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Ultrafast Igniting, Imidazolium based Hypergolic Ionic Liquids with Enhanced Hydrophobicity

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Exploring ultrafast igniting and hydrolytically stable ionic liquids (ILs) has a wide scope in hypergolic rocket fuels. Hydrophobicity of IL, induced by a smart change in alkyl substituents of imidazolium cation with energy-rich cyanoborohydride, $[BH_3CN]^-$ and dicyanamide, $[DCA]^-$ anions were examined for the first time. The physico-chemical properties and performance evaluation of ILs were also studied. Consequently, hydrolytic stability in terms of moisture study of all the ILs was thoroughly investigated under standard environmental conditions. The analysis indicates that the IL **14**, 1-allyl-3-octyl imidazolium cyanoborohydride is most hydrophobic and hydrolytically stable. The studies evaluating the role of cationic hydrocarbon chain and nature of anions of ILs on the properties of hypergolic fuel were carried out. All the ILs are liquid at room temperature and have exhibited a positive heat of formation. IL **10**, 1,3-diallyl-imidazolium cyanoborohydride exhibited the shortest ignition delay of 1.8 ms with WFNA and IL **11**, 1-allyl-3-ethyl imidazolium cyanoborohydride presented the lowest viscosity of 16.62 mPa·s. Therefore, these ILs can be suggested as potential candidates for replacing acutely toxic and carcinogenic, hydrazine and its methylated derivatives as hypergolic fuel.

Introduction

Hypergolic fuels (Monomethyl Hydrazine, MMH; Unsymmetrical Dimethyl Hydrazine, UDMH) present unique importance as a liquid rocket fuel because it has a self-igniting tendency while coming in contact with storable liquid oxidizers. Due to the peculiar properties of the fuel, it eliminates the external ignition source and thus, the system becomes more reliable. In addition, the hypergolic system offers the start-restart capability to the engine during multiple operations. Hypergolicity is measured in terms of ignition dealy (ID), which is a time lapse between physical contact of fuel and an oxidizer, and the appearance of the flame.[1,2] A shorter ID (< 50 ms) was in scope for the safe and reliable functioning of the liquid rocket engine.[3] However, hunting for the novel alternatives of MMH and UDMH, having ID < 5 ms (i.e Ultrafast ID) with attractive properties has great demand in space propulsion.[4] The ultrafast ID has significance as it lowers the risk of detonation and avoids an accident that may occur during space mission.

While developing the new rocket fuel for space propulsion, it is essential to consider the desirable properties such as liquid over temperature range -40 to +60 °C, large density, low viscosity and ignition delay, preferably positive heat of formation (ΔH_f), low molecular weight exhaust products, high specific heat and storage stability, minimum toxicity and cost.[5] Ionic liquids (ILs, melting below 100 °C[6,7]) are emerging very fast in the field of hypergolic fuel because of their unique properties such as negligible vapor pressure, liquideous over wide temperature range, low viscosity, high density, easy to synthesize by exchanging anion and cation, and hypergolic with storable oxidizers.[8–11] Therefore, the research community has immensely relied on ILs, which may have the potential to replace the conventional, acutely toxic, carcinogenic and highly volatile, MMH and UDMH fuels.[12] Due to the continuous endeavors by researchers, ILs are evolving as green hypergolic fuel in space propulsion, by gaining the desirable properties of rocket fuel. Theoretically, innumerable ILs are possible, but only a few of them will exhibit the experimental ignition test with storable oxidizers. Ignition is the redox (fuel as base and oxidizer as acid) type of reaction of hypergolic fuel,[13] which gets augmented due to the incorporation of an energy-rich group such as -C≡N, B-H, -N=N, -C=C-, -C≡C-, -C≡N, $-NH_2$, etc. in ILs. Therefore, it is essential to consider these groups, while designing the architecture of new hypergolic ILs. Sengupta et al. predicted the significance of energy-rich groups in hypergolic ILs using theoretical calculations.[14,15] Therefore the resultant ILs have been developed by culminating various energy-rich anions such as borohydride $[BH_4]^-$,[16,17] cyanoborohydride $[BH_3CN]^-$,[18–20] dicyanoboro-hydride $[BH_2(CN)_2]^-$,[21,22] nitrate $[NO_3]^-$,[22,23] azide $[N_3]^-$,[24–26] dicyanamide $[DCA]^-$,[4,18,22,25–32] nitrocynamide $[NCA]^-$,[22,25–28,33] aluminium borohydride $[Al(BH_4)_4]^-$,[34] $[BH_3(CN)BH_2(CN)]^-$,[35] bis(borono)hypophosphite $[PH_2(BH_3)_2]$,[36] with various

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saturated, unsaturated heterocyclic aromatic and non-aromatic cations.

