Journal of Fluorine Chemistry 132 (2011) 52–56

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

A new fluorinated anion for room-temperature ionic liquids

Mahesha B. Herath, Tom Hickman, Stephen E. Creager *, Darryl D. DesMarteau

Department of Chemistry, Clemson University, Clemson, SC 29634, United States

ARTICLE INFO

Article history:
Received 14 October 2010
Received in revised form 9 November 2010
Accepted 10 November 2010
Available online 17 November 2010

Keywords:
Bis(trifluoromethyl)phosphinate
Synthesis
Ionic liquids
Viscosity
Conductivity
Electrochemical stability
Thermal analysis

ABSTRACT

A new room-temperature ionic liquid (RTIL) consisting of the fluorinated anion bis(trifluoromethyl)-phosphinate($(CF_3)_2PO_2^-$) coupled with the 1-butyl-3-methyl-imidazoliuim (BMIM) cation has been synthesized and characterized by physicochemical and electrochemical means including differential scanning calorimetry (DSC), thermogravimetric analysis, viscosity, conductivity and cyclic voltammetry measurements. Properties are compared with those of the known RTIL consisting of BMIM coupled with the bis(trifluoromethyl)-sulfonylimide (TFSI) anion.

1. Introduction

There is great interest in room-temperature ionic liquids (RTILs) as alternative electrolytes for replacing conventional salt-in-solvent liquid electrolytes used in some electrochemical applications and in a wide range of other applications. This is due to their significant differences in physical and chemical properties compared to the conventional electrolytes and solvents. Many RTILs are non-volatile and non-flammable and have a high thermal stability (>300 °C), and they often possess other properties such as high ion content and wide electrochemical window (>4 V) that are considered advantageous for electrochemical applications [1,2].

Although many ionic liquids have been synthesized, most are not suitable for electrochemical applications because of poor conductivity (<1 mS) and/or high viscosity (>100 cP) at room temperature, also due to a poor electrochemical window. However, the combination of a fluorinated anion with a cation such as alkylimidazolium has resulted in ionic liquids that display relatively wide electrochemical windows and also low viscosities and high conductivities that are favorable for electrochemical applications [3]. Examples for fluorinated anions used to prepare such ionic liquids include the following: $[PF_6]^-$, $[BF_4]^-$, $[(CF_3SO_2)_2N]^-$, $[(FSO_2)_2N]^-$and $[CF_3SO_3]^-$.

In this paper we report the synthesis, characterization and properties of a new room-temperature ionic liquid based on a relatively understudied fluorinated anion, bis(trifluoromethyl)-phosphinate ($[CF_3)_2PO_2^-]$). Some of the key physical and chemical properties of an ionic liquid based on this anion are compared with those for a comparable ionic liquid based on the bis(trifluoromethyl)sulfonyl-imide-anion($[CF_3SO_2)_2N]^-$) or abbreviated from here on as [TFSI]. Chemical structures for the relevant anions and cations in these two ionic liquids are shown in Scheme 1. The common cation for these two ionic liquids is butyl-methyl-imidazolium ([BMIM]).

