Characteristics of Ignition delay of hypergolic ionic liquids combined with 1-amino-4-methylpiperazine

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Experimental Details

The typical procedure for synthesizing a highly energetic ionic liquid was previously reported elsewhere (1-3). Briefly, 1-methyl-1*H*-imidazole (99%, TCI) was dissolved in acetonitrile, and iodomethane or iodoethane was added dropwise to the solution, followed by stirring for 48 hours to allow for further reaction. The residual iodomethane and solvent were then removed through evaporation. By dissolving the corresponding parent iodide salts (R-I) in methanol and performing ion exchange with excess silver dicyanamide, 1-ethyl-3-methylimidazolium dicyanamide [EMIM][C_2N_3] and 1,3-dimethyl imidazolium dicyanamide [DMIM][C_2N_3] were obtained. For comparison, the synthesis was also performed without the solvent, and therefore, the direct reaction between alkyl iodide and 1-methyl-1*H*-imidazole was carried out using an ice bath to remove solvent impurities and minimize solvent usage. The subsequent steps were the same, with the solid product being recovered and followed by ion exchange as described above. The final product was obtained through filtration and subsequent removal of methanol using a rotary evaporator. At each reaction step, the structures of the compounds were analyzed using ^{1}H and ^{13}C NMR spectra.

In order to measure the vapor pressure, the sample bottle containing the ionic liquid with AMPZ was connected to the vacuum line and evacuated to 10^{-4} Torr using the freeze-thaw cycle to remove the dissolved impurities such as carbon dioxide. Subsequently, the pressure increased, and vapor pressure was measured directly at 298 K after the thermal equilibrium. The adsorption temperature was controlled at 298 ± 0.1 K using a constant-temperature circulation bath (Vision Scientific, VS-190CS).

The Shimadzu IR Prestige-21 instrument was used to record FT-IR spectra of a diluted sample consisting of the ionic liquid and AMPZ, which was prepared by dropping the sample diluted with acetone onto KBr pellets. The prepared samples were analyzed subsequent to solvent evaporation.

Thermogravimetric and differential thermal analyses (TG/DTA) of both [EMIM][C_2N_3] and [DMIM][C_2N_3] were conducted with a Shimadzu thermogravimetric analyzer (DTG-60H). Weight loss was measured as the temperature was increased to 673 K at a rate of 10 K/min under a nitrogen flow of 50 mL/min (Sinil, 99.9%).

For ignition delay (ID) time measurements, a single drop of the synthesized DCA-substituted compounds containing the desired amount of AMPZ was felled onto white fume nitric acid (WFNA, >93%, Daejung) in a 25 mL bottle. The subsequent explosion was observed using a high-speed camera with 1000 frames per second, where each frame corresponded to 1 msec. In this study, the ID time was defined as the time interval between the drop and the flash, and the measurement was repeated three times to ensure reproducibility.

DFT calculations for ILs were performed using the CP2K software and QUICKSTEP module, with consideration given to the impact of core electrons and nuclei on valence electrons through the use of Geodecker-Teter-Hutter (GTH) pseudopotentials. The treatment of valence electrons utilized triple-z double-polarized basis sets and an energy cutoff of 500 Ry. The Perdew, Burke, and Ernzerhof (PBE) exchange-correlation functional was employed[1], and van der Waals interactions were accounted for

with Grimme's DFT-D3 scheme. The IL and its corresponding complex were quenched in an isolated state, with nuclear coordinates and wave function gradients converging at 10^{-5} and 10^{-6}, respectively.

Using the Packmol program[2], the optimized structure was packed within a domain of 8000 $Å^3$ in the starting configuration, while keeping the number of ion pairs between 20-40 and the number of AMPZ consistent with the composition used for ignition delay measurement. For the BOMD simulation, a double-zeta valence polarized basis set with an energy cutoff of 400 Ry was utilized to manage the valence electrons, with all other conditions remaining the same. To achieve equilibrium, the Nose-Hoover thermostat was applied to raise the temperature of the system to 373 K, followed by a 5 ps production run under the NVT ensemble. The time step for the production run was 0.5 fs. Finally, the trajectory obtained was analysed with the TRAVIS program, which tracked the mean square displacement and radial distribution function.

Reference

1   J.P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865-3868.
2   L. Martínez, R. Andrade, E. G. Birgin, J. M. Martínez, *J. Comput. Chem.*, 2009, **30**, 2157-2164.

