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► **To cite this version:**

Mostefa Boumediene, Boumediene Haddad, Annalisa Paolone, Mohammed Amin Assenine, Didier Villemin, et al.. Synthesis, conformational studies, vibrational spectra and thermal properties, of new substituted dicationic based on biphenylenedimethylene linked bis-1-methylimidazolium ionic liquids. *Journal of Molecular Structure*, 2020, 1220, pp.128731. 10.1016/j.molstruc.2020.128731 . hal-02900552

HAL Id: hal-02900552

<https://normandie-univ.hal.science/hal-02900552>

Submitted on 16 Jul 2020

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Synthesis, conformational studies, vibrational spectra and thermal properties, of new substituted dicationic based on biphenylenedimethylene linked bis-1-methylimidazolium ionic liquids.

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[doi:10.1016/j.molstruc.2020.128731](https://doi.org/10.1016/j.molstruc.2020.128731)

ABSTRACT

Three new substituted dicationic ionic liquids (DILs) based on biphenylenedimethylene linked bis-1-methylimidazolium ionic liquids [Bis-(PhCH₂MIm)⁺], combined with three anions, namely dichloride[Cl]₂, di(hexafluorophosphate) [PF₆]⁻₂ and di(bis(trifluoromethylsulfonyl)Imide) [(CF₃SO₂)₂N]⁻₂ were synthesized. The three synthesized dicationic ionic liquids were characterized by Nuclear Magnetic Resonance and Fourier transform infrared (FTIR) and Raman spectroscopy in the region 4000–600 cm⁻¹ and 4000–45 cm⁻¹, respectively. A complete vibrational assignments have been performed; the biphenylene linkage spacer is confirmed by the presence of strong Raman band at 1616 cm⁻¹ related to the C=C vibration in all our investigated DILs. Moreover, a conformational investigation of the cation was performed by means of DFT calculations using the 6-31G** basis set and the B3LYP theory. The comparison of the computed and experimental Raman spectra further corroborate the structure of the cation. Finally, the thermal stability of the DILs was investigated by TGA and DTA measurements. The DILs with Cl⁻, PF₆⁻ and [(CF₃SO₂)₂N]⁻ anions decompose at 252, 323 and 420 °C, respectively.

KEYWORDS: Biphenylenedimethylene; Bis-imidazolium; Thermal analysis; Conformers; Raman measurements; DFT calculations.

1. INTRODUCTION

Ionic liquids (ILs) are habitually composed of a relatively large, structurally asymmetric organic cation and an (in) organic anion. Dicationic ionic liquids (DILs) are an interesting class of new ionic liquids formed of two cationic units combined with a linkage spacer (alkylene, phenylene, biphenylene groups) and paired with two anionic entities. Tailor-made dicationic ionic liquids (DILs) are becoming important, and have been shown to possess a larger variety of tunable interactions, better thermal stabilities, high density and designability. In the past decade, the exceptional portfolio of physi-chemical properties suggested them as a source of inspiration for novel materials. The knowledge of these properties can be obtained by studying the structure-property relationships, the nature of intermolecular interactions and hydrogen-bonding occurring between the dications and counterions in most dicationic ionic. The variety of properties of DILs give them a rich scientific and application connotation [1], as they are suggested for utilization in the fields of organic synthesis [2], electrochemistry [3] and material preparation [4]. DILs benefits of their higher thermal stability compared to traditional monocationic ILs [5]; moreover, their unique physical and chemical behavior distinguish them from other commonly used organic chemicals [6], as demonstrated by several intense investigations. A good application prospect has gradually moved from laboratory research to industrial application. The premise of industrial processes is an important basis for the design of new and functional ionic liquids.

In previous studies, we have investigated the meta and para-xylyl linked ionic liquids [7,8,9], and thus, we have deduced the influence of the position of xylyl groups on the thermal properties of these DILs. In our recent study, we have investigated in more detail the profound effect of the spacer group introduced between two imidazolium units (in the *para*-position of biphenyl rings) and then the role of the cation symmetry and the nature of the anion in changing the properties of the dicationic ionic liquids synthesized [10], in particular, thermal properties, such as melting point and decomposition temperature. Furthermore, the anions-cation interactions enlighten the occurrence of a larger number of hydrogen bonds, formed because structures of our DILs contain more hydrogen atoms in the cation and fluorine atoms in symmetrical hexafluorophosphate anion (octahedral) and lowest symmetrical anion (cis or trans form), the (bis(trifluoromethylsulfonyl) imide).

Additionally, theoretical chemical calculations of cation-anion energy were done in order to support experimental results. The advantages of using those DILs are due to their important thermal stability in comparison with their asymmetric counterparts [11-12].

In the present study, we report the synthesis of novel DILs, containing a symmetric cation based on the biphenylenedimethylene linked bis-1-methylimidazolium ionic liquids. The resulting DILs are further characterized to verify the desired structure of the cation and to assess their thermal stability.

2. EXPERIMENTAL

2.1. Materials

The reagents which have been used in all syntheses of the dicationic ionic liquids in this study are 1-methyl-1H-imidazole (> 99%), [4,4'- bis (chloromethyl)-1,1'- biphenyl] (95%), potassium hexafluorophosphate ($\geq 99\%$), lithium bis (trifluoromethylsulfonyl) imide (99%), that were purchased from Aldrich and used as received. The solvents N,N-dimethylformamide and diethyl ether used in the synthesis, purification and NMR characterization were provided from Fluka, while deuterated dimethyl sulfoxide (DMSO- d_6) obtained from Aldrich. Deionized water (H₂O) was produced with a Millipore ion-exchange resin deionizer.

2.2. Instrumentation

The structure and purity of all of the synthesized DILs were confirmed by spectral analysis: ¹H, ¹³C, ¹⁹F and ³¹P NMR spectra were recorded on a Bruker DRX with tetramethylsilane as the standard (at 500, 125.75, 470.62, 202.47 MHz respectively). All measurements of thermogravimetry (TGA) and differential thermal analysis (DTA) were performed by means of an apparatus model Setaram Setsys Evolution 1200, with a fixed temperature rate of 5°C/min, in an argon flux of 60 ml/min. An initial mass of ~20 mg was used for each sample.

Infrared spectroscopic analyses data were carried out for all of the synthesized DILs collecting 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 Limited, Slough, UK).

FT-RAMAN spectra were acquired by means of a Vertex 70-RAM II Bruker FTRAMAN spectrometer. This instrument is equipped with an Nd: YAG laser (yttrium aluminum 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 prealigned; 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

3. COMFORMATIONAL STUDY

The isolated cation (bis-phenyl) was investigated computationally by means of the Spartan software [13-14].