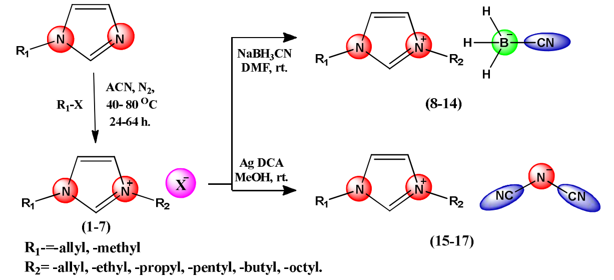
It was found that the ILs containing hydrogen rich anions such as $[BH_4]^-$, $[BH_3CN]^-$, $[BH_2(CN)_2]^-$, $[Al(BH_4)_4]^-$, and $[BH_3(CN)BH_2(CN)]^-$ manifested ultrafast ignition delay due to easy combustion with storable oxidizers. However, the hydrolytic stability of hypergolic ILs is of great concern in order to choose as a rocket fuel, because it gives poor water stability, while exposed in the environment.[21,35] Hence, it affects the physico-chemical properties of the IL, which is essential for liquid rocket fuel and consequently, hampers the performance of rocket engine. Therefore, development of ILs having ultrafast ignition delay with enhanced hydrophobicity is a very challenging task to accomplish. Overall, it is observed that the anions $[BH_2(CN)_2]^-$, $[BH_3(CN)BH_2(CN)]^-$ and $[PH_2(BH_3)_2]^-$ are found to be hydrolytically stable than corresponding ILs of $[BH_4]^-$, $[BH_3CN]^-$ anion.[21,35] However, synthesis of $[BH_2(CN)_2]^-$, $[BH_3(CN)BH_2(CN)]^-$, requires toxic $HgCl_2$ and increases the synthesis complication rendering low yield whereas, $[PH_2(BH_3)_2]^-$ exhibits low thermal stability and also, associated with synthesis complication. Therefore, the advancement in the area of probing new ultrafast igniting, hydrolytically stable ILs fuel has taken renewed interest.[35] The objective of this investigation also falls in the similar category.

In recent years, our research group also involved in finding alternatives to the existing liquid propellant fuels by testing various combinations of ILs.[18,37] In this article, development of new ultrafast igniting, hydrophobic ILs containing fuel rich $[BH_3CN]^-$ and $[DCA]^-$ with modified imidazolium cations have been explored. The $[BH_3CN]^-$ anion is known to improve ID by undergoing facile decomposition of B-H bond with a storable oxidizer and imidazolium-based salts are most likely result in a thermodynamically favorable liquid at room temperature. Additionally, these ILs are easy to synthesize with higher yield. Subsequently, the hydrolytic stability of ILs was improved by employing the unsaturated and long hydrocarbon side chain to imidazolium cation. The hydrophobic behavior of new ILs was examined by subjecting them to moisture analysis test. An attempt was also made to achieve the short ID of 5 ms with WFNA. Indeed, the impact of the side chain of imidazolium cation brings the change in physico-chemical and combustion properties of ILs. The developed hypergolic ILs are exhibiting reasonable fuel performance and properties including low viscosity, high density and thermal stability, low melting temperature, ultra short ignition delay with WFNA, positive ΔH_f, comparable specific impulse (I_{sp}) and high-density specific impulse (ρI_{sp}).Therefore, it could demonstrate great interest in the field of hypergolic rocket fuels.

Results and discussion

Synthesis

The imidazolium salts **1-7** were obtained by quaternization of allyl or methyl imidazole using n-alkyl or allyl halide. They were purified with ethyl acetate, dried and analyzed prior to the second step. ILs **8-17** were synthesized by metathesis reactions of purified salts **1-7** with sodium cyanoborohydride or silver dicyanamide (Scheme 1). The synthesis of cyanoborohydride based ILs **8-14** was efficiently carried out in DMF. ILs **8** & **9** were colorless and **11-14** were faint yellow liquids with good yields (78-92%). ILs **15-17** were obtained by metathesis of **3**, **6** & **7** salts with silver dicyanamide in methanol for 24 h in dark light (to avoid oxidation in presence of light). The reaction gave brown colored liquids with reasonable yields (78-83%). All the ILs were purified and stored in a capped vial under N_2 atmosphere. ILs **8-17** were soluble in acetonitrile, dichloromethane, chloroform, methanol, ethanol, acetone and insoluble in less polar solvents like diethyl ether and hexane.



