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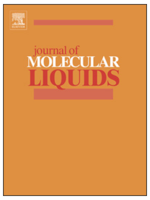

Phenyl/alkyl-substituted-3,5-dimethylpyrazolium ionic liquids

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ABSTRACT

The synthesis and characterization of a series of new phenyl/alkyl-substituted-3,5-dimethylpyrazolium ionic liquids ($[\text{Phpz}^R][X]$ $R = C_nH_{2n+1}$ n: 1,2,3,4,5,6,7 [X] = $CH_3SO_3^-$, BF_4^-, PF_6^-) are described. Their melting points, thermal stabilities, electrochemical windows, and solubility properties in common solvents were investigated. They were found to exhibit very good electrochemical and thermal stabilities. The results indicate that these ionic liquids have a high thermal stability up to 374 °C and a large electrochemical window of 4.63 V. The thermophysical properties such as density, viscosity and refractive index were also measured as a function of temperature for the ionic liquids which are in liquid state at room temperature.

1. Introduction

Ionic liquids (ILs) composed of cations and anions have a unique combination of properties such as low vapor pressure, non-flammability and high thermal stability as well as a wide liquid range and wide electrochemical window [1–5]. Furthermore, the physical and chemical properties of ILs can be adjusted or tuned by controlling the nature of cations and anions [6–9]. Numerous ILs based on imidazolium, pyridinium, and quarternary ammonium cations with a variety of anions such as PF_6^-, BF_4^-, $(CF_3SO_3)_2N^-$, and $CF_3SO_3^-$ have been successively synthesized and are widely utilized in organic synthesis, catalysis, and the preparation of nanostructured materials [10–15].

Researches involving pyrazolium-based ILs are quite rare in contrast with imidazolium-based ILs. This is probably due to the lower nucleophilicity of the imine nitrogen atoms of pyrazoles compared to those of imidazoles. From a structural viewpoint, the presence of two directly bounded nitrogen atoms could not be neglected being able to modify charge distribution and probably some of the physicochemical properties of the resulting salts.

Some 1,2-dialkylpyrazolium ILs have been investigated as electrolytes [16–19], catalysts for organic synthesis [20] and antibacterial cationic surfactants [21]. These salts, though structurally analogous to imidazolium-based ILs, are generally characterized by a relatively low viscosity and a high conductivity with relevant electrochemical properties [22]. Recently, ionic liquid crystals based on pyrazolium salts have been described [23].

Currently, attempts have been focused on the design and synthesis of ionic liquids based on aryl/alkyl-substituted ILs which constitute a new generation of ionic liquids termed TAAILs (Tunable Aryl Alkyl Ionic Liquids). This new concept has been applied for the synthesis of imidazole and 1,2,4-triazole-based tunable aryl/alkyl ILs with different chain lengths [24,25].

In this context, we decided to extend this new concept to aryl/alkyl-substituted-3,5-dimethylpyrazolium salts. We kept the aryl part constant (phenyl) and studied the influence of different alkyl chains (C_1–C_7) and anions ($CH_3SO_3^-$, BF_4^-, and PF_6^-) on the properties of the pyrazolium salts.

2. Results and discussion

2.1. Synthesis and characterization

As shown in Fig. 1, the synthesis of phenyl/alkyl-substituted-3,5-dimethylpyrazolium ILs starts with the preparation of 3,5-dimethyl-1-phenyl-1H-pyrazole (1). Compound 1 was synthesized by an improved procedure from phenylhydrazinium hydrochloride and acetylacetone under MW irradiation since using conventional heating methods [26] is time consuming. Subsequent quarternization by alkyl methanesulfonates of different alkyl chain lengths in acetonitrile at 80 °C under MW irradiation for a period of 30 to 120 min led to phenyl/alkyl-substituted-3,5-dimethylpyrazolium methanesulfonates (2a–2g). The yields of the methanesulfonate alkylation reactions were typically 75–91%. One advantage of the methanesulfonate ionic liquids is that the methanesulfonate anion is base stable, and very easy to exchange for other anions. Thus, the BF_4^- and PF_6^- salts (compounds 3a–3g and 4a–4g) were simply

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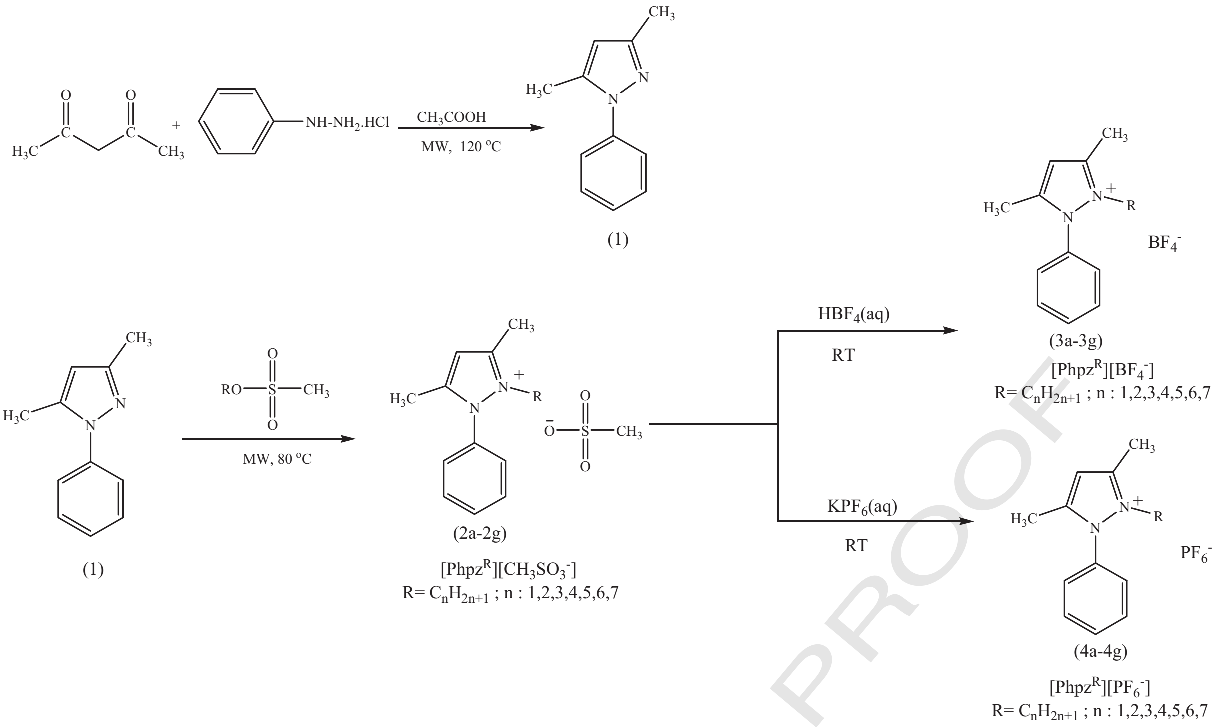

Fig. 1. Synthesis of the ionic liquids described in this work.

prepared by anion exchange reactions of corresponding methanesulfonate salts (2a–2g) with HBF_4 and KPF_6 in aqueous solution at room temperature with yields of 75–88% and 80–90%, respectively.

All of the pyrazolium salts were characterized by IR, ^{1}H NMR, ^{13}C NMR, TOF MS and elemental analysis. In addition, ^{19}F NMR spectra were recorded for the salts 3a–3g and 4a–4g. All the characterization data were consistent with the expected structures and compositions. The IR spectra of all the pyrazolium salts show the characteristic bands of the pyrazolium moiety as well as those of the corresponding counterions, where appropriate. In particular, the ν(C═N) and ν(C═C) absorption bands from the pyrazolium cation appear at ca. 1595–1560 cm^{-1}. In addition, characteristic bands of the BF_4^-, PF_6^- and $CH_3SO_3^-$ salts were observed at ca. 1030, 825 and 1198 cm^{-1}, respectively.