2. Results and discussion

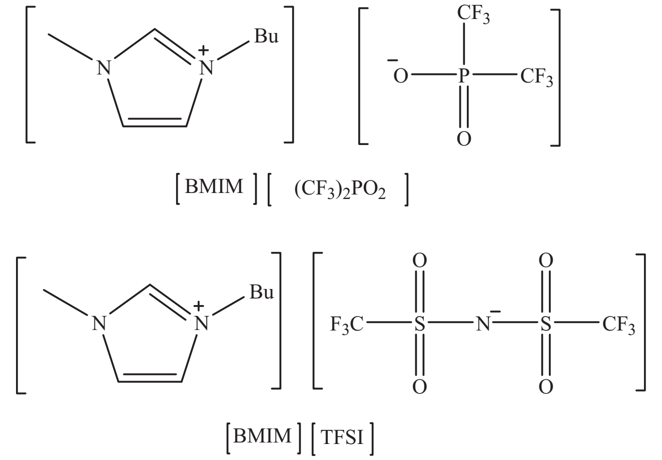
2.1. Synthetic aspects

$[BMIM][(CF_3)_2PO_2]$ was prepared by a metathesis reaction of 1-butyl-3-methylimidazolium bromide, [BMIM]Br, with an equimolar amount of $Ag[(CF_3)_2PO_2]$ as described in detail in the synthesis section. ^1H, ^{19}F and ^{31}P NMR spectra for the resulting RTIL did not show any signals for impurities and were in agreement with the expected chemical structure. Chemical analysis for C, H, F and N (see Section 4.3) gave results that agree with the chemical formula of $[BMIM][(CF_3)_2PO_2]$. A somewhat higher percentage of O than expected in the analysis suggests that the sample may contain some moisture. Energy-dispersive X-ray (EDS) spectral analysis (see supporting information) did not indicate the presence of bromide or any other inorganic impurities thus confirming that metathesis was complete. FT-IR spectroscopy of a film of the ionic liquid on the inside surface of one of the KBr windows of a gas cell was used to obtain a spectrum. The cell was evacuated for 30 min

---

* Corresponding author. Tel.: +1 864 656 2319; fax: +1 864 656 6613.
E-mail address: screage@clemson.edu (S.E. Creager).

0022-1139/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jfluchem.2010.11.005



Scheme 1. Chemical structures of (top) [BMIM] [$(CF_3)_2PO_2$] and (bottom) [BMIM][TFSI].

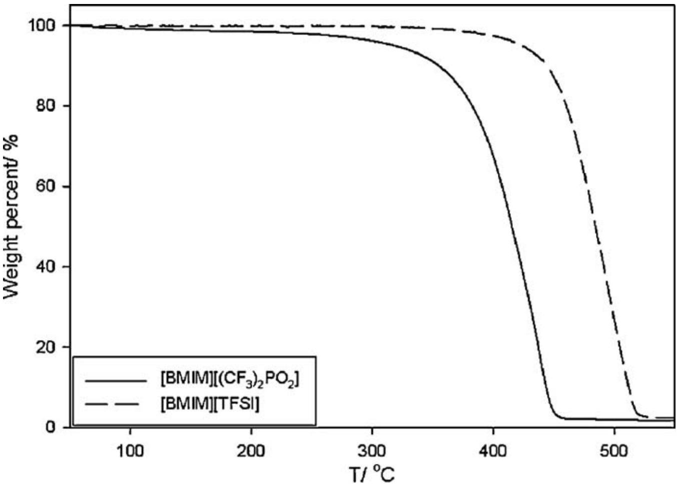


Fig. 1. TGA results for [BMIM][$(CF_3)_2PO_2$] and [BMIM][TFSI].

at 22 °C before recording the spectrum for [BMIM][$(CF_3)_2PO_2$] (see Fig. 3S in supporting information section). The absence of an –OH stretching band in the 3200–3800 cm^{-1} region showed that absorbed moisture in [BMIM][$(CF_3)_2PO_2$] can be completely removed by drying in vacuum for 30 min. All relevant FT-IR spectra are provided in the supporting information section. Comparison of the FT-IR spectra for [BMIM][TFSI] and [BMIM][$(CF_3)_2PO_2$] over time when in contact with moist air (introduced into the evacuated cell from the lab ambient) indicates that [BMIM][TFSI] takes up relatively small amounts of water from moist air whereas [BMIM][$(CF_3)_2PO_2$] appears to be more hygroscopic. Water uptake from air for the latter is much greater as indicated by the higher absorbance for the water-based –OH stretching peaks.