Supplementary Figures
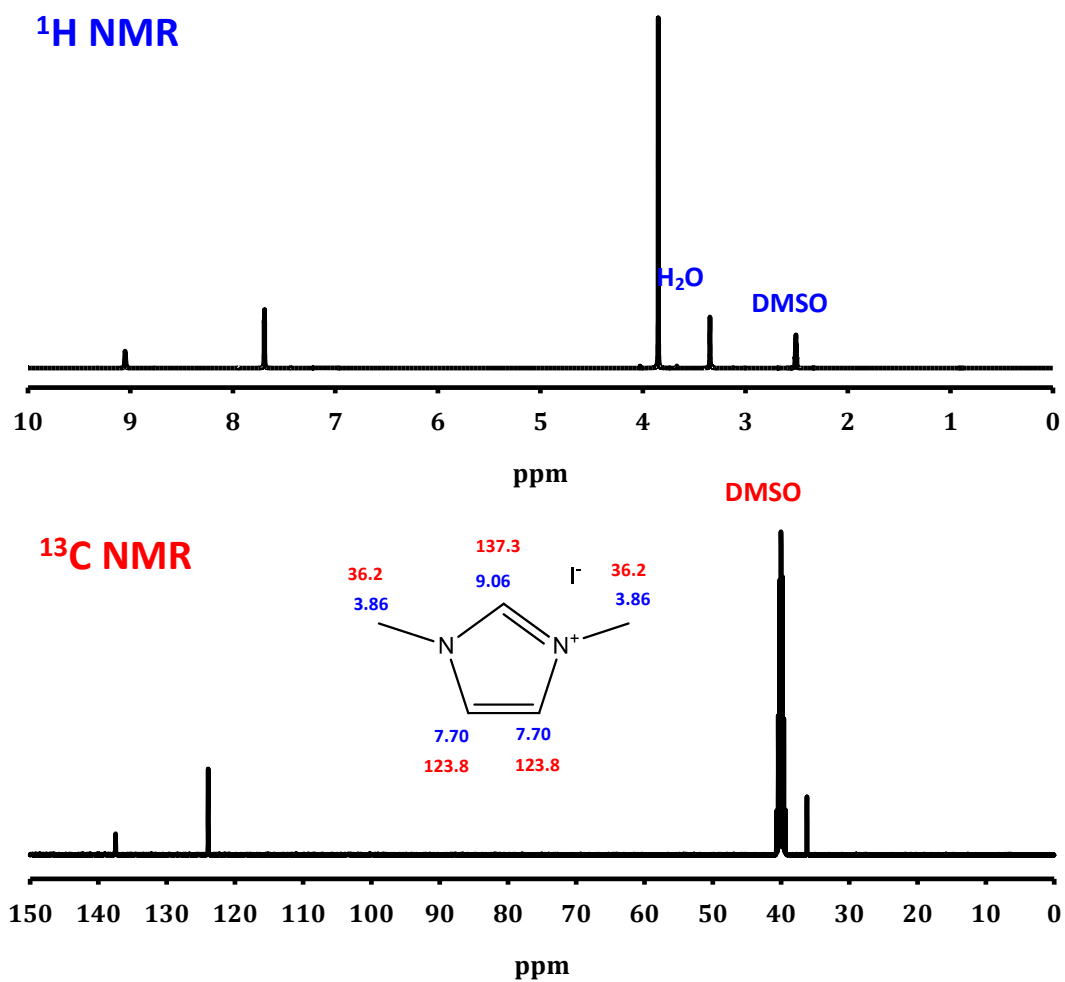
Fig.S1 ^{1}H and ^{13}C NMR spectrum of [DMIM]I in which the inset shows the corresponding chemical shift.

