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aSynthesis, thermal stability, vibrational spectra and conformational studies of novel dicationic meta-xylyl linked bis-1-methylimidazolium ionic liquids.

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ABSTRACT

In recent years, dicationic ionic liquids have been subject of a strongly growing research effort for their interesting and important properties that suggest them to be potential candidate for many applications. Therefore, the knowledge about the synthesis, thermal stability, vibrational spectra and conformational behaviour of these compounds is an important subject of study. The objective of the work presented in this paper is to investigate the influence of the substituent relative *meta*-position of dicationic ionic liquids (ILs), namely meta-xylyl linked bis-1-methylimidazolium ILs, on thermal stability, vibrational spectra and conformational studies. In the first step, 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, ^{19}F-NMR, ^{31}P-NMR and FT-IR spectroscopy. Also, their thermal properties were determined and compared. The thermal behavior confirmed that [m-$C_6H_4(CH_2ImMe)_2^+$] dicationic ILs containing $[(CF_3SO_2)_2N^-]_2$ and $[PF_6^-]_2$ are more stable that the dichloride $[Cl^-]_2$, and bis(tetrafluoroborate) $[BF_4^-]_2$ dicationic ILs, and they show a good thermal stability up to 340°C which makes them suitable for thermal application. In the next step, a computational study of the conformers of [m-$C_6H_4(CH_2ImMe)_2$], by means of DFT calculations with the 6-31G** basis set and the B3LYP theory was performed. Additionally, vibrational spectroscopy studies were conducted by infrared (FTIR) and Raman (FT-Raman) spectroscopy on the four dicationic ILs, differing for their anions. Finally a computational investigation of the interactions between anions and cation is presented.

KEYWORDS: Meta-xylyl; bis-imidazolium; Thermal analysis; conformers; Raman measurements; DFT calculations.

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1. INTRODUCTION

One of the principal aims of modern chemistry is to design effective solvents that will be alternative to organic solvents, and that would not have the same disadvantages (e.g: high toxicity, high flammability and high vapor pressure) [1-2].

Scientific researchers in this field have suggested several tracks for the discovery of a new class of solvents, less harmful and less volatile. One of them regards "ionic liquids", which have been developed in the last decade as new green solvents, more acceptable to the environment, with excellent physical and chemical properties [3] that make them green substitutes more attractive compared to conventional organic solvents. They exhibit several exciting properties, such as their low melting points [4], good solvation properties [5], their very low vaporization voltages [6], their thermal and chemical stabilities [7] and their high solubilities [8].

Concerning their structures, they are designable properties, determined by the molecular interactions between the ions [9]. Therefore, unravelling the structure-property relationships and finding universal correlations that can be utilized for a rational design is one of the main aim of the current research; in other words the coupled selected cations - anions can be adapted and adjusted to obtained ionic liquids with physicochemical properties desired for a specific application [10]; among these adjustments, it is possible to functionalize the imidazole as precursor in the synthesis reactions for the production of new substituted ionic liquids with new properties [11].

Recently, a new class of the ionic liquid family known as dicationic ionic liquids (ILs) has emerged as more effective and versatile compared to conventional monocationic ILs. Dicationic ionic liquids based on imidazolium [12], pyrrolidinium [13], piperidinium [14], and ammonium [15] cations represent the majority of the investigations in this field. A comparison between dicationic ILs and monocationic ILs, having a different length of grafted alkyl group was reported.[16-17].

The dicationic ILs have been the subject of many experimental and theoretical studies because of their properties makes them attractive for applications in a variety

of fields including organic synthesis, catalysis, electrochemistry, and separation. They are thermally more stable, with higher viscosities, melting point, densities [18-19],and have a greater d- spacing of the crystal structure than the monocationic ones [18].

The recent years have seen a strongly growing research effort regarding the influence of substituents functionalized in ionic liquids on the physical and chemical properties. In general, substituents in *ortho*, *meta* or *para*-positions alter the conformations, equilibrium relationships, vibrational spectra, the molecular structure, interionic interactions and thermal properties of the substituted in functionalized ionic liquids.

Very recently, we have investigated the conformers of the cation and the anion-cation hydrogen bonding in Para-xylyl linked bis-imidazolium ionic liquids by using IR and Raman spectroscopic studies with the help of DFT calculation [20-21].

The facile synthesis of the same dicationic ILs (bis-imidazolium group) followed by new substitution at the position meta for the cationic site can give rise to new dicationic ILs namely Meta-xylyl linked bis-imidazolium ionic liquids; however, to the best of our knowledge, the study of the thermal stability, vibrational spectra and conformational studies of these dicationic ILs are not covered yet by the literature.

In this study, four new dicationic ILs based on meta-xylyl linked bis-imidazolium pairing the dichloride, bis(hexafluorophosphate), bis(tetrafluoroborate) and di(bis (trifluoromethanesulfonyl) imide) anions were investigated by using spectroscopic and thermal analysis; the thermal stability of all these dicationic ILs and their decomposition process were investigated, with the aim to understand the relationship between the structure and properties.

2. MATERIALS, AND METHODS

The chemicals used in this study: 1-methyl-1H-imidazole (> 99%), [1,3-bis (chloromethyl) benzene], α, α′-dichloro-m-xylene (98%), potassium hexafluorophosphate (≥ 99%), lithium bis (trifluoromethylsulfonyl) Imide (99%), ammonium tetrafluoroborate (99.5 wt %), were purchased from Aldrich and used as

received. Diethyl ether and N,N-dimethylformamide were purchased from Fluka. Deionized H_2O was obtained with a Millipore ion-exchange resin deionizer.

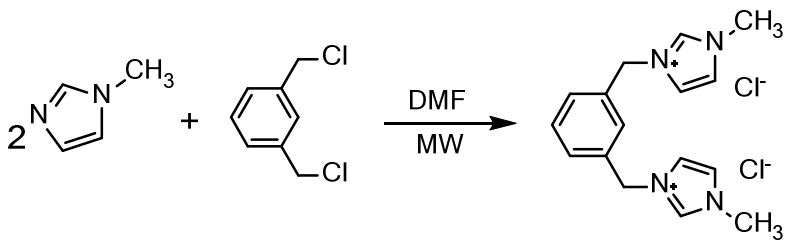
2.1 General procedure for the synthesis of dicationic ILs

The synthesis of 3,3'-dimethyl-1,1'-(1,3-phenylenedimethylene)-bis(1H-imidazolium) dichloride can be described as follows [22]. Briefly, The dicationic IL named [m-$C_6H_4(CH_2ImMe)^{+}{}_2][Cl^-]_2$ was prepared under microwave irradiation, from the mixture : 4.26 g (4.13 ml, 50 mmol) of 1-methylimidazole and 2.27g (10 mmol) of the m-xylene dichloride in N,N-dimethylformamide (3 ml) at 100 °C for 3 min . The resulting mixture was washed three times upon addition of diethyl ether (100 ml), and then dried in vacuo (< 1 mbar) for 8 h, to give a white hygroscopic solid compound in high yield (≈ 96%).

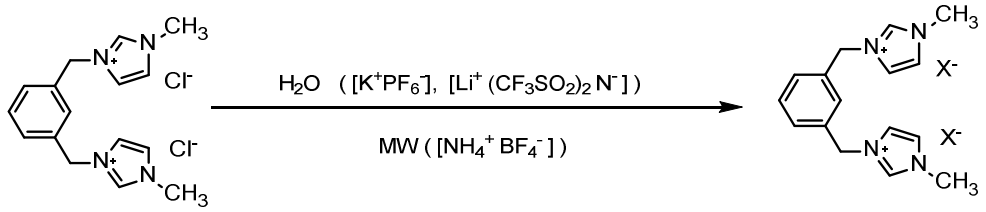
Three other dicationic ILs were synthesized by means of metathesis reactions (anion exchange) of the dichloride salts with:

- $[K^+ PF_6^-]$ (1.2g, 6.5 mmol) dissolved in 20 ml of demineralized water to give [m-C_6H_4 $(CH_2ImMe)^{+}{}_2]$ $[PF_6^-]_2$ after a separation process.
- $[Li^+ (CF_3SO_2)_2N^-]$ (1.86g, 6.5 mmol) to give [m-C_6H_4 $(CH_2ImMe)^{+}{}_2]$ $[(CF_3SO_2)_2N^-]_2$ following the same procedure.
- $[NH_4^+ BF_4^-]$ (0.68g, 6.5 mmol) under microwave heating to give [m-C_6H_4 $(CH_2ImMe)^{+}{}_2]$ $[BF_4^-]_2$

The summary of the synthesis reactions is depicted in the following Scheme 1 and Scheme 2:



Scheme 1. Synthetic route of dichloride salt [m-C_6H_4 $(CH_2ImMe)_2]$ Cl_2, MW microwave.



Scheme2.Metathesis reactions of [m-C_6H_4 (CH_2ImMe) $_2$] X_2 from dichloride dicationic IL, (with X = [PF_6], [$(CF_3SO_2)_2N$] and [BF_4]).

2.2 NMR characterization

The structures of synthesized dicationic ILs are confirmed by using ^{1}H, ^{13}C, ^{19}F and ^{31}P -NMR spectroscopy, in order to check the occurrence of the expected chemical reactions and confirm the absence of any impurities. ^{1}H-NMR (500 MHz), ^{13}C-NMR (125.75 MHz) and ^{19}F-NMR (470.62 MHz) spectra were recorded on a Bruker DRX 500 MHz spectrometer. Spectra were recorded in dimethylsulfoxide (DMSO-**d*6***), using the DMSO residual peak as the ^{1}H internal reference (δ = 2.5 and 3.3), and the central peak of DMSO-**d*6*** at δ = 39.5 as the ^{13}C reference. Chemical shifts (δ) are given in ppm and referred to the internal solvent signal, namely TMS and $CFCl_3$, respectively. All NMR spectra confirm that our dicationic ILs have been successfully synthesized and prove a good purity. The spectroscopic data are given below:

[m- C_6H_4 (CH_2ImMe) $_2^+$][Cl^-]$_2$:
^{1}H-NMR (DMSO-*d6*), δ_H ppm: 9.12 (s, 2H, NCHN), 7.69-7.67 (d, 4H, NCHCHN), 7.40-7.49 (m, 4H, C_6H_4), 5.41 (s, 4H, - CH_2-), 3.85 (s, 6H, 2 × CH_3).
^{13}C-NMR (DMSO-*d6*) δ ppm: 36.15, 51.96, 122.71, 124.46, 128.44, 129.08, 130.29, 135.86, 137.08

[m- C_6H_4 (CH_2ImMe) $_2^+$][BF_4^-]$_2$:
^{19}F-NMR (DMSO-d6) δ_F (ppm): -148.17 (s, B**F**$_4$).