2.2. Thermal properties

The thermal behavior of the phenyl/alkyl-substituted-3,5-dimethylpyrazolium salts was investigated with differential scanning calorimetry (DSC) (Table 1). Some of the pyrazolium salts (2b, 3a, 3b, 4a and 4c) have melting points above 100 °C and do not fulfill the IL criteria. Generally, increasing the alkyl chain length causing less efficient packing in the solid resulted in a lower melting point and starting with a chain length of more than three carbon atoms, all pyrazolium salts fulfill the IL criteria. It is also noteworthy that the melting points of phenyl/alkyl-substituted-3,5-dimethylpyrazolium salts are lower in comparison with dialkylpyrazolium salts having the same counterion [27].

Two effects were taken into account to discuss thermal behaviour of the compounds; the effect of the alkyl chain length and the effect of the counterion. When studying the alkyl chain length, some features have been determined. It is noticeable that most of the methanesulfonate salts are in liquid state at room temperature and increasing the substituent length initially increases the melting point with a major trend towards glass formation. As seen in Fig. 2, the BF_4^- salts show almost a linear dependency of the melting point on the alkyl chain length from one to four carbon atoms. Initial lengthening of the substitution leads to reduction of melting points through destabilization of coulombic

Table 1
Thermal properties of the phenyl/alkyl-substituted-3,5-dimethylpyrazolium ILs.

Entry	Salts	T_m[a] (°C)	T_g[b] (°C)	T_d[c] (°C)	Entry	Salts	T_m[a] (°C)	T_g[b] (°C)	T_d[c] (°C)
1	2a	–	−53.3	282.1	12	3e	–	−47.4	344.4
2	2b	122.5	–	274.9	13	3f	–	−46.6	342.7
3	2c	92.5	–	274.7	14	3g	56.3	–	343.2
4	2d	–	−45.7	291.0	15	4a	125.1	–	373.9
5	2e	–	−54.7	272.2	16	4b	95.1	–	371.2
6	2f	–	−56.4	274.9	17	4c	102.2	–	320.9
7	2g	–	−49.0	260.2	18	4d	60.8	–	347.3
8	3a	145.2	–	361.0	19	4e	61.5	–	353.5
9	3b	113.0	–	366.7	20	4f	38.9	–	356.5
10	3c	80.0	–	345.5	21	4g	43.0	–	341.1
11	3d	67.6	–	348.4					

[a] T_m — melting point.
[b] T_g — glass transition temperature.
[c] T_d — decomposition temperature.

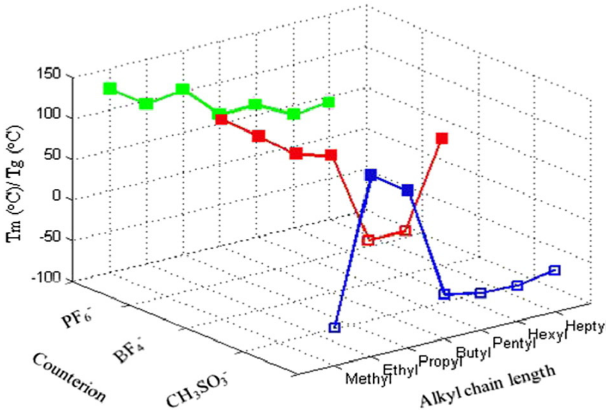

Fig. 2. Dependence of the melting points (closed square) or glass transitions (open square) of phenyl/alkyl-substituted-3,5-dimethylpyrazolium salts on the alkyl chain length with the counterions; BF_4^-, PF_6^- and $CH_3SO_3^-$.

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packing. Further increase in the chain length leads to glass formation for 3e and 3f. This trend was also observed for the series of tetrafluoroborate imidazolium salts [28]. No such trends in Tm values are observed for the PF_6^- salts 4a–4f. The behavior in the variation of the Tm from 4a to 4c and from 4d to 4f values shows similarity to that of aryl/alkyl-substituted imidazolium hexafluorophosphates [24]. Considering the effect of the counterion on the transition temperatures we found that the size seems to modulate the melting temperatures of the salts. Ionic liquids containing the smallest tetrafluoroborate anion displayed high melting transitions. In the case of hexafluorophosphate salts the melting points are lower than those of tetrafluoroborate salts for a given cation. These observations follow the general empirically observed trends for alkylimidazolium salts that the melting temperatures are in the order $[PF_6]^- < [BF_4]^-$. Thermal behavior of the ILs does not follow the same pattern with those of alkyloxyphenyl substituted pyrazolium salts whereas the melting temperatures were found to be in the order $[BF_4]^- < [SbF_6]^-$ for a given cation [23].

Thermal stability of the pyrazolium salts was measured by thermogravimetry analysis (TGA). The thermal decomposition temperatures are presented in Table 1. All the phenyl/alkyl-substituted-3,5-dimethylpyrazolium salts have thermal stability in the range of 260–374 °C. The onset of thermal decomposition temperatures was found to be nearly independent of alkyl chain length. With regard to the anion effect, Table 1 indicates that the thermal stability of PF_6^- containing salts does not significantly differ from that of BF_4^- containing salts. The methanesulfonate anion dramatically reduces the thermal stability, with the onset of decomposition occurring at least 50 °C below the corresponding ILs with BF_4^- and PF_6^- counterions. Relative anion stabilities have been suggested as $PF_6^-, BF_4^- \gg CH_3SO_3^-$.

2.3. Electrochemical stability

The electrochemical stability of the pyrazolium salts was evaluated by cyclic voltammetry (CV) at 50 mV/s sweep rate, starting from anodic to cathodic potentials and reversing back to the initial value. For the ILs based on the same anion, the difference in electrochemical stability is not so great. Most likely the length of the alkyl chain does not influence the stability of the cation. The pyrazolium salts with PF_6^- and BF_4^- anions possess higher electrochemical stability than those with $CH_3SO_3^-$ anion and follow the order of stability $PF_6^- > BF_4^- > CH_3SO_3^-$ by comparing them to the salts having the same cation (Table 2). The electrochemical windows (EW) of BF_4^- and PF_6^- salts were higher than 4.0 V, values which were better than some kinds of ILs, such as imidazolium, sulfonium and guanidinium ILs [29–33].

2.4. Thermophysical properties

The densities, viscosities, and refractive indices of the seven dried room temperature ionic liquids (RTILs) 2a, 2d–2g, 3e, and 3f were obtained as a function of temperature from 298 K to 333 K. Because of the difficulty in rigorously drying these RTILs, the values may be somewhat affected by the residual water content. For the five $CH_3SO_3^-$ and two BF_4^- RTILs studied, the experimental densities are presented in Table 3. As expected, the densities are related to the molar masses of the ions and the ILs containing heavy atoms are in general denser as was observed for those composed of methanesulfonate when compared to those with BF_4^-. This is not however valid for cationic counterparts; the density generally decreases with increasing alkyl chain length as was documented for imidazolium based cations [34,35]. Within a series of ionic liquids containing the same anion species, increasing cation mass corresponds to the decreasing ionic liquid density. The densities of the ILs are affected by the identity of the organic cation whereas the density for ILs composed of the same cation is $CH_3SO_3^- \sim BF_4^-$.