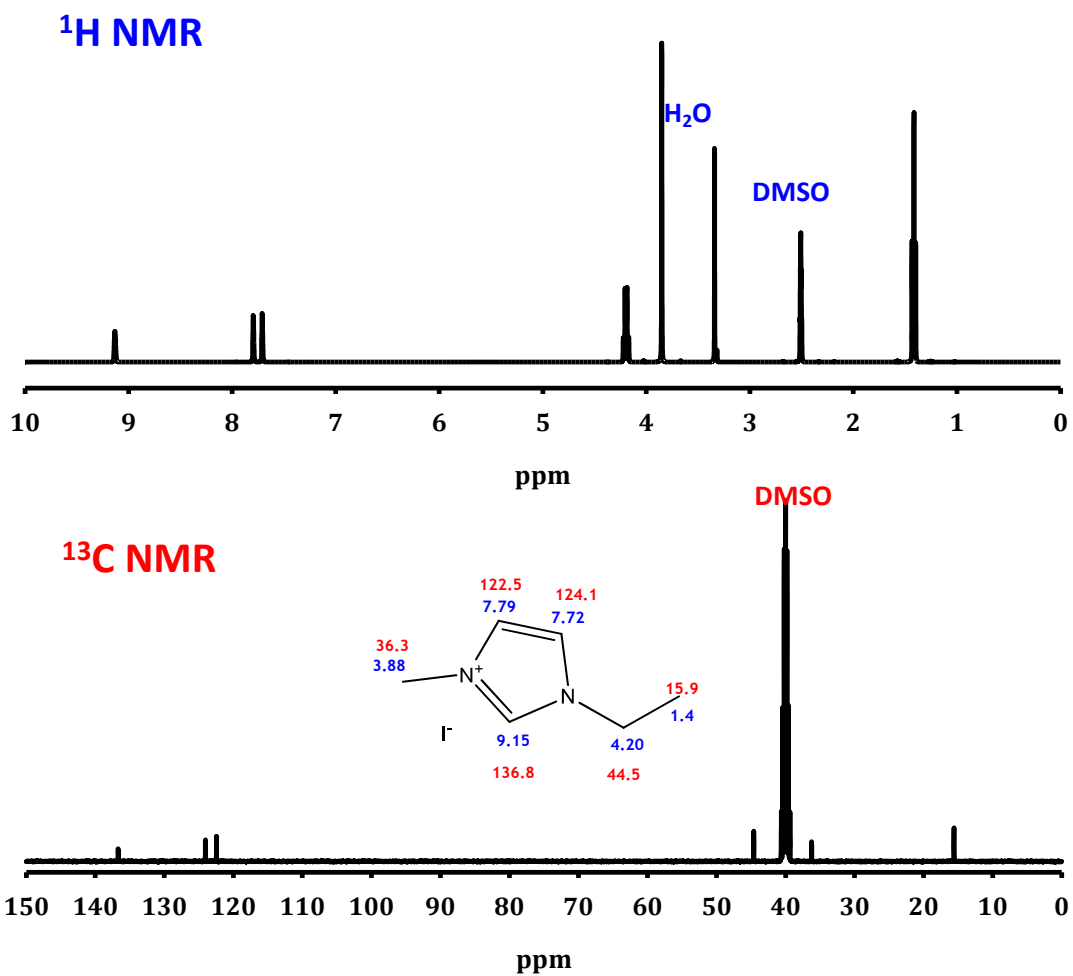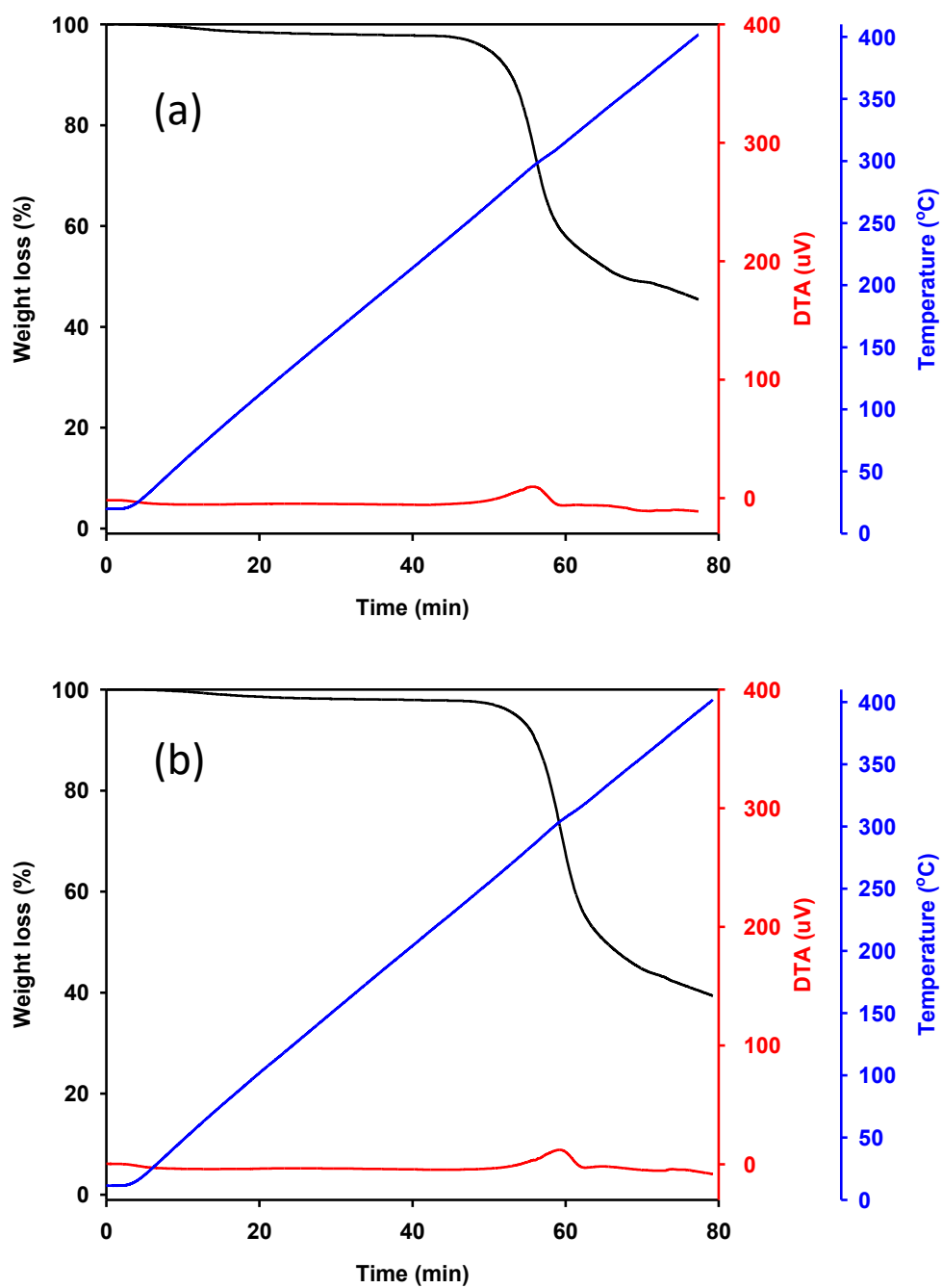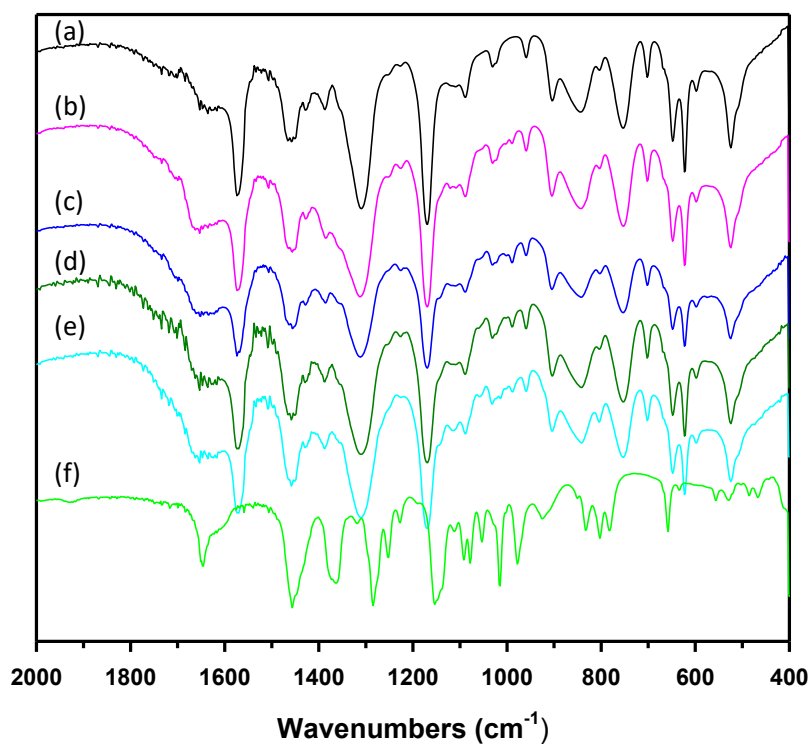