[m- C_6H_4 (CH_2ImMe) $_2^+$][PF_6^-]$_2$:
^{19}F-NMR (DMSO-*d6*) δ ppm: -69.63, -70.82.
^{31}P-NMR (DMSO-*d6*) δ ppm: -133.72, -137.27, -140.78, -144.30, -147.81, -151.19, 154.71(sept, **PF_6^-**)

[m- C_6H_4 (CH_2ImMe) $_2^+$][NTf_2^-]$_2$:
^{19}F-NMR (DMSO-d6) δ_F (ppm): -79.36 (s, [NT**F**$_2^-$]).

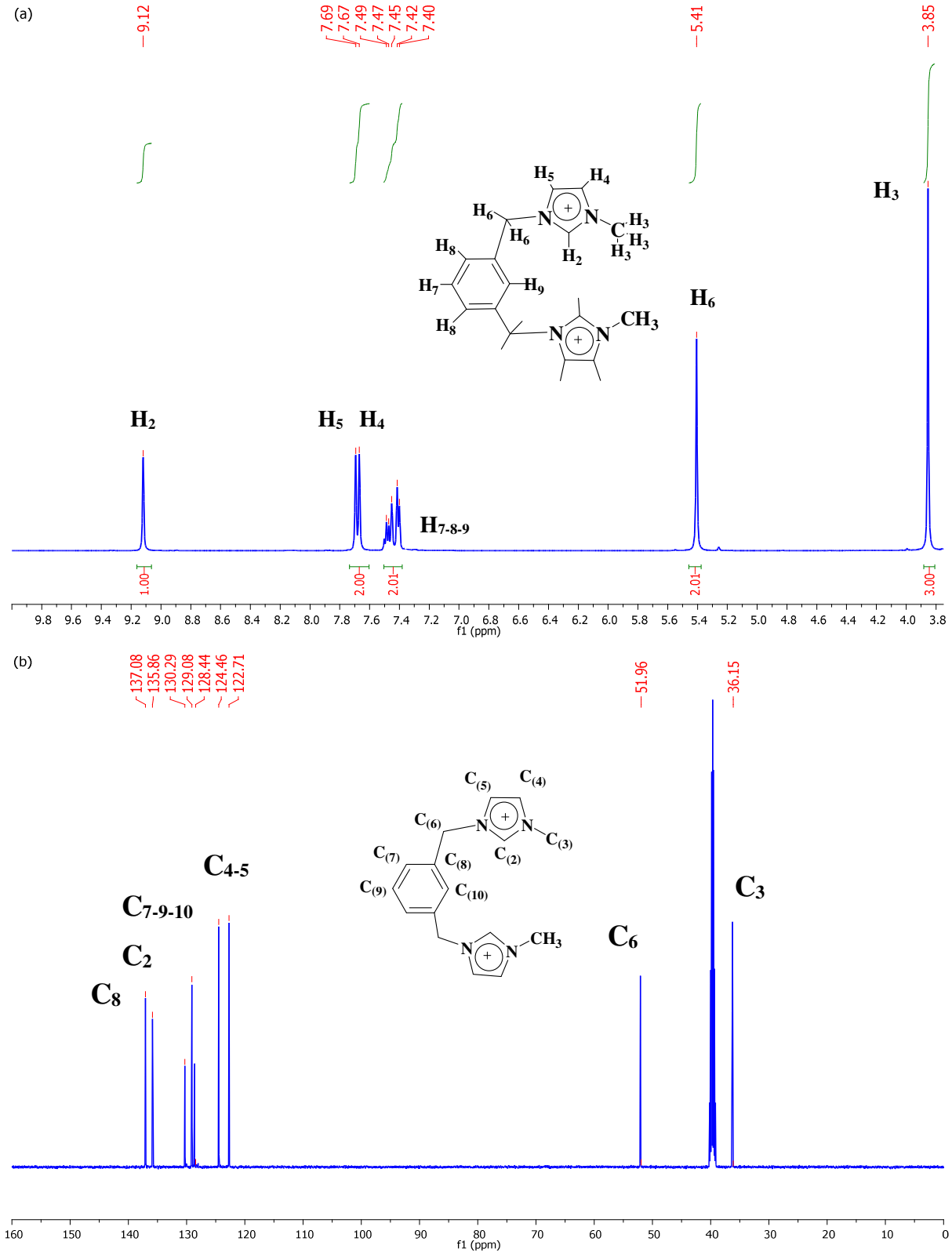


Figure 1. ^{1}H NMR (500 MHz) (a) and ^{13}C NMR (125.75 MHz) (b), spectra of [m-C_6H_4 (CH_2ImMe) $_2^+$][Cl^-]$_2$

2.3 THERMAL ANALYSIS

Concomitant measurements of thermogravimetry (TGA) and differential thermal analysis (DTA) were performed by means of a Setaram Setsys Evolution 1200 TG System, with a fixed temperature rate of 5°C/min, in an argon flux of 60 ml/min. For each sample, an initial mass of ~20 mg was used.

2.4 VIBRATIONAL SPECTROSCOPY

Infrared spectroscopy data were acquired by attenuated total reflectance spectra on a Vertex 70-RAM II Bruker spectrometer (Bruker Analytical, Madison, WI) operating with a Golden Gate TM diamond ATR accessory (Specac Ltd., Slough, UK). FTIR/ATR spectra [3500- 600 cm^{-1}] were collected with a nominal resolution of 1 cm^{-1} by co-adding 64 scans for each spectrum. Only for the sample containing Cl^- as anion, an additional spectrum was acquired in transmission mode by means of an Agilent Cary 660 with a resolution of 1 cm^{-1} in the frequency range between 4000 and 400 cm^{-1}, by dissolving the ionic salt in KBr in the proportion 1:100 in mass. The measurement was the mean of 100 scans. Prior of this measurement the sample was kept at 80°C for 48 hours in order to increase its crystallinity and remove hydration water.

FT-RAMAN spectra were acquired by means of a Vertex 70-RAM II Bruker FT-RAMAN spectrometer. This instrument is equipped with a Nd:YAG laser (yttrium aluminium garnetcrystal 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 focal point. The RAM II spectrometer is equipped with a liquid-nitrogen cooled Ge detector. FT-RAMAN spectra [3500-150 cm^{-1}] were collected with 1 cm^{-1} nominal resolution by co-adding 128 scans for each spectrum at room temperature.

3. COMPUTATIONAL

The isolated cation (m-xylene) was investigated computationally by means of the Spartan software [23-24]. Concerning the anions their spectra are well known both from an experimental and computational point of view [25-26].

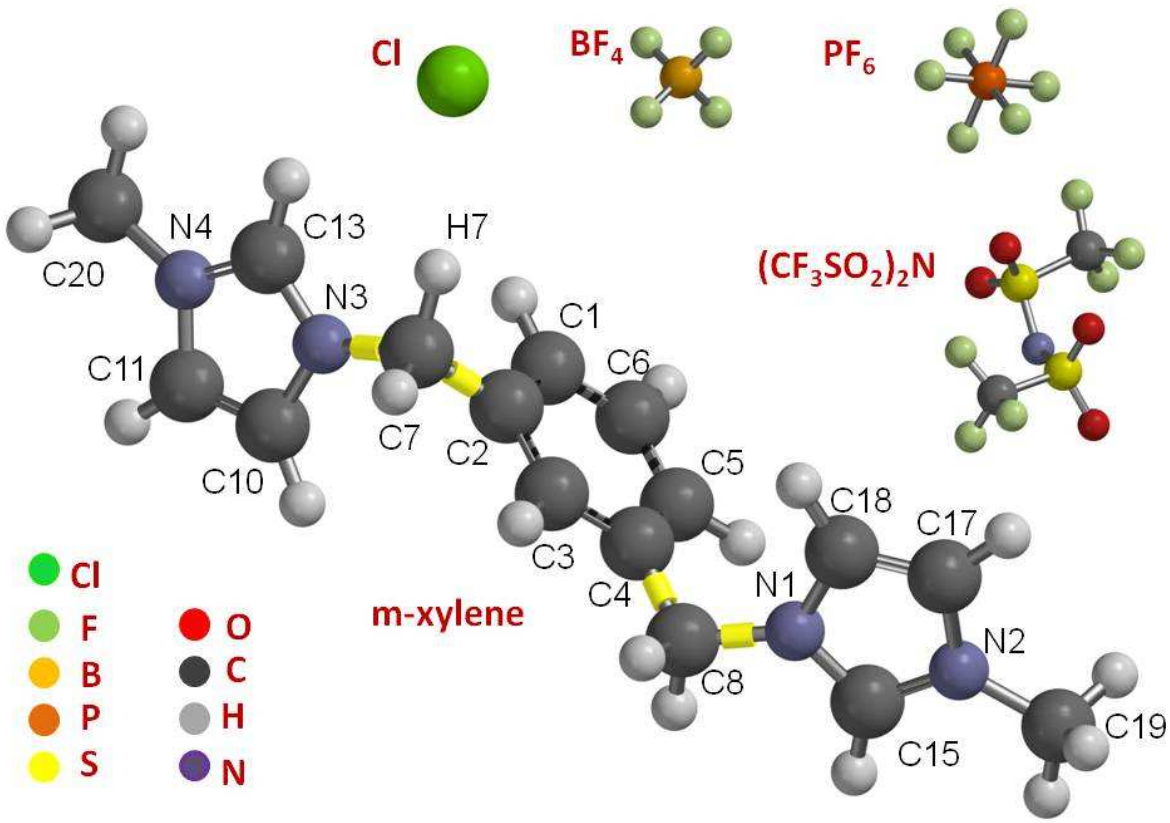


Figure 2. Schematics of the cation with labels identifying the atoms whose distances and angles are reported in Table 1 and schematics of the different anions.

