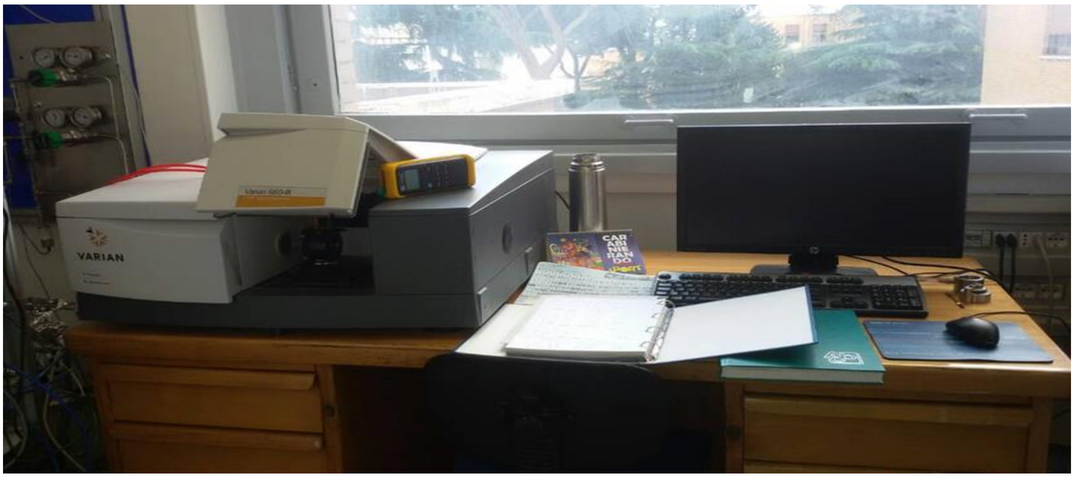
Fegure 2.19: Installation of thermal measurements (TGA-DTA) by Setaram Setsys 1200 TG.

Concomitant thermal gravimetric analysis (TGA) and Differential thermal analysis (DTA) measurements were performed using a Setaram Setsys Evolution 1200 TG system, with a fixed temperature step of 5 ° C / min, in an argon flow of 60 ml / min. For each sample, an initial mass of about 20 mg was used. These measurements were performed in Rome.

2.4.5 FT-Raman measurements:

The FT-RAMAN spectrum was acquired on a Vertex 70-RAM II Bruker FT-Raman spectrometer. This instrument is equipped with a Nd:YAG laser (yttrium aluminium garnet crystal doped with triply ionized neodymium) with a wavelength of 1064 nm and a maximum power of 1.5 W. The measurement accessory is pre-aligned: only the Z-axis of the scattered light is adjusted to set the sample in the appropriate position regarding the local measurement point. The RAM II spectrometer is equipped with a liquid nitrogen cooled Ge detector. FT-Raman spectra [454000cm-1] were collected with 1 cm-1 resolution by co-adding 128 scans for each spectrum at room temperature. The OPUS 6.0 software was used for the spectral acquisition, manipulation and transformation. These measurements were performed in the Walloon Agricultural Research Center (Craw) Belgium.

2.4.6 IR measurements:



Fegure 2.20: Agilent Cary 660 IR Spectrometer.

The absorbance spectrum of [*p*-$C_6H_4(CH_2ImBu)_2][(CF_3SO_2)_2N]_2$ was measured by means of an Agilent Cary 660 spectrometer equipped with a ceramic source, a DTGS detector and a KBr beams plitter. A few mg of powder were dissolved in KBr powder in a mass ratio of 3:100 and pressed in a dye in order to obtain a self-standing pellet. These measurements were performed in Rome.

References:

1. Ji, Y., Hou, Y., Ren, S., Yao, C., & Wu, W. (2018). Highly efficient extraction of phenolic compounds from oil mixtures by trimethylamine-based dicationic ionic liquids via forming deep eutectic solvents. *Fuel Processing Technology*, *171*, 183-191.
2. Patil, R. A., Talebi, M., Sidisky, L. M., & Armstrong, D. W. (2017). Examination of selectivities of thermally stable geminal dicationic ionic liquids by structural modification. *Chromatographia*, *80*(10), 1563-1574.
3. Haddad, B., Moumene, T., Villemin, D., Lohier, J. F., & Belarbi, E. H. (2016). Bis-methyl imidazolium methylidene bis (trifluoromethanesulfonyl) imide, crystal structure, thermal and dielectric studies. *Bulletin of Materials Science*, *39*(3), 797-801.
4. Haddad, B., Paolone, A., Villemin, D., Lohier, J. F., Drai, M., Bresson, S., ... & Belarbi, E. H. (2018). para-Xylyl bis-1-methylimidazolium bis (trifluoromethanesulfonyl) imide: Synthesis, crystal structure, thermal stability, vibrational studies. *Journal of Molecular Liquids*, *260*, 391-402.
5. Moumene, T., Belarbi, E. H., Haddad, B., Villemin, D., Abbas, O., Khelifa, B., & Bresson, S. (2014). Vibrational spectroscopic study of ionic liquids: Comparison between monocationic and dicationic imidazolium ionic liquids. *Journal of Molecular Structure*, *1065*, 86-92.
6. Chae, H., Lee, Y. H., Yang, M., Yoon, W. J., Yoon, D. K., Jeong, K. U., ... & Lee, M. (2019). Interesting phase behaviors and ion-conducting properties of dicationic N-alkylimidazolium tetrafluoroborate salts. *RSC advances*, *9*(7), 3972-3978.
7. Anderson, J. L., Ding, R., Ellern, A., & Armstrong, D. W. (2005). Structure and properties of high stability geminal dicationic ionic liquids. *Journal of the American Chemical Society*, *127*(2), 593-604.
8. Haddad, B., Villemin, D., Belarbi, E. H., Bar, N., & Rahmouni, M. (2014). New dicationic piperidinium hexafluorophosphate ILs, synthesis, characterization and dielectric measurements. *Arabian Journal of Chemistry*, *7*(5), 781-787.
9. Zhang, Z., Yang, L., Luo, S., Tian, M., Tachibana, K., & Kamijima, K. (2007). Ionic liquids based on aliphatic tetraalkylammonium dications and TFSI anion as potential electrolytes. *Journal of Power sources*, *167*(1), 217-222.
10. Ji, Y., Hou, Y., Ren, S., Yao, C., & Wu, W. (2018). Highly efficient extraction of phenolic compounds from oil mixtures by trimethylamine-based dicationic ionic liquids via forming deep eutectic solvents. *Fuel Processing Technology*, *171*, 183-191.
11. Moumene, T., Belarbi, E. H., Haddad, B., Villemin, D., Abbas, O., Khelifa, B., & Bresson, S. (2014). Vibrational spectroscopic study of ionic liquids: Comparison between monocationic and dicationic imidazolium ionic liquids. *Journal of Molecular Structure*, *1065*, 86-92.
12. Patil, R. A., Talebi, M., Xu, C., Bhawal, S. S., & Armstrong, D. W. (2016). Synthesis of thermally stable geminal dicationic ionic liquids and related ionic compounds: an examination of physicochemical properties by structural modification. *Chemistry of Materials*, *28*(12), 4315-4323.

13. Boumediene, M., Haddad, B., Paolone, A., Assenine, M. A., Villemin, D., Rahmouni, M., & Bresson, S. (2020). Synthesis, conformational studies, vibrational spectra and thermal properties, of new 1, 4-(phenylenebis (methylene) bis (methyl-imidazolium) ionic liquids. *Journal of Molecular Structure*, *1220*, 128731.

14. Haddad, B., Paolone, A., Villemin, D., Lohier, J. F., Drai, M., Bresson, S., ... & Belarbi, E. H. (2018). para-Xylyl bis-1-methylimidazolium bis (trifluoromethanesulfonyl) imide: Synthesis, crystal structure, thermal stability, vibrational studies. *Journal of Molecular Liquids*, *260*, 391-402.

15. Haddad, B., Paolone, A., Drai, M., Boumediene, M., Villemin, D., Belarbi, E. H., ... & Abbas, O. (2019). Para-xylyl linked bis-imidazolium ionic liquids: A study of the conformers of the cation and of the anion-cation hydrogen bonding. *Journal of Molecular Structure*, *1175*, 175-184.

16. Boumediene, M., Haddad, B., Paolone, A., Assenine, M. A., Villemin, D., Rahmouni, M., & Bresson, S. (2020). Synthesis, conformational studies, vibrational spectra and thermal properties, of new 1, 4-(phenylenebis (methylene) bis (methyl-imidazolium) ionic liquids. *Journal of Molecular Structure, 1220*, 128731.

17. Boumediene, M., Haddad, B., Paolone, A., Drai, M., Villemin, D., Rahmouni, M., ... & Abbas, O. (2019). Synthesis, thermal stability, vibrational spectra and conformational studies of novel dicationic meta-xylyl linked bis-1-methylimidazolium ionic liquids. *Journal of Molecular Structure, 1186*, 68-79.

18. Paschoal, V. H., Faria, L. F., & Ribeiro, M. C. (2017). Vibrational spectroscopy of ionic liquids. *Chemical reviews*, *117*(10), 7053-7112.

