

Ionicity and Electrochemical Properties of Visible Light Absorbing Pyrrolidinium m-Nitrophenolate

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Abstract

Here we report the synthesis of pyrrolidinium meta-nitrophenolate; a novel ultraviolet and visible light absorbing protic ionic liquid prepared using an environmentally friendly process via the proton transfer reaction. Characterization shows nearly complete ionization at a ΔpK_a separation of 3.31, which is much lower than that of conventional protic ionic liquids. We report that pyrrolidinium meta-nitrophenolate has a room temperature electrochemical window in excess of 10 V. The combined optical and electrochemical properties of pyrrolidinium meta-nitrophenolate suggest it could be used as an electrolyte additive in photovoltaic devices to improve device stability.

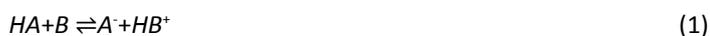
Keywords: Ionic liquid; Protic ionic liquid; Dye; Electrolyte; Solvent; Ion conductivity; Viscosity; Light absorbance; Walden plot; Dye sensitized solar cell

Abbreviations: DSC: Differential Scanning Calorimetry; PIL: Protic Ionic Liquid; RTIL: Room Temperature Ionic Liquid; UV: Ultra Violet; NMR: Nuclear Magnetic Resonance; DSSC: Dye Sensitized Solar Cell

Received: March 28, 2016; **Accepted:** April 15, 2016; **Published:** April 23, 2016

Introduction

Ionic liquids are a class of molten salts which have a melting point below 100°C [1]. The characteristic high thermal stability [2,3], low volatility [4], high ionic conductivity [4] and low flammability of ionic liquids has attracted interest in their use as electrolytes and solvents which can also serve as catalysts [5]. In particular ionic liquids with melting points below 100°C (or in some literature 25°C) commonly referred to as a room temperature ionic liquids (RTIL's) have attracted interest as green solvents and electrolytes [6]. Protic ionic liquids (PILs) are a type of ionic liquid synthesized by the transfer of a proton from an acid to a base forming a permanently charged anion (A^-) and a protonated cation (HB^+) [5].



This reversible reaction is driven by the difference in pKa values between the acid and base. There has been a great deal of discussion on a described pKa threshold that must be overcome in order to obtain good ionic liquid behavior with the previously mentioned characteristic properties [7-16]. Some propose that a ΔpK_a separation of 8 [9] or higher [7,10] is needed, while others have shown that a ΔpK_a separation of 4 is sufficient to obtain

99.9% proton transfer [12,13]. Strong Bronsted bases such as ammonia [17], pyrrolidine [18], guanidine [19] and imidazole [20] are commonly used in combination with strong acids such as nitric acid [21], sulfuric acid [22] and acetic acid [23] to drive the equilibrium of equation 1 further to the right. Many well-known protic ionic liquids are made by maximizing the ΔpK_a separation between the acid and the base however this drastically limits the available cations and anions that are considered usable in the synthesis of PIL's. When this limitation is removed new protic ionic liquids can be synthesized which incorporate weakly acidic dyes. Incorporating such dyes into the protic ionic liquid structure can introduce optical properties such as visible light absorption into these electrolytes. Recent studies have investigated the optical properties of aprotic ionic liquids. However, from a green chemistry perspective aprotic ionic liquid synthesis exhibits low atom economy due to the involved generation of waste products, solvent use and purification procedures [24-31]. The combined optical and electrochemical properties of these materials could lead to new avenues in the development of sensing materials and new directions in the field of photovoltaics. Here we seek