A preliminary investigation of the possible conformational geometries of the m-xylene cation was performed at the molecular mechanics level. The investigation of the possible stable structures started with a systematic search, varying the four dihedral angles that define the ionic structure highlighted in **Figure 2**. The Spartan software can automatically investigate up to 200 structures; therefore, we chose the steps of the angle variations in order to have a lower number of possible structures. The dihedral angles C3C2C7N3 and C3C4C8N1 were varied by steps of 60°, while the two dihedral angles C2C7N3C13 and C4C8N1C15 were varied by 180°, so that in total we investigated 6x6x2x2=144 possible structures. An optimization of these structures was performed by DFT calculations using the 6-31G** basis set and the B3LYP theory, as largely performed in the previous literature for ionic liquids [25-28]. After the optimization, we obtained many degenerate geometries, that were removed from the following procedures. The vibration frequencies and the infrared intensity and Raman activity of the optimized structures having an energy not higher than 5

kJ/mol from the lowest energy conformer were calculated by means of the Spartan software. Only 7 of them had all positive vibrational frequencies and can therefore, be considered as stable points of the potential energy surface. In order to compare the experimental infrared and Raman spectra with the calculated one, we constructed expected IR and Raman spectra summing Gaussian curves centered at each calculated vibration frequency, with an intensity proportional to the calculated one and a fixed line width of 10 cm^{-1}.

Moreover, the optimized geometry of the four ionic couples of m-xylene with 2 Cl^-, 2 BF_4^-, 2 PF_6^- or 2 NTf_2^- anions were obtained by DFT calculations using the 6-31G** basis set and the B3LYP theory.

4. RESULTS AND DISCUSSION

4.1 COMPUTATIONAL RESULTS

Table 1 reports the values of the four dihedral angles of the seven stable points of the potential energy surface (all vibrational frequencies are positive), after the optimization of geometries by means of DFT calculations using the 6-31G** basis set and the B3LYP theory. The two dihedrals C3C2C7N3 and C3C4C8N1 define the relative orientation of the two imidazolium rings, while the two dihedrals C4C8N1C15 and C2C7N3C13 describe the rotation of the imidazolium rings around its axis with respect to the xylene groups. In **Table 1** also the values of the energy difference with respect to the lowest energy conformer are reported.

Table 1. The label, the dihedral angles and the difference in relative energy with respect to the lowest energy one of the seven cation conformers.

Label	Dihedral C3C2C7N3	Dihedral C3C4C8N1	Dihedral C2C7N3C13	Dihedral C4C8N1C15	Relative Energy (kJ/mol)
A	-123.52	-123.99	-130.52	-131.32	0.00
B	122.49	85.63	133.55	-145.72	3.45
C	125.88	118.85	-45.82	133.75	3.61
D	-121.84	-122.43	37.64	-129.76	3.70
E	-143.20	136.94	-124.46	126.78	4.22
F	-97.20	-119.24	-14.94	-132.60	4.60
G	88.98	123.36	30.42	131.92	4.73

Table 2 displays some significative distances and angles of the lowest energy conformer. Similar values are obtained also for the other conformers, except for the four dihedral angles reported in **Table 1**. A comparison with experimental data is not possible because no study of the structure of meta-xylyl linked bis-1-methylimidazolium compounds is available. However, the presently calculated values of bond lengths and angles well compares with those obtained both computationally [20] and experimentally from X-Ray diffraction data [29-30] for the p-xylene compounds.

Table 2. Some significative distances and angles calculated for the lowest energy conformer of m-xylene. The labels of atoms refer to **Figure 2**.

distances (Å)									
C1-C2	C2-C7	C7-H7	C7-N3	N3-C10	N3-C13	C10-C11	C11-N4	C13-N4	N4-C20
1.400	1.516	1.093	1.484	1.384	1.341	1.363	1.383	1.337	1.473
angles (°)									
C3-C2-C7	C2-C7-N3	C7-N3-C10							
119.80	113.36	126.30							

Additionally **Table S1** of the Supplementing Information reports the calculated vibrational frequencies, their infrared intensities and the Raman activities, for all seven conformers.

4.2 THERMAL ANALYSIS

Decomposition studies are performed to investigate the influence that the structural parameters of anions have on the thermal degradation process of dicationic ILs, and to determine which ILs can be used in applications involving high temperatures [31].

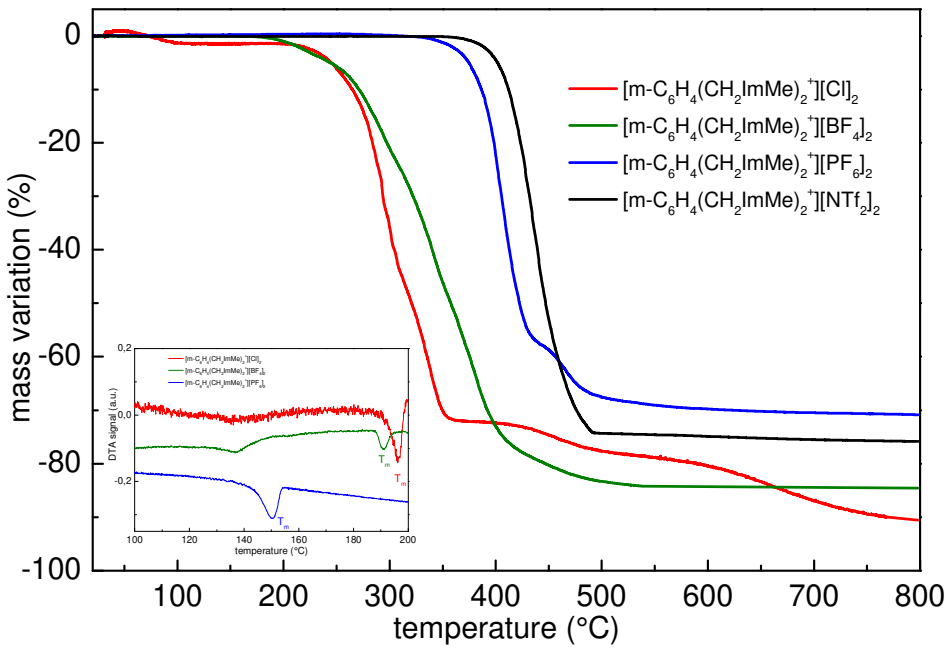


Figure 3. TGA and differential thermal analysis (DTA) thermographs for the synthesized dicationic ionic liquids (ILs).

Figure 3 shows the decomposition profiles of the four dicationic ILs based on the [m-C_6H_4 (CH_2ImMe)$_2$] dication from room-temperature up to 800°C. The present dicationic ILs were found to be thermally stable in a wide range of temperature. As reported for most dicationic ILs, the dicationic IL containing [NTf$_2$]$^-$ is more stable than those containing [PF$_6$]$^-$, [BF$_4$]$^-$ and Cl$^-$ [32-33]. We observed that dichloride salt begins to decompose (lose 0.07mg ≈ 0.5% of its initial mass) at 83°C probably due to the water of hydratation; the real decomposition of this salt is revealed in the range 300-357 °C (lose of ≈ 72%), to reach the maximum level of loss (≈ 90%) at 800°C. The analogue salt containing BF$_4$ anion loses the same amount compared to the halide salt, of its weight ≈ 0.5% at 190°C, but only 21% at 300°C, and reaches 84% of loss weight at 800°C. The two other salts containing [PF$_6$]$^-$ and [NTf$_2$]$^-$ have similar thermal behavior and are stable in a wider temperature range. The thermal stability of the salts generally increases in the order: halides < [BF$_4$]$^-$ < [PF$_6$]$^-$ < [NTf$_2$]$^-$. This trend indicates that the thermal stability of the dicationic ILs, therefore, depends on the anionic species, which have a significant impact on their thermal behavior, as observed in the imidazolium salts with these anions [34-35]. To realize the relationship of thermal behavior of the presently investigated dicationic ILs with

the structure of anion is difficult, probably due to a large number of parameters such as ion size, shape, charge density, polarizability and flexibility of ions and planarity of molecular geometry. The lower thermal stability of the dichloride salt relative to those containing $[BF_4]^-$, $[PF_6]^-$ and $[NTf_2]^-$, and his decomposition rate varied significantly during the pyrolysis, due to residual water. In addition to that, it is more nucleophilic than the larger fluoride containing anions and thus decompose by SN_1 or SN_2 nucleophilic decomposition [35-36]. The pyrolysis of the imidazolium based salts has been reported to proceed most likely via SN_2 process, and therefore, change in the basicity and/or nucleophilicity of the anions is likely to bring about a change in the thermal stability of the ILs [37]. The results indicated that dicationic ILs containing $[NTf_2]^-$ shows slightly higher stability, they are less nucleophilic compared to the halides ones, which provides higher thermal stabilities compared to others dicationic ILs. This result may be attributed to the size of the $[NTf_2]^-$ that is much larger and possesses higher polarizability than perfluorinated $[PF_6]^-$ and $[BF_4]^-$ ions. Moreover, the better flexibility and charge distribution of $[NTf_2]^-$ tend to increase the interactions (attractive forces), and finally the molecular weight of the combination cation/anion.

It was reported that the melting point (T_m) of a compound is determined by the strength of its crystal lattice, which in turn is controlled by three main factors: intermolecular forces, molecular symmetry, and the conformational degrees of the freedom of a molecule [38-39]. Increasing the size of the anion generally results in weaker coulombic interactions in the crystal lattice, poor packing of the ions, and a decrease in the melting temperatures (T_m: Cl, Br > PF_6 > BF_4 > NTf_2) [40].

Table 3. Thermal properties of synthesized dicationic ILs: melting point, T_m, and decomposition temperature, T_d.