19. Ngo, H. L., LeCompte, K., Hargens, L., & McEwen, A. B. (2000). Thermal properties of imidazolium ionic liquids. *Thermochimica Acta*, *357*, 97-102

Chapter 3

Results and discussions

3.1 Introduction :

In this fourth chapter, we will discuss the study of the vibrational and thermal analysis properties of three synthesis DILs

- $[p\text{-}C_6H_4(CH_2ImBu)_2][(CF_3SO_2)_2N]_2$ namely 3,3'–dibutyl–1,1'–(1,4–phenylenedimethylene)–bis(1H–imidazolium) di bis (trifluoromethylsulfonyl) imide.
- $[p\text{-}C_6H_4(CH2ImBu)_2][Br]_2$ namely 3,3' – dibutyl – 1,1 '- (1,4 – phenylenedimethylene) -bis (1H – imidazolium) dibromide.
- $[p\text{-}C_6H_4(CH_2ImBu)_2][PF_6]_2$ namely 3,3'–dibutyl–1,1'–(1,4–phenylenedimethylene)–bis(1H–imidazolium) dihexafluorophosphate.

All published papers indicate that DILs have higher thermal stabilities than monocationic ionic liquids (1, 2), they often exhibit higher melting points than ionic liquids (ILs), thermal stability is an important property of ILs, and analysis thermogravimetric (TGA) is generally the first analytical technique used for characterization, decomposition temperatures (T_d) are useful for comparing the thermal stabilities of different ILs (3).

The imidazolium cation has a positive charge delocalized in an aromatic ring, the hydrogens in $C_{(2)}$–H $C_{(4)}$-H and $C_{(5)}$–H are slightly acidic, of which the hydrogen $C_{(2)}$–H is the more acidic, these hydrogens are able to make hydrogen bonds. Imidazolium salts therefore have the ability to form cation-anion, π-anion and hydrogen bonds (4). Van der Waals-type interactions can take place if alkyl chains are present on the nitrogen atoms.

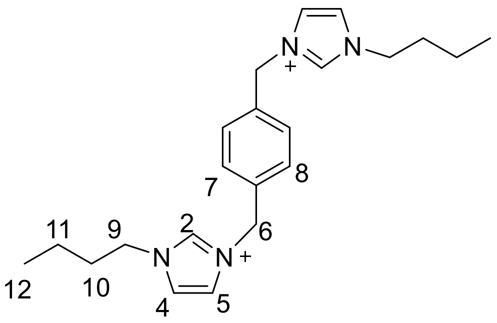
We will split this chapter into two parts:

- Structural study by NMR
- Vibrational study by IR and RAMAN
- Thermal study by ATG and DTG

3.2 Experimental characterization of structural, thermal properties and vibrational spectroscopic of ionic liquids:

3.2.1 Structural study:

In order to confirm the structure of all the DILs and to demonstrate the absence of impurities, the NMR technique is applied.



Scheme 3.1: The chemical structure of cation, the numbers indicate the atoms numbering used in discussion.

- **3,3'–dibutyl–1,1'–(1,4–phenylenedimethylene)–bis(1H–imidazolium dibromide:** $[p\text{-}C_6)\ H_4(CH_2ImBu)_2][Br]_2$:

^{1}H–NMR (DMSO–d_6) δ_H (ppm): 1.02 (t, J = 7.2 Hz, 3 H,CH_3); 1.43 (m, 2 H,CH_2); 1.91 (m, 2 H,CH_2); 4.25 (t, J = 7.5 Hz, 2H,CH_2N); 5.51 (s, 4H, CH_2-Ar), 7.56 (d, 4H, CH_{Im}), 7.76 (d, 4H,CH_{Im}), 7.89 (s, 2H, CH_{Ar}), 7.95 (s, 2H, CH_{Ar}), 9.45 (s,2H, NCHN).

^{13}C–NMR (DMSO–d_6) δ ppm: 13.17 (CH_3); 19.31 (CH_2); 31.87 (CH_2); 50.06 (CH_2N); 52.12 (CH_2Ar), 122.87 (CH_{im}), 124.61 (CH_{im}), 127.86, 137.37, 140.10 (NCHCH).

First, the ^{1}H NMR spectrum of $[p\text{-}C_6H_4(CH_2ImBu)_2][Br^-]_2$showed a singlet at δ = 9.45 ppm of the NC $_{(2)}$ HN corresponding to the protons of the imidazolium fragment and a doublet at δ = 7.56 / 7.76 ppm of the protons NC $_{(4)}$ HC $_{(5)}$ HN. The resonances of the aromatic phenyl group

($–C_6H_4–$) are observed as a singlet at δ = 7.95 ppm. On the other hand, the resonance of the methylene protons ($–C_{(6)}H_2–$) is observed in the form of a singlet at δ = 5.51 ppm.

Second, examination of the ^{13}C NMR spectrum of DIL shows the appearance of five signals corresponding to the carbon atoms of the imidazole and phenyl rings located at 122.87, 124.61, 127.86, 137.37 and 140.10 ppm respectively. The spectrum also shows the appearance of four signals corresponding to the carbon atoms of the side chain located at 13.17, 19.31, 31.87and 50.06 ppm respectively.

- **3,3'–dibutyl–1,1'–(1,4–phenylenedimethylene)–bis(1H–imidazolium) ^{1}H bis(hexafluorophosphate):** [p-$C_6H_4(CH_2ImBu)_2][PF_6]_2$:

^{1}H–NMR (DMSO–d_6) δ_H (ppm): ^{1}H–NMR (DMSO–d_6) δ_H (ppm): 1.03 (t, J = 7.2 Hz, 3 H,CH_3); 1.44 (m, 2 H,CH_2); 1.92 (m, 2 H,CH_2); 4.26 (t, J = 7.5 Hz, 2H,CH_2N); 5.52 (s, 4H, CH_2-Ar), 7.57 (d, 4H, CH_{Im}), 7.77 (d, 4H,CH_{Im}), 7. 9 (s, 2H, CH_{Ar}), 7.96 (s, 2H, CH_{Ar}), 9.46 (s, 2H, NCHN).

^{13}C–NMR (DMSO–d_6) δ ppm: 13.18 (CH_3); 19.32 (CH_2); 31.88 (CH_2); 50.07 (CH_2N); 52.13 (CH_2Ar), 122.88 (CH_{im}), 124.61 (CH_{im}), 127.87, 137.38, 140.13 (NCHCH).

^{19}F–NMR (DMSO–d_6) δ_F (ppm): - 70.10 (d, J_{F-P} 711 Hz) [PF_6^-]

^{31}P–NMR (DMSO–d_6) δP (ppm): -144.22 (sept, J_{P-F} 711 Hz) [PF_6^-]

From the proton NMR spectrum of DIL [p-C_6H_4 (CH_2ImBu) $_2$] [PF_6] $_2$ we can distinguish a singlet at δ = 9.46 ppm of the NC $_{(2)}$ HN corresponding to the proton at position (2) of the imidazolium fragment and a doublet at δ = 7.57 / 7.77 ppm of the NC $_{(4)}$ HC $_{(5)}$ HN protons. The resonances of the aromatic phenyl group ($–C_6H_4–$) are observed as a singlet at δ = 7.9 ppm. On the other hand, the resonance of the methylene protons ($–C_{(6)}H_2–$) is observed in the form of a singlet at δ = 5.52 ppm. Finally, the characteristic signal of N-butyl (NCH_2) appeared at δ = 4.26 ppm and 1.44, 1.92 ppm for ($-CH_2-$) and 1.03 ppm for (CH_3).

the ^{13}C NMR spectrum of DIL containing the PF_6^- anion shows the appearance of seven signals corresponding to the carbon atoms of the imidazole, phenyl (aromatic), located at 140.13, 137.38, 127.87, 124.61, 122.88, 52.13 for ($-CH_2-$) and ($-CH_3$) of butyl chain 50.07,31.88,19.32and 13.18 ppm respectively.

- **3,3'–dibutyl–1,1'–(1,4–phenylenedimethylene)–bis(1H–imidazolium) di(bis (trifluoromethylsulfonyl) imide:** [*p*-$C_6H_4(CH_2ImBu)_2$][$(CF_3SO_2)_2N^-$]$_{2:}$

^{1}H–NMR (DMSO–d_6) δ_H (ppm): ^{1}H–NMR (DMSO–d_6) δ_H (ppm): 1.02 (t, J = 7.2 Hz, 3 H,CH_3); 1.43 (m, 2 H,CH_2); 1.91 (m, 2 H,CH_2); 4.25 (t, J = 7.5 Hz, 2H,CH_2N); 5.51 (s, 4H, CH_2-Ar), 7.56 (d, 4H, CH_{Im}), 7.76 (d, 4H,CH_{Im}), 7.89 (s, 2H, CH_{Ar}), 7.95 (s, 2H, CH_{Ar}), 9.51 (s,2H, NCHN).

^{13}C–NMR (DMSO–d6) δ ppm: 13.17 (CH_3); 19.31 (CH_2); 31.87 (CH_2); 50.06 (CH_2N); 52.12 (CH_2Ar),122.87 (CH_{im}), 124.61 (CH_{im}), 127.87, 137.38, 140.18 (NCHCH), 143.2 (CF_3).

^{19}F–NMR (DMSO–d_6) δ_F (ppm): -78.75 (s), [$(CF_3SO_2)_2N^-$]

For the DIL [*p*-C_6H_4 $(CH_2ImBu)^+_2$] [$(CF_3SO_2)_2N^-$]$_2$, the resonance of the proton $NC_{(2)}$ HN of the imidazolium fragment recorded the lowest value δ = 9.51 ppm, this probably due to the nature of the anion [$(CF_3SO_2)_2N^-$], which has a low symmetry with respect to the other anions, in addition to its complexity and its volume (size).