2.2. Thermal properties

Table 1 lists glass transition temperatures, melting points and thermal decomposition/volatilization temperatures for the two investigated ionic liquids. The glass transition temperature for [BMIM][$(CF_3)_2PO_2$] was obtained from the differential scanning calorimetry (DSC) curve recorded in the temperature range −120 to 100 °C at a heating rate of 5 °C min^{-1}. Compared to the [BMIM][TFSI], the new ionic liquid [BMIM][$(CF_3)_2PO_2$] did not show a melting point in this temperature range suggesting that it has a weaker tendency than [BMIM][TFSI] for crystallization. The absence of a melting point and roughly the same low glass transition temperature for [BMIM][$(CF_3)_2PO_2$] compared to [BMIM][TFSI] indicate that this new ionic liquid is a good glass former. TGA data were recorded with similar sample sizes, near 12 mg, and at sample heating rate of 20 °C min^{-1}. Fig. 1 shows TGA weight loss curves recorded for these two ionic liquids. [BMIM][$(CF3)_2PO_2$] shows some minor weight loss, <1%, below 200 °C. [BMIM][$(CF_3)_2PO_2$] appears to be somewhat less thermally stable than its TFSI analog; the thermal decomposition and/or volatilization temperature of the new ionic liquid is somewhat lower than that of the TFSI analog (see Table 1).

2.3. Fluidity and conductivity

Fluidity (inverse of viscosity) and conductivity in ionic liquid electrolytes are both expected to vary significantly with temperature (higher fluidity and conductivity at higher temperatures) and to approximately correlate with each other. Figs. 2 and 3 show that this is indeed the case for both [BMIM][$(CF_3)_2PO_2$] and [BMIM][TFSI]. Conductivity and fluidity both increase with increasing temperature, with [BMIM][TFSI] having the higher fluidity (lower viscosity) and also the higher conductivity over the full temperature range studied. This findings is as expected if the two ILs have approximately the same ion content and ion transport occurs by simple viscous flow. A more detailed analysis of the temperature-dependent data in terms of a simple Arrhenius model is not possible because the Arrhenius plots are curved, therefore the data were analyzed using the Vogel–Fulcher–Tammann(VTF) formalism, for which the governing equations are given by Eqs. (1) and (2).

$$\sigma = \sigma_0 \exp\left(\frac{-B_\sigma}{T - T_0}\right) \tag{1}$$

$$\frac{1}{\eta} = \frac{1}{\eta_0} \exp\left(\frac{B_\eta}{T - T_0}\right) \tag{2}$$

In these equations σ and η are the conductivity and viscosity respectively, σ_0 (S cm^{-1}) and η_0 (P) are constants associated with conductivity and viscosity, B_σ (K) and B_η (K) are pseudo-activation energies for conductivity and fluidity, and T_0 (K) is a characteristic temperature corresponding to freezing of molecular motions in the liquid within the VTF theory. Values for these parameters were

Table 1
Physical parameters determined for ionic liquids.

IL	MW (g mol^{-1})	ρ (g ml)	T_g (°C)	T_m (°C)	T_d (°C)	η (cP)	σ (mS cm^{-1})
[BMIM][TFSI]	419.4	1.45	−84	−3	459[a]	49.7 ± 2.1	3.70 ± 0.10)
[BMIM][$(CF_3)_2PO_2$]	340.2	1.35	−88[b]	[c]	380[a]	101.8 ± 5.1	2.40 ± 0.07

Molecular weight (MW); density (ρ); glass transition temperature (T_g); melting point (T_m); decomposition temperature (T_d); dynamic viscosity (η); specific conductivity (σ) are given. T = 25 °C.

[a] Determined by TGA analysis.

[b] Determined by DSC exotherm.

[c] Melting point was not observed.