Dicationic ILs	Physical State at 25 °C	T_m (°C)	T_d (°C)
$[m\text{-}C_6H_4(CH_2ImMe)_2][Cl]_2$	Solid	196	357
$[m\text{-}C_6H_4(CH_2ImMe)_2][PF_6]_2$	Solid	150	476
$[m\text{-}C_6H_4(CH_2ImMe)_2][BF_4]_2$	Solid	136	407
$[m\text{-}C_6H_4(CH_2ImMe)_2][NTf_2]_2$	Liquid	--	491

The comparison of the T_m values of the dichloride salt with those containing the $[BF_4]^-$, $[PF_6]^-$ and $[NTf_2]^-$ clearly shows the impact of the anion symmetry (see **Table 3**). For the same cation, the salts with fluoro anions ($[BF_4]^-$ …) generally exhibit a lower melting point than those with higher symmetry $[Cl]^-$, because this fluoro anions not only possesses chemical and electrochemical stability, but they also have low symmetry, high flexibility, and a weakly coordinating nature. These results suggest that packing efficiency of the salt could be disrupted by reducing the anion symmetry, thus lowering the melting point.

4.3 INFRARED SPECTROSCOPY

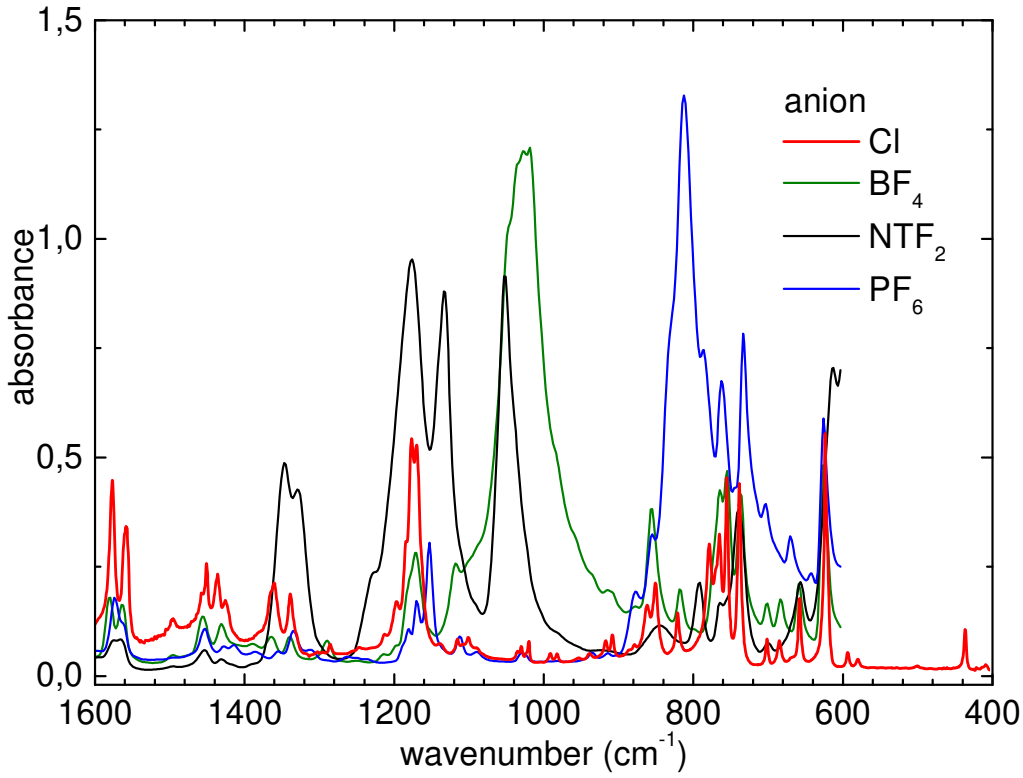


Figure 4. Comparison of the infrared absorption spectra of the four dicationic ILs.

Figure 4 reports the infrared absorbance spectra of the four dicationic ILs synthesized in this study. Most of the absorption lines of the dicationic IL containing NTF_2 as anion are due to the vibrations of the anion, as reported in **Table 4**. In the dicationic ILs with the BF_4 anion the strong absorption lines centered around 761 and 1026 cm^{-1} are due to the anion; in the dicationic IL with PF_6, the intense lines

around 742 and 852 cm^{-1} are attributable to the vibrations of the anion [25]. Apart for these lines, the other absorption bands are common to the dicationic ILs and are therefore attributable to the vibrations of the common m-xylene cation. Their detailed attributions are reported in **Table 4**.

Table 4. Observed FTIR/ATR bands and their assignment of the four dicationic ILs. (vw = very weak; w = weak; m = medium, s = strong; sh = shoulder; v = Str = stretch; δ = deformation; bend = bending deformation; ω = wagging; ρ = rocking; ϒ = out-of-plane; s = symmetric; as = antisymmetric).

[m-C_6H_4 (CH_2ImMe) $_2$]				Vibrational assignment	Refs
[Cl] $_2$	[PF_6] $_2$	[BF_4] $_2$	[NTf_2] $_2$		
				Range: 3300-2700 cm^{-1}	
	3170(s)	3161(w)	3157(m)	H-C-C-H symmetric stretch	[44]/[45]/[46/ [47]/[55]/[59]/[60]/[69]
3138(sh)	3134(sh)	3132(sh)		H-C-C-H asymmetric stretch	[44]/[45]/[46]/[47]/[55]/[59]/[60]/[69]
3115(sh)	3120(sh)	3116(w)	3120(vw)	H-C-C-H asymmetric stretch	[44]/ [45]/ [46]/[47]/[55]/ [59]/[60]/[70]
3088(w)				v (C-H) / v (CH)	[55]/[70]/[70]
3059(w)				v (C-H)	[41]/[60]/[69]/[70]
2981(w)	2974(vw)	2970(vw)	2968(vw)	(N)CH_3 asymmetric stretch,CH_2HCH asym Str	[59]/ [60]/[69]/[70]
				Range : 1700- 900cm^{-1}	
1660(m)				Imidazole ring : C=C str, N =C-N str	[59]
1612(vw)	1631(w)	1618(vw)	1612(w)	Phenyl ring : v C=C	[41] /[42]/[44]/[45]/[46]/[47]
1595(vw)				v C=C , Asym Str CH_2(N)/CH_3(N)CN Str	[55]/[58]
1573(m)	1573(m)	1581(w)	1571(vw)	Phenyl ring :C=C stretching, (N)CH_2 str	[41] /[42]/[44]/[45]/[46]/[47]
1558(m)		1562(w)		Phenyl ring :vC=C, Imidazole ring v(N=C)	[41] /[42]/[44]/[45]/[46]/[47]
1494(vw)	1496(vw)	1494(vw)		Imidazole ring ip asym str, (N)CH_3 HCH sym bend	[53]/[58]/[69]/[70]
1471(sh)				δ (CH_2)/CCH HCH as bend	[44] /[55]/[60]/[70]
1446(m)	1452(w)	1454(w)	1452(vw)	δ (CH_2)/CCH HCH as bend	[44] /[55]/[60]
1429(sh)	1427(vw)	1429(w)	1431(vw)	Imidazole ring :C–N/ C=N stretching band, δ_s(CH_2), C–H deformation	[41] /[42]/[44]/[45]/[46]/[47]/[58]
	1413(vw)			ρ (N-H)	[41]/ [55]/[61]
1383(w)	1384(vw)			ρ(CH_2), ρ(CH)/δ(CH_2) [op], ω(CH)	[41] /[60]/[61]
1359(w)	1353(vw)		1346(m)	Imidazole ring :C–N/ C=N stretching band, Trans[NTf_2]$^-$: v_{as}(SO_2), (N)CH_2 str , v CC	[41] /[42]/[43]/[44]/[45]/[46]/[47]
1328(w)	1332(w)	1338(vw)	1328(m)	Imidazole ring :C–N/ C=N stretching, SO_2 asym str	[41] /[42]/[44]/[45]/[46]/[47]
	1311(sh)			ρ C4-H, C5-H, twist CH_2	[58]
1282(w)	1261(vw)	1290(vw)		Phenyl ring: C–C stretching, v BF_4	[41] /[44]/[45]/[46]/[47]/[58]
1238(vw)	1236(vw)	1217(vw)	1224(sh)	v CN, CF_3 sym Str	[41]
1195(vw)				Ring s CH_2(N) and CH_3(N)CN Str	[44]/[55]
	1178(sh)	1170(m)	1174(s)	Ring asym Str CH_2(N) and CH_3(N)CN Str/CC Str,BF_4 FBF asym str	[44] / [53]/[55]
1153(s)	1151(s)			δ CH, (N)-CH_2-, (N)-CH_3	[44]/[58]
1110(vw)	1110(sh)	1116(sh)	1132(s)	δ CH, ring HCCH sym bend, CC str	[53]/[55]/[57]
1091(w)	1087(sh)		1051(s)	Ring ip asym str, CC str,NCH_3 twist, SNS asym str	[41]/ [43][48]/[49]/[50]/[51]/[56]
1028(vw)	1028(w)	1026(s)		CH_3N Str/CH_2N Str , v C-C	[41]/ [44]/ [48] /[49]/[50] /[51]/ [55]
1016 (vw)		1016(s)		BF_4 asym str, ring ip sym str	[53]
983(vw)				*v* CC, ring ip asym bend	[53]
960(vw)				Ring ip sym bend, CC str	[53]
931(vw)	933(vw)	933(vw)		ρ_{as} (CH_2), BF_4 asym str, ϒ CH	[53]/[44] /[55]
912(vw)	912(vw)	908(vw)		ϒ C-H	[58]