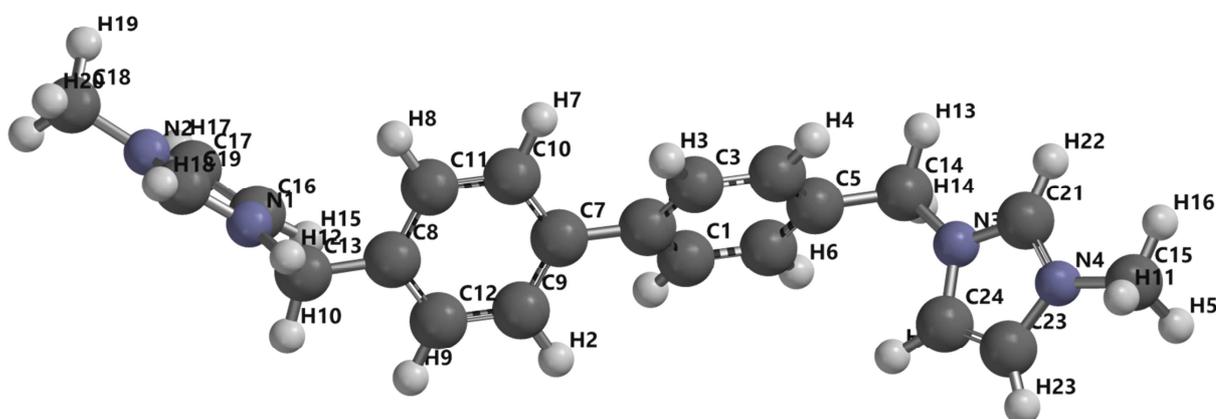


Figure 1. Schematics of the bis-phenyl cation with labels for each atom.

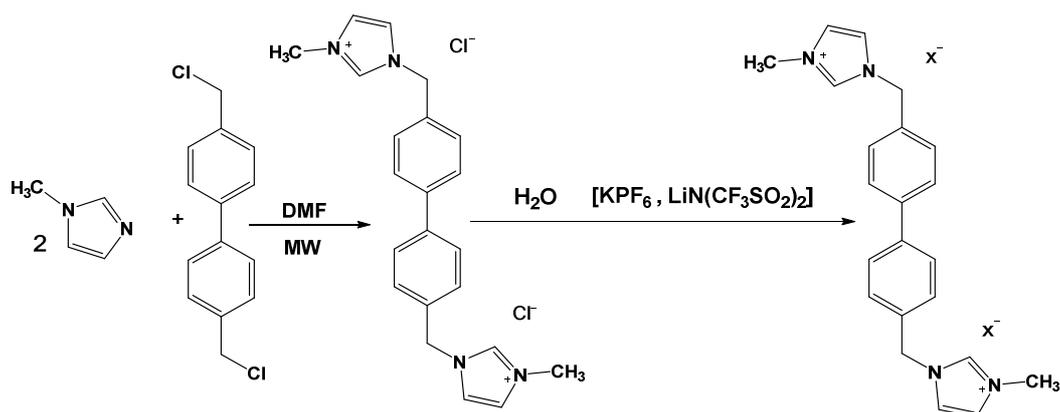
A preliminary investigation of the possible conformational geometries of the cation was performed at the molecular mechanics level. The investigation of the possible stable structures started with a systematic search, varying the four dihedral angles that define the ionic structure reported in Figure 1. 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 N3,C14,C5,C6 and C12,C8,C13,N1 were varied by steps of 60°, while the two dihedral angles C24,N3,C14,C5 and C8,C13,N1,C16 were varied by 180°, so that in total we investigated $6 \times 6 \times 2 \times 2 = 144$ 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. After the optimization, we obtained much degenerate geometries, which were removed from the following procedures. The vibration frequencies and the infrared intensity and Raman activity of the optimized structures having energy not higher than 1 kJ/mol from the lowest energy conformer were calculated by means of the Spartan software. Only five 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 intensity proportional to the calculated one and a fixed line width of 10 cm^{-1} .

4. Preparation of Dicationic Ionic Liquids

The synthesis of three dicationic ILs implies two steps. The first one is to obtain the ionic salt namely 3,3'-dimethyl-1,1'-(biphenylenedimethylene)-bis(1H-imidazolium) dichloride or namely 4,4'-bis-(3-methylimidazolium-1-yl-methyl) biphenyl dichloride, which can be synthesized and described as cited in literature [15] with slight modifications. Briefly, The DIL named $[\text{Bis}-(\text{PhCH}_2\text{MIm})^+][\text{Cl}^-]_2$ was prepared under microwave irradiation, as following: 3.28 g (3.18 ml, 40 mmol) of 1-methylimidazole were mixed with 5.02 g (20 mmol) of the [4,4'- bis (chloromethyl) -1,1'- biphenyl] in N,N- dimethylformamide (3 ml) at $100\text{ }^\circ\text{C}$ for 3 min. The resulting crude precipitate was collected by filtration and washed three times upon addition of diethyl ether (100 ml) to remove any unreacted reactants, and then dried under high vacuum for 8 h, to afford a white hygroscopic solid in high yield ($\approx 97\%$). The second step involves the synthesis of two other dicationic ionic liquids by performing anion exchange for the chloride anions with $[\text{PF}_6^-]$ and $[\text{NTf}_2^-]$ anions. For this, one (1) molar equivalent of the dichloride salt (2 g, 6.25 mmol) dissolved with two (2) molar equivalents (2.14 g, 11.5 mmol) of hexafluorophosphate potassium salt (KPF_6) in 20 ml of deionized water, to give $[\text{Bis}-(\text{PhCH}_2\text{MIm})^+][\text{PF}_6^-]_2$ after a separation and washing process. The same procedure was followed in the preparation of $[\text{Bis}-(\text{PhCH}_2\text{MIm})^+][(\text{CF}_3\text{SO}_2)_2\text{N}^-]_2$ by using the dichloride salt with 2 molar equivalents (3.33 g, 11.5 mmol) of bis (trifluoromethylsulfonyl) imide lithium salt (LiNTf_2). All synthesis reactions (two steps) are summarized and depicted in the following scheme 1:



Scheme 1: The synthesizing process of dicationic ionic liquids (DILs),
MW: Microwave (with X = [PF₆] and [(CF₃SO₂)₂N]).

5. RESULTS AND DISCUSSION

5.1. NMR spectroscopy characterization

The dichloride, di-hexafluorophosphate and di-bis (trifluoromethylsulfonyl) imide DILs were characterized by NMR spectral method over the range $\delta = 0 - 12$. As it is observed, in the ¹H NMR spectra of the dichloride DIL, the signals between $\delta = 9.45 - 7.89$ ppm corresponds to the imidazolium ring protons at C2 and C4/C5 positions. The DILs containing the same cation and differing in the structure of the fluorinated anion exhibited similar ¹H NMR profiles with downfield resonance.