A second series of measurements, analogous to those for densities, allowed us to obtain dynamic viscosities of the RTILs. Again it should be kept in mind that these RTILs contain traces of water, and as shown for other ILs, the presence of water can affect the viscosity significantly [36,37]. In the temperature range studied, the viscosity decreases with increasing temperature. As seen in Table 3, viscosity of the RTILs increases with increasing alkyl chain length. This may be attributed to the increase in Van der Waals interactions as the length of alkyl chain increases. No such trend was observed for 1-alkyl-2,3,5-trimethylpyrazolium-based room temperature ionic liquids [17]. It is also seen that the RTILs comprising $CH_3SO_3^-$ anion have higher viscosities compared with those having BF_4^- anion.

The refractive indices of these RTILs were found to decrease with increasing temperature and to depend on the anion following the trend $BF_4^- < CH_3SO_3^-$ (Table 3). For the RTILs with $CH_3SO_3^-$ anion, refractive indices decreased with increasing length of the alkyl chain in the cation while for those with BF_4^- anion increased.

It can be concluded that the density, viscosity and refractive indices of the RTILs were found to depend on temperature and the nature of

Table 2
Cathodic and anodic potentials vs. Ag/Ag^+ for EWs of the pyrazolium salts at a cut-off current density of 1.0 mA/cm^2 using GC macro-electrode as a working electrode at 25 °C.

Entry	Salts	$E_{cathodic}$ (V)	E_{anodic} (V)	EW (V)	Entry	Salts	$E_{cathodic}$ (V)	E_{anodic} (V)	EW (V)
1	2a	−0.71	2.08	2.79	12	3e	−2.19	2.44	4.63
2	2b	−0.63	1.84	2.47	13	3f	−2.03	2.45	4.48
3	2c	−0.61	2.04	2.65	14	3g	−1.97	2.43	4.40
4	2d	−0.60	2.03	2.63	15	4a	−1.65	2.73	4.38
5	2e	−0.62	2.04	2.66	16	4b	−1.71	2.81	4.52
6	2f	−0.65	2.06	2.71	17	4c	−1.74	2.84	4.58
7	2g	−0.61	2.06	2.67	18	4d	−1.70	2.77	4.47
8	3a	−1.82	2.28	4.10	19	4e	−1.73	2.87	4.60
9	3b	−2.04	2.25	4.29	20	4f	−1.71	2.80	4.51
10	3c	−1.92	2.39	4.31	21	4g	−1.63	2.79	4.42
11	3d	−1.81	2.27	4.08					

Table 3
Experimental densities (ρ), dynamic viscosities (η) and refractive indices (n_r) of the RTILs as a function of temperature at atmospheric pressure.[a]

Compound	T (K)	ρ (g/cm^3)	η (mPa·s)	n_r
2a	298	1.2466	–[b]	1.5192
	308	1.2451	1440.71	1.5167
	313	1.2261	844.84	1.5153
	333	1.2111	162.03	1.5100
2d	298	1.1862	–[b]	1.5164
	308	1.1788	–[b]	1.5137
	313	1.1708	886.67	1.5125
	333	1.1559	212.22	1.5065
2e	298	1.1691	–[b]	1.5141
	308	1.1512	–[b]	1.5117
	313	1.1503	1548.22	1.5104
	333	1.1356	285.67	1.5043
2f	298	1.1416	–[b]	1.5119
	308	1.1368	–[b]	1.5092
	313	1.1290	1602.09	1.5075
	333	1.1148	315.00	1.5011
2g	298	1.1238	–[b]	1.5104
	308	1.1225	–[b]	1.5079
	313	1.1170	1666.61	1.5065
	333	1.1035	346.86	1.5008
3e	298	1.1585	–[b]	1.4705
	308	1.1536	1665.73	1.4722
	313	1.1515	1044.10	1.4708
	333	1.1376	226.11	1.4651
3f	298	1.1366	–[b]	1.4772
	308	1.1336	2131.24	1.4740
	313	1.1299	1284.84	1.4728
	333	1.1164	253.82	1.4671

[a] Data were measured on samples which had a water content (wt.%) in the range of 0.2–0.32 according to coulometric Karl-Fischer titration.
[b] Not determined by a viscometer.

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both the cation and the anion. Such trends were also well documented for imidazolium-based ionic liquids [38–40].

2.5. Solubility

All of the pyrazolium salts synthesized were immiscible with nonpolar solvents such as toluene, Et_2O, benzene and hexane and were completely miscible with polar solvents such as acetonitrile, acetone, DMSO and chloroform. However, in water and low carbon alcohols such as methanol and ethanol, all $CH_3SO_3^-$ ionic liquids were miscible while BF_4^- and PF_6^- salts were immiscible.

3. Conclusions

We synthesized and characterized a new series of tunable phenyl/alkyl-substituted-3,5-dimethylpyrazolium salts. The decomposition temperatures were found to be dominated by anion effects and to be nearly independent of the alkyl chain length. The electrochemical stabilities of BF_4^- and PF_6^- salts up to 4.63 V make these salts attractive for electrochemical applications. It may also be expected that substituents at phenyl ring will have a significant effect on the properties of the resulting pyrazolium salts. We therefore plan to study the effect of substituents on the phenyl ring and current research in our laboratory is ongoing.

4. Experimental section

4.1. General methods

Chemicals were supplied by Acros, Fluka, Merck and Aldrich as well as other common suppliers and used without further purification. Microwave-assisted reactions were performed in a professional multimode oven (Microsynth — Milestone). IR spectra were obtained from samples in neat form with an ATR (Attenuated Total Reflectance) accessory. ^1H, ^{13}C, and ^{19}F NMR spectra were recorded on a Bruker-Avance-300 MHz spectrometer, in $CDCl_3$ or DMSO-d_6 at 300, 75 and 282 MHz respectively. Elemental analysis was carried out using a LECO, CHNS-932 elemental analyzer. Mass spectra were recorded on Waters LCT Premier XE (TOF MS). Differential scanning calorimetry experiments were performed using a DSC-60 (Shimadzu), with a ramp temperature of 10 °C min^{-1} under nitrogen atmosphere. The thermal stability of the ionic liquids was investigated on a TA-60WS Thermal Analyzer (Shimadzu) at a heating rate 10 °C min^{-1} with nitrogen as the purge gas.

The water content was determined using a coulometric Karl-Fischer titrator, Cou-Lo Aquamax KF moisture meter.

Density of the RTILs was measured using a Anton Paar DMA-4500 M digital densimeter based on the "oscillating U-tube principle" and thermostated at different temperatures. Two integrated Pt 100 platinum thermometers were provided for good precision in temperature control internally ($T \pm 0.01$ K). The densimeter protocol includes an automatic correction for the viscosity of the sample. The apparatus is precise to within 1.0×10^{-5} g/cm^3, and the uncertainty of the measurements was estimated to be better than $\pm 1.0 \times 10^{-4}$ g/cm^3. Calibration of the densimeter was performed at an atmospheric pressure using doubly distilled and degassed water.

The dynamic viscosity of the RTILs was measured using an Anton Paar Microviscosimeter based on a falling-ball principle. A laser sensor detects the time, t_1, taken by the ball to fall a given distance in a capillary tube of calibrated diameter filled with the mixture.

Refractive index measurements were conducted with a refractometry DR 6300-TF, A. Krüss Optronic GmbH equipped with a temperature control using a He–Ne light source with a wavelength of 633 nm.

Cyclic voltammetry was conducted on a Electrochemical Workstation CHI-660B instrument. 0.1 M solution of the salts was prepared in anhydrous acetonitrile and then the solution was purged with nitrogen for at least 10 min to minimize the effect of water and oxygen on cyclic voltammograms. The experiments were performed at 25 °C, using glassy carbon macro-electrode (surface area: 7.065×10^{-2} cm^2) as a working electrode, Pt as a counter electrode and Ag/AgCl as a reference electrode.

