

Plastic Crystal Phases with High Proton Conductivity

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Received (in XXX, XXX) Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX

DOI: 10.1039/b000000x

The effect of annealing on [Choline][DHP]

Figures and Tables

Table S1. Glass transition temperatures (T_g), heat capacity change (ΔC_p) values for the glass transitions and enthalpy change (ΔH) values as calculated from the peak area of different solid-solid phase transitions for annealed [Choline][DHP] system.

Material	T_g T °C \pm 2 °C	(T_g) ΔC_p (J/(g K) \pm 5%	III>>II ΔH / kJ mol ⁻¹ \pm 5%	II>>I ΔH / kJ mol ⁻¹ \pm 5%
Annealed [Choline][DHP] 2nd heating cycle	-22	25	5.5	1

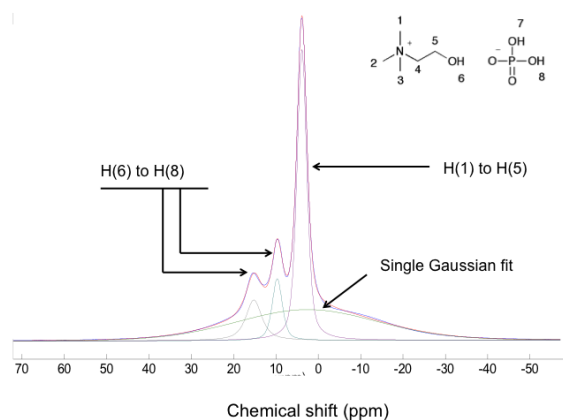


Figure S1. ¹H static NMR spectrum of as-prepared [Choline][DHP] at 100 ± 0.5 °C temperature. The dmfit program was used for the deconvolution of NMR into various peaks and simulated fit.

The effect of addition of 4 mol% acid to [Choline][DHP]

Figures and Tables

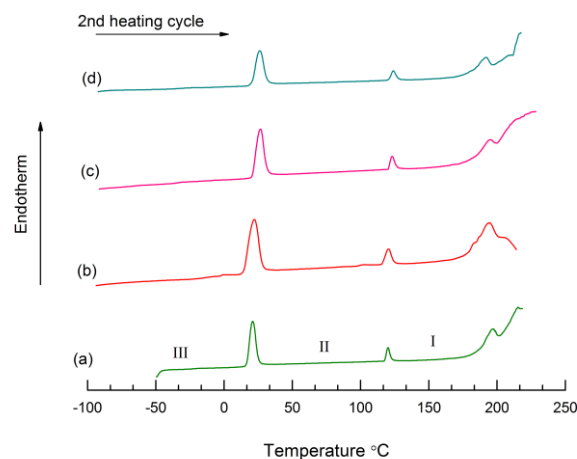
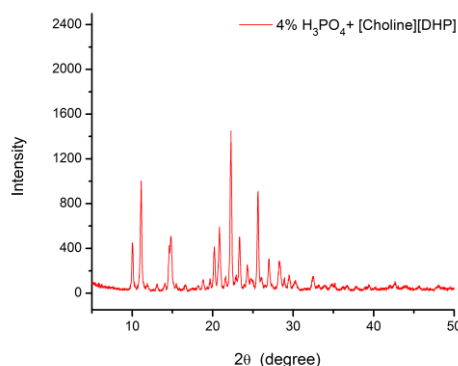


Figure S2. DSC thermograms of (a) Annealed [Choline][DHP], (b) 4 mol % H₃PO₄ + [Choline][DHP], (c) 4 mol% HN(Tf)₂ + [Choline][DHP] and (d) 4 % TfOH + [Choline][DHP] samples. All samples were annealed and the DSC traces are reported for the second heating cycle.



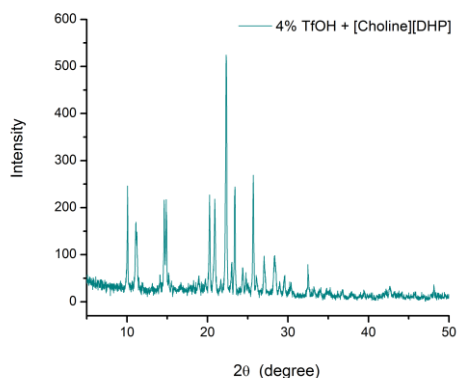


Figure S3. Powder X-Ray diffraction patterns of 4 mol% H₃PO₄ and 4 mol% TfOH containing [Choline][DHP] samples at 22 ± 1 °C temperature.