Firstly, the ¹H NMR spectrum of [Bis-(PhCH₂MIm)⁺][2Cl⁻] showed a singlet at $\delta = 9.45$ ppm corresponding to the NC₂HN of the protons of the imidazolium fraction and a doublet at $\delta = 7.95 / 7.89$ ppm for NC₄HC₅HN protons. The resonance of the aromatic biphenyl group (-C₆H₄)₂ is seen in the form of a doublet at $\delta = 7.76 / 7.56$ ppm. On the other hand, the proton resonance of methylene (-CH₂-) is seen as a singlet at $\delta = 5.51$ ppm. The characteristic singlet peak for N-methyl (CH₃) appeared at $\delta = 3.88$ ppm. On the hand, for the DIL [Bis-(PhCH₂MIm)⁺][2PF₆⁻], the signal of the imidazolium proton NC₂HN appears as a singlet at $\delta = 9.22$ ppm, and a doublet at $\delta = 7.80 / 7.77$ ppm for imidazolium protons NC₄HC₅HN. Three resonances at $\delta = 7.73 / 7.52$, 5.45 and 3.81 ppm can also be observed for the aromatic biphenyl group (-C₆H₄)₂, the methylene protons (-CH₂-) and the N-methyl (-CH₃), respectively. The ¹³C-NMR spectra of the DILs showed direct information about the carbon skeleton and the number of equivalents/non-equivalents carbons of these DILs.

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. ^{31}P NMR spectrum of the synthesized DIL was found to have sextuplet (multiplet, m) between -130 to -159 ppm confirming the presence of the phosphorous atom coupled with six fluorine atoms. On the other hand, for the dihexafluorophosphate salt, the ^{19}F -NMR spectra were found to contain doublets (d) between $\delta = -69.35$ to -70.86 ppm that confirmed the coupling of six fluorine atoms with one phosphorous atom. The ^{19}F -NMR spectra for (di-bis (trifluoromethylsulfonyl) imide DIL was found to contain a singlet (s) at $\delta = -78.75$ ppm.

[Bis-(PhCH₂MIm)⁺][2Cl⁻]:

^1H NMR (500 MHz, DMSO-*d*₆): 3.88 (s, 6H, 2 × CH₃), 5.51 (s, 4H, 2 × N-CH₂-Ar), 7.56 (d, 4H, 2 × HC-C(CH₂)-CH), 7.76 (d, 4H, 2 × HC-C(C)-CH), 7.89 (s, 2H, H₃C-NCH), 7.95 (s, 2H, -NCH), 9.45 (s, 2H, 2 × NCHN). ^{13}C NMR (125.75 MHz, DMSO-*d*₆): 36.6, 52.1, 122.8, 124.6, 127.8, 129.3, 134.7, 137.3, 140.1

[Bis-(PhCH₂MIm)⁺][2PF₆⁻]:

^{31}P NMR (DMSO-*d*₆) δ ppm: -133.68, -137.19, -140.71, -144.22, -147.74, -151.25, -154.76 (sept, PF₆⁻)

[Bis-(PhCH₂MIm)⁺][2NTF₂⁻]:

^{19}F NMR (DMSO-*d*₆) δ F (ppm): -78.56 (s, [NTF₂⁻]).

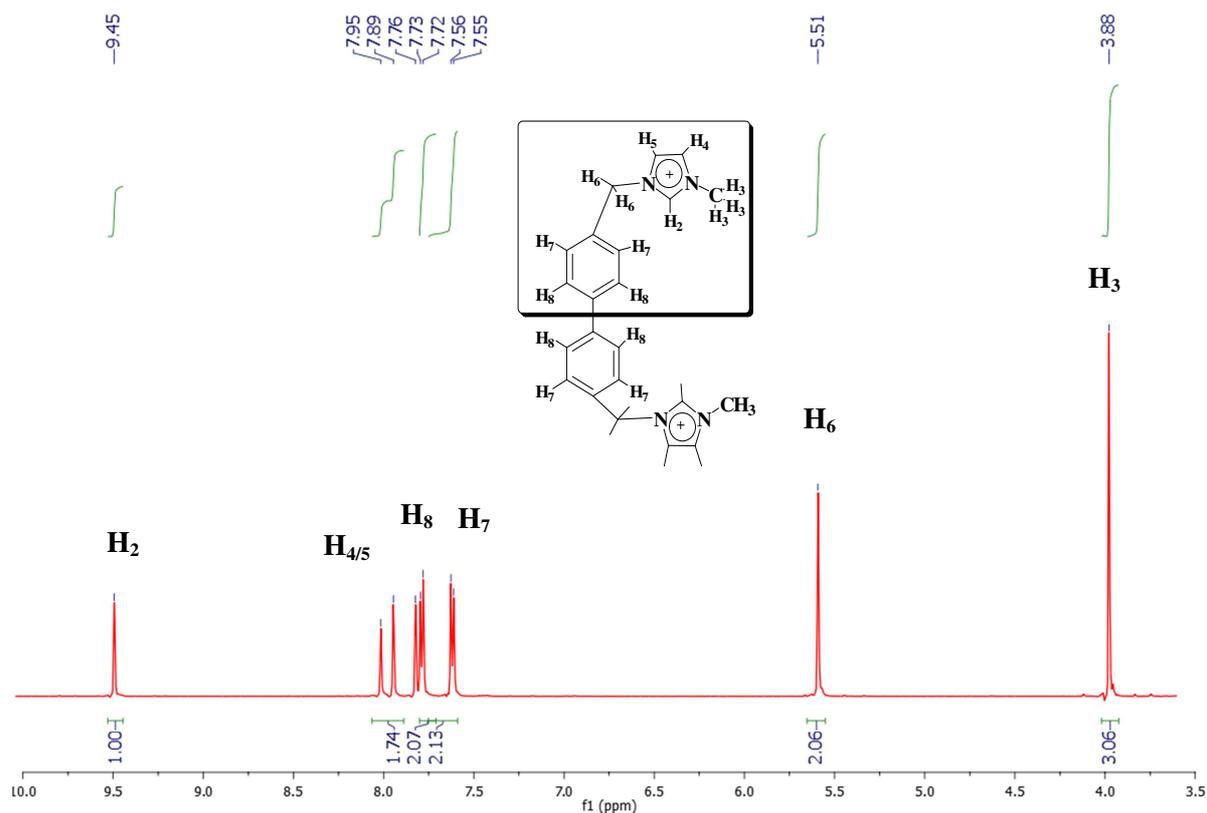


Figure 2. ¹H NMR (500 MHz) spectra of [Bis-(PhCH₂MIm)]⁺[Cl]⁻₂.

5.2. Vibrational spectroscopy

The identification of different vibrations remains a challenging task in vibrational spectroscopy, especially when complex structures (such that of the presently investigated cations) are present. Normally, to interpret the IR and Raman spectra one starts with the base of most organic compounds, namely the basic skeleton or parent hydrocarbon structure. The infrared and Raman spectrum can furnish information on the existence of these structures, directly or by inference. The presence of the functionalities was identified by these powerful tools, while additional information on the interaction of the group with other parts of the ion pair could be obtained.