1: R_1= -methyl, R_2= pentyl, X^-= Br
2: R_1= -methyl, R_2= octyl, X^-= Cl
3: R_1= -allyl, R_2= -allyl, X^-= Cl
4: R_1= -allyl, R_2= -ethyl, X^-= Br
5: R_1= -allyl, R_2= propyl, X^-= Br
6: R_1= -allyl, R_2= butyl, X^-= Cl
7: R_1= -allyl, R_2= octyl, X^-= Cl
8: R_1= -methyl, R_2= pentyl
9: R_1= -methyl, R_2= octyl
10: R_1= -allyl, R_2= -allyl
11: R_1= -allyl, R_2= -ethyl
12: R_1= -allyl, R_2= propyl
13: R_1= -allyl, R_2= butyl
14: R_1= -allyl, R_2= octyl
15: R_1= -allyl, R_2= -allyl
16: R_1= -allyl, R_2= butyl
17: R_1= -allyl, R_2= octyl

Scheme 1. Synthesis of new imidazolium-based ILs.

Characterisation

ILs **8-10, 13, 14 & 17** were water insoluble and ILs **11, 12, 15 & 16** were water soluble as confirmed by visual test at 30 °C. The structural identification of ILs was carried out by using FT-IR, ^1H & ^{13}C-NMR and HR-MS (Supporting information, SI-A). The physico-chemical properties of ILs **8-17** including viscosity (η), density (ρ), melting temperature (T_m), decomposition temperature (T_d), the heat of combustion (ΔH_c) and heat of formation (ΔH_f) were calculated. The performance evaluation parameters such, ID, I_{sp} and ρI_{sp} were also measured/computed.

Hydrolytic stability

Hydrolytic stability of hypergolic ILs has vital importance as they are salts, being hygroscopic absorbs a significant amount of moisture, though they are known to be hydrophobic.[38] This impurity lowers the quality of ILs that are being utilized for various applications.[39,40] In bipropellant, quality of fuel has key significance as it affects the performance of rocket engine. The handling and storage of ILs for a longer duration could absorb the moisture present in the environment. Longer exposure of some of the borane based compounds in moisture environment formed white precipitation.[41] ^1H-NMR study of one of the hydrophilic IL, **11** in D_2O revealed the chemical change when the acidic C2-H of imidazolium cation is replaced by Deuterium (Supporting Information fig. SI-A35). It confirms

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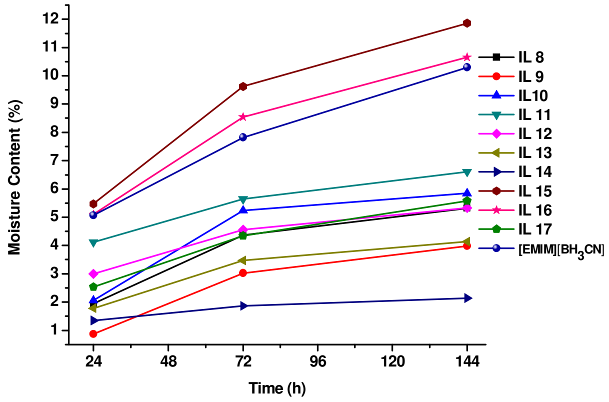

Fig. 1 Moisture content (%) of ILs **8-17**and **[EMIM][BH$_3$CN]**

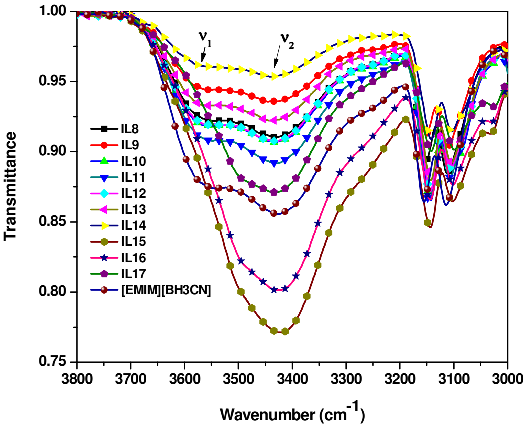

Fig. 2 FT-IR study of ILs **8-17** and **[EMIM][BH$_3$CN]**

the instability of imidazolium cation in water. Therefore understanding the water stability of IL has special worth in liquid hypergolic fuel.