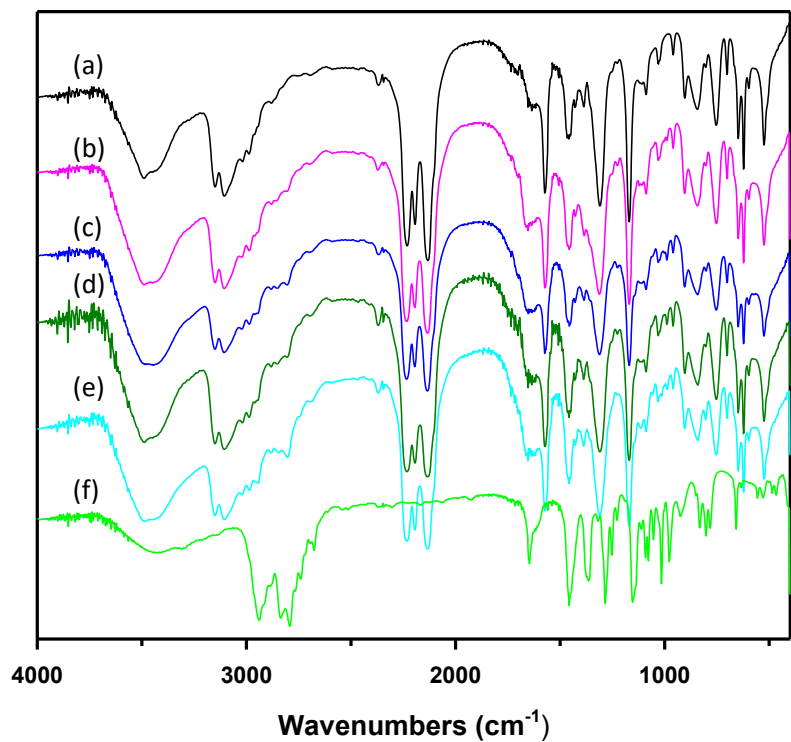**Fig.S2** ^{1}H and ^{13}C NMR spectrum of [EMIM]I in which the inset shows the corresponding chemical shift.