5.2.1 FT-Raman spectroscopy characterization

It is of importance to study the spectral features in Raman spectra, for several regions, to attribute the vibrational modes. In the spectral zone 200 - 60 cm⁻¹, we

observed strong bands correspond to intermolecular vibrations with the halide $[\text{Cl}]^-$ and fluorinated anions $[\text{PF}_6]^-$, $[\text{NTf}_2]^-$ at 72, 68 and 62 cm^{-1} respectively. Moreover, weak intermolecular interactions at around 200, 190 and 170 cm^{-1} were visible in the three DILs.

In general, the most dominant bands can be found in the region between 1500 and 1000 cm^{-1} for the $[\text{NTf}_2]^-$ anion. These bands correspond to the O=S=O and C-F stretching modes. For $[\text{PF}_6]^-$, the anionic vibrations as weak bands at 856, 570 and 470 cm^{-1} , two medium intensity band around 826 and 740 cm^{-1} and a strong band at 751 cm^{-1} [16,20,36].

The frequencies in the spectral zone occurring between 3200 and 2800 cm^{-1} are assigned to the ν CH stretching modes, and are remarkably very weak. The absorptions at around 2970 (medium) and 2895 cm^{-1} are characteristic of asymmetric stretching vibrations of C-H (sp^3 -s) from the alkyl chain (-CH₃) and symmetric stretching methylene vibrations (N-CH₂-Phenyl) group, respectively. The vibrational bands with wavenumbers more than 3000 cm^{-1} correspond to the aromatic stretching modes of the C_{Im}-H, and C_{Phenyl}-H bonds. As depicted in Fig.3A, the FT-Raman spectrum of $[\text{Bis}-(\text{PhCH}_2\text{MIm})^+][\text{PF}_6^-]_2$ shows a band at 3106 cm^{-1} assigned to the $\nu\text{C}(2)\text{H}$ vibration, absorption line at 3137 cm^{-1} , attributable to $\nu_{\text{ip}}\text{C}(4,5)\text{H}$, and a band at 3175 cm^{-1} attributed to $\nu_{\text{op}}\text{C}(4,5)\text{H}$ vibrations. Thus, the C (2)-H bond would establish stronger hydrogen bonds than the other two CH bonds, in agreement with its stronger acidity. In the spectra one can note also a very weak band at 3158 cm^{-1} which can be attributed to =C-H stretching in *ortho* and *meta* positions of the biphenyl cation. The C-H out-of-plane bending vibration bands appear in the range of 1000-750 cm^{-1} for substituted benzenes. In aromatic compounds, the C-H in plane bending appears in the zone of 1300-1000 cm^{-1} . The zone from 700 to 580 cm^{-1} include various vibration modes from CH, NC(H), CCH, CF₃ symmetric bending at 625 cm^{-1} , O=S=O asymmetric bending at 615 cm^{-1} , S-N-S asymmetric bending at 615 cm^{-1} and other atomic groups of the cation and the anions. The spectral zone 340-260 cm^{-1} is dominated by the $[\text{NTf}_2]^-$ anion, which produces 4 bands of very low intensities at 280, 313, 327 and 340 cm^{-1} . Also, the vibration bands of $[\text{NTf}_2]^-$ anion are shown in the spectral range 1360-1100 cm^{-1} , which was originally believed to be exclusively due to symmetric stretching of the anionic CF groups and symmetric stretching of SO₂ groups. The deformation

(scissoring) mode of CH₂ group gives rise to a characteristic band around 1430 cm⁻¹; however the rocking mode is identified in the zone of 300-200 cm⁻¹.

The vibration bands with wavenumbers in the range of 1750–1300 cm⁻¹ represent mainly the C=C, and C=N bond stretching within the imidazole ring and phenyl ring modes. The bands at around 1566 cm⁻¹ and 1430 cm⁻¹, 1335 cm⁻¹ and 1416 cm⁻¹ can be assigned to the C=C and C=N stretching vibrations of the imidazolium cation, respectively. The typical (strong) band for the C=C vibration of the aromatic phenyl ring was located at 1615 cm⁻¹. The stretching C-N vibration of imidazole ring (ν CH₃-N-CN) was observed in the zone of 1430- 1330 cm⁻¹.

Table 1. Observed FT-Raman bands and their assignment of 3 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, γ = out-of-plane; s = symmetric; as = antisymmetric).

[Bis-(PhCH ₂ MIm)]			Vibrational assignment	References
[Cl] ₂	[PF ₆] ₂	[NTf ₂] ₂		
Range: 3500- 2700 cm⁻¹				
3171 (vw)	3175 (vw)		H-C-C-H asymmetric stretch	[16]/[17]/[18]/[19]/[20]
3158 (vw)	3158 (vw)		H-C-C-H asymmetric stretch	[16]/[17]/[18]/[19]/[20]
3130 (vw)	3137 (vw)	3127 (vw)	H-C-C-H asymmetric stretch	[21]/[19]/[22]/[18]/[20]
	3106 (vw)		H-C-C-H asymmetric stretch	[21]/[19]/[18]/[20]
3083 (w)	3083 (vw)	3074 (vw)	C-H stretching	[23]/[24]/[25]
	3056 (vw)		C-H stretching	[23]/[24]/[25]
3048 (w)	3040 (w)	3049 (w)	C-H stretching	[17]/[26]/[23]/[20]
	3000 (sh)	3002 (sh)	(N)CH ₃ asymmetric stretch	[26]/[27]/[18]/[20]
2968 (m)	2971(m)	2969 (m)	(N)CH ₃ asymmetric stretch, ν_{as} (CH ₃)	[27]/[24]/[25]
2890 (vw)	2896 (vw)	2895 (vw)	(N)CH ₂ , (N)CH ₃ symmetric stretch	[16]/[20]
2846 (vw)	2842 (vw)	2835 (vw)	(N)CH ₂ , (N)CH ₃ symmetric stretch	[26]/[28]/[18]
Range: 1700-1000 cm⁻¹				
1616(s)	1616 (s)	1615 (s)	Phenyl ring: ν C=C	[29]/[30]/ [31]/[32]
1579 (vw)	1580 (vw)		Phenyl ring: ν C=C	[29]/[30]/ [31]/[32]
1569 (vw)	1563 (vw)	1566 (vw)	Phenyl ring ν C=C,(N)CH ₂ str	[34]/[21]/[29]/[30]/ [31]/[32]
1536 (m)	1532 (w)	1532(w)	Phenyl ring: ν C=C , Im ring ν (N=C)	[34]/[21]
1457 (w)	1448 (w)	1455(w)	Phenyl ring ν C=C,(N)CH ₃ str, C-H deformation	[29]/[30]/ [31]/[32]
1433 (w)		1431 (sh)	Im ring:C-N/C=N stretching band, δ (CH ₂)	[37]/ [29]/[27]/ [39]
1416 (w)	1418 (w)	1416(w)	Imidazole ring:C-N/C=N stretching band, (N)CH ₂ str ,C-H deformation	[38]/ [33]/[32]
1387 (w)	1391 (vw)	1390 (vw)	Imidazole ring:C-N/C=N stretch band	[28]/[38]/[33]/[24]
1362 (vw)		1355 (vw)	Trans [NTf ₂]: ν_{as} (SO ₂), (N)CH ₂ str	[37]/[28]/ [27]/[36]
1339 (vw)	1339 (vw)	1335 (vw)	Imidazole ring :C-N/ C=N stretching band,	[29]/[30]/ [31]/[32]/[36]
1290 (s)	1289 (s)	1288 (s)	Phenyl ring: C-C stretching	[32]/[27]/[18]
	1231 (vw)	1242 (w)	Phenyl ring: C-C stretching/ Trans [NTf ₂]: ν_s (CF ₃)	[29]/[30]/ [31]/[32]/[36]/[40]
1202 (m)	1204 (m)		Phenyl ring: C-C stretching	[33]/[42]
	1195 (w)	1197(w)	Phenyl ring: C-C stretching, C- C-H _{ip} bend, C- C- H _{ip} bend	[32]/[45]/[18]
1175 (vw)	1169(vw)		δ CH, CH ₃ N	[38]/ [32]/[18]
		1135 (w)	Trans [NTf ₂]: $\nu_{s,ip}$ (SO ₂)	[36]/ [37]/ [19]
1121 (vw)	1114(vw)	1106 (vw)	δ CH, ring HCCH sym bend	[38]/[31]
1031(w)			δ CC, CH ₃ (N) str	[27]/[35]
	1021(w)	1022 (w)	δ CC, δ CH,	[33]/ [27]/[35]
Range: 1000- 45 cm⁻¹				
	973 (vw)	973 (vw)	(N)CH ₂	[42]/[33]/[37]