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Table S2. ¹H NMR full width at half maximum (FWHM) linewidths, chemical shift values and % area of NMR peaks for 4 mol% H₃PO₄, 4 mol% TfOH and 4 mol% HN(Tf)₂ containing [Choline][DHP] samples at 30 and 100 °C. The NMR spectra of these samples were deconvoluted and simulated by the dmfit program

4 mol% H ₃ PO ₄ + [Choline][DHP] @ 30 °C	Area (%)	Chemical shift (ppm)	FWHM (Hz) ± 100 Hz	4 mol% H ₃ PO ₄ + [Choline][DHP] @ 100 °C	Area (%)	Chemical shift (ppm)	FWHM (Hz) ± 100 Hz
Broad peak	96	3.3	18000	Broad peak 1	56	3.7	12000
–	–	–	–	Broad peak 2	5	15.5	7000
Narrow peak [H(1) to H(5)]	3.5	3.5	1500	Broad peak 2	28	3.8	900
Narrow peak 1 [H(6) to H(8)]	0.5	9.3	1000	Narrow peak [H(1) to H(5)]	6	10	1000
Narrow peak 2 [H(6) to H(8)]	–	–	–	Narrow peak 1 [H(6) to H(8)]	5	15	1000
4 mol% TfOH + [Choline][DHP] @ 30 °C	Area (%)	Chemical shift (ppm)	FWHM (Hz) ± 100 Hz	4 mol% TfOH + [Choline][DHP] @ 100 °C	Area (%)	Chemical shift (ppm)	FWHM (Hz) ± 100 Hz
Broad peak	83	1.3	20000	Broad peak 1	47	3.7	12000
–	–	–	–	Broad peak 2	6	16.7	9000
Narrow peak [H(1) to H(5)]	16	3.7	800	Narrow peak [H(1) to H(5)]	29	3.8	800
Narrow peak 1 [H(6) to H(8)]	1	8.2	800	Narrow peak 1 [H(6) to H(8)]	7	9.7	900
Narrow peak 2 [H(6) to H(8)]	–	–	–	Narrow peak 2 [H(6) to H(8)]	11	15.3	1300
4 mol% HN(Tf) ₂ + [Choline][DHP] @ 30 °C	Area (%)	Chemical shift (ppm)	FWHM (Hz) ± 100 Hz	4 mol% HN(Tf) ₂ + [Choline][DHP] @ 100 °C	Area (%)	Chemical shift (ppm)	FWHM (Hz) ± 100 Hz
Broad peak	78	2.2	17000	Broad peak	53	3.3	12000
Narrow peak [H(1) to H(5)]	17	3	800	Narrow peak [H(1) to H(5)]	27	3.3	700
Narrow peak 1 [H(6) to H(8)]	5	10.3	1000	Narrow peak 1 [H(6) to H(8)]	8	10.2	700
Narrow peak 2 [H(6) to H(8)]	–	–	–	Narrow peak 2 [H(6) to H(8)]	12	15.3	1000

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The effect of acid composition on structure and dynamics of [Choline][DHP]

Figures and Tables

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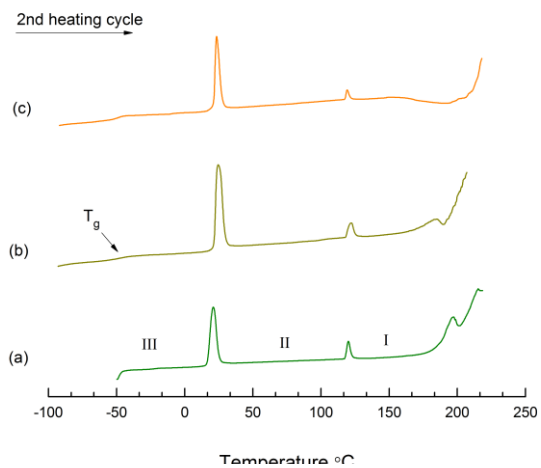


Figure S4. DSC thermograms of (a) Annealed [Choline][DHP], (b) 8 mol% TfOH + [Choline][DHP] and (c) 12 mol% TfOH + [Choline][DHP] samples.