Table 3. 1: H-NMR peaks and assignments.

	[p-$C_6H_4(CH_2ImBu)_2$] [$(CF_3SO_2)_2N$]$_2$	**[p-$C_6H_4(CH_2ImBu)_2$] [PF_6]$_2$**	**[p-$C_6H_4(CH_2ImBu)_2$] [Br]$_2$**
$C_{(2)}$–H	9.51	9.46	9.45
$C_{(7)}$–H	7.89	7.90	7.89
$C_{(8)}$–H	7.95	7.96	7.95
$C_{(4)}$–H	7.76	7.77	7.76
$C_{(5)}$–H	7.56	7.57	7.56
$C_{(6)}$–H	5.51	5.52	5.52
$C_{(9)}$–H	4.25	4.26	4.25

To better understand the structural effect of the anion, an overview on the table shows that, for the imidazolium nucleus, the chemical shift of C (2) –H a increases by 9.45 ppm for [p-C_6H_4 (CH_2ImBu)$_2$] [Br] $_2$; 9.46 ppm for DIL [p-C_6H_4 (CH_2ImBu)$_2$] [PF_6] $_2$ and finally at 9.51 ppm for DILs [p-C_6H_4 (CH_2ImBu)$_2$] [$(CF_3SO_2)_2N^-$]$_2$.

This clearly showed that the anion ([$(CF_3SO_2)_2N^-$]) is close to the H – C $_{(2)}$ site of the cation to form a specific hydrogen bond, which is much stronger than that of other DILs. In summary, the chemical shifts of the ^{1}H NMR of our DILs follow the order:

C $_{(2)}$ –H> H – C $_{(7)}$ / C $_{(8)}$ –H> (H – C $_{(5)}$ / C $_{(4)}$ –H)> (–C $_{(6)}$ H2 -)> –C $_{(9)}$ H2

3.2.2 Vibrational spectroscopic analysis:

The DIL coupled with the three anions were analyzed by vibrational spectroscopy which is a powerful tool for exploring the structure of an ionic liquid and characterizing the different interactions

3.2.2.1 Infrared spectroscopy study of DILs:

In this part, IR study allows us to find the different intra / intermolecular interactions and vibration modes for the three dicationic liquids (DILs).

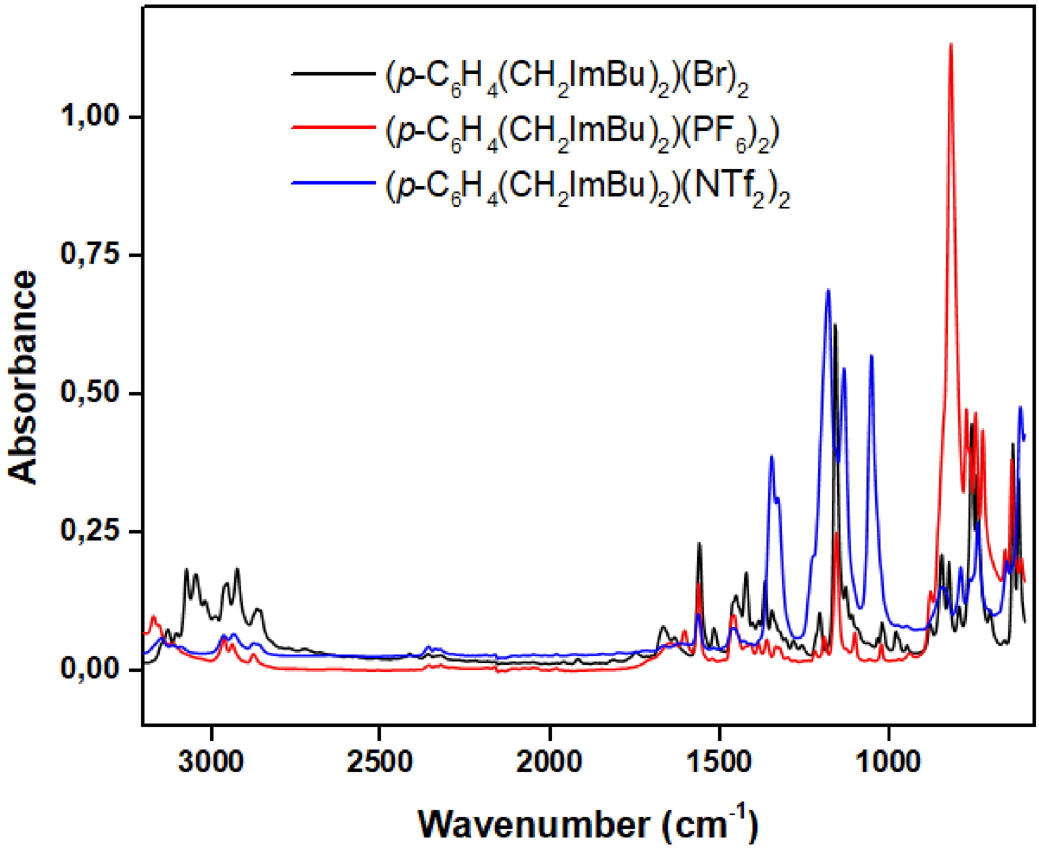


Figure 3.1: Comparison of the infrared absorption spectra of the three DILs in the spectral range [3500-400 cm^{-1}].

The bands shown in Figure 4.1 will be discussed in terms of vibrations, as follows:

- **C – H vibrations:**

The spectra of the three DILs were measured in the frequency range 4000 –500 cm^{-1}. In general, vibrations of symmetrical and asymmetric stretching of C – H bonds give bands in the spectral range of 3200 to 3000 cm^{-1} in all aromatic compounds (benzene and imidazole rings), the frequencies of this mode in our DILs are observed in a narrow range between 3174 and 3018 cm^{-1}, the bands are low, medium (3074 cm^{-1}), the stretching vibrations of the aliphatic C – H bond of ionic liquids ($-CH_2$ and $-CH_3$) have been observed in the range between 2987 and 2857 cm^{-1}, spectra show bands of low and medium intensity, we observe 3 strong bonds corresponding to (1180,1159,1053 cm^{-1}) in-plane bending vibration which relate to the C-H bonds , and the out of plane bending CH deformation vibrations between 879 -740 cm^{-1}.

- **C – C and C – N vibrations:**

C – C stretching frequencies are generally predicted in the region of 1650–1200 cm-1 (5). In the present study, the C − C stretching of our ionic liquids were observed at 1367 (m) and 1346 (s) cm^{-1}. The infrared spectrum of [*p*-$C_6H_4(CH_2ImBu)_2$] [$(CF_3SO_2)_2N$]$_2$ shows bands at 1346 (s), [*p*-$C_6H_4(CH_2ImBu)_2$] [Br]$_2$ at 1367 (m) and [*p*-C_6H_4 $(CH_2ImBu)_2$] [PF_6]$_2$ at1409 (w) cm-1 which can be attributed to the stretching of the imidazole ring consisting of C – N stretching, N –C – H in plane bending for the spectra DILs [*p*-$C_6H_4(CH_2ImBu)_2$] [$(CF_3SO_2)_2N$]$_2$ and [*p*-$C_6H_4(CH_2ImBu)_2$][PF_6]$_2$ around 1562 cm^{-1}.

- **C = C vibrations:**

In the present study, C = C elongation bands are observed around 1560 (m), 1604 (w), 1666 (vw) cm^{-1} for the spectra of the studied DILs.

- **Anionic vibrations:**

Another important indicator of intermolecular interactions is the infrared bands corresponding to the anionic species of the ionic liquid. In the spectra, the presence of a strong band characteristic of [$(CF_3SO_2)_2N^-$] are observed at 613 cm^{-1}, assigned to a symmetrical stretching SO_2 (1134 (s), 1346 (s) cm^{-1}) and bending vibrations of SNS at 613 (s) cm^{-1}, and bending of CF_3 at 738 (m) cm^{-1}, we also observe in the spectra two bands: a strong intensity at 817 (s) cm^-

^{1} and another medium band at 744 cm^{-1} correspond to the asymmetric stretching of hexafluorophosphate (PF_6^-).

Table 4.2 FTIR / ATR bands observed and their assignment for the three DILs . vw = very weak; w = weak; m = medium, s = strong; sh = shoulder; ν = Str = stretch; δ = deformation; bend = bending deformation; ω = wagging; ρ = rocking; ɤ = out-of-plane; s = symmetric; as = antisymmetric.