934 (vw)	942 (vw)		(N)CH ₂	[42]/[33]
880(sh)	878(sh)		ρ (CH ₂), NC(H)N bend/CCH bend	[21]/[27]
	856 (sh)	864 (sh)	NC(H)N bend, FPF asym str	[16]/[17]/[38]/[20]/[36]
832 (m)	826(m)	835 (m)	FPF asym str/ring HCCH asym bend	[21]/[24]
813 (vw)		797 (sh)	ν_s (CS), ν_s CC	[36]/[24]
788(w)	782 (vw)		ν_s CC, HCCH sym bend	[21]/[22]/[24]
767 (m)	740 (m) / 751 (s)	766 (sh)	ν_s (SNS), (N) CH ₂ str, NCH ₃ , δ CC, C=C-H, ring HCCH asym bend, ν (PF ₆)	[28]/[17]/[38]/[20]
726 (vw)	725 (vw)	742 (s)	ν (PF ₆), Trans-[NTf ₂]: δ_s (CF ₃),	[36]/[16]/[17]/[38]/[20]
693 (vw)	693 (vw)	693 (vw)	C=C-H, H-C-C-H	[30]
657(vw)	651 (vw)	651 (w)	δ CC, C=C-H, CH ₂ (N)/CH ₃ (N)CN Str	[29]/[30]/ [31]/[32]/ [27]
634 (w)	633 (w)	634 (w)	δ CC, (N-C), (N)CH ₂ str, ν N-CH ₃	[29]/[35]
614 (w)	616 (w)	615 (w)	δ CC, NCH ₃ Trans-[NTf ₂]: δ SNS, δ_{op} as(SO ₂), Phenyl ring ν C=C.	[16]/[17]/[38]/[20]/[36]
		590 (vw)	Trans-[NTf ₂]: δ_{as} (CF ₃), δ_{as} (CF ₃), δ ip as(SO ₂), δ_s (NSO ₂)	[36] / [37]/[16]/[17]/[38]/ [20]
	570 (w)	571 (w)	ν (PF ₆), Trans-[NTf ₂]: δ_{as} (CF ₃), δ ip as(SO ₂), δ_s (NSO ₂)	[36] / [37]/[16]/[17]/ [20]
550 (vw)	552(vw)	553(w)	CH ₂ (N)/CH ₃ (N)CN Str, Trans-[NTf ₂]: δ_s (SO ₂)	[36] / [37]/[16]/[17]/[20]
522(vw)		513(vw)	Trans-[NTf ₂]: δ_{as} (CF ₃), SO ₂ sym bending	[16]/[36]
440 (vw)	470 (w)		(N)CH ₂ str, ν (PF ₆)	[36]/ [21]/[19]/[35]
423(vw)	416 (w)	408 (vw)	(N)CH ₂ str, NCH ₃ , Trans-[NTf ₂]: ω (SO ₂)	[16]/[17]/[38]/ [20]/[36]
387 (vw)	386 (vw)		ρ (CH ₂), (N) CH ₂ str	[16]/[17]/[38]/ [20]/[36]
	360 (vw)		δ NCH ₃ , CC	[16]/[17]
342(vw)	353(vw)	340 (m)	δ NCH ₃ , Trans-[NTf ₂]: τ (SO ₂), CC	[16]/[17]/[38]/ [20]/[36]
	329 (vw)	327(w)	CC,(N)CH ₂ str, ρ (SO ₂)	[35]/[43]/ [23]/[36]
		313(w)	CN stretch, CC str, Trans-[NTf ₂]: ρ (SO ₂), ρ (CF ₃)	[16]/[17]/[38]/ [20]/[36]
290 (vw)	290 (vw)	280 (w)	ρ (CH ₂), CN stretch, Trans-[NTf ₂]: ρ CF ₃ , ν_{as} (CS)	[16]/ [17]/[38]/[19] [20]/[36]
261 (vw)	257 (vw)		ρ (CH ₂), τ N-CH ₃ ,	[33]/[34]/[19]/ [22]
215 (vw)	225(vw)	211(vw)	τ (N-C)/ ρ (CH ₂), NCH ₃	[33]/[34]/[19]/ [22]
190 (vw)	200 (vw)	170(vw)	Intermolecular vibration, ω (N-C), τ (N-C)/ ρ (CH ₂)	[34]/[19]/ [22]/[41]
72 (s)	68 (s)	62(s)	Intermolecular vibration	[41]
[C] ₂	[PF₆]₂	[NTf₂]₂	Vibrational assignment	References

5.2.2 FT-IR spectroscopy characterization

Frequently, we are confronted with the anionic vibrations of polyatomic anions such as SCN⁻, BF₄⁻, PF₆⁻ or NTf₂⁻ in vibrational spectroscopic investigations of ILs. Their vibrational assignment is mostly documented in the literature [18, 33-40].

There is a clear similarity between FT-Raman and FT-IR spectra, with small discrepancies in shift wavenumbers. We observe in Fig.3B, a characteristic band around 1415 cm⁻¹, which will be attributed to the scissoring mode of CH₂ group [48]. Also, a strong and sharp intense bands observed at 812 cm⁻¹ ascribed to the stretching modes of vibrations ν PF₆ [19].