In this investigation, the hydrolytic stability of all the synthesized ILs **8-17** and the proven ultrafast igniting IL, [EMIM][BH$_3$CN][20] were evaluated by exposing them in Orbital Incubator Shaker (SAII-OS-S25, India) containing 50.89 (±5) % moisture content and 32 (±2) °C temperature for several days at 100 rpm. Finally, the amount of moisture content absorbed was estimated by using UniBloc Moisture Analyzer (Shimadzu, MOC63u, halogen heater). Three readings of each experiment were recorded and the average mean value was noted. As evident from Fig. 1, IL **15** absorbs the highest (11%) whereas IL **14** absorbs the lowest amount of water content (1.5%). The ILs **8, 10, 12 & 17** exhibited nearly same affinity towards water. Additionaly, ILs **8-17** & [EMIM][BH$_3$CN] were analyzed by FT-IR spectrometer[42] with Zn-Se ATR crystal and gold coated mirror (Fig. 2). The moisture content absorbed by ILs was observed by the transmittance of the H_2O in FT-IR. Lower the transmittance of O-H bond, higher the moisture content present in ILs. It is found that ILs **8-14** and [EMIM][BH$_3$CN] exhibited the IR band at υ_1 (3570-3556 cm^{-1} of asymmetric stretching) & υ_2 (3430-3420 cm^{-1} of symmetric stretching) and ILs **15-17** display only one broad band at 3425-3420 cm^{-1} due to the strong coupling of υ_1 & υ_2 frequency band for O-H bond of water. It is due to the stronger interaction of [DCA]$^-$ and weaker interaction of [BH$_3$CN]$^-$ with H_2O. These two techniques were satisfying in predicting the trend of moisture content absorbed by ILs, except IL **17**. In moisture analysis study, IL **17** exhibits lower water content, however, IR study shows maximum absorbance. Perhaps, the bulkiness of the molecule due to its long octyl chain and the large voids between the anion and cation must have retained the water molecule which might have resulted different trend in Moisture Analyzer. Thus, the Moisture Analyzer and FTIR data interpret that the ILs that absorb low moisture content are having enhanced hydrophobicity than other ILs. The reported IL, [EMIM][BH$_3$CN] absorbs high moisture content than ILs **8-14** and hence, exhibit lower hydrolytic stability.

Overall, it is important to note that only ILs **15** & **16** have shown increasing trend of moisture content analysis while the others have tried to attain the equilibrium.

Hydrophobicity of the ILs was improved with the smart choice of hydrocarbon chain length of cation with the same anion. ILs **9** & **14** having octyl chain length of cation are hydrophobic and exhibit high moisture stability. It is due to the high molar volume of ILs reduces the interaction with water.[43] Nevertheless, IL **10** also exhibits hydrophobicity; though having shorter hydrocarbon chain. In this case, unsaturated hydrocarbon chain may diminish the hydrogen bond interactions with water and results in the hydrophobicity. The [DCA]$^-$ based ILs were found to have high moisture affinity (except IL **17**) than the [BH$_3$CN]$^-$ based ILs of the same cation. The synthesized [BH$_3$CN]$^-$ based ILs have showed better moisture stability than the reported IL, [EMIM][BH$_3$CN]. No doubt, new family of hydrolytically stable hydrophobic ILs based on [BH$_3$CN] anion has emerged in present findings.

Thermal Properties

The thermal properties of ILs such as glass transition temperature (T_g) and decomposition temperature (T_d), are important to measure the operational temperature range of hypergolic ILs. A liquid over wide temperature range ensures that IL can be safely stored. The T_g of all the synthesized ILs were found to be < -50 °C except IL **9** (T_m = -38.22 °C). Therefore, it fulfills the desirable property ($T_m \geq -40$ °C) of liquid rocket fuel.[5] The T_d of ILs **8-17** was analyzed by Differential Thermal Analysis (DTA) in a nitrogen atmosphere at a heating rate of 20 °C min^{-1} (Table 1). The IL **10** exhibited the lowest T_d (242 °C) and IL **17** shows highest T_d (326 °C). The results depicts that the thermal stability of ILs is directly linked with the **type of** anion and hydrocarbon chain of the cation. The ILs **8-14** exhibited low thermal stability than ILs **15-17** because [BH$_3$CN]$^-$ undergoes easy decomposition as compared to the [DCA]$^-$. Furthermore, the allyl-substituted cation has