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Citation: Pettipas RD, Mahimwalla ZS, Johnson MB, et al. Ionicity and Electrochemical Properties of Visible Light Absorbing Pyrrolidinium M-Nitrophenolate. Insights Anal Electrochem. 2016, 2:1

to address an issue with dye sensitized solar cell (DSSC) devices regarding the absorption of ultraviolet (UV) light by TiO_2 resulting in efficiency losses and also the depletion of I_3^- in the I_3^-/I^- redox couple following absorption of < 500 nm light [32,33]. These devices are typically shielded from this light using an UV filter, here we seek to develop an electrolyte which absorbs ultraviolet and visible light by incorporating a chromophore into the protic ionic liquid structure. The chromophore can be introduced by deprotonating a weakly acidic pH sensitive dye using a Bronsted base to induce a bathochromic shift allowing absorption of UV-Vis light while retaining the characteristic ion transport properties of protic ionic liquids. Our investigation involves the use of *m*-nitrophenol, a weakly acidic dye which absorbs UV and visible light to undergo an intramolecular charge transfer [34-36]. To deprotonate *m*-nitrophenol we have selected the strong base pyrrolidine, previously shown to generate PILs with favorable ion transport properties [18,37].

Materials and Methods

Materials

m-Nitrophenol $\geq 99\%$ and pyrrolidine $\geq 99\%$ were purchased from Sigma Aldrich and used as received.

Synthesis of pyrrolidinium *m*-nitrophenolate

m-Nitrophenol (1 g, 7.2 mmol) was added to pyrrolidine (0.6 mL, 7.2 mmol) in a 20 mL reaction vessel. Contents were stirred at 50°C for 30 minutes under solvent free conditions to obtain a viscous red liquid at $\geq 99\%$ yield. ^1H NMR (200 MHz, D_2O) δ 7.36-6.98 (3H, m), δ 6.80 (1H, d), δ 3.10-2.95 (4H, m), δ 1.26-1.17 (4H, m). ATR-FTIR (neat, cm^{-1}): 2971, 2416, 1866, 1599, 1510, 1456, 1345, 1301, 1267, 1241, 1076, 989, 934, 864, 813, 789, 736, 672 cm^{-1} .

Structural characterization

^1H NMR spectra were recorded on a 200 MHz Varian MercuryPlus. FTIR spectra were recorded on a Thermo Scientific Nicolet iS5 FT-Infrared spectrometer with an iD5 ATR Diamond accessory.

Physical characterization

Ionic Conductivity was recorded using a SUNTEX Conductivity Meter-SC170 with a cell constant of 1 cm calibrated using 0.01M KCl. Ionic conductivity measurements were taken at 2°C intervals in a calibrated reaction vessel while increasing the temperature of the oil bath in which the reaction vessel was immersed. Viscosity was measured using a BrookField-LV viscometer in a calibrated reaction vessel, heated by immersion in an oil bath. The oil bath was gradually heated and the temperature of sample and reaction vessel calibrated in relation to the oil bath temperature. Mass and volume measurements were determined using an analytical balance and a graduated cylinder at room temperature.

Light absorbance

UV/Vis spectra were recorded in a 1 cm quartz cuvette using a Varian Cary 100 Bio UV-Vis spectrometer.

Cyclic voltammetry

Scans were conducted using a Biologic SP-150 potentiostat using EC LAB software. A standard three electrode system was used consisting of a platinum wire counter electrode (BASi MW-4130), a reference electrode, composed of a Ag/AgCl wire (BASi, MF-2052) in 3 M NaCl solution and a glassy carbon working electrode (BASi, MF-2015) filled with carbon paste (BASi, CF-1010). All measurements were conducted under atmospheric conditions.

Thermal phase behavior

Differential scanning calorimetry was performed using 11.85 mg of the sample into a tared hermetic aluminum sample pan. The pan and lid were hermetically sealed and the sample was loaded into a TA instruments Q200 differential scanning calorimeter for measurement. Measurements were performed under a helium atmosphere (25 mL min^{-1} flow rate) using the liquid nitrogen cooling accessory as the cooling unit. The cell is first calibrated with indium as standard reference material ($T_{\text{melt}}=156.6^\circ\text{C}$ and $\Delta H_{\text{fus}}=28.71\text{ J g}^{-1}$) and with mercury as a second temperature standard ($T_{\text{melt}}=-38.8^\circ\text{C}$). The sample was equilibrated at -150°C , held for 5 minutes and then held at a ramp rate of $10^\circ\text{C min}^{-1}$ to 130°C and held at that temperature for one minute before cooling at a ramp rate of $10^\circ\text{C min}^{-1}$ to -150°C .