The stretching modes of the phenyl group were observed between 1650 and 1200 cm⁻¹. The peaks were located around 1612, 1579 and 1552 cm⁻¹ (band typical for the C=C vibration), respectively, and are attributed to the stretching of C-C phenyl, while the aromatic C-C deformation in plane was observed at 1005 cm⁻¹ (Ring stretching). It should be noted that strong band of C-C conjugated with benzenic cycle was

shown at 1662 cm^{-1} . The C-N stretching band of imidazole ring ($\nu\text{CH}_3\text{-N-CN}$) was found to be present at 1346 cm^{-1} (with medium intensity).

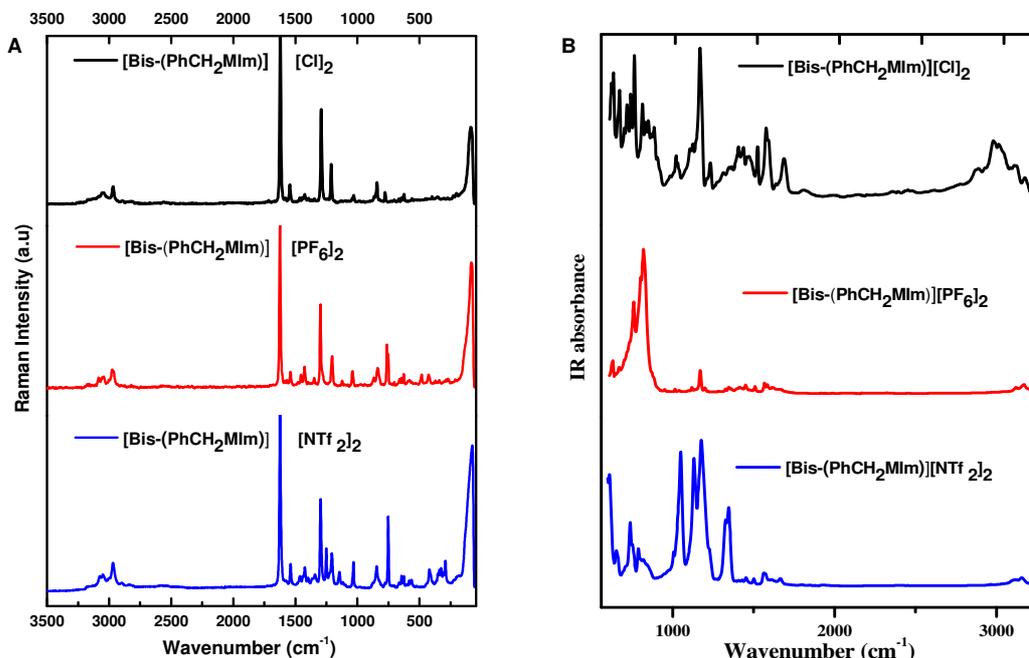


Figure 3. Experimental IR / Raman vibrational spectra of investigated DILs.

Table 2. Observed FTIR/ATR bands and their assignment of the DILs: (vw = very weak; w = weak; m = medium, s = strong; sh = shoulder; v = Str = stretch; δ = deformation; bend = bending deformation; ω = wagging; ρ = rocking; τ = out-of-plane; s = symmetric; as = antisymmetric).

[Bis-(PhCH ₂ MIm)]			Vibrational assignment	References
[Cl] ₂	[PF ₆] ₂	[NTf ₂] ₂		
Range: 3300-2300 cm⁻¹				
	3170(w)	3155(w)	H-C-C-H symmetric stretch	[38]/ [16]/[17]/ [20]/ [19]/ [43]/[22]/[18]
3126(w)	3122(vw)	3116(vw)	H-C-C-H asymmetric stretch	[38]/ [16]/[17]/ [20]/ [19]/ [43]/[22]/[18]
3074(w)			ν (C-H) / ν (CH)	[19]/[18]/[40]
	3041(sh)	3040(sh)	ν (C-H)	[34]/[22]/[18]/[40]
2968(sh)	2976(vw)	2966(vw)	(N)CH ₃ asymmetric stretch, CH ₂ HCH asym Str	[43]/ [22]/ [18]/ [40]
2854(vw)	2858(vw)	2855(vw)	(N)CH ₂ , (N)CH ₃ symmetric stretch	[16] / [19]/[22]/[40]
Range : 1700- 900cm⁻¹				
1662(m)	1654(sh)	1664(w)	Im ring : C=C str, N =C-N str ,C-C cong	[43]
1612(sh)	1612(vw)	1612(w)	Phenyl ring : ν C=C	[34] / [37]/[38]/[16]/[17]/[20]
1569(sh)	1579(w)	1573(w)	Phenyl ring :C=C stretching, (N)CH ₂ str	[34] / [37]/[38]/[16]/[17]/[20]
1552(m)	1562(w)	1564(w)	Phenyl ring : ν C=C, Imidazole ring ν (N=C)	[34] / [37]/[38]/[16]/[17]/[20]
1500(m)	1503(vw)	1502(w)	Imidazole ring ip asym str, (N)CH ₃ HCH sym bend	[33]/[42]/[18]/[40]
1446(m)	1445(w)	1454(w)	δ (CH ₂)/CCH HCH as bend	[16] / [19]/[22]/[40]
	1421(vw)	1429(vw)	Imidazole ring :C-N/ C=N stretching band, δ_s (CH ₂), C-H deformation	[34] / [37]/[38]/[16]/[17]/[20]/[42]
1415(m)	1407(vw)	1407(vw)	ρ (N-CH), Imidazole ring :C-N / C=N stretching band, (N)CH ₂ str, δ (CH ₂), C-H deformation	[34]/ [19]/[27]/[48]