Fig.S3 TG and DTG of (a) [DMIM][C_2N_3] and [EMIM][C_2N_3] under nitrogen to examine the decomposition temperature. Both samples were found to decompose above 473 K.
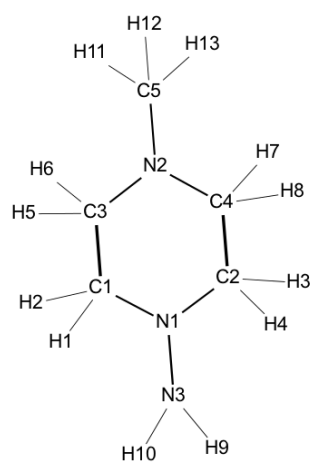
Fig.S4 FT-IR spectrum of (a) [EMIM][C_2N_3], (b) [EMIM][C_2N_3]+10 wt%AMPZ, (c) [EMIM][C_2N_3]+20 wt%AMPZ, (d) [EMIM][C_2N_3]+30 wt%AMPZ, (e) [EMIM][C_2N_3]+40 wt%AMPZ, and (f) AMPZ.
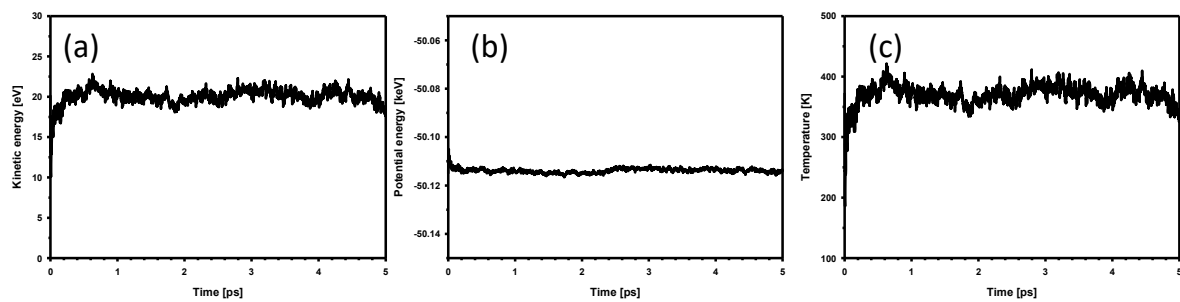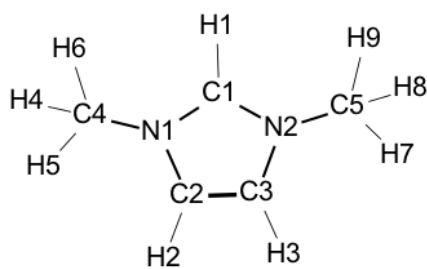
Fig.S5 The preliminary result of molecular dynamic simulation on the [DMIM][C_2N_3] and AMPZ aggregate in 20 Å × 20 Å × 20 Å using Nose-Hoover thermostat at 373 K for 5 ps: (a) the kinetic energy, (b) potential energy and (c) temperature.
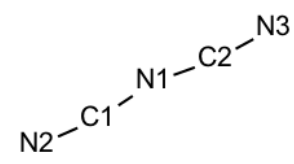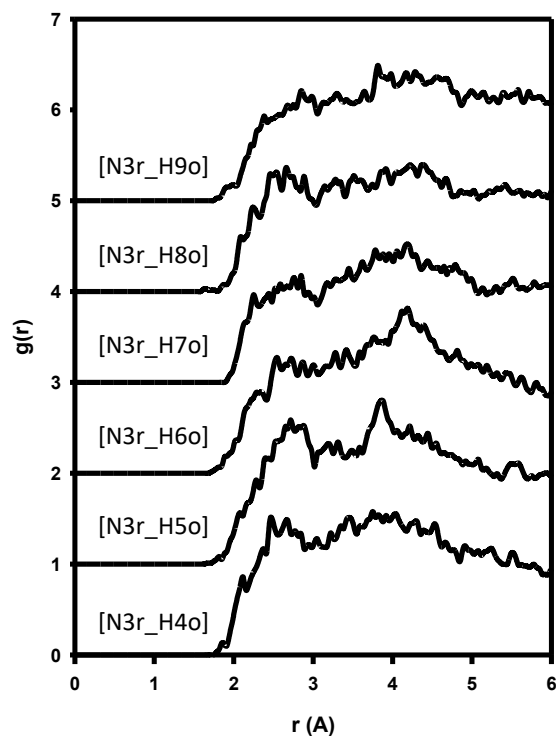
(a)   (b)   c)