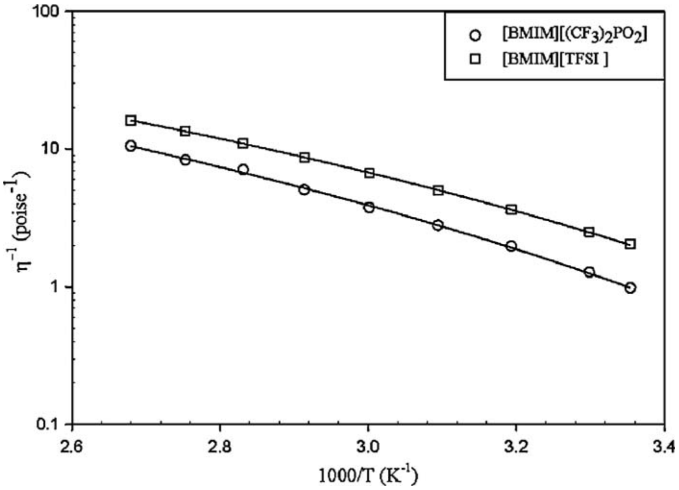


Fig. 2. Fluidity data for [BMIM][$(CF_3)_2PO_2$] in comparison with [BMIM][TFSI].

obtained by non-linear fits of Eqs. (1) and (2) to η^{-1}–T and σ–T datasets and are given in Tables 2 and 3 respectively.

A close inspection of the VTF fitting parameters in Tables 2 and 3 and the plots in Figs. 2 and 3 reveals some interesting features. In particular, we see that the curvature in the Arrhenius plots for fluidity is quite similar for both ionic liquids, whereas in the conductivity plots there is much higher curvature for [BMIM][$(CF_3)_2PO_2$] than for [BMIM][TFSI]. The same is true for VTF fitting parameters; the values are similar for both ILs for the fluidity data, whereas for the conductivity data the VTF fit parameters are very different for [BMIM][$(CF_3)_2PO_2$] and [BMIM][TFSI]. It appears that temperature variation causes changes in [BMIM][$(CF_3)_2PO_2$], but not in [BMIM][TFSI], that affect conductivity differently, and to a greater extent, than they affect viscosity. One possibility is that [BMIM][$(CF_3)_2PO_2$] undergoes ion-pairing to a greater extent at low temperature than does [BMIM][TFSI], perhaps due to the smaller size of the $(CF_3)_2PO_2^-$ anion relative to TFSI. Ion pairing (or more generally ion association) would decrease the charge carrier concentration and thereby decrease conductance, whereas it might have only a minimal effect on viscosity/fluidity. This is only one possibility; a more in-depth analysis that includes other data (not currently available) relating to ion pairing and transport would be required to say anything further.

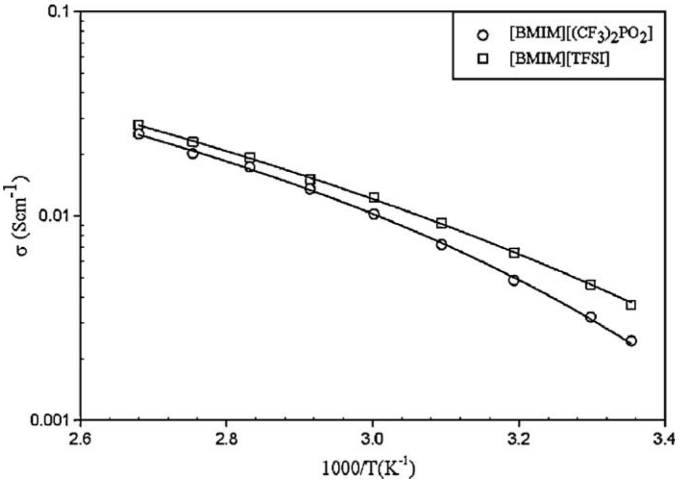


Fig. 3. Ionic conductivity of data for [BMIM] [$(CF_3)_2SO_2N$] in comparison with [BMIM][$(CF_3)_2PO_2$] conductivity values.

Table 2
The best-fit VTF parameters for the fluidity data.

	$1/\eta_0$ (P)	B_η (K)	T_0 (K)
[BMIM][TFSI]	609.7 ± 87.6	740.5 ± 50.9	168.2 ± 5.9
[BMIM][$(CF_3)_2PO_2$]	598.8 ± 505.0	827.7 ± 289.3	169.4 ± 30.2

Table 3
The best-fit VTF parameters for the conductivity data.