5 The 8 mol% TfOH sample was annealed and the 12 mol% TfOH sample was non annealed but all DSC traces were reported for the second heating cycle.

10 Table S3. Glass transition temperatures (T_g), heat capacity change (ΔC_p) values for the glass transitions and enthalpy change (ΔH) values as calculated from the peak area of different solid-solid phase transitions for 8 mol% TfOH and 12 mol% TfOH containing [Choline][DHP] samples. The DSC data of the pure material is given for reference.

Material	T_g T °C \pm 2 °C	(T_g) ΔC_p (J/(g K) \pm 5%)	III>>II ΔH / kJ mol ⁻¹ \pm 5%	II>>I ΔH / kJ mol ⁻¹ \pm 5%
Annealed [Choline][DHP] 2 nd heating cycle	-22	25	5.5	1
8 mol% TfOH + [Choline][DHP]	-46	55	6.2	0.9
12 mol% TfOH + [Choline][DHP]	-48	82	3.9	0.3

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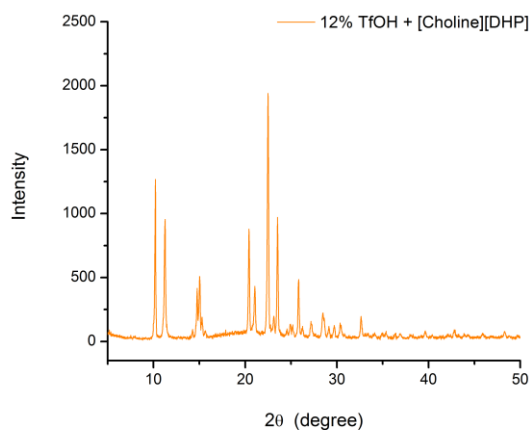


Figure S5. Powder X-Ray diffraction patterns of 8 mol% TfOH and 12 mol% TfOH containing [Choline][DHP] samples at 22 ± 1 °C temperature.

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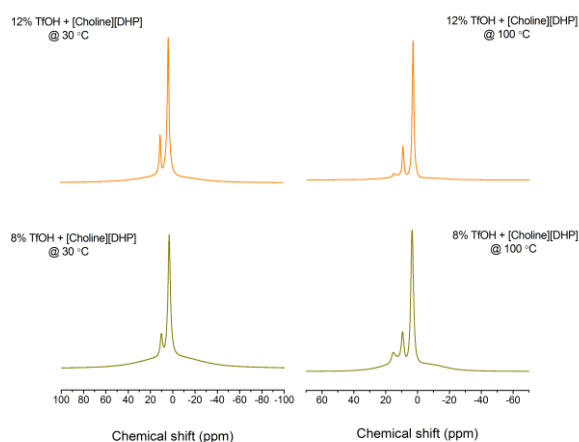
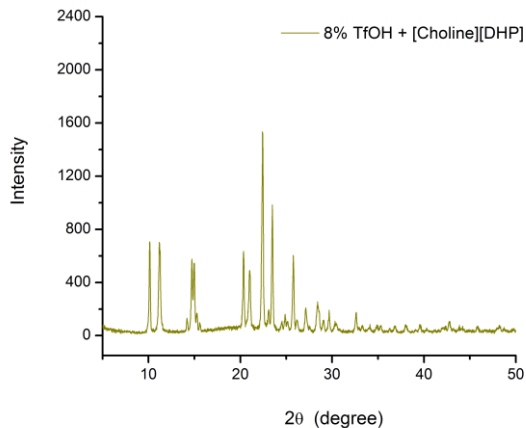


Figure S6. ¹H NMR spectra of 8 mol% TfOH, 12 mol% TfOH containing [Choline][DHP] samples at 30 and 100 °C \pm 1 °C.