[P-$C_6H_4(CH_2ImBu)_2$]			**Vibrational assignment**	**References**
$[Br]_2$	**$[PF_6]_2$**	**$[NTf_2]_2$**		
Range: 3300-2700 cm^{-1}				
	3172(w)	3174(w)	H-C-C-H symmetric stretch	[7]/ [11]/[12]/ [16]/ [24]/ [25]/[26]/[8]
3130(w)	3155(w)	3120(vw)	H-C-C-H asymmetric stretch	[7]/ [11]/[12]/ [16]/ [24]/ [25]/[26]/[8]
3105(vw)	3116(vw)	3109(vw)	H-C-C-H asymmetric stretch	[7]/ [11]/[12]/ [16]/ [24]/ [25]/[26]/[8]
3074(m)			ν (C-H) / ν (CH)	[24]/[8]/[13]
3047(m)			ν (C-H)	[15]/[26]/[8]/[13]
3018(w)			ν (C-H)	[15]/[26]/[8]/[13]
2987(vw)			(N)CH_2- asymmetric stretch,CH_2HCH asym Str	[25]/ [26]/ [8]/ [13]
2954(m)	2964(w)	2964(w)	(N)CH_2- asymmetric stretch,CH_2HCH asym Str	[25]/ [26]/ [8]/ [13]
2925(m)	2939(w)	2937(w)	(N)CH_2- asymmetric stretch,CH_2HCH asym Str	[25]/ [26]/ [8]/ [13]
2864(w)	2857(vw)	2873(vw)	(N)CH_2- symmetric stretch	[11] /[24]/[26]/[13]
			Range : 1700- 900cm^{-1}	

1666(w)	1651(sh)	1666(vw)	Imidazole ring : C=C str, N =C-N str	[25]
1631(vw)	1604(w)	1620(vw)	Phenyl ring : ν C=C	[15] /[9]/[7]/[11]/[12]/[16]
1560(m)	1562(m)	1562(w)	Phenyl ring :C=C stretching, (N)CH_2 str	[15] /[9]/[7]/[11]/[12]/[16]
1516(w)	1521(vw)	1517(vw)	Imidazole ring ip asym str, HCH sym bend	[22]/[29]/[8]/[13]
1452(w)	1458(w)	1460(w)	δ (CH2)/CCH HCH as bend	[11] /[24]/[26]/[13]
1423(m)	1421(vw)	1427(vw)	Imidazole ring :C–N/ C=Nstretching band, δs(CH_2), C–H Deformation	[16] /[9]/[7]/[32]/[12]/[16]/[29]
	1409(vw)	1407(vw)	ρ (N-CH), Imidazole ring :C–N / C=N stretching band, (N)CH_2 str, C–H deformation	[15]/ [24]/[27]
1384(vw)	1384(vw)		ρ(CH_2), ρ(CH)/δ(CH_2) [op], ω(CH)	[15] /[26]/[27]
1367(m)	1361(vw)		Imidazole ring : C–N/ C=N stretching band, (N)CH_2 str , ν CC	[15] /[9]/[10]/[11]/[12]/[7]/[16]
1346(w)		1346(s)	Imidazole ring :C–N/ C=N stretching, SO_2 asym str	[15] /[9]/[11]/[12/[7]/[16]
	1326(vw)	1328(sh)	Imidazole ring :C–N/ C=N stretching, SO_2 asym str	[15] /[9]/[11]/[12/[7]/[16]
1305(w)	1299(vw)		ρ C4-H, C5-H, twist CH_2,	[29]/[9]
1282(vw)	1278(vw)		Phenyl ring: C–C stretching	[15] /[11]/[12]/[7/[16]/[29]
1205(w)	1218(vw)	1224(sh)	ν CN, CF_3 sym Str	[15]
	1191(s)	1180(s)	Ring s CH2(N) and CH_2(N)CN Str	[11]/[24]

1159(s)	1155(w)	1161(sh)	δ CH, (N)-CH_2-, (N)-CH_2	[11]/[29]
1128(w)	1126(vw)	1134(s)	Trans [NTf_2]: νs(SO_2)	[6]/ [9]/ [24]
1109(sh)	1101(w		δ CH, ring HCCH sym bend, CC str	[22]/[24]/[36]
1039(sh)	1058(vw)	1053(s)	CH_2N Str/CH_2N Str , ν C-C	[15]/ [11]/ [17] /[18]/[19] /[20]/[24]
1022(vw)	1024(w)		ring ip sym str	[22]
979(w)	972(vw)	974(vw)	ν CC, ring ip asym bend	[22]
			Range : 900- 600 cm^{-1}	
879(w)	877(w)		NC(H) N bend, ρ as(CH_2)	[11]/[16]/[27]
844(m)		840(w)	NC(H) N bend /CCH bend / NC2(H)N CH bend	[9]/[10]/[24]
823(m)	817(s)		νas (PF_6), Ring CC bend	[22]/[27]
792(w)	773(m)	788(w)	ring HCCH asym bend / CS St	[9]/ [21]/[23]
756(s)	761(m)	761(sh)	δ (HCCH)/ ring HCCH asym bend, νs SNS,	[10]/[21]/[22]/ [24]
740(s)	744(m)	738(m)	Tans[NTf2] : δs (CF_3), ring HCCH sym bend, CF_3 sym bend, ν (PF_6)	[21]/ [10]/[22]/ [24]/[19]
	723(m)		Anion interaction, CH_2(N) and CN str,	[10]/ [21]/[24]/[19]/[22]
	657(w)	653(w)	ω (C-H) , δ CC, C=C-H, Ring HCCH sym bend	[15]/ [17] /[18]/[19] /[20]/[25]/[27]
634(s)	638(m)		CH_2(N) str, ring op bend, Trans[NTf_2] : δSNS	[15] /[21]/[10]/[11]/[12]/[7]/[16]
619(s)	609(w)	613(s)	CH_2-(N) CN Str,, δSNS	[23]

3.2.2.2 Raman spectroscopy study of DILs:

The spectra of the three DILs were measured in the frequency range 3500 –60 cm-1 for Raman,

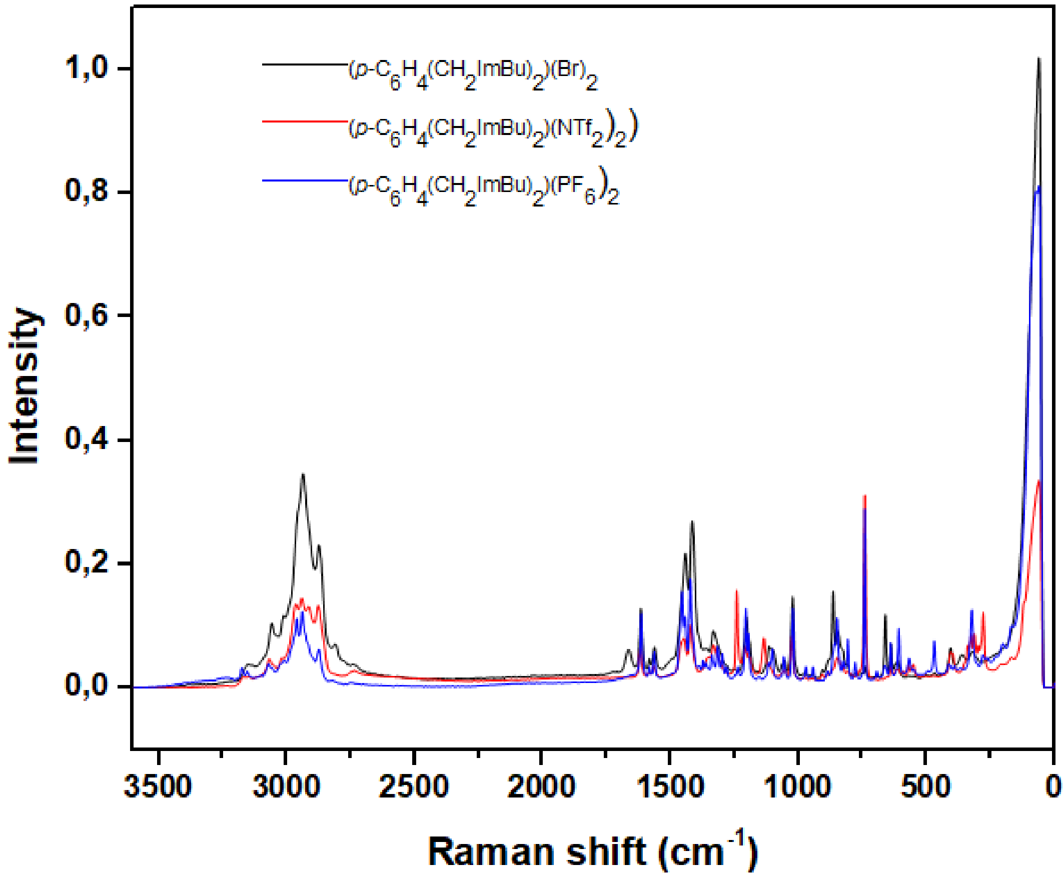


Figure 3.2: Comparison of Raman spectra of the three dicationic ionic liquids in the frequency range 3500 - 60 cm^{-1}

The bands shown in Figure 4.2 will be discussed in terms of vibrations, as follows:

- **Range 1000- 45 cm^{-1} :**

The bands in the area [200-50 cm-1] correspond to intermolecular vibrations with the anions $[Br]^-$, $[PF_6]^-$, $[(CF_3SO_2)_2N^-]$

1. [$(CF_3SO_2)_2N^-$] shows a strongly intense peak at 60 cm^{-1} and other weak peaks at 118, 167 cm^{-1}, asymmetric and symmetrical bending of CF_3 was distributed to the bands of 533, 571 and 741 cm^{-1}, rocking SO_2 at (312 and 325 cm^{-1}), wagging SO_2 at (404 cm^{-1}), bending (a)symmetrical with SO_2 at (571 cm^{-1}), another mode is observed at 763 cm^{-1} attributed to symmetrical stretching of S – N – S .
2. In the dibromide salt, we notice the presence of the following vibration mode: 60 (s) cm^{-1} attributed to the intermolecular interaction.
3. The spectrum relating to the PF_6^- anion shows peaks, in particular a stretching at 470 cm^{-1}.
4. The bending movements of these links (HCCH) have a contribution in the weak bands of the zone between 750 and 900 cm^{-1}.