Fig.S6 The molecular structures are generated in the TRAVIS program[2] to extract the radial distribution function o for AMPZ, [DMIM]$^+$, and [C$_2$N$_3$]$^-$.

Fig.S7 Radial distribution function of the terminal nitrogen in dicyanamide ion to hydrogen in the imidazolium cation.   Both molecular structures are shown in ESI with the label, which is generated from the analysis using the TRAVIS program.   The inset label denoted the RDF for N3 in the reference molecule, dicyanamide, and the Hn in the observed molecule, DMI cation.
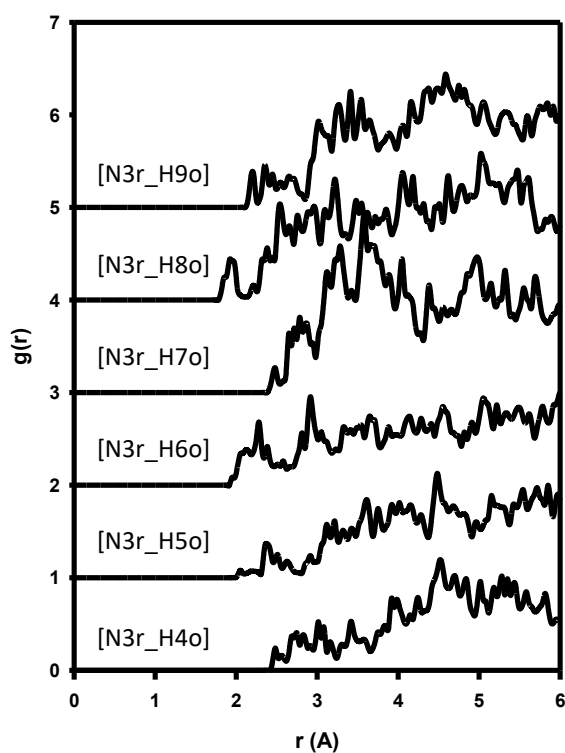
Fig.S8 Radial distribution function of the terminal nitrogen in AMPZ ion to hydrogen in the imidazolium cation.   Both molecular structures are shown in ESI with the label, which is generated from the analysis using the TRAVIS program.   The inset label denoted the RDF for N3 in the reference molecule, AMPZ and the Hn in the observed molecule, [DMIM]$^+$ cation.