	σ_0 (S cm^{-1})	B_σ (K)	T_0(K)
[BMIM][TFSI]	0.800 ± 0.296	678.8 ± 125.2	171.7 ± 15.5
[BMIM][$(CF_3)_2PO_2$]	0.382 ± 0.140	442.6 ± 95.9	211.1 ± 13.9

2.4. Pulsed-field-gradient NMR measurements

The self-diffusion coefficients of the anions and the cations at 25 °C and 60 °C was estimated by using pulsed-field-gradient nuclear magnetic resonance spectroscopy. The cation consists of ^{1}H NMR sensitive nuclei and the anion consist of ^{19}F NMR sensitive nuclei. Therefore the self-diffusion coefficients of the cation and the anion can be independently determined. However, this method does not distinguish between neutral molecules, ion aggregates and the independently moving free ions. Table 4 shows the diffusion coefficients for [BMIM][$(CF_3)_2PO_2$] and [BMIM][TFSI] at these two temperatures. At both these temperatures the self-diffusion coefficients of the anion and the cation of TFSI based ionic liquid are higher than the self-diffusion coefficients of the anion and the cation of the $(CF_3)_2PO_2^-$-based ionic liquid. This observation is in agreement with the conductivity and the fluidity (viscosity) trend observed for these two ionic liquids. As indicated above, the conductivity and fluidity trend from 25 °C to 100 °C was observed to be [BMIM][TFSI] > [BMIM][$(CF_3)_2PO_2$]. The higher fluidity results in higher self-diffusion coefficients for [BMIM][TFSI] which, for similar ion concentrations, results in higher conductivity for [BMIM][TFSI].

2.5. Electrochemical stability

The electrochemical stability windows were determined for both ionic liquids using cyclic voltammetry (CV) at platinum electrodes vs. a silver quasi-reference electrode in the neat liquids. CV scans were always first recorded from positive to negative direction. Cyclic voltammograms for the ionic liquids are shown in Fig. 4. The region where the current as a function of voltage was nearly constant ($< \pm 5$ μA) was taken as the region that shows the electrochemical stability of these ionic liquids. Based on this method, for [BMIM][$(CF_3)_2PO_2$] an electrochemical window of 4.5 V was determined whereas the electrochemical window of [BMIM][TFSI] was about 4.2 V. This suggests that [BMIM][$(CF_3)_2PO_2$] is somewhat more electrochemically stable than [BMIM][TFSI]. The small additional voltammetric peaks at −2 V and −1 V could be due to reduction of absorbed H_2O or dissolved O_2.

Table 4
The self-diffusion coefficients of cation (D^+, cm^2 s^{-1}) and anion (D^-, cm^2 s^{-1}) of the ILs.

Compound	At 25 °C		At 60 °C	
	$D^+/10^{-7}$	$D^-/10^{-7}$	$D^+/10^{-7}$	$D^-/10^{-7}$
[BMIM] [$(CF_3)_2PO_2$]	1.10(±0.03)	0.90(±0.02)	4.90(±0.15)	4.10(±0.10)
[BMIM] [$(CF_3)_2SO_2N$]	2.50(0.06)	1.90(±0.05)	8.90(±0.25)	7.20(±0.20)
[BMIM] [$(CF_3)_2SO_2N$][a]	2.8	2.2	9.0	7.5

[a] The diffusion data were obtained from Ref. [6].