4.2. The synthesis of 3,5-dimethyl-1-phenyl-1H-pyrazole

Phenylhydrazinium hydrochloride (5.0 mmol), acetylacetone (5.0 mmol) and acetic acid (30.0 mL) were added to a round bottom flask fitted with a reflux condenser. The mixture was heated at 120 °C under MW irradiation. The progress of the reaction was monitored by TLC (20% EtOAc–hexane). After completion of the reaction, acetic acid was removed by rotary evaporation. The residue was dissolved in ethyl acetate. The mixture was washed with diluted sodium hydrogen carbonate, water and saturated brine, respectively. The separated organic phase was dried over anhydrous sodium sulfate. After removing of ethyl acetate the remaining liquid product was purified with column chromatography (silica gel: 20% EtOAc–hexane). Yield: 90%, orange liquid. ^1H NMR (300 MHz, DMSO-d_6, ppm): $\delta = 2.18$ (s, 3H, 5-CH_3); 2.28 (s, 3H, 3-CH_3); 6.05 (s, 1H, CH); 7.35–7.48 (m, 5H, Ph). ^{13}C NMR (75 MHz, DMSO-d_6, ppm) $\delta = 12.57$; 13.72; 107.55; 127.47–129.46; 139.48; 140.16 and 148.26.

4.3. General procedure for the synthesis of alkyl methanesulfonates

Methanesulfonate esters of alcohols were synthesized (except methyl methanesulfonate and ethyl methanesulfonate) from methanesulfonyl chloride and corresponding n-alkyl alcohols (n-propyl, n-butyl, n-pentyl, n-hexyl or n-heptyl alcohol) using a previously described procedure [41]. Their ^1H NMR and ^{13}C NMR spectra were recorded.

4.3.1. Propyl methanesulfonate: (colorless liquid)

^1H NMR (300 MHz, DMSO-d_6, ppm): $\delta = 0.92$ (t, 3H, $–OCH_2CH_2\underline{CH_3}$); 1.68 (m, 2H, $–OCH_2\underline{CH_2}CH_3$); 4.15 (t, 2H, $–O\underline{CH_2}CH_2CH_3$); 3.15 (s, 3H, S-$CH_3$).$^{13}C$ NMR (75 MHz, $CDCl_3$, ppm) $\delta = 9.53$; 22.17; 36.48; 71.91.

4.3.2. Butyl methanesulfonate: (colorless liquid)

^1H NMR (300 MHz, $CDCl_3$, ppm): $\delta = 0.96$ (t, 3H, $–OCH_2CH_2CH_2\underline{CH_3}$); 1.46 (m, 2H, $–OCH_2CH_2\underline{CH_2}CH_3$); 1.76 (m, 2H, $–OCH_2\underline{CH_2}CH_2CH_3$); 4.23 (t, 2H, $–O\underline{CH_2}CH_2CH_2CH_3$); δ 3.0 (s, 3H, S-CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) $\delta = 13.08$; 16.34; 30.75; 36.52; 70.12.

4.3.3. Pentyl methanesulfonate: (colorless liquid)

^1H NMR (300 MHz, DMSO-d_6, ppm): $\delta = 0.87$ (t, 3H, $–OCH_2CH_2CH_2CH_2\underline{CH_3}$); 1.33 (m, 4H, $–OCH_2CH_2\underline{CH_2CH_2}CH_3$); 1.70 (m, 2H, $–OCH_2\underline{CH_2}CH_2CH_2CH_3$); 4.19 (t, 2H, $–O\underline{CH_2}CH_2CH_2CH_2CH_3$); 2.95 (s, 3H, S-$CH_3$). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) $\delta = 13.51$; 21.81; 27.23; 28.48; 36.49; 70.37.

4.3.4. Hexyl methanesulfonate: (colorless liquid)

^1H NMR (300 MHz, $CDCl_3$, ppm): $\delta = 0.83$ (t, 3H, $-OCH_2CH_2CH_2CH_2CH_2\underline{CH_3}$); 1.25 (m, 6H, $-OCH_2CH_2\underline{CH_2CH_2CH_2}CH_3$); 1.67 (m, 2H, $-OCH_2\underline{CH_2}CH_2CH_2CH_2CH_3$); 4.14 (t, 2H, $-O\underline{CH_2}CH_2CH_2CH_2CH_2CH_3$); 2.93 (s, 3H, S-$CH_3$). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) $\delta = 13.85$; 22.44; 24.99; 28.99; 31.11; 37.12; 70.34.

4.3.5. Heptyl methanesulfonate: (colorless liquid)

^1H NMR (300 MHz, $CDCl_3$, ppm): $\delta = 0.90$ (t, 3H, $-OCH_2CH_2CH_2CH_2CH_2CH_2\underline{CH_3}$); 1.31 (m, 8H, $-OCH_2CH_2\underline{CH_2CH_2CH_2CH_2}CH_3$); 1.76 (m, 2H, $-OCH_2\underline{CH_2}CH_2CH_2CH_2CH_2CH_3$); 4.23 (t, 2H, $-O\underline{CH_2}CH_2CH_2CH_2CH_2CH_2CH_3$); 3.01 (s, 3H, S-$CH_3$). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) $\delta = 13.82$; 22.36; 25.21; 28.54; 28.96; 31.49; 36.87; 70.33.

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4.4. General procedure for the synthesis of 1-phenyl-2-alkyl-3,5-dimethylpyrazolium methanesulfonates (2a–2g)

3,5-Dimethyl-1-phenyl-1H-pyrazole (5.0 mmol), appropriate alkyl methanesulfonate (5.0 mmol), and acetonitrile (5.0 mL) were added to a round-bottomed flask equipped with a reflux condenser and heated at 80 °C under MW irradiation. The progress of the reaction was monitored by TLC (80% EtOAc–hexane). After completion of the reaction, acetonitrile was removed by rotary evaporation. The resulting product was washed two times with 20.0 mL of hexane and then two times with 20.0 mL of diethylether. After this, active charcoal and 20.0 mL acetonitrile were and stirred for 24 h and then filtered. The filtrate was dried over anhydrous sodium sulfate and concentrated. The synthesized salts were set under vacuum for 48 h at 75 °C.

4.4.1. 1-Phenyl-2,3,5-trimethylpyrazolium methanesulfonate (2a)

Yield: 91%, yellow liquid. IR (ATR, cm^{-1}) ν_{max} = 3055, 2970–2930, 1592, 1564, 1496, 1195, 1036, 100–750. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 2.23 (s, 3H, 5-CH_3); 2.63 (s, 3H, 3-CH_3); 2.73 (s, 3H, S-CH_3); 3.78 (s, 3H, NCH_3); 6.51 (s, 1H, CH); 7.68 (m, 5H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ = 12.34; 12.44; 35.07; 39.34; 108.17; 128.92–132.58; 146.65 and 148.11. Analysis: calcd for $C_{13}H_{18}N_2O_3S$: C 55.30, H 6.43, N 9.92, S 11.36. Found: C 55.16, H 6.44, N 9.90, S 11.49. TOF MS (ES^{+}) m/z calcd. for $C_{12}H_{15}N_2$: 187.1235. Found: 187.1234. TOF MS (ES^{-}) m/z calcd. for CH_3O_3S: 94.9803. Found: 94.9801.