				Range : 900- 600 cm^{-1}	
894(vw)				NC(H)N bend/CCH bend	[55]
877(w)	875(sh)	877(vw)		NC(H) N bend, $\rho_{as}(CH_2)$	[42]/[47]/[61]
840(w)	852(sh)	854(m)	844(vw)	NC(H) N bend /CCH bend / NC2(H)N CH bend	[42]/[43]/[55]
808(w)	810(s)	815(w)		v (PF_6), Ring CC bend	[53]/[61]
788(w)	783(vw)	794(vw)	789 (w)	ring HCCH asym bend / CS St	[42]/ [52]/[54]/[71]
760(vw)	760(m)	761(vw)	762 (vw)	δ (HCCH)/ ring HCCH asym bend, V_s SNS, BF_4 sym str	[43]/[52]/[53]/ [55]
748(w)	742(vw)	752(w)	746(vw)	Trans-[NTf_2] : δs (CF_3), ring HCCH sym bend, CF_3 sym bend, v (PF_6), BF_4 FBF sym str	[42]/ [43]/[53]/ [55]/[61]
729(m)	731(m)	735(m)	736(m)	Anion interaction, CH_2(N) and CH_3(N)CN str, CF_3 sym bend	[42]/[43]/ [52]/[55]/[61]
696(w)	699(sh)	698(w)	696 (vw)	Ring ip asym bend, CH_2(N) str, CH_3(N) CN str	[41]/[42]
675(w)	667(w)	679(w)		ω (C-H) , δ CC, C=C-H, Ring HCCH sym bend	[41]/ [48] /[49]/[50] /[51]/[55]/[61]
655 (w)	640(vw)	655(w)	653(w)	CH_2(N) str, CH_3(N) CN str/v N–CH_3 , δSNS	[43]/[61]
613 (s)	622 (s)	622 (m)	610 (s)	CH_3(N) CN Str,, Trans-[NTf_2] : δSNS, Phenyl ring v C=C, v (PF_6)	[41] /[42]/[43]/[44]/[45]/[46]/[47]

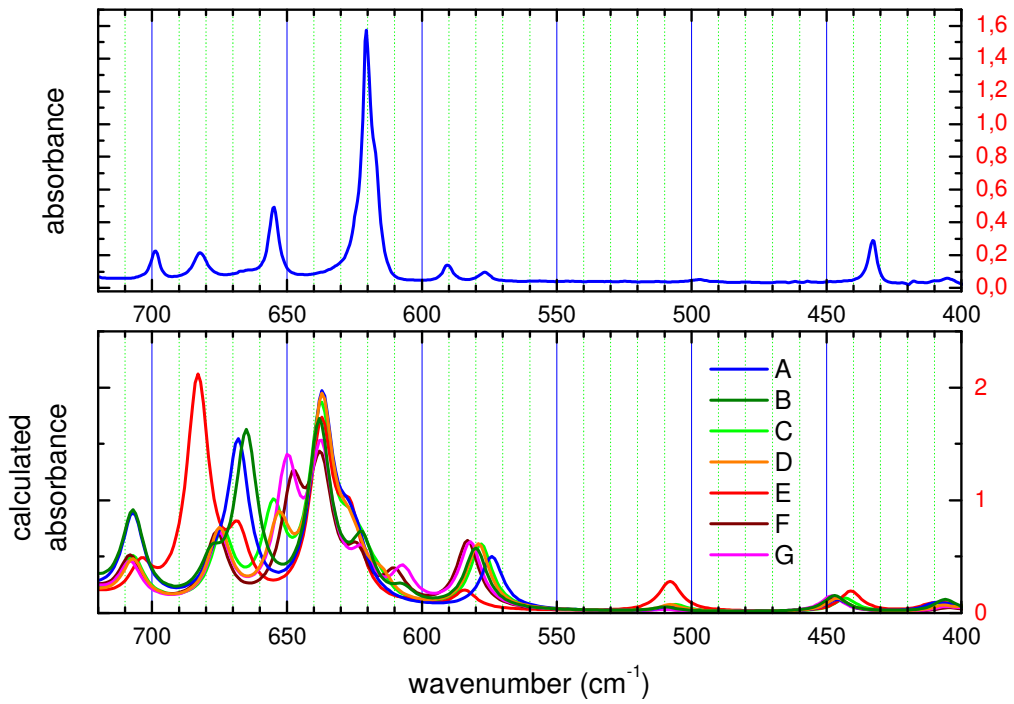


Figure 5. Comparison of the calculated infrared absorption spectra of the seven conformers of the cation and the experimentally measured spectrum of [m-C_6H_4 (CH_2ImMe) $_2$][Cl] $_2$.

Figure 5 reports a comparison in the frequency range between 720 and 400 cm^{-1} of the calculated infrared absorption spectra of the seven conformers of the cation and the experimentally measured spectrum of [m-C_6H_4 (CH_2ImMe) $_2$][Cl] $_2$, that has no contribution coming from the anion. It is evident that all calculated lines should be displaced towards lower frequency multiplying them by a factor in the range 0.97-0.99. The strong experimental absorption line centered around 620 cm^{-1} is found computationally around 636 cm^{-1} in all conformers. The lines measured around 654 cm^{-1} and 698 cm^{-1} are obtained computationally around 665 and 707 cm^{-1} in Conf A and around 668 and 707 cm^{-1} in Conf B (the conformers with the lowest energies). The experimental absorption around 681 cm^{-1} could be attributed to Conf E that is expected to show a line around 683 cm^{-1} from the DFT calculations. The lack of any experimental absorption band between 610 and 636 cm^{-1} suggests the occurrence of very limited concentrations of conformers B, C, F and G, that should present clear absorptions in this frequency range (after scaling).

4.4 RAMAN SPECTROSCOPY

Complementary to infrared absorption spectroscopy, Raman spectroscopy is a vibrational spectroscopy technique used in chemistry to identify molecules and study chemical bonding and intramolecular bonds.

In **Figures** 6, 7 and 8, we present a comparison between FT-Raman spectra of our four substituted dicationic ionic liquids (ILs) in the spectral ranges 1000-50, 1700-1000 and 3500- 2700 cm^{-1}, respectively. **Figure S1**, reported in the **Supplementing Information**, shows a comparison of the FT-Raman bands [50-3500 cm^{-1}] of the studied dicationic ionic liquids; their assignment is reported in the following with a discussion for each spectral region.

Region 1000- 45 cm^{-1}

In this region, the most characteristic modes were discussed in several zones. The bands appearing in the zone [200- 50 cm^{-1}] correspond to intermolecular vibrations with the spherical anions Cl^-, PF_6^-, BF_4^- (the symmetry of the anions; the chloride anion has the most symmetrical sphere, whereas PF_6^- anion is an octahedron, BF_4^- is an tetrahedron and the complexed $[NTf_2]^-$ anion has the lowest symmetry in cis or

trans forms and it also has S-N-S charge delocalization). Firstly, we observe three peaks for each anion except in the case of $[NTf_2]^-$, that has only two peaks at 72 and 192 cm^{-1}.

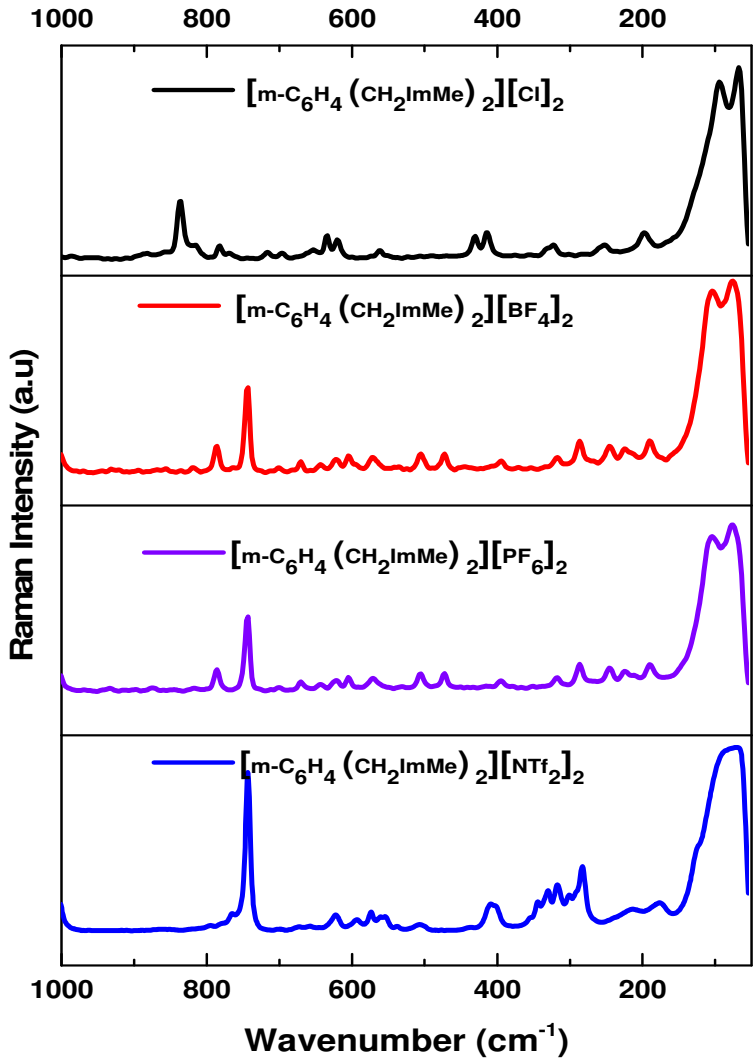


Figure 6. Raman spectra of the four dicationic ILs in the frequency range 1000- 45 cm^{-1}.