- **Range 1700-1000 cm^{-1} :**
    1. This spectral region, begins with (C – C) appearing in the range [1000-1200 cm^{-1}], a band of (bending at 1026 cm^{-1}).
    2. For the anion [$(CF_3SO_2)_2N^-$] an antisymmetric stretching mode for SO_2 is expected at 1350 cm^{-1}, the contributions of the symmetrical vibration stretching of the CF_3 (medium band at 1242cm^{-1}).
    3. The presence of the C = C stretching bands located in the spectral range [1650 -1550 cm^{-1}] in the form of bands could also identify the phenyl cycle of dicationic ILs.
- **Range 3500-2700 cm^{-1} :**

In the region 3200-2700 cm-1, the dicationic spectrum is richer in vibration modes

1. New medium band is present around 2876 (m) cm^{-1} (attributed to symmetrical stretching CH_3 of butyl chain

2. At 3067 cm^{-1}, 3071 cm^{-1} and 3059 cm^{-1} these bonds are stretching (CH) for the three DILs).
3. Frequencies above 3117 cm^{-1} attributed to (HCCH) aromatic rings.

Table 3.3: FT-RAMAN bands observed and assignment for the three DILs at room temperature ,vw = Very weak; w = weak; m = medium, s = strong; sh = shoulder; ν = Str = stretch; δ = deformation; bend = bending deformation; ω = wagging; ρ = rocking; τ = torsion, s = symmetric; as = antisymmetric

[*p*-$C_6H_4(CH_2ImBu)_2$]			**Vibrational assignment**	**References**
$[Br]_2$	**$[PF_6]_2$**	**$[NTf_2]_2$**		
			Range: 3500- 2700 cm^{-1}	
	3175(vw)	3172(vw)	H-C-C-H asymmetric stretch	[11]/[12]/[24]/[8]/[37]
3145(vw)	3154(vw)	3146(vw)	H-C-C-H asymmetric stretch	[11]/[12]/[45]/[29]/[16]
		3117(sh)	H-C-C-H asymmetric stretch	[21]/[24]/[8]/[16]
	3071(vw)	3067(vw)	C-H stretching	[31]/[32]/[34]
3059(w)	3059(vw)		C-H stretching	[37]/[39]/[10]/[38]
3011(sh)	3010(vw)	3017(w)	C-H stretching	[24]/[34]/[7]
	2961(w)	2964(m)	(N)CH_2 asymmetric stretch, νas (CH_3)	[27]/[32]/[34]
2935(m)	2939(w)	2941(m)	(N)CH_2 symmetric stretch	[22]/[26]/[9]
	2917(vw)	2916(m)	(N)CH_2 symmetric stretch	[22]/[26]/[9]
2875(m)	2875(vw)	2876(m)	(N)CH_2 symmetric stretch	[23]/[10]/[8]
2811(w)			νs(CH_3), (N)CH_2, sym stretch	[29/[8]/[16]

			Range: 1700-1000 cm^{-1}	
1616(w)	1615(w)	1619(w)	Phenyl ring: ν C=C	[17]/[18]/ [19]/[20]
1581(w)	1583(w)	1585(w)	Phenyl ring ν C=C,(N)CH_2 str	[15]/[21]/[17]/[18]/ [19]/[20]
1563(w)	1564(w)	1566(w)	Phenyl ring: ν C=C , Im ring ν (N=C)	[15]/[21]
1441(m)	1454(m)	1448(w)	Im ring:C-N/C=N stretching band, δ (CH_2)	[9]/[17]/[27]/ [35]
1416(m)	1423(m)	1421(w)	Imidazole ring:C-N/C=N stretching band, (N)CH_2 str ,C–H deformation	[7]/ [22]/[20]
	1388(vw)		Imidazole ring:C-N/C=N stretch band	[10]/[7]/ [22]/[32]
1362(vw)	1363(vw)	1350(sh)	Trans[NTf_2]: νas(SO_2), (N)CH_2 str	[9]/[10]/ [22]/ [27]/[6]
1333(w)	1338(vw)	1332(w)	Imidazole ring :C–N/ C=N stretching band,	[17]/[18]/ [19]/[20]/[6]
	1317(vw)		Imidazole ring:C-N/C=N stretch band, Trans [NTf_2]: νas, op(SO_2)	[9]/[10]/ [22]/ [27]/[6]
	1298(vw)		henyl ring: C-C stretching	[20]/[27]/[8]
1250(vw)	1246(vw)	1242(m)	Phenyl ring: C–C stretching/Trans [NTf_2]: νs(CF_3)	[17]/[19]/ [19]/[20]/[6]/[13]
1203(w)	1206(w)	1206(w)	Phenyl ring: C-C stretching	[22]/[29]
1193(vw)	1196(vw)	1191(w)	Phenyl ring: C-C stretching, C- C-H i p bend, C- C- H ip bend	[20]/[33]/[8]
1156(vw)	1153(vw)		δ CH, CH_2N	[7]/[22]/[8]
		1135(w)	Trans[NTf_2]: νs,ip(SO_2)	[6]/ [9]/ [24]
1115(vw)	1117(vw)	1116(sh)	δ CH, ring HCCH sym bend	[7]/ [22]/[19]
1023(w)	1022(w)	1026(w)	δ CC, CH_2(N) str	[27]/[14]
			Range: 1000- 45 cm^{-1}	

975(vw)	972(vw)	975(vw)	(N)CH_2 asym str	[29]/[30]
884(sh)	885(vw)	881(vw)	ρ (CH_2), NC(H)N bend/CCH bend	[21]/[27]
865(w)			(N)CH_2 str, NC(H)N bend/CCH bend	[7]/[6]
845(w)	850(w)	848(vw)	NC(H)N bend, FPF asym str	[11]/[12]/[7]/ [16]
827(sh)	824(vw)	826(sh)	FPF asym str/ring HCCH asym bend	[21]/[22]/[32]
810(sh)	807(w)	807(vw)	FPF asym str/ring HCCH asym bend	[21]/[22]/[32]
	778(vw)	793(vw)	νsCC, HCCH sym bend	[21]/[26]/[32]
		763(sh)	νs(SNS), (N) CH_2 str, δ CC, C=C-H, ring HCCH asym bend	[10]/[12]/[7]/ [16]
741(vw)	742(m)	741(s)	ν (PF_6) , Trans[NTf_2]: δS(CF_3)	[6]/[11]/[12]/[7]/[16]/[22]/[16]
	694(vw)		C=C-H, H-C-C-H	[39]
661(w)	662(vw)	656(vw)	δ CC, C=C-H, CH_2(NCN Str	[17]/[18]/[19]/ [20]/ [27]
639(w)	640(vw)	640(vw)	δ CC, (N-C), (N)CH_2 Str	[17]/[14]
610(vw)	608(w)	611(vw)	δ CC, NCH_2 ,Trans[NTf_2] : δSNS, δop as(SO_2), Phenyl ring ν C=C	[11]/[12]/[7]/ [16] /[6]
		590(vw)	Trans[NTf_2] : δas(CF_3), δ ip as(SO_2), δs(NSO_2)	[6] /[9]/[11]/[12]/[7]/ [16]
	568(vw)	571(vw)	Trans[NTf_2] : δas(CF_3), δ ip as(SO_2), δs(NSO_2)	[6] /[9]/[11]/[12]/[7]/ [16]
		551(vw)	Trans[NTf_2] : δs(SO_2)	[6] /[9]/[11]/[12]/[7]/ [16]
		533(vw)	Tans[NTf_2] : δas(CF_3),	[11]/[6]
	470(vw)		ν (PF6)	[6]/ [21]/[24]/[14]
405(w)	412(vw)	404(w)	(N)CH_2 str , Tans[NTf_2]: ω (SO_2)	[11]/[13]/[7]/ [16]/[6]

		339(w)	δ NCH$_2$, Trans[NTf$_2$]:: τ(SO$_2$),	
321(w)	323(w)	325(w)	CC,(N)CH$_2$ str, ρ(SO$_2$)	[22]/[14]/[30]/ [31]/[6]
		312(w)	CN stretch, CC str, Trans[NTf$_2$]: ρ(SO$_2$), ρ(CF$_3$)	[11]/ [12]/[7]/ [16]/[6]
		297(w)	ρ (CH$_2$), CN stretch, Trans[NTf$_2$]: : ρCF$_3$, νas(CS)	[11]/ [12]/[7]/ [24] [16]/[6]
	202(vw)	209(w)	Intermolecular vibration, ω (N–C), τ (N–C)/ρ(CH$_2$)	[15]/ [24]/ [26]/ [28]
	167(sh)	167(sh)	Intermolecular vibration	[28]
		118(sh)	Intermolecular vibration	[28]
	71(vw)		Intermolecular vibration	[28]
60(s)	61(s)	60(s)	Intermolecular vibration	[28]

generally the position of H-bonding C$_{(2)}$-H/C$_{(4)}$-H,C$_{(5)}$-H/C$_{Ar}$-H/C$_{(But)}$-H/C$_{(methylidene)}$-H are important for any interaction with anions, all values noted in the range of (3000-3500 cm^{-1}) but this interaction it depends on symmetry of combined anion-cation and specially related to basicity of anion.