1384(m)	1388(vw)	1388(vw)	$\rho(\text{CH}_2)$, $\rho(\text{CH})/\delta(\text{CH}_2)$ [op], $\omega(\text{CH})$, $\omega(\text{NCH}_3)$	[34] / [22]/[27]
1346(vw)	1341(vw)	1346(m)	Imidazole ring :C–N/ C=N stretching band, Trans-[NTf ₂]: vas(SO ₂), (N)CH ₂ str, ν CC	[34] / [37]/[28]/[16]/[17]/[38]/[20]
1328(vw)	1320(w)	1328(m)	Imidazole ring :C–N/ C=N stretching, SO ₂ asym str	[34] / [37]/[16]/[17]/[38]/[20]
1292(vw)	1280(vw)		Phenyl ring: C–C stretching	[34] / [16]/[17]/[38]/[20]/[42]
1213(w)		1224(sh)	ν CN, CF ₃ sym Str	[34]
1191(vw)	1191(vw)		Ring str CH ₂ (N) and CH ₃ (N)CN Str	[16]/[19]
		1177(s)	Ring asym Str CH ₂ (N) and CH ₃ (N)CN Str/CC Str	[16] / [33]/[19]
1151(s)	1163(m)		δ CH, (N)-CH ₂ -, (N)-CH ₃	[16]/[42]
		1132(s)	Trans-[NTf ₂]: vs(SO ₂)	[36]/ [37]/ [19]
1107(vw)	1112(vw)		δ CH, ring HCCH sym bend, CC str	[33]/[19]/[47]
1089(w)	1089(vw)	1051(s)	Ring ip asym str, CC str, NCH ₃ twist, SNS asym str	[34]/ [28]/[29]/[30]/[31]/[32]/[46]
1015 (sh)	1033(vw)		ring ip sym str, ν C-C, CH ₃ N Str/ CH ₂ N Str	[34]/ [16]/ [29] / [30]/[31] / [32]/[19]
1005 (w)	1006 (vw)	1006 (sh)	ν CC, ring ip asym bend	[37]/[33]
968(vw)	943(vw)	948(vw)	CC str, ring ip asym bend	[37]/[33]
Range : 900- 600 cm⁻¹				
871(w)	877(sh)	871(vw)	NC(H) N bend, ρ as(CH ₂)	[37]/[20]/[27]
852(vw)	862(sh)	844(vw)	NC(H) N bend /CCH bend / NC2(H)N CH bend	[37]/[28]/[19]
817(w)	812(s)	817(w)	vas (PF ₆), Ring CC bend	[27]/[19]
800(m)	795(sh)	788 (w)	ring HCCH asym bend / CS St	[37]/ [21]/[26]
	769 (sh)	761 (sh)	δ (HCCH)/ ring HCCH asym bend, vs SNS	[28]/[21]/[19]
729/752(s)	750(s)	752(sh)	Trans-[NTf ₂]: δ s (CF ₃), ring HCCH sym bend, CF ₃ sym bend, ν (PF ₆),	[21]/ [28]/ [19]/[31]
705(m)	709(sh)	738(m)	Anion interaction, CH ₂ (N) and CH ₃ (N)CN str, CF ₃ sym bend	[21]/[28]/ [21]/[19]/[31]
690(w)	694(sh)	692 (vw)	Ring ip asym bend, CH ₂ (N) str, CH ₃ (N) CN str	[32]/[21]
661(s)	660(w)	663(sh)	ω (C-H), δ CC, C=C-H, Ring HCCH sym bend	[34]/ [29] / [30]/[31] / [32]/[19]/[27]
651 (sh)	646(vw)	653(w)	CH ₂ (N) str, CH ₃ (N) CN str/ ν N–CH ₃ , δ SNS	[34] / [21]/[28]/[16]/[17]/[38]/[20]
613/624(s)	621 (m)	610 (s)	CH ₃ (N) str, CH ₂ (N) str, Trans-[NTf ₂]: δ SNS ; Phenyl ring ν C=C, ν (PF ₆)	[34] / [21]/[28]/[16]/[17]/[38]/[20]

5.3. Computational Results

Table 3 reports the values of the four dihedral angles of the five 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 N3,C14,C5,C6 and C12,C8,C13,N1 define the relative orientation of the two imidazolium rings, while the two dihedrals C24,N3,C14,C5 and C8,C13,N1,C16 describe the rotation of the imidazolium rings around their 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 3. The label, the difference in relative energy with respect to the lowest energy one and the dihedral angles of the five lowest energy cation conformers.

Label	Relative Energy (kJ/mol)	Dihedral (C24,N3, C14,C5)	Dihedral (N3,C14, C5,C6)	Dihedral (C1,C2, C7,C9)	Dihedral (C12,C8, C13,N1)	Dihedral (C8,C13, N1,C16)
A	0.00	43.62	-105.70	38.28	-111.88	45.35
B	0.09	44.51	-108.53	37.64	-76.68	-40.06
C	0.27	46.17	70.34	36.08	76.69	43.02
D	0.35	42.41	75.74	37.60	107.53	-42.61
E	0.85	42.58	-106.17	36.50	-85.58	166.75

Figure 4 reports the comparison of the calculated Raman spectra and of the spectra measured for bis-phenyl-PF₆. This particular DIL was chosen for the comparison with the computational results because only few lines are due to the anion and the sample is not as hydroscopic as the one containing Cl⁻. The lines attributable to the PF₆ anions are those centered around 470, 570, 751 and 856 cm⁻¹, that are marked by magenta asterisks in the figure. Apart for these lines all other bands can be attributed to vibrations of the cation. Indeed, after a scaling of the frequencies of 0.98 for the calculated Raman spectrum, one obtains a straightforward correspondence between the calculated and experimental bands. However, it seems not possible to discriminate between the different conformers of the cation, due to the practical superposition of their computed spectra. By the way, it must be noted that the strict resemblance of the calculated and experimental spectra further suggest that the synthesized cation possess the desired structure.

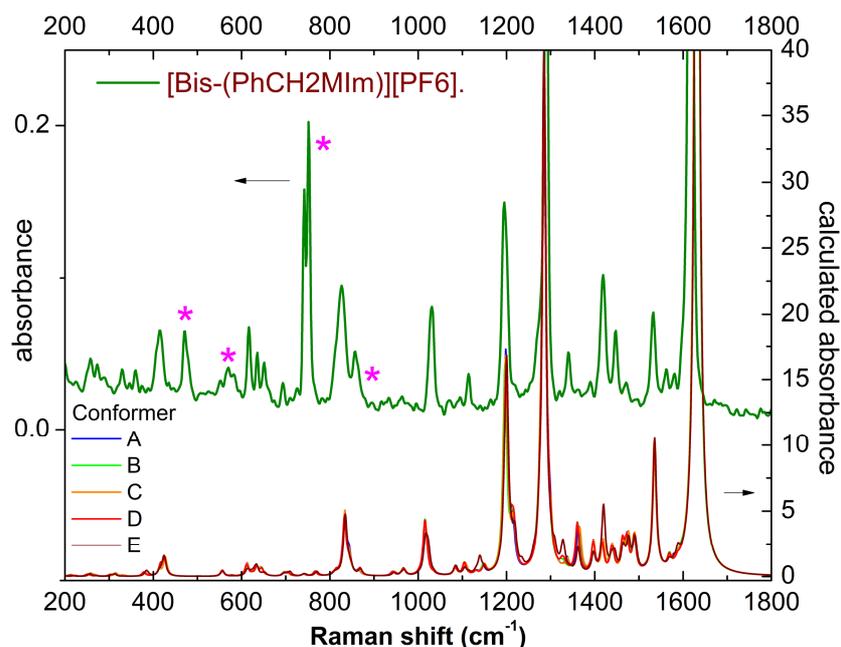


Figure 4. Comparison of the calculated Raman spectra and the spectra measured for [Bis-(PhCH₂MIm)][PF₆].

6 THERMAL ANALYSIS

6.1. Thermal Stability

A large number of dicationic ILs evoke melting points higher than 100°C [49]. The higher thermal stability in the dicationic ILs than the monocationic ILs would be related to the higher liquid density in the dicationic ILs than the monocationic ones. It has been supposed that the decomposition temperature of the ionic liquids depends on the structure and molecular weight of cations and anions [50]. TGA and DTA analysis was accomplished to study the thermal behavior of these DILs; the change in weight of DILs by increasing the temperature at a constant heating rate of 5 °C min⁻¹ like depicted in Fig. 5.