4.4.2. 1-Phenyl-2-ethyl-3,5-dimethylpyrazolium methanesulfonate (2b)

Yield: 89%, yellow solid. IR (ATR, cm^{-1}) ν_{max} = 3048, 2970–2930, 1591, 1558, 1483, 1190, 1037, 100–750. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 1.16 (t, 3H, $–NCH_2\underline{CH_3}$); 4.37 (q, 2H, $–N\underline{CH_2}CH_3$); 2.21 (s, 3H, 5-CH_3); 2.65 (s, 3H, 3-CH_3); 2.70 (s, 3H, S-CH_3); 6.53 (s, 1H, CH); 7.69 (m, 5H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 11.95; 12.16; 14.20; 39.19; 43.08; 108.51; 128.65–132.57; 147.19; 147.22. Analysis: calcd for $C_{14}H_{20}N_2O_3S$: C 56.73, H 6.80, N 9.45, S 10.82. Found: C 56.60, H 6.81, N 9.43, S 10.95. TOF MS (ES^{+}) m/z calcd. for $C_{13}H_{17}N_2$: 201.1392. Found: 201.1389. TOF MS (ES^{-}) m/z calcd. for CH_3O_3S: 94.9803. Found: 94.9799.

4.4.3. 1-Phenyl-3,5-dimethyl-2-propylpyrazolium methanesulfonate (2c)

Yield: 80%, yellow solid. IR (ATR, cm^{-1}) ν_{max} = 3055, 2970–2879, 1592, 1560, 1495, 1206, 1038, 1000–750. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 0.78 (t, 3H, $–NCH_2CH_2\underline{CH_3}$); 1.52 (m, 2H, $–NCH_2\underline{CH_2}CH_3$); 4.2 (t, 2H, $–N\underline{CH_2}CH_2CH_3$); 2.22 (s, 3H, 5-$CH_3$); 2.66 (s, 3H, 3-$CH_3$); 2.72 (s, 3H, S-$CH_3$); 6.55 (s, 1H, CH); 7.69 (m, 5H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 10.66; 12.33; 12.41; 22.32; 39.33; 49.21; 108.57; 128.93–132.49; 147.20; 147.93. Analysis: calcd for $C_{15}H_{22}N_2O_3S$: C 58.04, H 7.14, N 9.02, S 10.33. Found: C 57.91, H 7.15, N 9.0, S 10.47. TOF MS (ES^{+}) m/z calcd. for $C_{14}H_{19}N_2$: 215.1548. Found: 215.1549. TOF MS (ES^{-}) m/z calcd. for CH_3O_3S: 94.9803. Found: 94.9802.

4.4.4. 1-Phenyl-2-butyl-3,5-dimethylpyrazolium methanesulfonate (2d)

Yield: 89%, yellow liquid. IR (ATR, cm^{-1}) ν_{max} = 3055, 2970–2873, 1592, 1560, 1494, 1198, 1036, 100–750. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = δ 0.76 (t, 3H, $-NCH_2CH_2CH_2\underline{CH_3}$); 1.19 (m, 2H, $-NCH_2CH_2\underline{CH_2}CH_3$); 1.48 (m, 2H, $-NCH_2\underline{CH_2}CH_2CH_3$); 4.26 (t, 2H, $-N\underline{CH_2}CH_2CH_2CH_3$); 2.23 (s, 3H, 5-$CH_3$); 2.65 (s, 3H, 3-$CH_3$); 2.80 (s, 3H, S-$CH_3$); 6.56 (s, 1H, CH); 7.70 (m, 5H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 12.13; 12.18; 12.96; 19.09; 30.60; 39.17; 47.35; 108.50; 128.72–132.51; 147.22; 147.53. Analysis: calcd for $C_{16}H_{24}N_2O_3S$: C 59.23, H 7.46, N 8.63, S 9.88. Found: C 59.10, H 7.46, N 8.62, S 9.98. TOF MS (ES^{+}) m/z calcd. for $C_{15}H_{21}N_2$: 229.1705. Found: 229.1703. TOF MS (ES^{-}) m/z calcd. for CH_3O_3S: 94.9803. Found: 94.9805.

4.4.5. 1-Phenyl-3,5-dimethyl-2-pentylpyrazolium methanesulfonate (2e)

Yield: 78%, orange liquid. IR (ATR, cm^{-1}) ν_{max} = 3053, 2927–2857, 1593, 1560, 1495, 1198, 1037, 100–750. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 0.77 (t, 3H, $-NCH_2CH_2CH_2CH_2\underline{CH_3}$); 1.12 (m, 4H, $-NCH_2CH_2\underline{CH_2CH_2}CH_3$); 1.49 (m, 2H, $-NCH_2\underline{CH_2}CH_2CH_2CH_3$); 4.25 (t, 2H, $–N\underline{CH_2}CH_2CH_2CH_2CH_3$); 2.23 (s, 3H, 5-$CH_3$); 2.65 (s, 3H, 3-$CH_3$); 2.79 (s, 3H, S-$CH_3$); 6.55 (s, 1H, CH); 7.70 (m, 5H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 12.40; 12.45; 13.56; 21.68; 28.09; 28.56; 39.33; 47.90; 108.61; 129.02–132.63; 147.22; 147.81. Analysis: calcd for $C_{17}H_{26}N_2O_3S$: C 60.33, H 7.74, N 8.28, S 9.47. Found: C 60.20, H 7.75, N 8.26, S 9.61. TOF MS (ES^{+}) m/z calcd. for $C_{16}H_{23}N_2$: 243.1861. Found: 243.1868. TOF MS (ES^{-}) m/z calcd. for CH_3O_3S: 94.9803. Found: 94.9799.

4.4.6. 1-Phenyl-3,5-dimethyl-2-hexylpyrazolium methanesulfonate (2f)

Yield: 75%, orange liquid. IR (ATR, cm^{-1}) ν_{max} = 3055, 2930–2859, 1593, 1560, 1495, 1197, 1037, 1000–750. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 0.80 (t, 3H, $-NCH_2CH_2CH_2CH_2CH_2\underline{CH_3}$);1.12 (m, 6H, $NCH_2CH_2\underline{CH_2CH_2CH_2}CH_3$); 1.48 (m, 2H, $NCH_2\underline{CH_2}CH_2CH_2CH_2CH_3$); 4.28 (t, 2H, $N\underline{CH_2}CH_2CH_2CH_2CH_2CH_3$); 2.23 (s, 3H, 5-$CH_3$); 2.66 (s, 3H, 3-$CH_3$); 2.77 (s, 3H, S-$CH_3$); 6.54 (s, 1H, CH); 7.70 (m, 5H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 12.43; 12.54; 13.76; 22.15; 25.75; 28.88; 30.72; 39.38; 48.02; 108.51; 129.17–132.55; 146.99; 147.88. Analysis: calcd for $C_{18}H_{28}N_2O_3S$: C 61.33, H 8.01, N 7.95, S 9.10. Found: C 61.21, H 8.01, N 7.93, S 9.24. TOF MS (ES^{+}) m/z calcd. for $C_{17}H_{25}N_2$: 257.2018. Found: 257.2018. TOF MS (ES^{-}) m/z calcd. for CH_3O_3S: 94.9803. Found: 94.9800.