3.2.3 Thermal analysis:

The thermal stability of ionic liquids is subject to intermolecular interactions. These anion-cation interactions mainly include hydrogen bond energy and electrostatic energy. The three most important are the H bonds, the hydrogen bond is formed between a hydrogen atom and a heteroatom (of the anion), the Coulomb interactions (electrostatic) between anionic and cationic charges and finally, the Van der Waals interactions between the side chains of imidazolium rings. Research teams (40-42) recently discovered that the correct adjustment of the structure of ionic liquids can improve the anion-cation interaction energy, thus improving the thermophysical properties of ILs. The choice or the evaluation of an ionic liquid for a particular application requires knowing these thermophysical properties, especially the melting point (M_p), which is the point of the appearance of an endothermic peak during heating, and the thermal decomposition temperature(T_d).

3.2.3.1 Thermal stability and melting point:

The thermal behaviors of the three solid dicationic ionic liquids based on the dication [*p*-$C_6H_4(CH_2ImBu)^+{}_2$] from room temperature up to ≈ 800 ° C, their thermal stability and their fusion were studied in this work.

All three DILs are thermally stable, the bromide salt [*p*-C_6H_4(CH2ImBu)][Br]$_2$ begins to decompose rapidly from 253 ° C and decompose completely at 343° C , in one step in a short temperature range [253-343 ° C] by losing 70% of its initial mass , While the salt [*p*-C_6H_4 (CH_2ImBu)] [PF_6]$_2$ does not begin to lose its initial mass until at 265 ° C and decompose completely at 349° C, also in one step in a temperature range [265-349 ° C] with a mass loss of up to 68%.The results of the thermogravimetric analysis of [*p*-C_6H_4 (CH_2ImBu)] [$(CF_3SO_2)_2N$]$_2$, indicated to us that thermal decomposition, upon heating, occurred in the temperature range [293 –604 ° C] in two steps from 293 to 372 ° C with a mass loss of up to 50 %, and it decompose completely at 604 °C. These results are in agreement with the literature where the thermal stability, with the common cation follows the following order: $(CF_3SO_2)_2N^-$ > $PF_6{}^-$ > $BF_4{}^-$ > Oms^- > OTf^- > I^- > Br^- (43). The thermal stability and the occurrence of melting of the three DILs studied in this work were investigated by means of concomitant (DTA) measurements , The former compound displays one endothermic peaks around 138°C for [p-$C_6H_4(CH_2ImBu)$][PF_6]$_2$,and at 167°C for [p-$C_6H_4(CH_2ImBu)$][Br]$_2$, For the [*p*-$C_6H_4(CH_2ImBu)^+{}_2$] [$(CF_3SO_2)_2N^-$]$_2$ melting process, nothing was observed, even after a change in the baseline of the thermograms.

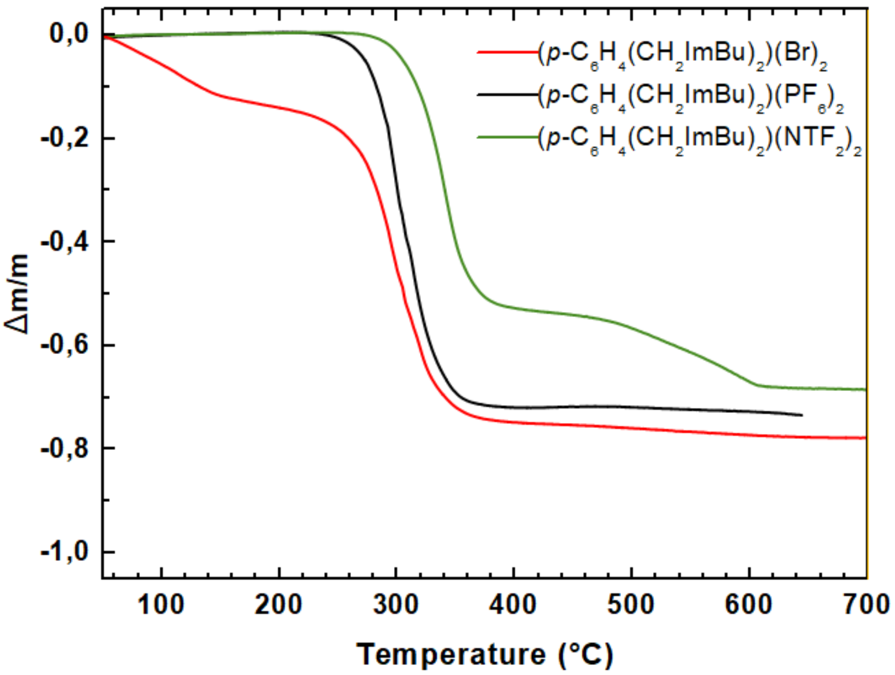


Figure 3.3: Thermogravimetric analysis (TGA) thermograms for synthesized dicationic ionic liquids (DILs).

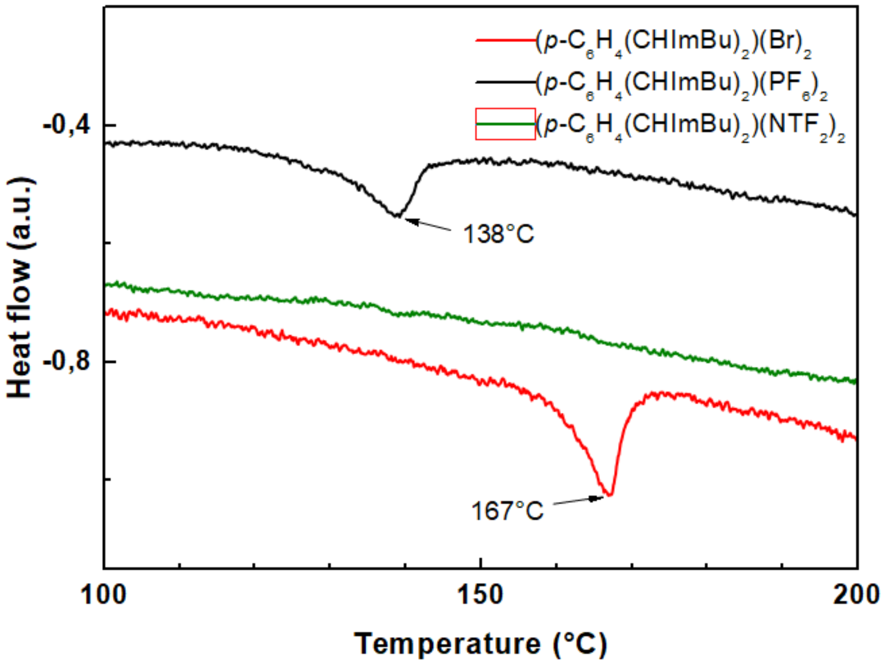


Figure 3.4: Differential thermal analysis (DTA) thermograms for synthesized dicationic ionic liquids (DILs).

The following table summarizes the thermal properties (Tm and Td) of our DILs:

Table 3.4: Thermal properties of synthesized DILs.

T_m: Melting point; T_d: Decomposition temperature.

DILs	Physical state at 25 ° C	M_P	T_d
[*p*-$C_6H_4(CH_2ImBu)$][Br]$_2$	Solid	167° C	343° C
[*p*-$C_6H_4(CH_2ImBu)$][PF_6]$_2$	Solid	138° C	349° C
[*p*-$C_6H_4(CH_2ImBu)$][$(CF_3SO_2)_2N$]$_2$	Liquid	---	604° C

3.3 Conclusion

Three new DILs based on bis-1-butylimidazolium linked to para-xylyl, combined with three anions, namely dibromide, di-bis (trifluoromethylsulfonyl) imide and di-hexafluorophosphate were synthesized. With the common cation, TGA / DTA thermal measurements indicate that the thermal stability of DILs follows the following order: $(CF_3SO_2)_2N$ > PF_6> Br, two samples are solid at room temperature and its melting points are in the order PF_6 <Br. In addition, the vibrational behavior of these DILs was studied using FTIR and FT-RAMAN spectroscopies, they indicate that the position of H-bonding $C_{(2)}$-H/$C_{(4)}$-H,$C_{(5)}$-H/C_{Ar}-H/$C_{(But)}$-H/$C_{(methylidene)}$-H are important for any interaction with anions, ^{1}H, ^{13}C, ^{19}F and ^{31}P NMR spectroscopies confirm the good purity of our targeted DILs and showed that the anion [$(CF_3SO_2)_2N^-$] is close to the H – C $_{(2)}$ site of the cation to form a specific hydrogen bond.

References

1. Payagala, T., Huang, J., Breitbach, Z. S., Sharma, P. S., & Armstrong, D. W. (2007). Unsymmetrical dicationic ionic liquids: manipulation of physicochemical properties using specific structural architectures. *Chemistry of Materials*, *19*(24), 5848-5850.

2. Shirota, H., Mandai, T., Fukazawa, H., & Kato, T. (2011). Comparison between dicationic and monocationic ionic liquids: liquid density, thermal properties, surface tension, and shear viscosity. *Journal of Chemical & Engineering Data*, *56*(5), 2453-2459.

3. Patil, R. A., Talebi, M., Xu, C., Bhawal, S. S., & Armstrong, D. W. (2016). Synthesis of thermally stable geminal dicationic ionic liquids and related ionic compounds: an examination of physicochemical properties by structural modification. *Chemistry of Materials*, *28*(12), 4315-4323.

4. Matthews, R. P., Welton, T., & Hunt, P. A. (2015). Hydrogen bonding and π–π interactions in imidazolium-chloride ionic liquid clusters. *Physical Chemistry Chemical Physics*, *17*(22), 14437-14453.