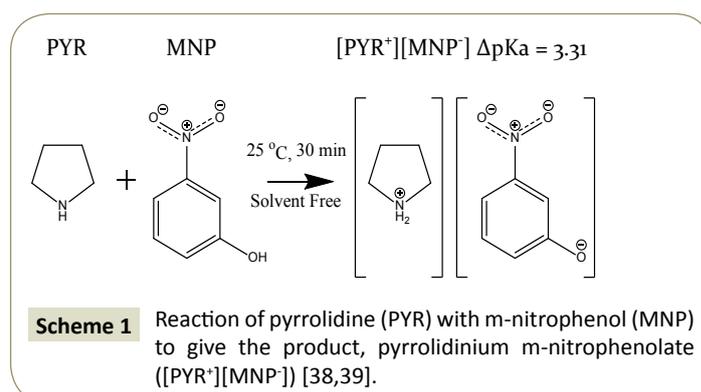
Results and Discussion

We first synthesized pyrrolidinium *m*-nitrophenolate [PYR^+][MNP^-] by the proton transfer from pyrrolidine to *m*-nitrophenol at a mild reaction temperature in the absence of a solvent as shown in **Scheme 1**. NMR and Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) show that the reaction went to completion with no side products formed. This process was determined to be thermodynamically favorable according to equation 2 where the theoretical Gibbs free energy value is equal to -17.1 kJ mol^{-1} [9].

$$\Delta G^\circ = -2.303RT\Delta pK_a \quad (2)$$

The thermal phase behavior of [PYR^+][MNP^-] was investigated to predict the range of potential applications and experiments that could be performed. The thermal phase transitions were investigated using Differential Scanning Calorimetry (DSC) as shown in **Figure 1**.

In **Figure 1** it can be seen that [PYR^+][MNP^-] remains in the liquid state until cooled to -44°C . Further cooling resulted in organization



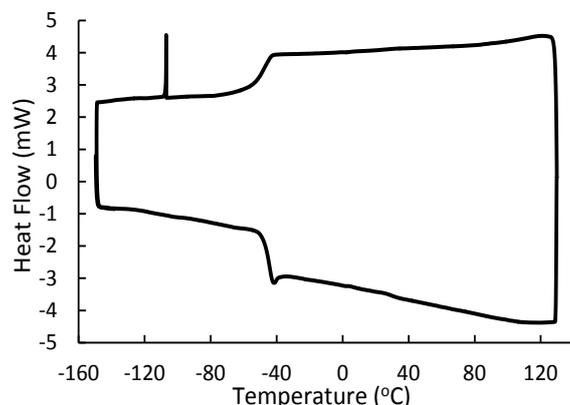


Figure 1 DSC thermogram of [PYR⁺][MNP⁻] over one complete heating and cooling cycle, positive heat flow indicates an exothermic process.

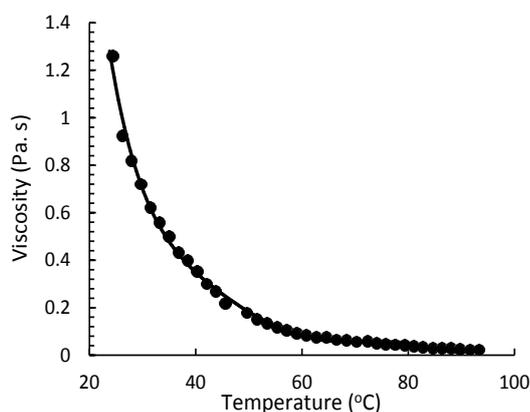


Figure 2 Viscosity of [PYR⁺][MNP⁻].