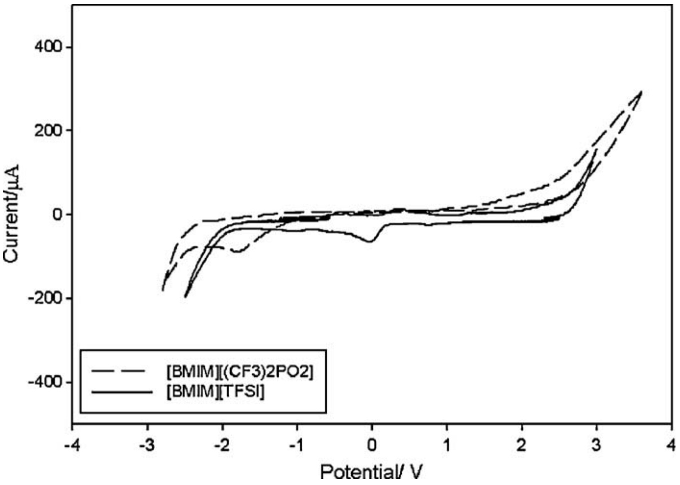


Fig. 4. Cyclic voltammetry of neat [BMIM][$(CF_3)_2PO_2$)] and neat [BMIM][TFSI] at 23 °C, on a platinum electrode, with a platinum counter electrode and Ag/Ag^+ pseudo reference electrode with a sweep rate of 100 mV/s.

3. Conclusions

A new ionic liquid [BMIM][$(CF_3)_2PO_2$] based on a new fluorinated anion $(CF_3)_2PO_2{}^-$ is reported. Its chemical and physical properties were investigated, including thermal stability, viscosity, voltage window, and conductivity. This substance may be useful as an electrolyte in batteries or in other electrochemical power sources/devices.

4. Experimental

4.1. Chemicals

Imidazolium bromide [4] and bis(trifluoromethyl)phosphonic acid [5] were prepared by procedures described in literature. [BMIM][TFSI] ionic liquid was purchased from Sigma–Aldrich.

4.2. Analytical procedures

^{1}H, ^{19}F and ^{31}P NMR spectra were measured on JEOL 300 (300.13 MHz for ^{1}H, 282.40 for ^{19}F and 121.5 MHz for ^{31}P) and BruckerAvance 300 instruments in acetonitrile-D3 except where noted. ^{19}F chemical shifts were referenced to internal standard $CFCl_3$. ^{1}H chemical shifts were referenced to lock solvent CD_3CN. The external reference for ^{31}P NMR, 85% H_3PO_4 was positioned at 0 ppm. Infra-red spectra were obtained using a Perkin-Elmer Spectrum 2000 FTIR. Energy dispersive X-ray (EDX) spectra were recorded by a SiLi detector (Oxford) attached to a SEM (S-3400N, Hitachi). Thermogravimetric analyses (TGA) were recorded on a Perkin-Elmer TGA 7 under N_2 (g).

Ionic conductivities were measured as a function of temperature by electrochemical impedance spectroscopy (EIS). Data were collected using a Solatron model SI 1286 electrochemical interface coupled to a Solatron model 1254 frequency response analyzer. The conductivity experiments were carried out inside of a stainless steel apparatus using a conductivity cell constructed from PEEK (polyether-ether-ketone) material and under a nitrogen atmosphere as previously described in reference [5]. The conductivity was calculated by dividing the cell constant value by the impedance value extracted from the high-frequency intercept on the real axis of a Nyquist plot. Conductivity data were determined with a precision of ±3%.

Viscosities were measured using a set of calibrated Cannon-Manning Semi-Micro Extra-Low-Charge capillary viscometers. Viscosity data were determined with a precision of ±5%. Densities were determined from measuring the weight of the 1 mL volume dispensed by an Eppendorf micropipette. Cyclic voltammograms were recorded on neat ionic liquids using a platinum (Pt) working electrode and a Pt auxiliary electrode and silver (Ag) wire as a reference electrode on CH 660 A (CH instruments) instrument.

Pulsed-field-gradient nuclear magnetic resonance (PFG NMR) experiments were performed on a BrukerAvance 300 spectrometer with 5 mm ^{13}C/^{19}F/^{31}P-^{1}H QNP z-gradient liquid probes at 300.13 MHz for ^{1}H, 282.7 MHz for ^{19}F at 20 and 85 °C. Temperatures were regulated by a BVT3000 temperature controller and calibrated against ethylene glycol. The experiments were performed without deuterium lock and without sample rotation. The stimulated echo sequence using one spoil gradient (stegp1 s from the Bruker library) was used in pseudo-two-dimensional mode with constant diffusion time and a linearly ramped gradient from 5 to 95% of maximum power in 16 increments. Diffusion time Δ was kept constant at 100 ms and gradient pulse length δ was optimized for each sample, nucleus, and temperature using the one-dimensional variant of the pulse sequence stegp1s1d. The data were processed in pseudo-two-dimensional mode then analyzed using SimFit included with Bruker (v 3.5), fitting the signal integration (area) to gradient strength. Diffusion data were determined with a precision of ±3%.