4.4.7. 1-Phenyl-3,5-dimethyl-2-heptylpyrazolium methanesulfonate (2 g)

Yield: 75%, orange liquid. IR (ATR, cm^{-1}) ν_{max} = 3053, 2928–2857, 1593, 1560, 1495, 1198, 1037, 1000–750. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 0.80 (t, 3H, $–NCH_2CH_2CH_2CH_2CH_2CH_2\underline{CH_3}$); 1.11 (m, 8H, $–NCH_2CH_2\underline{CH_2CH_2CH_2CH_2}CH_3$);1.46 (m, 2H, $–NCH_2\underline{CH_2}CH_2CH_2CH_2CH_2CH_3$); 4.23 (t, 2H, $–N\underline{CH_2}CH_2CH_2CH_2CH_2CH_2CH_3$); 2.23 (s, 3H, 5-$CH_3$); 2.65 (s, 3H, 3-$CH_3$); 2.79 (s, 3H, S-$CH_3$); 6.54 (s, 1H, CH); 7.71 (m, 5H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 12.42; 12.50; 13.92; 22.34; 26.02; 28.26; 28.90; 31.25; 39.35; 47.96; 108.57; 129.12–132.58; 147.10; 147.85. Analysis: calcd for $C_{19}H_{31}N_2O_3S$: C 62.09, H 8.50, N 7.62; S 8.72. Found: C 61.97, H 8.51, N 7.61, S 8.84. TOF MS (ES^{+}) m/z calcd. for $C_{18}H_{27}N_2$: 271.2174. Found: 271.2173. TOF MS (ES^{-}) m/z calcd. for CH_3O_3S: 94.9803. Found: 94.9799.

4.5. General procedure for the synthesis of 1-phenyl-2-alkyl-3,5-dimethylpyrazolium tetrafluoroborates (3a–3g)

Tetrafluoroboric acid (40% solution in water, 5.0 mmol) was added dropwise to a solution of the appropriate methanesulfonate salt (5.0 mmol) in water (10.0 appropriate mL) and the mixture was stirred at room temperature for 2 h. The resulting solid salt was collected and recrystallized from ethanol. The resulting liquid salt, which formed two phases, was purified by the decantation of the aqueous layer and washed two times with 20.0 mL of hexane and diethylether, respectively. After this, 20.0 mL of acetonitrile and active charcoal was added and refluxed over 24 h. The solution was filtered and the filtrate was dried over anhydrous sodium sulfate and concentrated. The synthesized salts were set under vacuum at 75 °C for 48 h.

4.5.1. 1-Phenyl-2,3,5-trimethylpyrazolium tetrafluoroborate (3a)

Yield: 88%, white solid. IR (ATR, cm^{-1}) ν_{max} = 3072, 2970–2930, 1594, 1571, 1499, 1032, 834. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 2.22 (s, 3H, 5-CH_3); 2.56 (s, 3H, 3-CH_3); 3.68 (s, 3H, NCH_3); 6.50 (s, 1H, CH); 7.58 (m, 2H, Ph); 7.70 (m, 3H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ = 11.93; 12.14; 34.43; 108.07; 128.77–132.62; 146.64 and 147.96. ^{19}F NMR (282 MHz, $CDCl_3$, ppm): δ = −153.97, −154.03. Analysis: calcd for $C_{12}H_{15}N_2BF_4$: C 52.59, H 5.52, N 10.22. Found: C 53.03, H

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5.37, N 10.10. TOF MS (ES$^+$) m/z calcd. for $C_{12}H_{15}N_2$: 187.1235. Found: 187.1229.

4.5.2. *1-Phenyl-2-ethyl-3,5-dimethylpyrazolium tetrafluoroborate (3b)*

Yield: 78%, white solid. IR (ATR, cm^{-1}) $\nu_{max} = 3077, 2970–2943$, 1594, 1562, 1498, 1032, 827. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): $\delta = 1.16$ (t, 3H, $–NCH_2\underline{CH_3}$); 4.18 (q, 2H, $–N\underline{CH_2}CH_3$); 2.18 (s, 3H, 5-CH_3); 2.55 (s, 3H, 3-CH_3); 6.51 (s, 1H, CH); 7.56 (m, 2H, Ph); 7.68 (m, 3H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): $\delta = 11.75$; 12.14; 14.21; 42.89; 108.54; 128.79–132.72; 147.29; 147.42. ^{19}F NMR (282 MHz, $CDCl_3$, ppm): $\delta = -153.59, -153.64$. Analysis: calcd for $C_{13}H_{17}N_2BF_4$: C 54.20, H 5.95, N 9.72. Found: C 54.05, H 5.84, N 9.72. TOF MS (ES$^+$) m/z calcd. for $C_{13}H_{17}N_2$: 201.1392. Found: 201.1391.

4.5.3. *1-Phenyl-3,5-dimethyl-2-propylpyrazolium tetrafluoroborate (3c)*

Yield: 75%, white solid. IR (ATR, cm^{-1}) $\nu_{max} = 3068, 2971–2886$, 1593, 1557, 1494, 1031, 827. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): $\delta = 0.74$ (t, 3H, $-NCH_2CH_2\underline{CH_3}$); 1.54 (m, 2H, $-NCH_2\underline{CH_2}CH_3$); 4.06 (t, 2H, $-N\underline{CH_2}CH_2CH_3$); 2.19 (s, 3H, 5-$CH_3$); 2.54 (s, 3H, 3-$CH_3$); 6.53 (s, 1H, CH); 7.54 (m, 2H, Ph); 7.67 (m, 3H, Ph).^{13}C NMR (75 MHz, $CDCl_3$, ppm): $\delta = 10.64$; 12.06; 12.22; 22.37; 48.93; 108.55; 128.80–132.72; 147.55; 147.79. ^{19}F NMR (282 MHz, $CDCl_3$, ppm): $\delta = -153.63, -153.68$. Analysis: calcd for $C_{14}H_{19}N_2BF_4$: C 55.66, H 6.34, N 9.27. Found: C 55.66, H 6.06, N 9.28. TOF MS (ES$^+$) m/z calcd. for $C_{14}H_{19}N_2$: 215.1548. Found: 215.1546.

4.5.4. *1-Phenyl-2-butyl-3,5-dimethylpyrazolium tetrafluoroborate (3d)*

Yield 87%, white solid. IR (ATR, cm^{-1}) $\nu_{max} = 3062, 2970–2857$, 1592, 1561, 1485, 1032, 847. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): $\delta = 0.75$ (t, 3H, $-NCH_2CH_2CH_2\underline{CH_3}$); 1.18 (m, 2H, $-NCH_2CH_2\underline{CH_2}CH_3$); 1.49 (m, 2H, $-NCH_2\underline{CH_2}CH_2CH_3$); 4.12 (t, 2H, $-N\underline{CH_2}CH_2CH_2CH_3$); 2.21 (s, 3H, 5-$CH_3$); 2.57 (s, 3H, 3-$CH_3$); 6.53 (s, 1H, CH); 7.58 (m, 2H, Ph); 7.70 (m, 3H, Ph).^{13}C NMR (75 MHz, $CDCl_3$, ppm): $\delta = 11.97$; 12.18; 13.07; 19.29; 30.74; 47.28; 108.56; 128.83–132.71; 147.49; 147.65. ^{19}F NMR (282 MHz, $CDCl_3$, ppm): $\delta = -153.55, -153.60$. Analysis: calcd for $C_{15}H_{21}N_2BF_4$: C 56.99, H 6.70, N 8.86. Found: C 57.23, H 6.38, N 8.93. TOF MS (ES$^+$) m/z calcd. for $C_{15}H_{21}N_2$: 229.1705. Found: 229.1708.

