

Supplementary Information

Sample preparation

[Choline][triflate] was made by the neutralization reaction of triflic acid with Choline hydroxide. Typically the synthesis involves a drop wise addition of aqueous solution of 1 mole of triflic acid (Aldrich) (5.9g) to 1 mole of 20% aqueous Choline hydroxide (Aldrich) solution (23.9g) in an ice bath and the contents were stirred for about 2 hours at room temperature. The neutralized product was then treated with activated charcoal for decolorization. The solvent was removed by distillation and the final product was dried under vacuum at 60 °C for two days and the yield of pale yellow crystalline product was found to be 96%.

Identification of compound

The product was identified by Electrospray mass spectroscopy and NMR spectroscopic techniques as follows:

Electrospray mass spectroscopy analysis, (cone ±25V) : CTf, m/z (relative intensity, %): ES+, 103.9 (Me₃N+CH₂CH₂OH, 100); ES-, 149.0 (CF₃SO₃⁻, 100)

¹H NMR (300.13 MHz in D₂O, δ, ppm relative to TMS): 3.16(s,9H), 3.49-3.46(m,2H), 4.04-4.0(m, 2H). The ¹H NMR peak of the hydroxyl group of [Choline]⁺ cation was exchanged with the solvent peak. ¹⁹F NMR shows a strong signal for the fluorine atom of the triflate anion at -78.7 ppm.

TGA Measurements

The thermal stability and moisture content in materials were investigated by employing TGA measurement using a Pyris 1 TGA in a flowing dry nitrogen atmosphere between 25 to 700 °C with a heating rate of 10 °C min⁻¹. Additional isothermal TGA measurements were undertaken at 110 °C. Samples were ramped up to the 110 °C temperature at the rate of 2 °C min⁻¹, maintained at this temperature for 10 hrs and then ramped to 700 °C at the rate of 10 °C min⁻¹.

DSC Measurement

The thermal properties of materials were studied using a TA differential scanning calorimeter (DSC) model Q 100 over a temperature range of -120 to 300 °C at a scanning rate of 10 °C min⁻¹. The samples were sealed in the gold-coated stainless steel pans under the dry N₂ gas in glove boxes to avoid any moisture absorption and acid corrosion

issues. Three consecutive cyclic runs were carried out, with the first two cycles up to 140 °C and the third cycle increasing to 300 °C. The entropy changes (ΔS) reported in Table 1 are calculated from the enthalpy change (ΔH) occurring at each transition, which is obtained from the area under the DSC transition peaks. The DSC traces were analyzed using the TA instruments universal analysis 2000 program. The enthalpies and entropies reported are based on the quantity of plastic crystal in each of the doped samples, i.e by subtracting the amount of added acid in the calculations.

Conductivity Measurements

The ionic conductivities of all samples were measured using AC impedance spectroscopy using a frequency response analyzer (FRA, Solartron, 1296), impedance software version 3.2.0. The conductivities were obtained by measurement of the complex impedance spectra between 10 MHz and 0.1 Hz on a Solartron SI 1296 Dielectric interface and Solartron SI 1270 frequency response analyzer using two shielded BNC connectors. A Eurotherm 2204e temperature controller under serial control was used to control a 240 V cartridge heater for some experiments. The Eurotherm was under Solatron impedance measurement software control. A 240 V cartridge heater and K type thermocouple, mounted in a brass block, were used to control the sample temperature.

All sample handling was conducted within a nitrogen filled dry box to avoid any moisture uptake. The temperature range over which the impedance is measured is different for different compositions of samples and is taken from -50 °C to 140 °C.

PXRD studies

The powder X-ray diffraction (PXRD) patterns of pure and acid containing [Choline][DHP] samples were obtained at 22 ± 2 °C using Scintac powder diffractometer. A microcrystalline sample of 1-2 g was placed randomly on a flat brass made sample holder fitted with an o-ring sealed covered Mylar sheet providing an airtight atmosphere. CuKα1 radiation ($\lambda = 1.5405981 \text{ \AA}$) was produced at 40 kV and 25 mA by the X-Ray generator. The data were collected in the Brag-Brentano ($\theta/2\theta$) horizontal geometry using a 2θ -range of 5 to 60.0° with a step size of 0.02° 2θ with an accompanying scan speed of 0.5 ° / min.