4.3. Synthesis

[BMIM][$(CF_3)_2PO_2$] in water (2 mL), solid Ag_2O (1.1 g, 4.9 mol) and $(CF_3)_2PO_2H$ (2.0 g, 9.9 mmol) prepared as described in reference [5] were stirred until the Ag_2O had reacted completely giving a clear solution. 1-Butyl-3-methyl-imidazolium bromide (2.2 g, 9.9 mmol) dissolved in water was then added to this solution. After 1 h of stirring, the AgBr precipitate was filtered off, and the filtrate was concentrated on a rotary evaporator. The resulting slightly yellow color liquid was further dried overnight in a vacuum oven at 120 °C to give 2.9 g of [BMIM][$(CF_3)_2PO_2$] (85% yield).^{1}H NMR ($CDCN_3$, 300.13 MHz): $\delta = 0.91$ (t, 3H, $-CH_3$, $J = 7.2$ Hz), 1.26 (m, 2H, $-CH_2$), 1.78 (m, 2H, $-CH_2$), 3.8 (s, 3H, $-CH_3$), 4.10 (t, 2H, $-CH_2$, $J = 7.2$ Hz), 7.35 (d, 2H, –CH, $J = 11.6$ Hz), 8.59 (s, 1H, –CH). ^{19}F NMR ($CDCN_3$, 282.40 MHz): $\delta = -72.73$ (d, 6F, $-CF_3$, $J = 88.7$ Hz). ^{31}P NMR ($CDCN_3$, 121.5 MHz): $\delta = -6.10$ (septet, $-(CF_3)_2P$, $J = 90.7$ Hz).

Elemental analysis. Elemental analysis was performed by Atlantic Micro Labs, Atlanta, GA. The sample was dried in vacuo for 2 h at 120 °C. Anal. Calculated for $C_{10}H_{15}F_6N_2O_2P$: C, 35.3; H, 4.44; F, 33.5; N, 8.2; O, 9.4%. Found C, 34.85; H, 4.73; F, 33.49; N, 8.0; Br, 0.0; O, 12.5%.

We note that [BMIM][$(CF_3)_2PO_2$] is fully soluble in/miscible with the following solvents: (1) acetonitrile, (2) dimethylsulfoxide, (3) dichloromethane, (4) tetrahydrofuran and (5) water.

Acknowledgement

Financial support for this work was provided by the United States Department of Energy (US DOE) hydrogen program via grant number DE-FG36-06GO16031.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jfluchem.2010.11.005.

References

[1] J. Fuller, R.T. Carlin, R.A. Osteryoung, J. Electrochem. Soc. 144 (1997) 3881–3886.
[2] A.B. McEwen, H.L. Ngo, K. LeCompte, J.L. Goldman, J. Electrochem. Soc. 146 (1999) 1687–1695.
[3] R. Hagiwara, Y. Ito, J. Fluorine Chem. 105 (2000) 221–227.
[4] P. Bonhote, A.P. Dias, N. Papageorgiou, K. Kalyanasundaram, M. Gratzel, Inorg. Chem. 35 (1996) 1168–1178.
[5] M.B. Herath, S. Creager, A. Kitaygorodskiy, D.D. Desmarteau, Chem. Phys. Chem. 11 (2010) 2871–2878.
[6] H. Tokuda, K. Hayamizu, K. Ishii, M. Abu Bin Hasan Susan, M. Watanabe, J. Phys. Chem. B 108 (2004) 16593–16600.