In dichloride salt, we notice the presence of the following vibrational modes: 61, 90 and 190 cm^{-1} assigned to intermolecular interactions. The same observation for the two fluorinated dicationic ILs, with slight difference in the position of the peak, which depends on the strength of the anion - cation interaction.We note that the size of the anion adjacent imidazolium rings affected the vibrational behavior of the modes

situated in this spectral zone. The larger the anion, the higher the wavenumbers of the intermolecular Raman modes: 61 and 90 cm^{-1} for Cl^- against 69; 95 / 70; 99 and 72 cm^{-1} for, PF_6^-, BF_4^- , and $[NTf_2]^-$ respectively. In the spectral zone [1000- 200 cm^{-1}], the changes are more spectacular, as we observed very different vibrational modes between dicationic ionic liquids according to the paired anion. In the case of the $[NTf_2]^-$ anion, the CF_3 asymmetric and symmetric deformation contributes to the 571, 591 and 741 cm^{-1} bands respectively. In addition, other assignable modes of vibrations from the trans-$[NTf_2]^-$ anion are: a SO_2 rocking (313 and 326 cm^{-1}), a SO_2 wagging (399 and 404cm^{-1}), a SO_2 symmetric deformation (552 cm^{-1}) and a SO_2 symmetric bending (507 cm^{-1}). As for the other anions, a great similarity is observed between the spectra relating to PF_6 and BF_4 anions especially at 471 $cm^{-}1$ as reported by Talaty et al. [46] and 742 cm^{-1} concerning the stretching and scissoring modes of vibration with a clear difference in intensities. Further two modes are observed at 620 and 766 cm^{-1}, assigned to a bending, and symmetric stretching S–N–S respectively.

Moreover, in this zone, we showed the characteristic bands corresponding to all modes of the C–H bond (in the N–C(H)–N fragment) and the stretching vibrations of the N-heterocyclic ring that used before as the diagnostic bands in spectroscopic similar studies on molecules containing the imidazolium ring as investigated by Haddad et al. [9, 20-21, 65] and by Kausteklis et al. [69]. The bending motions of these bonds (HCCH) have predominant contribution in the weak bands in the zone from 750 to 900 cm^{-1}.

Region 1700-1000 cm^{-1}

At the beginning of this spectral region, (C–C) skeletal modes are shown in the range [1000- 1200 cm^{-1}], as intense band (symmetric stretching at 1005 cm^{-1}). According to literature [42-45], all fundamental vibrations of the $[NTf_2]^-$ anion are situated below 1400 cm^{-1}, then two SO_2 antisymmetric stretching modes are expected between 1335 and 1352 cm^{-1} and the symmetric one, ν_s SO_2 (1160 cm^{-1}), with contributions from the ν_s CF_3 symmetric stretching (intense polarized band at 1244 cm^{-1}) [70]. In monocationic ionic liquids, the chloride was found in the plane of the ring, while BF_4 is positioned over the ring and has short contacts not only with H-C (2), but also with a proton of the methyl group, as suggested by Katsyuba et al.

[58] thanks to the observation of the BF_4 antisymmetric stretching mode of vibration (1025 cm^{-1}). The spectral zone [1500–1400 cm^{-1}] particularizes δ (CH_2) bending [69].

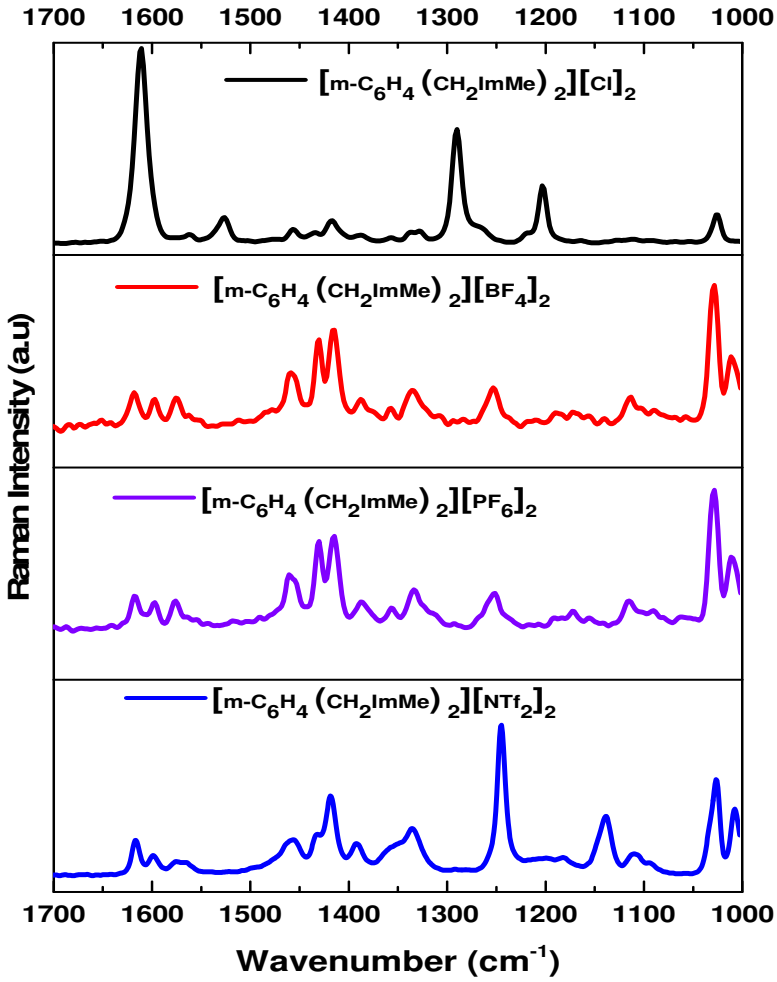


Figure 7. Raman spectra of the four dicationic ILs in the frequency range 1700-1000 cm^{-1}.

The presence of the phenyl ring could be identifying also by C= C stretching bands in the spectral range [1650 - 1500 cm^{-1}], undoubtedly, the most characteristic vibration of the phenyl group is observed as a clear band around 1596 cm^{-1} for the fluorinated dicationic ILs, and 1610 cm^{-1} for the dichloride dicationic IL, that was assigned to v (C=C).

Region 3500- 2700 cm^{-1}

This region namely C-H region, is characterized notably by the stretching vibrations of the C-H bonds occur in the range from 3000 to ~ 2700 cm^{-1} attributed to aliphatic C-H symmetric and asymmetric stretching modes, while the aromatic CH groups vibrate at higher frequency manifesting between 3200 and 3000 cm^{-1}. The band observed in the Raman spectrum near 2970 cm^{-1} can be assigned to a ν_{as} CH_3 asymmetric stretching, as reported by Kausteklis et al. [69-70]. Moreover, the C-H stretching vibration bands of the aromatic phenyl ring, the methylene and the methyl group attached to the imidazolium ring appear in the Raman spectra at 3027, 3043, 3065 cm^{-1} for $[m\text{-}C_6H_4(CH_2ImMe)_2^+][Cl^-]_2$; 3071 cm^{-1} for $[m\text{-}C_6H_4(CH_2ImMe)_2^+][BF_4^-]_2$; 3031, 3071 cm^{-1} for $[m\text{-}C_6H_4(CH_2ImMe)_2^+][PF_6^-]_2$; 3022, 3075 cm^{-1} for $[m\text{-}C_6H_4(CH_2ImMe)_2^+][NTF_4^-]_2$. The C-H stretching of the imidazole ring are observed at 3119, 3152 cm^{-1} for $[m\text{-}C_6H_4(CH_2ImMe)_2^+][Cl^-]_2$, 3127, 3158, 3179 cm^{-1} for $[m\text{-}C_6H_4(CH_2ImMe)_2^+][PF_6^-]_2$, 3135, 3158, 3179 cm^{-1} for $[m\text{-}C_6H_4(CH_2ImMe)_2^+][BF_4^-]_2$, , 3134, 3153, 3178 cm^{-1} for $[m\text{-}C_6H_4(CH_2ImMe)_2^+][NTF_2^-]_2$, (**Figure** 6). In this region, the vibrational bands at higher wavenumbers can be referred to C(4,5)-H stretching modes, whereas those at lower wavenumbers can be assigned to the C(2)-H stretching modes.

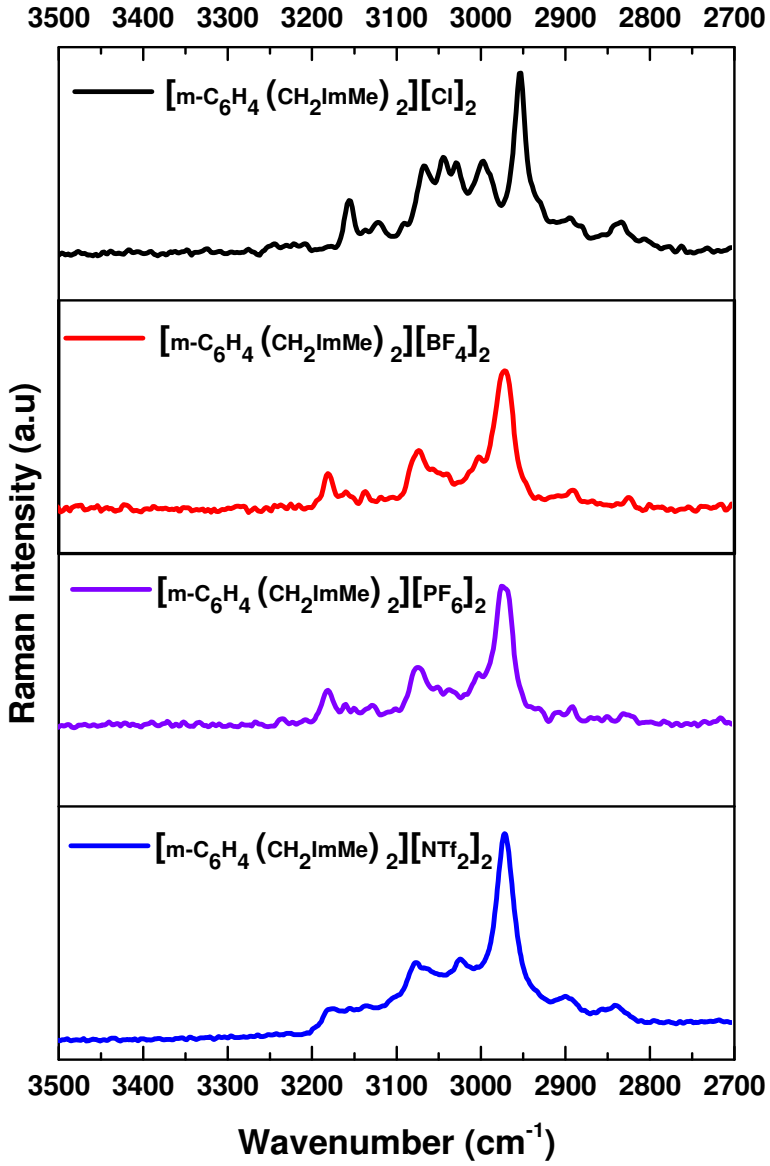


Figure 8. Raman spectra of the four dicationic ILs in the frequency range 3500 – 2700 cm^{-1}.