Nuclear Magnetic resonance (NMR) Studies

1D ¹H and ¹⁹F static NMR experiments have been performed to identify the static and mobile species and to conduct the Full Width at Half Maximum

(FWHM) calculations on NMR peaks. Pulsed field gradient stimulated spin echo nuclear magnetic resonance (PFGSTE-NMR) spectroscopy experiments have been performed to determine the self-diffusion coefficients of the H^+ , the $[\text{Choline}]^+$ cation and the $[\text{triflate}]^-$ anion in the $[\text{Choline}][\text{triflate}]$ and its acid doped compositions using ^1H and ^{19}F nuclei respectively. Because the T1 (longitudinal relaxation time) of viscous samples is much longer than T2 (transverse relaxation time), the stimulated spin echo sequence was used. A Bruker Ultrashield 300 MHz NMR spectrometer with Avance I console fitted with a Diff 30 diffusion probe and GREAT 60 amplifier, held at 80°C ($\pm 0.5^\circ\text{C}$) and tuned to the corresponding nuclei was used in the diffusion studies. For each sample the gradient, gradient pulse length and diffusion time were optimized as well. The same setup was held at 30°C ($\pm 0.5^\circ\text{C}$) for 1D ^1H and ^{19}F static NMR experiments. The pulse lengths, duration between pulses and number of scans were optimized for each experiment.

Cyclic Voltammetry (CV)

Electrochemical characterization was carried out in a locally designed three-electrode cell, which consisted of a platinum working, Pt counter and Pt quasi-reference electrode. All experiments were performed in an Ar dry box at varying temperatures at a scanning rate of 20 mV/sec on a VMP2/Z potentiostat (Princeton Applied Research) under the control of EC-Lab V8.31 software. Samples were equilibrated for $\frac{1}{2}$ an hour before running the cyclic voltammograms. Since the Pt quasi reference electrode is not a standard reference electrode; therefore, separate control CV experiments were conducted on the solutions of pure and acid doped $[\text{Choline}][\text{triflate}]$ samples in acetonitrile using Ferrocene/ferrocenium ($\text{Fc}^{0/+}$) redox couple as an internal reference. ($\text{Fc}^{0/+}$) redox couple has been widely studied as a standard internal reference to assign the oxidation/reduction potentials of redox couples and ionic liquids, where it is difficult to employ a reference electrode of known potential^{1,2}. IUPAC also recommended $\text{Fc}^{0/+}$, a standard internal reference for non aqueous systems especially³. The voltage axis in the cyclic voltammograms was then rescaled using the known conversion between $\text{Fc}^{0/+}$ and the Normal Hydrogen Electrode (NHE)⁴.

Figures and Tables

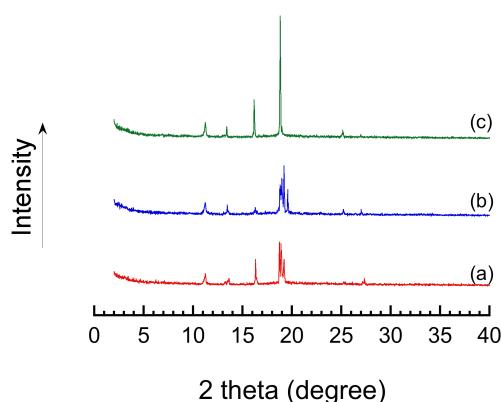


Figure S 1. PXRD traces of (a) pure $[\text{Choline}][\text{triflate}]$, (b) 4 mol% and (c) 8 mol% triflic acid doped $[\text{Choline}][\text{triflate}]$ samples respectively.

Material	$\text{III} \gg \text{II}$ $\Delta H/\text{kJ mol}^{-1} \pm 5\%$	$\text{II} \gg \text{I}$ $\Delta H/\text{kJ mol}^{-1} \pm 5\%$	$\text{I} \gg \text{melt}$ $\Delta H/\text{kJ mol}^{-1} \pm 5\%$
Pure $[\text{Choline}][\text{triflate}]$	1.6	0.2	2.3
4% $\text{CF}_3\text{SO}_3\text{H} + [\text{Choline}][\text{triflate}]$	14.3	0.2	1.4
8% $\text{CF}_3\text{SO}_3\text{H} + [\text{Choline}][\text{triflate}]$	12.2	0.2	1.6
Material	$\text{III} \gg \text{II}$ $\Delta S/\text{J K}^{-1} \text{mol}^{-1} \pm 5\%$	$\text{II} \gg \text{I}$ $\Delta S/\text{J K}^{-1} \text{mol}^{-1} \pm 5\%$	$\text{I} \gg \text{melt}$ $\Delta S/\text{J K}^{-1} \text{mol}^{-1} \pm 5\%$
Pure $[\text{Choline}][\text{triflate}]$	7.1	0.4	5.2
4% $\text{CF}_3\text{SO}_3\text{H} + [\text{Choline}][\text{triflate}]$	52.1	0.5	3.2
8% $\text{CF}_3\text{SO}_3\text{H} + [\text{Choline}][\text{triflate}]$	44.6	0.5	3.6

Table 1. Enthalpy and entropy values for different phase transitions calculated from the peak areas of DSC thermograms of pure and acid doped $[\text{Choline}][\text{triflate}]$ samples

References

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