4.5.5. *1-Phenyl-3,5-dimethyl-2-pentylpyrazolium tetrafluoroborate (3e)*

Yield:75%, yellow liquid. IR (ATR, cm^{-1}) $\nu_{max} = 3065, 2958–2872$, 1593, 1561, 1496, 1030, 826. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): $\delta = 0.75$ (t, 3H, $-NCH_2CH_2CH_2CH_2\underline{CH_3}$); 1.11 (m, 4H, $-NCH_2CH_2\underline{CH_2CH_2}CH_3$); 1.52 (m, 2H, $-NCH_2\underline{CH_2}CH_2CH_2CH_3$); 4.09 (t, 2H, $-N\underline{CH_2}CH_2CH_2CH_2CH_3$); 2.20 (s, 3H, 5-$CH_3$); 2.55 (s, 3H, 3-$CH_3$); 6.53 (s, 1H, CH); 7.58 (m, 2H, Ph); 7.70 (m, 3H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): $\delta = 11.97$; 12.17; 13.53; 21.58; 28.02; 28.41; 47.49; 108.56; 128.81–132.70; 147.49; 147.63. ^{19}F NMR (282 MHz, $CDCl_3$, ppm): $\delta = -153.52, -153.57$. Analysis: calcd for $C_{16}H_{23}N_2BF_4$: C 58.20, H 7.02, N 8.48. Found: C 58.30, H 7.04, N 8.56. TOF MS (ES$^+$) m/z calcd. for $C_{16}H_{23}N_2$: 243.1861. Found: 243.1861.

4.5.6. *1-Phenyl-3,5-dimethyl-2-hexylpyrazolium tetrafluoroborate (3f)*

Yield: 86%, yellow liquid. IR (ATR, cm^{-1}) $\nu_{max} = 3068$, 2970–2860, 1593, 1561, 1496, 1031, 837. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): $\delta = 0.78$ (t, 3H, $–NCH_2CH_2CH_2CH_2CH_2\underline{CH_3}$); 1.09 (m, 6H, $–NCH_2CH_2\underline{CH_2CH_2CH_2}CH_3$); 1.52 (m, 2H, $–NCH_2\underline{CH_2}CH_2CH_2CH_2CH_3$); 4.12 (t, 2H, $–N\underline{CH_2}CH_2CH_2CH_2CH_2CH_3$); 2.21 (s, 3H, 5-$CH_3$); 2.56 (s, 3H, 3-$CH_3$); 6.54 (s, 1H, CH); 7.57 (m, 2H, Ph); 7.69 (m, 3H, Ph).^{13}C NMR (75 MHz, $CDCl_3$, ppm): $\delta = 12.01$; 12.20; 13.74; 22.10; 25.67; 28.72; 30.60; 47.52; 108.56; 128.87–132.69; 147.44; 147.63. ^{19}F NMR (282 MHz, $CDCl_3$, ppm): $\delta = -153.60, -153.65$. Analysis: calcd for $C_{17}H_{25}N_2BF_4$: C 59.32, H 7.32, N 8.14. Found: C 59.10, H 7.13, N 8.27. TOF MS (ES$^+$) m/z calcd. for $C_{17}H_{25}N_2$: 257.2018. Found: 257.2007.

4.5.7. *1-Phenyl-3,5-dimethyl-2-heptylpyrazoliumtetrafluoroborate (3g)*

Yield: 84%, pinky solid. IR (ATR, cm^{-1}) $\nu_{max} = 3068, 2951–2865$, 1595, 1562, 1495, 1034, 824. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): $\delta = 0.80$ (t, 3H, $-NCH_2CH_2CH_2CH_2CH_2CH_2\underline{CH_3}$); 1.09 (m, 8H, $–NCH_2CH_2\underline{CH_2CH_2CH_2CH_2}CH_3$); 1.49 (m, 2H, $–NCH_2\underline{CH_2}CH_2CH_2CH_2CH_2CH_3$); 4.09 (t, 2H, $–N\underline{CH_2}CH_2CH_2CH_2CH_2CH_2CH_3$); 2.20 (s, 3H, 5-$CH_3$); 2.55 (s, 3H, 3-$CH_3$); 6.54 (s, 1H, CH); 7.57 (m, 2H, Ph); 7.69 (m, 3H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): $\delta = 11.91$; 12.12; 13.89; 22.27; 25.87; 28.06; 28.66; 31.16; 47.41; 108.53; 128.78–132.67; 147.44; 147.54. ^{19}F NMR (282 MHz, $CDCl_3$, ppm): $\delta = -153.50, -153.55$. Analysis: calcd for $C_{18}H_{27}N_2BF_4$: C 60.35, H 7.60, N 7.82. Found: C 60.33, H 7.45, N 7.91. TOF MS (ES$^+$) m/z calcd. for $C_{18}H_{27}N_2$: 271.2174. Found: 271.2170.

4.6. *General procedure for the synthesis of 1-phenyl-2-alkyl-3,5-dimethylpyrazolium hexafluorophosphates (4a–4g)*

Potassium hexafluorophosphate (5.0 mmol) solution in 5.0 mL of water was added dropwise to a solution of the appropriate methanesulfonate salt (5.0 mmol) in water (5.0 mL) and the mixture was stirred at room temperature for 2 h. The resulting solid salt was collected and recrystallized from ethanol.

4.6.1. *1-Phenyl-2,3,5-trimethylpyrazolium hexafluorophosphate (4a)*

Yield: 90%, white solid. IR (ATR, cm^{-1}) $\nu_{max} = 3073, 2960–2833$, 1594, 1561, 1496, 825, 769. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): $\delta = 2.19$ (s, 3H, 5-CH_3); 2.50 (s, 3H, 3-CH_3); 3.61 (s, 3H, NCH_3); 6.46 (s, 1H, CH); 7.50 (m, 2H, Ph); 7.66 (m, 3H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) $\delta = 11.77$; 12.07; 34.23; 108.12; 128.62–132.73; 146.75 and 147.91. ^{19}F NMR (282 MHz, $CDCl_3$, ppm): $\delta = -72.39–74.91$. Analysis: calcd for $C_{12}H_{15}N_2PF_6$: C 43.38, H 4.55, N 8.43. Found: C 43.45, H 4.57, N 8.41. TOF MS (ES$^+$) m/z calcd. for $C_{12}H_{15}N_2$: 187.1235. Found: 187.1229. TOF MS (ES$^-$) m/z calcd. for PF_6: 144.9642. Found: 144.9639.

4.6.2. *1-Phenyl-2-ethyl-3,5-dimethylpyrazolium hexafluorophosphate (4b)*

Yield: 87%, white solid. IR (ATR, cm^{-1}) $\nu_{max} = 3080, 2979–2946$, 1594, 1560, 1496, 825, 776. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): $\delta = 1.19$ (t, 3H, $–NCH_2\underline{CH_3}$); 4.17 (q, 2H, $–N\underline{CH_2}CH_3$); 2.22 (s, 3H, 5-CH_3); 2.57 (s, 3H, 3-CH_3); 6.52 (s, 1H, CH); 7.54 (m, 2H, Ph); 7.71 (m, 3H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): $\delta = 11.61$; 12.05; 14.15; 42.81; 108.60; 128.66–132.81; 147.23; 147.58. ^{19}F NMR (282 MHz, $CDCl_3$, ppm): $\delta = -72.21; -74.73$. Analysis: calcd for $C_{13}H_{17}N_2PF_6$: C 45.09, H 4.95, N 8.09. Found: C 44.82, H 4.94, N 8.04. TOF MS (ES$^+$) m/z calcd. for $C_{13}H_{17}N_2$: 201.1392. Found: 201.1388. TOF MS (ES$^-$) m/z calcd. for PF_6: 144.9642. Found: 144.9644.