Table 5. Observed FT-RAMAN bands and their assignment of 4 dicationic ILs at room temperature. (vw = Very weak; w = weak; m = medium, s = strong; sh = shoulder; v = Str = stretch; δ = deformation; bend = bending deformation; ω = wagging; ρ = rocking; τ = torsion, s = symmetric; as = antisymmetric).

[m-C_6H_4 (CH_2ImMe) $_2$]				Vibrational assignment	Refs
[Cl] $_2$	[PF_6] $_2$	[BF_4] $_2$	[NTf_2] $_2$		
				Range: 3500- 2700 cm^{-1}	
	3179 (w)	3179 (w)	3178 (vw)	H-C-C-H asymmetric stretch , v_{as} (H-C(4)), v_{as} (H-C(5))	[44]/[45]/[55]/[69]/[70]
3152 (w)	3158 (vw)	3158 (vw)	3153 (vw)	H-C-C-H asymmetric stretch	[52]/[63]/[60]/[69]/[70]
3119 (vw)	3127 (vw)	3135 (vw)	3134 (vw)	H-C-C-H asymmetric stretch , v_{as} (H-C(2))	[52]/[55]/[69]/[70]
3065 (w)	3071 (w)	3071 (w)	3075 (w)	C-H stretching	[65]/[66]/[68]
3043 (vw)				C-H stretching	[45]/[54]/[65]/[70]
3027 (vw)		3031 (vw)	3022 (vw)	C-H stretching	[54]/[68]/[69]
2994 (w)	2999 (sh)	2999 (sh)		(N)CH_3 asymmetric stretch	[54]/[61]/[69]/[70]
	2971(m)	2969 (m)	2969 (m)	(N)CH_3 asymmetric stretch, v_{as} (CH_3)	[61]/[66]/[68]
2949 (m)		2928 (vw)		(N)CH_2, (N)CH_3 symmetric stretch	[53]/[60]/[42]
2890 (vw)	2890 (vw)	2890 (vw)	2897 (vw)	(N)CH_2, (N)CH_3 symmetric stretch	[44]/[70]
2830 (vw)	2828 (vw)		2838 (w)	(N)CH_2, (N)CH_3 symmetric stretch	[54]/[43]/[69]
		2822 (vw)		v_s(CH_3), (N)CH_2, (N)CH_3 sym stretch	[58]/[21]/[69]/[70]
				Range: 1700-1000 cm^{-1}	
1610 (s)	1616 (vw)	1616(vw)	1615 (vw)	Phenyl ring: v C=C	[48]/[49]/ [50]/[51]
	1596 (m)	1597 (m)	1596 (m)	Phenyl ring: v C=C	[48]/[49]/ [50]/[51]
1572 (vw)	1575 (vw)	1575 (vw)	1574(vw)	Phenyl ring v C=C,(N)CH_2 str	[41]/[52][48]/[49]/ [50]/[51]
1525 (w)				Phenyl ring: v C=C , Im ring v (N=C)	[41]/[52]
1455(w)	1457(w)	1457 (w)	1457(w)	Phenyl ring v C=C,(N)CH_3 str, C–H deformation	[48]/[49]/ [50]/[51]
1434 (vw)	1429 (w)	1429 (w)	1430 (sh)	Im ring:C-N/C=N stretching band, δ (CH_2)	[42]/[48]/[61]/ [66]
1417(w)	1415 (m)	1415 (m)	1418 (w)	Im ring:C-N/C=N stretching band, (N)CH_2 str ,C–H deformation	[46]/ [53]/[51]
1384 (vw)	1387 (w)	1387 (w)	1390 (w)	Imidazole ring:C-N/C=N stretch band	[43]/[46]/ [53]/[66]
			1352 (sh)	Imidazole ring :C–N/ C=N stretching band, Trans [NTf_2]: v_{as}(SO_2),(N)CH_2 str	[48]/[49]/ [50]/[51]/[25]
1334 (vw)	1332 (w)	1334 (w)	1335 (m)	Imidazole ring:C-N/C=N stretch band, Trans [NTf_2]: $v_{as,op}$(SO_2)	[42]/[43]/ [53]/ [61]/[25]
1288 (m)	1289 (vw)	1291 (vw)		Phenyl ring: C-C stretching	[51]/[61]/[69]
	1251 (m)	1249(w)	1244 (m)	Phenyl ring: C–C stretching/ Trans [NTf_2]: v_s(CF_3)	[48]/[49]/ [50]/[51]/[25]/[70]
		1205 (vw)		BF_4 asym str, Phenyl ring: C-C stretching	[53]/[63]
1199 (m)	1190 (vw)	1190 (vw)	1195 (vw)	Phenyl ring: C-C stretching, C- C-H i p bend, C- C- H ip bend	[51]/[67]/[69]
	1168(vw)	1169 (vw)	1178 (vw)	δ CH, CH_3N	[46]/ [51]/[53]/[69]
			1135 (m)	Trans [NTf_2]:: $v_{s,ip}$(SO_2)	[25]/ [42]/ [55]
	1110(w)	1112 (w)	1106 (vw)	δ CH, ring HCCH sym bend	[46]/ [53]/[61]
1023 (m)	1025(m)	1025(m)	1023 (m)	δ CC, δ CH, BF_4 asym str, v_{as} (BF(4)), v_{as} (BF(2))	[53]/ [61]/[58]
	1006(sh)	1008 (sh)	1003 (sh)	C-C ring stretch	[51]/[67]
				Range: 1000- 45 cm^{-1}	
	931 (vw)	932 (vw)		(N)CH_2, BF_4 asym str	[21]/[53]
882 (vw)	876 (vw)	882 (vw)		ρ (CH_2), NC(H)N bend/CCH bend	[52]/[61]
	864 (vw)			PF_6 asym str	[46]/[25]
		855 (vw)	856 (vw)	NC(H)N bend	[44]/[45]/[46]/ [47]
836(m)		834 (vw)		Ring HCCH asym bend	[53]/[66]
815 (sh)	817 (vw)	818 (vw)		HCCH sym bend	[52]/[66]
			795 (sh)	v_s (CS)	[25]
782(w)	784 (w)	786 (w)		V_sCC, HCCH sym bend	[52]/[60]/[66]
767(sh)		766 (vw)	766 (sh)	v_s(SNS), (N) CH_2 str, NCH_3, δ CC, C=C-H, ring HCCH	[43]/[45]/[46]/ [47]

				asym bend	
	742 (s)	743 (s)	741 (s)	v (PF_6) , BF_4 scissors , v_s (BF_4),Trans [NTf_2]: $\delta_S(CF_3)$,	[25]/[44]/[45]/[46]/ [47]/[53]/[70]
711(vw)	700(vw)	701 (vw)	696 (vw)	C=C-H, H-C-C-H	[21]/[49]
652(vw)	667 (vw)	668 (vw)	659 (w)	δ CC, C=C-H, CH_2(N)/CH_3(N)CN Str	[48]/[49]/[50]/ [51]/ [61]
632(w)	641 (w)	642 (w)		δ CC, (N-C), (N)CH_2 str, v N-CH_3	[48]/[63]
616(w)	618 (w)	618 (w)	620 (w)	δ CC, NCH_3 Trans-[NTf_2] : δSNS, δ op $_{as}(SO_2)$, Phenyl ring v C=C	[44]/[45]/[46]/ [47] /[25]
			591 (w)	Trans-[NTf_2] : $\delta_{as}(CF_3)$, δ ip $_{as}(SO_2)$, $\delta_s(NSO_2)$	[25] /[42]/[44]/[45]/[46]/ [47]
			552(w)	Trans-[NTf_2]: $\delta_s(SO_2)$	[44]/[25]
	503(vw)	504(vw)	507(vw)	BF_4 scissors, δ (BF_4), SO_2 sym bending	[52]/[[53]/[63] /[25]
	470 (vw)	470 (vw)		v (PF_6), δ (BF_4), v (BF)	[25]/ [52]/[55]/[63]
412(w)			404 (vw)	(N)CH_2 str , NCH_3, Trans-[NTf_2]: ω (SO_2)	[44]/[45]/[46]/ [47]/[25]
	391 (vw)	391 (vw)	399 (m)	ρ(CH_2), (N) CH_2 str, Trans-[NTf_2] : ω (SO_2)	[44]/[45]/[46]/ [47]/[25]
		351(vw)		δ NCH_3, BF_4 scissors, δ (BF_4), CC	[53]/[63]/[64]/ [65]/[25]
			340 (sh)	δ NCH_3, Trans-[NTf_2] : τ (SO_2)	[44]/[45]/[46]/ [47]/[25]
			326(m)	ρ(SO_2)	[44]/[45]/[46]/ [47]/[25]
319(w)	313(m)	313(m)	313(m)	CN stretch , SC Str Trans-[NTf_2]: ρ(SO_2), ρ(CF_3)	[44]/[45]/[46]/ [47]/[25]
	282(vw)	282(vw)	282(m)/288(sh)	ρ (CH_2), CN stretch, Trans-[NTf_2] : ρ CF_3, v_{as}(CS)	[45]/[46]/ [55]
248(vw)	240(vw)	242(vw)		ρ (CH_2), ϒ N-CH_3,	[21]]/[53]
	221(vw)	219(vw)	208(vw)	τ (N-C)/ ρ (CH_2), NCH_3	[41]/[55]/ [60]
190(w)	185(w)	186(w)	172(w)	Intermolecular vibration, ω (N–C), τ (N–C)/ρ(CH_2)	[41]/ [55]/ [60]/[62]
90(sh)	95 (sh)	99(sh)		Intermolecular vibration	[62]
90(sh)	95 (sh)	99(sh)		Intermolecular vibration	[62]
90(sh)	95 (sh)	99(sh)		Intermolecular vibration	[62]
61 (sh)	69 (sh)	70 (sh)	72(s)	Intermolecular vibration	[62]