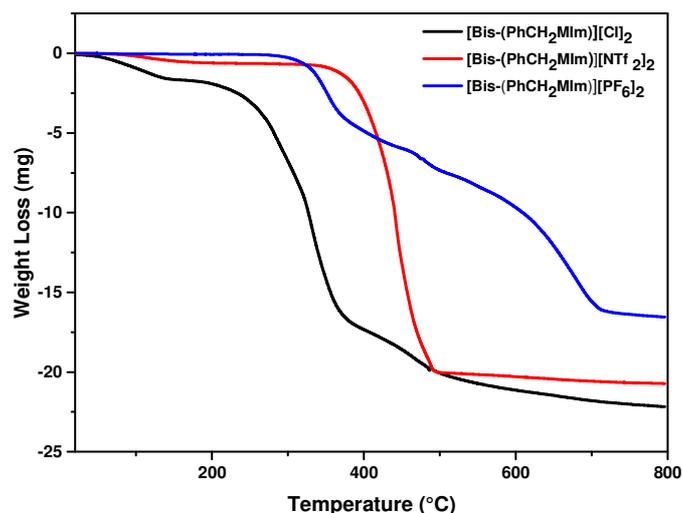


Figure 5. TGA thermographs for synthesized dicationic ionic liquids

The TGA curve recorded for the di-(hexafluorophosphate) DIL in Fig.5 shows two mass losses at 323, 479 °C and one broad loss at 604 °C. The first mass loss may correspond to the volatilization of residual water or organic solvent that was used during the separation process. The second stage can be associated to the thermal decomposition of anion $[PF_6]^-$ in the temperature range of 420–600 °C and the third process can be the rupture of the $[(Bis-(PhCH_2Mlm))^+]$ cation in the temperature range 620–720 °C.

At first sight, the thermal gravimetric analysis results indicated that the DIL containing the halide anion decomposed rapidly (abrupt decrease) and loses the majority of its mass in a broad range of temperature [220-450°C], differently from both perfluorinated DILs: a strong mass loss onset (5.5 mg, \approx 25% Wt) is seen below 420 °C, while the DIL containing the $[NTf_2]^-$ anion loses its total mass gradually above 400 °C. The dicationic ionic liquid containing $[PF_6]^-$ anion loses 3% of its mass at 323°C, however the other DIL containing $[NTf_2]^-$ anion loses only 3% of its weight at 350°C. But the first DIL retains 2/3 of its mass at 500°C when the other loses almost the totality of its weight above 500°C. We can deduce that the type of the anion play an important role in these degradation reactions and the thermal stability was observed to increase in the following order: $[Cl]^- < [PF_6]^- < [NTf_2]^-$. The observed high thermal stability in this DIL is ascribed to strong van der Waals and non-covalent interactions.

6.2. Melting point

The melting points of the halide and fluorinated DILs synthesized in this study are collected in Table 4. Previous investigations report that the melting point of dicationic ILs was affected by the nature of the anions and increased following the order: $[\text{Cl}]^- > [\text{PF}_6]^- > [\text{NTf}_2]^-$, moreover the lower melting point of the $[\text{NTf}_2]^-$ anion is related to its inability to Hydrogen-bonding owing to its bulky structure (steric effect) and also to its better charge delocalization (S-N-S) and aromaticity (additional electron mobility).

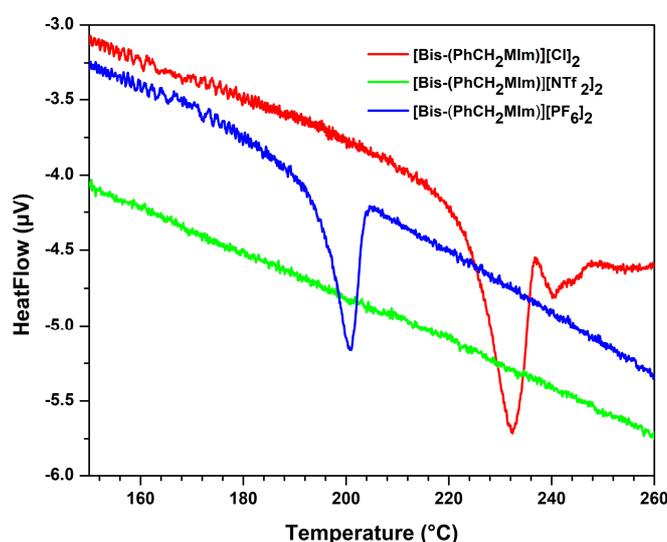


Figure 6. DTA thermographs for synthesized dicationic ionic liquids

In literature [51,52], it is found that in general when the anions are $[\text{BF}_4]^-$, $[\text{PF}_6]^-$ and $[\text{NTf}_2]^-$, the melting points and heat of fusion are lower than in the case of a halogenated anion.

Table 4. Melting points and thermal stability of analyzed dicationic ionic liquids.

T_m : Melting point; T_d : Decomposition temperature.

Structure of DIL	Physical state at 25 °C	T_m (°C)	T_d (°C)
$[(\text{Bis-Ph CH}_2\text{MIm})][\text{Cl}]_2$	Solid	232	252
$[(\text{Bis-Ph CH}_2\text{MIm})][\text{PF}_6]_2$	Solid	200	323
$[(\text{Bis-Ph CH}_2\text{MIm})][\text{NTf}_2]_2$	Liquid	--	420

From a structural point of view, when the anion volume increases the interaction between the anions and the cations decreases [53]. In the present case the melting point of the DIL with the $[\text{Cl}]^-$ anion is higher than in the case of the $[\text{PF}_6]^-$ anion and $[\text{NTf}_2]^-$.

CONCLUSION

In this paper, three bis-1-methylimidazolium-based DILs linked to biphenyl, paired with two inorganic anions, namely di-hexafluorophosphate and dichloride, and an organic anion, namely di-bis (trifluoromethylsulfonyl) imide, have been synthesized. ^1H , ^{13}C , ^{19}F and ^{31}P -NMR spectroscopies confirm the good purity of our targeted DILs. TGA / DTA thermal measurements with the common dication indicate that the thermal stability of the DILs follows the following order: $\text{NTf}_2 > \text{PF}_6 > \text{Cl}$. The samples melting points are in the order $\text{NTf}_2 < \text{PF}_6 < \text{Cl}$. In addition, the vibrational behavior of these DILs was studied using FTIR and FT-RAMAN spectroscopies and a complete attribution of the observed experimental bands is reported. The theory of quantum chemistry (at the DFT level) was used to calculate the possible conformers of the bis-phenyl cation. Due to the complex structure of the cation, there are five conformers with an energy difference of less than 1 kJ / mole. The comparison of the experimental and calculated Raman spectra for these conformers further corroborated the proper synthesis of the desired cation.

ACKNOWLEDGEMENTS

Prof: HB gratefully acknowledge the financial support by The Ministry of Higher Education and Scientific Research (MESRS) of Algeria in PRFU project code: B00L01UN200120180002.

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