5. Shirini, F., Khaligh, N. G., & Akbari-Dadamahaleh, S. (2012). Preparation, characterization and use of 1, 3-disulfonic acid imidazolium hydrogen sulfate as an efficient, halogen-free and reusable ionic liquid catalyst for the trimethylsilyl protection of hydroxyl groups and deprotection of the obtained trimethylsilanes. *Journal of Molecular Catalysis A: Chemical*, *365*, 15-23.

6. El Khoury, Y., & Hellwig, P. (2017). Far infrared spectroscopy of hydrogen bonding collective motions in complex molecular systems. *Chemical communications*, *53*(60), 8389-8399.

7. Talaty, E. R., Raja, S., Storhaug, V. J., Dölle, A., & Carper, W. R. (2004). Raman and infrared spectra and ab initio calculations of C2-4MIM imidazolium hexafluorophosphate ionic liquids. *The Journal of Physical Chemistry B*, *108*(35), 13177-13184.

8. Kausteklis, J., Aleksa, V., Iramain, M. A., & Brandán, S. A. (2018). Effect of cation-anion interactions on the structural and vibrational properties of 1-buthyl-3-methyl imidazolium nitrate ionic liquid. *Journal of Molecular Structure*, *1164*, 563-576.

9. Kiefer, J., Fries, J., & Leipertz, A. (2007). Experimental vibrational study of imidazolium-based ionic liquids: Raman and infrared spectra of 1-ethyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide and 1-ethyl-3-methylimidazolium ethylsulfate. *Applied spectroscopy*, *61*(12), 1306-1311.

10. Moschovi, A. M., Ntais, S., Dracopoulos, V., & Nikolakis, V. (2012). Vibrational spectroscopic study of the protic ionic liquid 1-H-3-methylimidazolium bis (trifluoromethanesulfonyl) imide. *Vibrational Spectroscopy*, *63*, 350-359.

11. Moumene, T., Belarbi, E. H., Haddad, B., Villemin, D., Abbas, O., Khelifa, B., & Bresson, S. (2014). Vibrational spectroscopic study of ionic liquids: Comparison between monocationic and dicationic imidazolium ionic liquids. *Journal of Molecular Structure, 1065*, 86-92.

12. Drai, M., Mostefai, A., Paolone, A., Haddad, B., Belarbi, E., Villemin, D., ... & Rahmouni, M. (2017). Synthesis, experimental and theoretical vibrational studies of 1-

methyl and 1, 2-dimethyl, 3-propyl imidazolium bis (trifluoromethanesulfonyl) imide. *Journal of Chemical Sciences*, *129*(6), 707-719.

13. Kausteklis, J., Aleksa, V., Iramain, M. A., & Brandán, S. A. (2019). DFT and vibrational spectroscopy study of 1-butyl-3-methylimidazolium trifluoromethanesulfonate ionic liquid. *Journal of Molecular Structure*, *1175*, 663-676.

14. Katsyuba, S. A., Dyson, P. J., Vandyukova, E. E., Chernova, A. V., & Vidiš, A. (2004). Molecular structure, vibrational spectra, and hydrogen bonding of the ionic liquid 1-ethyl-3-methyl-1H-imidazolium tetrafluoroborate. *Helvetica Chimica Acta*, *87*(10), 2556-2565.

15. Malek, K., Puc, A., Schroeder, G., Rybachenko, V. I., & Proniewicz, L. M. (2006). FT-IR and FT-Raman spectroscopies and DFT modelling of benzimidazolium salts. *Chemical physics*, *327*(2-3), 439-451.

16. Haddad, B., Paolone, A., Villemin, D., Taqiyeddine, M., Belarbi, E. H., Bresson, S., ... & Kiefer, J. (2017). Synthesis, conductivity, and vibrational spectroscopy of tetraphenylphosphonium bis (trifluoromethanesulfonyl) imide. *Journal of Molecular Structure*, *1146*, 203-212.

17. Güllüoğlu, M. T., Erdogdu, Y., Karpagam, J., Sundaraganesan, N., & Yurdakul, Ş. (2011). DFT, FT-Raman, FT-IR and FT-NMR studies of 4-phenylimidazole. *Journal of Molecular Structure*, *990*(1-3), 14-20.

18. Sudha, S., Karabacak, M., Kurt, M., Cinar, M., & Sundaraganesan, N. (2011). Molecular structure, vibrational spectroscopic, first-order hyperpolarizability and HOMO, LUMO studies of 2-aminobenzimidazole. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, *84*(1), 184-195.

19. Cui, S., Wang, T., & Hu, X. (2014). Synthesis, characterization, and DFT studies of a new chiral ionic liquid from (S)-1-phenylethylamine. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, *133*, 778-784.

20. Erdogdu, Y., Güllüoğlu, M. T., Yurdakul, S., & Dereli, Ö. M. E. R. (2012). DFT simulations, FT-IR, FT-raman, and FT-NMR spectra of 4-(4-chlorophenyl)-1H-imidazole molecules. *Optics and Spectroscopy*, *113*(1), 23-32.

21. Noack, K., Schulz, P. S., Paape, N., Kiefer, J., Wasserscheid, P., & Leipertz, A. (2010). The role of the C2 position in interionic interactions of imidazolium based ionic liquids: a vibrational and NMR spectroscopic study. *Physical Chemistry Chemical Physics*, *12*(42), 14153-14161.

22. Heimer, N. E., Del Sesto, R. E., Meng, Z., Wilkes, J. S., & Carper, W. R. (2006). Vibrational spectra of imidazolium tetrafluoroborate ionic liquids. *Journal of molecular liquids*, *124*(1-3), 84-95.

23. Chaker, Y., Ilikti, H., Debdab, M., Moumene, T., Belarbi, E. H., Wadouachi, A., ... & Bresson, S. (2016). Synthesis and characterization of 1-(hydroxyethyl)-3-methylimidazolium sulfate and chloride ionic liquids. *Journal of Molecular Structure*, *1113*, 182-190.

24. Moumene, T., Belarbi, E. H., Haddad, B., Villemin, D., Abbas, O., Khelifa, B., & Bresson, S. (2015). Study of imidazolium dicationic ionic liquids by Raman and FTIR spectroscopies: The effect of the nature of the anion. *Journal of Molecular Structure*, *1083*, 179-186.

25. Socrates, G. (2004). *Infrared and Raman characteristic group frequencies: tables and charts*. John Wiley & Sons.

26. Kadari, M., Belarbi, E. H., Moumene, T., Bresson, S., Haddad, B., Abbas, O., & Khelifa, B. (2017). Comparative study between 1-Propyl-3-methylimidazolium bromide and trimethylene bis-methylimidazolium bromide ionic liquids by FTIR/ATR and FT-RAMAN spectroscopies. *Journal of Molecular Structure*, *1143*, 91-99.

27. Moumene, T., Belarbi, E. H., Haddad, B., Villemin, D., Abbas, O., Khelifa, B., & Bresson, S. (2016). Vibrational spectroscopic study of imidazolium dicationic ionic liquids: effect of cation alkyl chain length. *Journal of Applied Spectroscopy*, *83*(2), 165-171.

28. Penna, T. C., Faria, L. F., Matos, J. R., & Ribeiro, M. C. (2013). Pressure and temperature effects on intermolecular vibrational dynamics of ionic liquids. *The Journal of chemical physics*, *138*(10), 104503.

29. Katsyuba, S. A., Zvereva, E. E., Vidiš, A., & Dyson, P. J. (2007). Application of density functional theory and vibrational spectroscopy toward the rational design of ionic liquids. *The Journal of Physical Chemistry A*, *111*(2), 352-370.

30. Panja, S. K., Boumediene, H., Drai, M., Villemin, D., & Bresson, S. (2018). Probing effect of weak H-bonding on conformational change in ionic liquid: Experimental and DFT studies. *Journal of Molecular Liquids*, *266*, 727-732.

31. Haddad, B., Kiefer, J., Brahim, H., Belarbi, E. H., Villemin, D., Bresson, S., ... & Palumbo, O. (2018). Effects of C (2) methylation on thermal behavior and interionic interactions in imidazolium-based ionic liquids with highly symmetric anions. *Applied Sciences*, *8*(7), 1043.

32. Sharma, S. K., Misra, A. K., & Sharma, B. (2005). Portable remote Raman system for monitoring hydrocarbon, gas hydrates and explosives in the environment. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, *61*(10), 2404-2412.

33. Steinert, R., Bettermann, H., & Kleinermanns, K. (1997). Identification of xylene isomers in high-pressure liquid chromatography eluates by Raman spectroscopy. *Applied spectroscopy*, *51*(11), 1644-1647.

34. Haddad, B., Mokhtar, D., Goussem, M., Belarbi, E. H., Villemin, D., Bresson, S., ... & Kiefer, J. (2017). Influence of methyl and propyl groups on the vibrational spectra of two imidazolium ionic liquids and their non-ionic precursors. *Journal of Molecular Structure*, *1134*, 582-590.

35. Marsh, K. N., Boxall, J. A., & Lichtenthaler, R. (2004). Room temperature ionic liquids and their mixtures—a review. *Fluid phase equilibria*, *219*(1), 93-98.

36. Shirini, F., Khaligh, N. G., & Akbari-Dadamahaleh, S. (2012). Preparation, characterization and use of 1, 3-disulfonic acid imidazolium hydrogen sulfate as an efficient, halogen-free and reusable ionic liquid catalyst for the trimethylsilyl protection of hydroxyl groups and deprotection of the obtained trimethylsilanes. *Journal of Molecular Catalysis A: Chemical*, *365*, 15-23.