of the glass as evidenced by the exothermic peak at -107°C. It can be implied from **Figure 1** that [PYR⁺][MNP⁻] is thermally stable to at least 100°C allowing a higher temperature investigation of the transport properties. The low ΔpK_a separation between m-nitrophenol and pyrrolidinium goes against conventional recommendations of large ΔpK_a separation and might suggest the possibility of incomplete proton transfer. To further investigate the degree of proton transfer using a Walden plot, which requires knowledge of the density, viscosity and ion conductivity of the ionic liquid was created. We first investigated the viscosity of [PYR⁺][MNP⁻], a graph illustrating the change in viscosity as a function of temperature is shown in **Figure 2**.

In **Figure 2** the expected decrease in viscosity with increasing temperature can be seen through temperature dependent viscosity measurements. The PIL is a viscous liquid at 25°C (1.26 Pa.s) becoming considerably more fluid with increasing temperature. Conventional knowledge of protic ionic liquids would suggest that a low ΔpK_a separation would result in poor ion conductivity, however we find that the ion conductivity of [PYR⁺][MNP⁻] shown in **Figure 3** compares well to that of typical protic ionic liquids with much greater ΔpK_a separations [40].

As shown in **Figure 3**, the ion conductivity of **3** increases from

0.381 mS cm⁻¹ at 25°C to 8.29 mS cm⁻¹ at 92°C illustrating moderate to high ion conductivity. Using this information we can compare the degree of proton transfer of [PYR⁺][MNP⁻] to that of ideal 0.01M KCl for which complete ionization is said to occur, the comparison is shown in **Figure 4** using a Walden Plot [42].

In **Figure 4** we find that [PYR⁺][MNP⁻] demonstrates good ionic liquid behavior approaching that of ideal 0.01M KCl indicating nearly complete proton transfer and ionization. The degree of proton transfer can be calculated using equation 3 to predict 99.9% proton transfer at a ΔpK_a separation of 3.3 [13].

$$K = \frac{K_{a, aq}(HA)}{K_{a, aq}(HB^+)} \quad (3)$$

These results suggest that even weak acids could be used in protic ionic liquid synthesis. With almost complete proton transfer we investigated the optical properties of [PYR⁺][MNP⁻] by studying the wavelengths of light absorbed in the UV/Vis region as shown in **Figure 5**.

In **Figure 5** a maximum absorbance of **3** is obtained at 382 nm ($\epsilon=1.23 \times 10^3$ L mol⁻¹cm⁻¹) which persists beyond 400 nm ($\epsilon=1.14 \times 10^3$ L mol⁻¹cm⁻¹) into the visible region. Absorption of light in this range is beneficial as it allows [PYR⁺][MNP⁻] to absorb light which would otherwise harm dye sensitized solar cell components in addition to facilitating ion transport as an electrolyte. Application of this material in such devices requires an investigation into the electrochemical stability. We investigated the electrochemical stability using cyclic voltammetry over the range of -5 to 5 V in reference to a Ag/AgCl reference electrode, the results of this investigation are shown in **Figure 6**.

In **Figure 6** we see no evidence of oxidation or reduction over an electrochemical window of 10 V indicating remarkable electrochemical stability. This finding suggests that [PYR⁺][MNP⁻] is well suited towards photovoltaic applications however further study is needed to determine the stability of the electrolyte over time. Further study is required in order to establish the

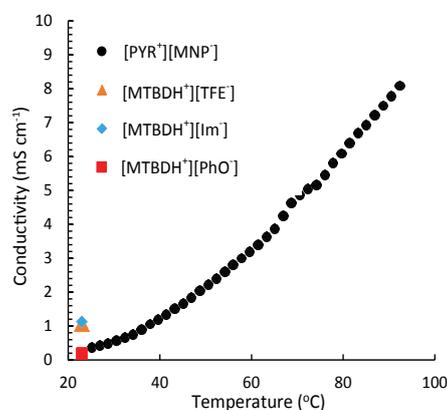


Figure 3 Ion Conductivity of neat [PYR⁺][MNP⁻] in comparison to [MTBDH⁺][TFE⁻] ($\Delta pK_a=12.9$), [MTBDH⁺][TFE⁻] ($\Delta pK_a=10.9$) and [MTBDH⁺][PhO⁻] ($\Delta pK_a=15.4$) [40,41]. The solid line is used as a guide for the eye.