4.5 COMPUTATIONAL INVESTIGATION OF THE STRUCTURE ANIONS-CATION

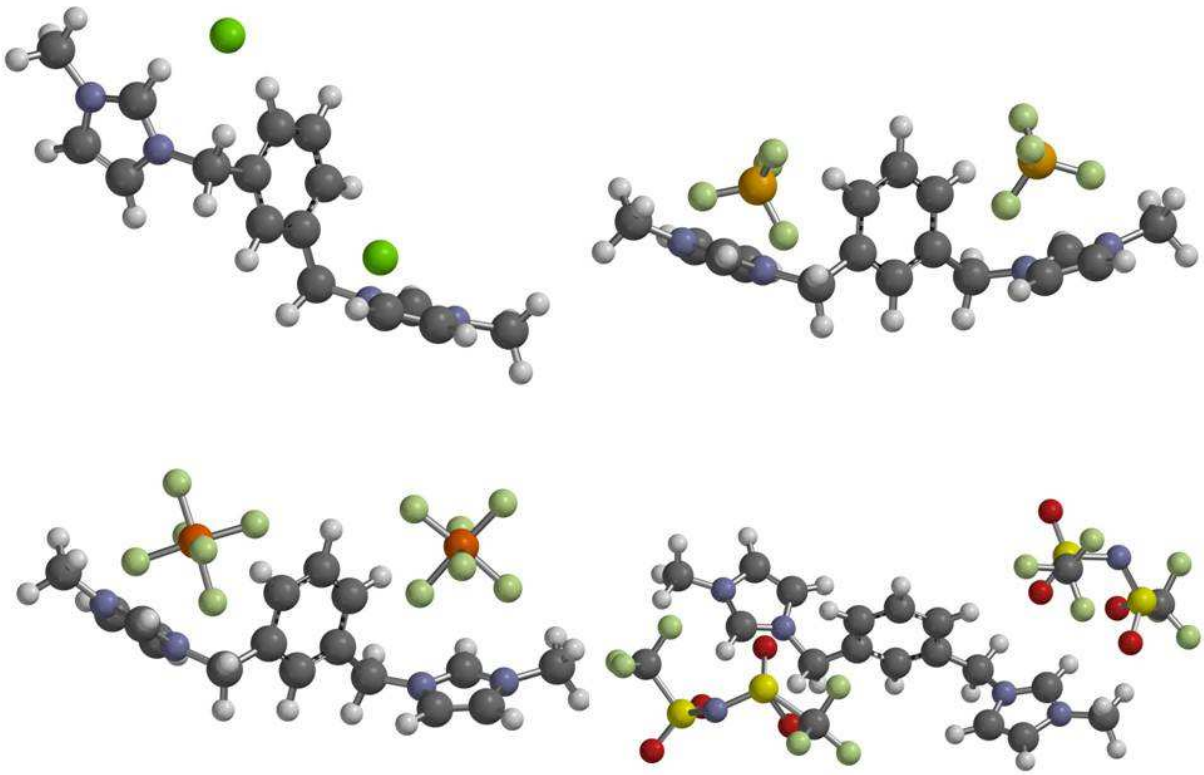


Figure 9. Schematics of the optimized structures of the four ILs with different anions (top-left: Cl; top-right: BF_4; bottom-left: PF_6; bottom-right: NTf_2).

The optimized structures of the four ionic couples of m-xylene with 2 Cl^-, 2 BF_4^-, 2 PF_6^- or 2 NTf_2^- anions were obtained by DFT calculations using the 6-31G** basis set and the B3LYP theory. Different starting geometries were investigated. For all the four possible anions, the cation preserves its structure close to that found for conformer A, reported in Section 4.1 (see Figure 9). Moreover, in all cases the two anions prefer to reside both in the same half plane were the benzene ring is placed, in positions close to the imidazolium C13 and C15 carbon atoms (see Figure 2) and the attached H atoms. The only exception is observed in the case of the two Cl^- anions, which prefer to displace toward the methylene groups with carbon atoms C7 and C8. In this case the distances between Cl and the hydrogen atoms of the imidazolium ring (H14, Figure 9), of the methyl group (H7) and of the benzene ring (H1) are 2.027, 2.521 and 2.861 Å, respectively. In the case of the BF_4 anions the F2 and F1 atoms (figure 2) distance from H14 are 2.030 and 2.091 Å, while for PF_6 the F1 and F2 distance from H14 increases to 2.046 and 2.105 Å. Finally in the case of NTf_2, the closest oxygen atom has a distance of 1.929 Å from H14. In all cases the anions reside outside the planes defined by the imidazolium rings, with increasing distance for Cl, BF_4, PF_6 and NTf_2. However, these results need to be compared to experimental structural data, that at present are not available, due to the lack of X-ray diffraction data in the solids.

5. CONCLUSION

Four new substituted dicationic ionic liquids based on meta-xylyl linked bis-1-methylimidazolium, combined with four anions, namely dichloride $[Cl^-]_2$, di(bis(trifluoromethylsulfonyl) Imide) $[(CF_3SO_2)_2N^-]_2$, di(tetrafluoroborate) $[BF_4^-]_2$ and di(hexafluorophosphate) $[PF_6^-]_2$ were synthesized for the first time. ^1H, ^{13}C, ^{19}F and ^{31}P-NMR spectroscopies confirm the production of the desired ILs. Combined TGA/DTA measurements indicate that the thermal stability of the ILs is in the following order $NTf_2>PF_6>BF_4>Cl$; the latter compound is highly hygroscopic. While the NTf_2 based sample is liquid at room temperature, the other three samples are solid and the melting points are in the order $NTf_2<BF_4<PF_6<Cl$. Moreover, the vibrational spectra of these ionic liquids were investigated by using FTIR and FT-

RAMAN spectroscopies. Quantum chemical theory (at the DFT level) was used to calculate the possible conformers of the cation. Due to the complex structure of the cation seven conformers exists with a difference in energy of less than 5 kJ/mol. The comparison with the experimental IR spectrum suggests that at least three of them could be present in the samples. Finally a computational investigation of the interaction between anions and cation is presented.

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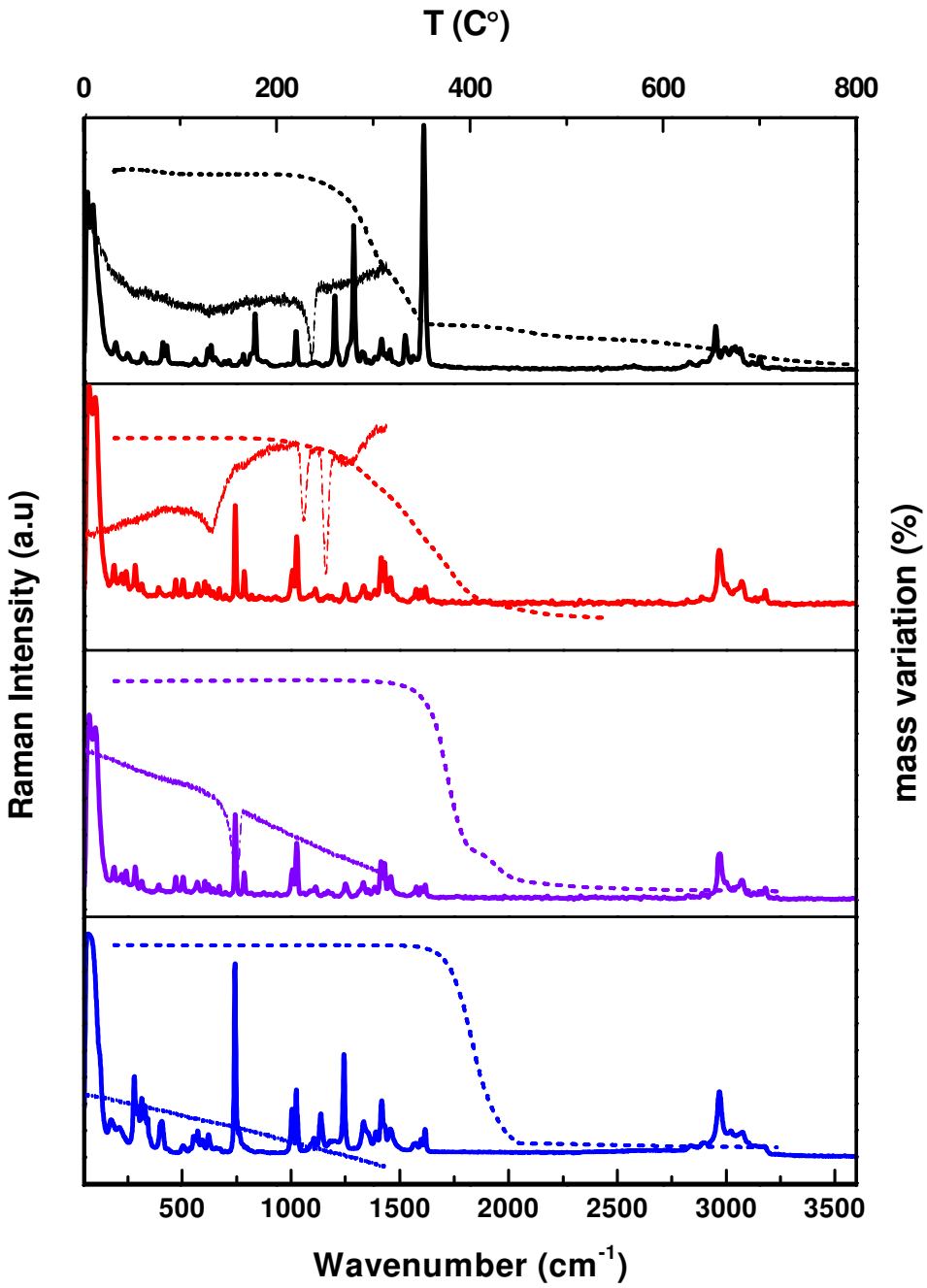
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