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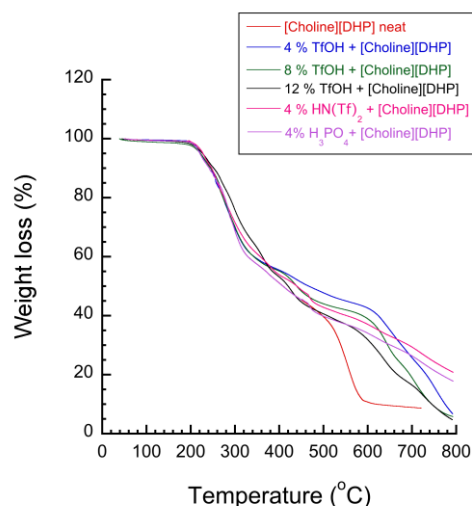
Supplementary Information

Table S4. ¹H NMR full width at half maximum (FWHM) linewidths, chemical shift values and % area of NMR peaks for 8 mol% TfOH and 12 mol% TfOH containing [Choline][DHP] samples at 30 and 100 °C. The NMR spectra of these samples were deconvoluted and simulated by the dmfit program.

8 mol% TfOH + [Choline][DHP] @ 30 °C	Area (%)	Chemical shift (ppm)	FWHM (Hz) ± 100 Hz	8 mol% TfOH + [Choline][DHP] @ 100 °C	Area (%)	Chemical shift (ppm)	FWHM (Hz) ± 100 Hz
Broad peak	59	0.6	19000	Broad peak 1	39	2	12500
Narrow peak [H(1) to H(5)]	37	3.2	800	Narrow peak [H(1) to H(5)]	42	3.4	600
Narrow peak 1 [H(6) to H(8)]	4	10.2	800	Narrow peak 1 [H(6) to H(8)]	9	9.4	600
Narrow peak 2 [H(6) to H(8)]	–	–	–	Narrow peak 2 [H(6) to H(8)]	10	14.7	1400
12 mol% TfOH + [Choline][DHP] @ 30 °C	Area (%)	Chemical shift (ppm)	FWHM (Hz) ± 100 Hz	12 mol% TfOH + [Choline][DHP] @ 100 °C	Area (%)	Chemical shift (ppm)	FWHM (Hz) ± 100 Hz
Broad peak	46	6.8	7300	Broad peak 1	9	2.8	4000
Narrow peak [H(1) to H(5)]	47	3	500	Narrow peak [H(1) to H(5)]	68	3.2	300
Narrow peak 1 [H(6) to H(8)]	7	10.3	400	Narrow peak 1 [H(6) to H(8)]	17	9.5	300
Narrow peak 2 [H(6) to H(8)]	–	–	–	Narrow peak 2 [H(6) to H(8)]	6	15	800

²⁰ [Choline][DHP], where the H₂O protons were found to be exchanging with the OH group protons of the [DHP] anion¹.

Thermal Stability of the acid/[Choline][DHP] mixtures



⁵ Figure S7. Single scan TGA plot of pure [Choline][DHP], 4, 8 and 12 mol% TfOH containing [Choline][DHP] and 4 mol% HN(Tf)₂ and H₃PO₄ containing [Choline][DHP] samples at a scan rate of 10 °C/min.

Table S5. Isothermal TGA data of annealed, as-prepared and acid containing samples of [Choline][DHP].

Material	Weight loss (%) ± 5 % at 120 °C isothermal temperature
Annealed and as-prepared [Choline][DHP]	2
4 mol% TfOH + [Choline][DHP]	2
8 mol% TfOH + [Choline][DHP]	1.8
12 mol% TfOH + [Choline][DHP]	1
4 mol% H ₃ PO ₄ + [Choline][DHP]	2
4 mol% HN(Tf) ₂ + [Choline][DHP]	1.8

²⁵ Table S5 also indicates a reductions in the weight loss for 8 and 12 mol% TfOH containing sample and 4 mol% HN(Tf)₂ containing sample. This weight loss data suggest less bound water in the fluorinated anion containing samples compared to the neat plastic crystal or H₃PO₄ acid containing sample. This observation can be explained by the fact that the Tf⁻¹ anion of TfOH and N(Tf)₂⁻¹ anion of HN(Tf)₂ are comparatively weakly basic compared to the [DHP] anion and therefore shows less affinity towards water. Another important observation from the isothermal TGA data is the same weight loss seen in as prepared and annealed [Choline][DHP] samples, which eliminates the possibility of the annealing process merely being a drying process.

Notes and references

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References

1. L. S. Cahill, U. A. Rana, M. Forsyth and M. E. Smith, *Physical Chemistry Chemical Physics*, 2010, **12**, 5431-5438.