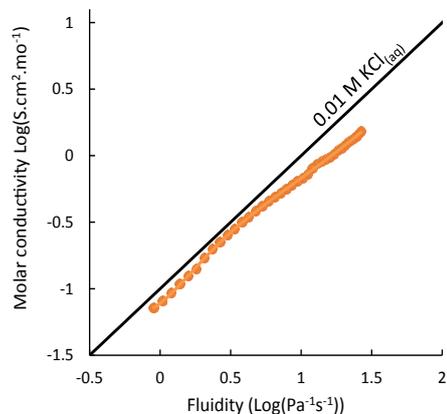


Figure 4 Walden plot of $[\text{PYR}^+][\text{MNP}^-]$, the solid line indicates ideal 0.01 M KCl behavior [42]. The solid line serves to guide the eye.

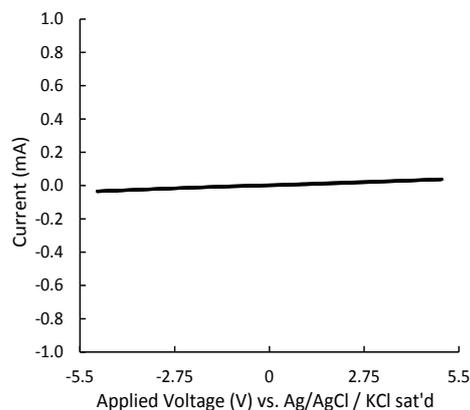


Figure 6 Cyclic voltammogram for neat $[\text{PYR}^+][\text{MNP}^-]$ at 25°C measured at a scan rate of 100 mV/s.

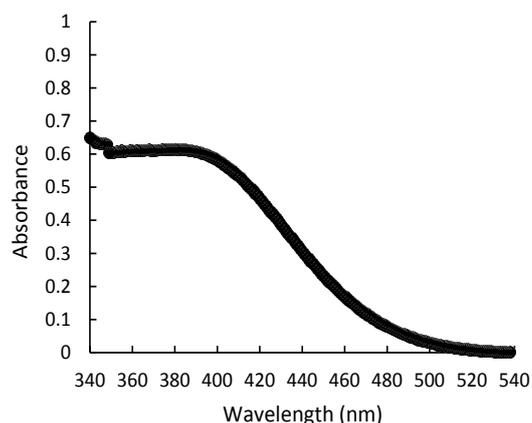


Figure 5 Light absorbance of 5×10^{-4} M $[\text{PYR}^+][\text{MNP}^-]$ in distilled water.

performance of this material as an electrolyte and its potential to function as a sensitizer in photovoltaic applications.

Conclusion

We have shown that complete proton transfer can be obtained at a ΔpKa separation of 3.31 indicating that weak acid and base combinations may be used in protic ionic liquid synthesis. We also report a green synthetic technique to generate a liquid dye capable of absorbing ultraviolet and visible wavelengths of light by using a pH sensitive dye as the anion. We find that the electrochemical window of $[\text{PYR}^+][\text{MNP}^-]$ is in excess of 10 V suggesting it can be used in applications such as dye sensitized solar cells among other electrochemical devices.

Acknowledgements

Synthetic and experimental work was supported by Natural Sciences and Engineering Research Council, NBIF and H.E Bigelow Fund. We acknowledge the support of the Canada Foundation for Innovation, the Atlantic Innovation Fund, and other partners which fund the Facilities for Materials Characterization, managed by the Institute for Research in Materials.

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