37. Johansson, P., Gejji, S. P., Tegenfeldt, J., & Lindgren, J. (1998). The imide ion: potential energy surface and geometries. *Electrochimica acta*, *43*(10-11), 1375-1379.

38. Dearden, J. C. (1991). The QSAR prediction of melting point, a property of environmental relevance. *Science of the total environment*, *109*, 59-68.

39. Capitani, F., Trequattrini, F., Palumbo, O., Paolone, A., & Postorino, P. (2016). Phase transitions of PYR14-TFSI as a function of pressure and temperature: the competition between smaller volume and lower energy conformer. *The Journal of Physical Chemistry B, 120*(11), 2921-2928.

40. Zhang, H., Li, M., & Yang, B. (2018). Design, synthesis, and analysis of thermophysical properties for imidazolium-based geminal dicationic ionic liquids. *The Journal of Physical Chemistry C*, *122*(5), 2467-2474.

41. Zhang, H., Xu, W., Liu, J., Li, M., & Yang, B. (2019). Thermophysical properties of dicationic imidazolium-based ionic compounds for thermal storage. *Journal of Molecular Liquids*, *282*, 474-483.

42. Zhang, H., Liu, J., Li, M., & Yang, B. (2018). Functional groups in geminal imidazolium ionic compounds and their influence on thermo-physical properties. *Journal of Molecular Liquids*, *269*, 738-745.

43. Blake, D. M., Moens, L., Rudnicki, D., & Pilath, H. (2006). Lifetime of imidazolium salts at elevated temperatures.

General conclusion

General conclusion

This work divided into several studies, we demonstrated the effect of different structural modifications, including the aromatic bond spacer, the side chain, and the type of dications and anions on the spectroscopic vibrational and thermal properties of ionic liquids dicationics (DILs). The new series of synthesized dicationic ILs exhibited excellent ATG thermal stability up to 604 ° C. This made it possible to design the type of system suitable for various applications (e.g: thermal batteries, electrochemistry, organic, inorganic and enzymatic synthesis, catalysis, etc.).

The structural symmetry of dications and anions of dicationic ionic liquids also appears to affect their thermal stability. For a common dication, we have studied that the decrease in the anionic symmetry of the dicationic ionic liquids, leads to the decrease in the melting temperature, in addition the molecular asymmetry increases the thermal stability (1), which is the case for the symmetry of the dication for a common anion. These DILs are mainly structured by electrostatic interactions and hydrogen bonds, for this purpose, electrostatic interactions play an essential role in the change of the temperature of the fusion and the thermal decomposition resistance of these dicationic compounds.

Our research strategy in the first stage, was the incorporation of an aryl group (xylyl) between two units-1-butylimidazolium of ionic liquids, in the para position of the xylyl group, spectroscopic and thermal studies were carried out to identify the effect of structural parameters such as: 1_ the nature of the anion, 2_ the structural symmetry of dicationic ILs (anions and dications). The results obtained during these studies demonstrated that the three DILs linked to para-xylyl are thermally stable. It can be seen that the symmetrical molecular structure has a negative impact on the thermal stability of dicationic ionic compounds. In the same series of DILs (keeping the same dication) with various paired anions, the phenomenon of symmetry still persists. This observation is attributed to the nature of the anion (its size). Spherical [Br^-]

bromide is completely symmetrical, octahedral hexafluorophosphate [PF_6^-] is less symmetrical than halide, while the organic anion named bis-(trifluoromethylsulfonyl) imide has poor symmetry compared to other anions, this anion has planar symmetry which makes it possible to diffuse the charge over the entire anionic structure, tends to lower the melting points (2).

In summary, the melting temperature (T_m) of a salt strongly reflects its Helmholtz free energy, which is influenced by three important factors: intermolecular forces, molecular symmetry, and degrees of freedom in rotation and configuration. For these organic salts, the short-range interactions include attractive components such as $\pi - \pi$ interactions, hydrogen bond interactions and Van der Waals interactions, these interactions make a more significant contribution to the T_m of ILs with large organic cations than in simple inorganic salts

The vibrational spectroscopic study stage represents the cornerstone of our research work. The aim is to study the spectroscopic properties of LIDs by purely vibrational methods, such as FTIR / ATR and Raman. These two techniques have provided a better understanding of the mechanisms and types of cation-anion interaction within these ionic liquids and for obvious attribution of each band observed in vibrational spectroscopic measurements. On the other hand, knowledge of this type of molecular-scale interactions of these synthesized LIDs will make it possible to establish a relationship between structural, thermal and vibrational properties.

This step offers the advantage of being able to control all these properties and of course lead to the targeted application

References

1. Ngo, H. L., LeCompte, K., Hargens, L., & McEwen, A. B. (2000). Thermal properties of imidazolium ionic liquids. *Thermochimica Acta*, *357*, 97-102.
2. Siedlecka, E. M., & Stepnowski, P. (2009). The effect of alkyl chain length on the degradation of alkylimidazolium-and pyridinium-type ionic liquids in a Fenton-like system. *Environmental Science and Pollution Research*, *16*(4), 453-458.

التوليف والخصائص الاهتزازية والحرارية للسوائل الأيونية الجديدة DILs

الملخص:
تعد معرفة التركيب ، والاستقرار الحراري ، والأطياف الاهتزازية لمركباتنا موضوعًا مهمًا للدراسة. الهدف من العمل المعروض في هذه المخطوطة هو دراسة تأثير الهيكل على السوائل الأيونية ، لدينا خصائص حرارية واهتزازية طيفية لأربعة سوائل أيونية (LIDs) dicationic ، المرحلة الاولى توليف أربعة سوائل أيونية جديدة مرتبطة بـ-1-bis xylyl Buthylimidazolium (LIDs) تحتوي على الأنيونات :ثنائي كلوريد2 [-BR] ، ثنائي (مكرر (ثلاثي فلورو ميثيل سلفونيل) إيميد) 2 [-CF3SO2) 2N)] ومكررسداسي فلورو الفوسفات 2 [-PF6] تم تصنيعها.
تميزت LIs dicationic التي تم الحصول عليها بـمطيافية الرنين المغناطيسي النووي 1H-NMR ,13C-NMR 31P-NMR , 19P-NMRو FT-IR و .FT-Raman بالإضافة إلى ذلك ، كانت خصائصها الحرارية مصممة ومقارنة.
أكد السلوك الحراري أن LIs الوظيفية [pC6H4 (CH2ImBu) 2+] التي تحتوي على الأنيون 2 [-CF3SO2) 2N)] أكثر استقرارًا حرارياً من غيرها.

الكلمات المفتاحية:السوائل األيونية – الخواص- البنيوية - االهتزازية الطيفية- الحرارية

« Synthèse, propriétés vibrationnelles et thermiques de nouveaux liquides ioniques dicationiques LIDs »

Résumé:

La connaissance de la synthèse, de la stabilité thermique, des spectres vibrationnels de nos composés est un sujet d'étude important. L'objectif du travail présenté dans ce manuscrit est d'étudier l'influence de la structurede nos liquide ioniques a les propriétés thermiques et vibrationelle spectroscopiques de trois liquides ioniques dicationiques (LIDs) synthétisés, Lors de la première étape, trois nouveaux liquides ioniques (LIDs) bis-1-Buthylimidazolium liés au xylyle, contenant les anions : dichlorure $[Br^-]_2$, di-(bis(trifluorométhylsulfonyl) imide) $[(CF_3SO_2)_2N^-]_2$ et bis (hexafluorophosphate) $[PF_6^-]_2$ ont été synthétiser. Les LIs dicationiques obtenus ont été caractérisés par les spectroscopies RMN-1H, RMN-13C, RMN-19F, RMN-31P, FT-IR et FT-Raman. De plus, leurs propriétés thermiques ont été déterminées et comparées. Le comportement thermique a confirmé que les LIs dicationiques fonctionnalisées $[p\text{-}C_6H_4(CH_2ImBu)_2^+]$ contenant l'anion $[(CF_3SO_2)_2N^-]_2$ sont plus stables thermiquement que d'autres.

Mots clés : Liquides ioniques - – propriétés - structurales - spectroscopiques vibrationnelles-thermiques.

"Synthesis, vibrational and thermal properties of new dicationic ionic liquids DILs"

Abstract:
Knowledge of the synthesis, thermal stability, vibrational spectra of our compounds is an important subject of study. The objective of the work presented in this manuscript is to study the influence of the structure of our ionic liquids has the spectroscopic thermal and vibrational properties of three dicationic ionic liquids (DILs) synthesized, three new ionic liquids (DILs) bis-1-Buthylimidazolium linked to xylyl, containing the anions: dichloride $[Br^-]_2$, di- (bis (trifluoromethylsulfonyl) imide) $[(CF_3SO_2)_2N^-]_2$ and bis (hexafluorophosphate) $[PF_6^-]_2$ were synthesized. The dicationic LIs obtained were characterized by the NMR spectroscopies1H, NMR-13C,NMR-19F, NMR-31P, FT-IR and FT-Raman. In addition, their thermal properties have beendetermined and compared. The thermal behavior confirmed that the functionalized dicationic LIs $[p\text{-}C_6H_4(CH_2ImBu)_2^+]$ containing the anion $[(CF_3SO_2)_2N^-]_2$ are more thermally stable than others.

Keywords: Ionic liquids - structural-thermal-vibrational spectroscopic- properties.