4.6.3. *1-Phenyl-3,5-dimethyl-2-propylpyrazolium hexafluorophosphate (4c)*

Yield: 80%, white solid. IR (ATR, cm^{-1}) $\nu_{max} = 3078, 2967–2882$, 1593, 1557, 1494, 825, 763. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): $\delta = 0.77$ (t, 3H, $-NCH_2CH_2\underline{CH_3}$); 1.56 (m, 2H, $-NCH_2\underline{CH_2}CH_3$); 4.02 (t, 2H, $-N\underline{CH_2}CH_2CH_3$); 2.19 (s, 3H, 5-$CH_3$); 2.54 (s, 3H, 3-$CH_3$); 6.52 (s, 1H, CH); 7.51 (m, 2H, Ph); 7.70 (m, 3H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): $\delta = 10.56$; 11.90; 12.11; 22.34; 48.86; 108.60; 128.66–132.82; 147.71; 147.73. ^{19}F NMR (282 MHz, $CDCl_3$, ppm): $\delta = -72.23; -74.75$. Analysis: calcd for $C_{14}H_{19}N_2PF_6$: C 46.67, H 5.32, N 7.78. Found: C 46.47, H 4.95, N 7.75. TOF MS (ES$^+$) m/z calcd. for $C_{14}H_{19}N_2$: 215.1548. Found: 215.1540. TOF MS (ES$^-$) m/z calcd. for PF_6: 144.9642. Found: 144.9646.

4.6.4. *1-Phenyl-2-butyl-3,5-dimethylpyrazolium hexafluorophosphate (4d)*

Yield: 85%, white solid. IR (ATR, cm^{-1}) $\nu_{max} = 3073, 2971–2865$, 1591, 1557, 1494, 826, 766. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): $\delta = 0.75$ (t, 3H, $-NCH_2CH_2CH_2\underline{CH_3}$); 1.18 (m, 2H, $-NCH_2CH_2\underline{CH_2}CH_3$); 1.50 (m, 2H, $-NCH_2\underline{CH_2}CH_2CH_3$); 4.06 (t, 2H, $-N\underline{CH_2}CH_2CH_2CH_3$); 2.21 (s, 3H, 5-$CH_3$); 2.54 (s, 3H, 3-$CH_3$); 6.51 (s, 1H, CH); 7.53 (m, 2H, Ph); 7.71 (m, 3H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): $\delta = 11.80$; 12.05;

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12.99; 19.23; 30.66; 47.18; 108.57; 128.67–132.79; 147.55; 147.61. ^{19}F NMR (282 MHz, $CDCl_3$, ppm): δ = −72.12; −74.64. Analysis: calcd for $C_{15}H_{21}N_2PF_6$: C 48.13, H 5.65, N 7.48. Found: C 47.99, H 5.47, N 7.30. TOF MS (ES^+) m/z calcd. for $C_{15}H_{21}N_2$: 229.1705. Found: 229.1700. TOF MS (ES^-) m/z calcd. for PF_6: 144.9642. Found: 144.9647.

4.6.5. 1-Phenyl-3,5-dimethyl-2-pentylpyrazolium hexafluorophosphate (4e)

Yield: 90%, white solid. IR (ATR, cm^{-1}) ν_{max} = 3078, 2958–2868, 1596, 1564, 1495, 824, 766. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 0.78 (t, 3H, $-NCH_2CH_2CH_2CH_2\underline{CH_3}$); 1.14 (m, 4H, $-NCH_2CH_2\underline{CH_2CH_2}CH_3$); 1.52 (m, 2H, $-NCH_2\underline{CH_2}CH_2CH_2CH_3$); 4.06 (t, 2H, $-N\underline{CH_2}CH_2CH_2CH_2CH_3$); 2.21 (s, 3H, 5-$CH_3$); 2.55 (s, 3H, 3-$CH_3$); 6.52 (s, 1H, CH); 7.53 (m, 2H, Ph); 7.71 (m, 3H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 11.83; 12.06; 13.49; 21.53; 27.98; 28.37; 47.44; 108.61; 128.69–132.78; 147.56; 147.63. ^{19}F NMR (282 MHz, $CDCl_3$, ppm): δ = −72.15; −74.67. Analysis: calcd for $C_{16}H_{23}N_2PF_6$: C 49.49, H 5.97, N 7.21. Found: C 49.31, H 5.82, N 7.25. TOF MS (ES^+) m/z calcd. for $C_{16}H_{23}N_2$: 243.1861. Found: 243.1859. TOF MS (ES^-) m/z calcd. for PF_6: 144.9642. Found: 144.9641.

4.6.6. 1-Phenyl-3,5-dimethyl-2-hexylpyrazolium hexafluorophosphate (4f)

Yield: 90%, white solid. IR (ATR, cm^{-1}) ν_{max} = 3076, 2969–2861, 1593, 1564, 1495, 824, 764. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 0.81 (t, 3H, $-NCH_2CH_2CH_2CH_2CH_2\underline{CH_3}$); 1.13 (m, 6H, $-NCH_2CH_2\underline{CH_2CH_2CH_2}CH_3$); 1.52 (m, 2H, $-NCH_2\underline{CH_2}CH_2CH_2CH_2CH_3$); 4.08 (t, 2H, $-N\underline{CH_2}CH_2CH_2CH_2CH_2CH_3$); 2.22 (s, 3H, 5-$CH_3$); 2.56 (s, 3H, 3-$CH_3$); 6.51 (s, 1H, CH); 7.55 (m, 2H, Ph); 7.72 (m, 3H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 11.80; 12.00; 13.67; 22.02; 25.55; 28.60; 30.47; 47.40; 108.56; 128.67–132.72; 147.46; 147.56. ^{19}F NMR (282 MHz, $CDCl_3$, ppm): δ = −72.23; −74.75. Analysis: calcd for $C_{17}H_{25}N_2PF_6$: C 50.75, H 6.26, N 6.96. Found: C 50.85, H 6.02, N 7.03. TOF MS (ES^+) m/z calcd. for $C_{17}H_{25}N_2$: 257.2018. Found: 257.2013. TOF MS (ES^-) m/z calcd. for PF_6: 144.9642. Found: 144.9642.

4.6.7. 1-Phenyl-3,5-dimethyl-2-heptylpyrazolium hexafluorophosphate (4g)

Yield: 85%, pinky solid. IR (ATR, cm^{-1}) ν_{max} = 3076, 2970–2863, 1595, 1562, 1496, 826, 764. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 0.84 (t, 3H, $-NCH_2CH_2CH_2CH_2CH_2CH_2\underline{CH_3}$); 1.12 (m, 8H, $-NCH_2CH_2\underline{CH_2CH_2CH_2CH_2}CH_3$); 1.52 (m, 2H, $-NCH_2\underline{CH_2}CH_2CH_2CH_2CH_2CH_3$); 4.07 (t, 2H, $-N\underline{CH_2}CH_2CH_2CH_2CH_2CH_2CH_3$); 2.22 (s, 3H, 5-$CH_3$); 2.56 (s, 3H, 3-$CH_3$); 6.52 (s, 1H, CH); 7.54 (m, 2H, Ph); 7.72 (m, 3H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 11.92; 12.15; 13.93; 22.34; 25.95; 28.12; 28.77; 31.23; 47.46; 108.61; 128.76–132.80; 147.54; 147.55. ^{19}F NMR (282 MHz, $CDCl_3$, ppm): δ = −72.25; −74.77. Analysis: calcd for $C_{18}H_{27}N_2PF_6$: C 51.92, H 6.54, N 6.73. Found: C 52.16, H 6.48, N 6.83. TOF MS (ES^+) m/z calcd. for $C_{18}H_{27}N_2$: 271.2174. Found: 271.2168. TOF MS (ES^-) m/z calcd. for PF_6: 144.9642. Found: 144.9640.

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Appendix A. Supplementary data

This material includes ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra; TGA curves, DSC thermograms, and cyclic voltammograms of all the pyrazolium salts. Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.molliq.2014.10.014.

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