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Table 1. Physical and chemical properties, and performance parameters of ILs

ILs	T_m[a] (°C)	T_d[b] (°C)	ρ[c] ($g.cm^{-3}$)	η[d] (mPa·s)	$ΔH_c$[e] ($kJ.mol^{-1}$)	$ΔH_f$[f] ($kJ.mol^{-1}$)	ID[g] (ms)	I_{sp}[h] (s)	$ρI_{sp}$[i] ($s.g/cm^3$)
8	<-50	275	0.9251	38.17	-7207 (1.5)	217	4.7 (0.25)	234	300
9	-36.22	283	0.9056	85.90	-9267 (3.5)	371	31.2 (2.0)	236	301
10	<-50	247	0.9582	21.68	-6885 (2.5)	379	1.9 (0.1)	233	299
11	<-50	265	0.9533	16.62	-6350 (3)	237	3.1 (0.1)	232	296
12	<-50	256	0.9403	25.56	-7037 (1)	289	3.4 (0.15)	233	301
13	<-50	264	0.9310	32.62	-7749 (1.5)	366	4.0 (0.05)	234	302
14	<-50	265	0.9078	74.34	-10460 (2.5)	536	32.6 (4.6)	234	299
15	<-50	325	1.0861	20.00	-6325 (2.5)	425	16.9 (1.3)	227	304
16	<-50	324	1.0473	35.48	-7284 (2)	507	41.1 (3.1)	230	305
17	<-50	326	0.9976	47.72	-9983 (3.5)	665	272.0 (38)	233	302
[EMIM][BH_3CN][20,37]	<-50	221	0.9611	18.00	-5169	85.47	1.5	230	295
UDMH[44]	-57.2	62.3[j]	0.7860	0.492	-1989	51.63	4.8[16]	239	292

[a] Melting temperature , [b]Decomposition temperature was observed using DTA at heating rate 20 ˚$C.min^{-1}$, [c]Density at 25 ˚C, [d]Viscosity at 25˚C, [e]The average heat of combustion measured using ELECTRO CERAMICS Bomb Calorimeter BC 8000 with standard deviation, [f]Heat of formation. [g]Ignition delay measured with WFNA (98.40 % HNO_3) along with standard deviation, [h]Specific impulse measured using NASA-CEC-71 code, [i]Density specific impulse, [j]Boiling Point

lower thermal stability than alkyl substituted cation with the same anion. It was also observed that the size of the alkyl chain length of cation does not influence on the T_d. The T_d of BH_3CN based ILs was found to improve in comparison with proven IL, [EMIM][BH_3CN].

Density and viscosity

Density (ρ) and viscosity (Ƞ) are significant physical properties of liquid rocket fuel. It directly reflects on the propulsion performance of fuel. A high-density fuel offers an efficient loading of fuel with low space and therefore, it minimizes the dead weight of storage tank and possibly increases the range of space vehicle. As evident from Table 1, it is clear that the [BH_3CN]$^-$ based ILs **8-14** have density ≥ 0.91 $g.cm^{-3}$ which is comparable with reported [$BH_2(CN)_2$]$^-$, [$BH_3(CN)BH_2(CN)$]$^-$ based ILs.[20,35] ILs with dicyanamide anion **15-17** have density ≥ 1.0 $g.cm^{-3}$, which is higher than the [BH_3CN]$^-$ based ILs. Amongst the ILs **8-17,** the density varies with hydrocarbon chain length of cation as allyl > ethyl > propyl > butyl > pentyl > octyl, which is ascribed to the increasing molecular size of the cation. The low density of IL can be attributed interstices between cation and anion. A bulky cation cannot to the pack closely with anion.[45] Moreover, the densities of new ILs are comparable with known hypergolic ILs, and are much higher than the hydrazine-based fuel (e.g. UDMH, 0.79 $g.cm^{-3}$).[44] It indicates high loading capacity of ILs in rocket fuel tank.

Low viscosity of ILs is an eminent property for choosing the fuel for bipropellant formulation. The low viscous fuel aids facile transport of fuel from the tank to the combustion chamber, thus, favoring rapid mixing with oxidizer for instant combustion.[1] Amongst the ILs **8-17,** the IL **11** exhibited lowest viscosity of 16.62 mPa·s and it is lesser than the proven IL, [EMIM][BH_3CN]. Table 1, it can be seen that the viscosity varies with hydrocarbon chain length of cation as ethyl < allyl < propyl < butyl < pentyl < octyl. The increase in the chain length of cation obviously increases the viscosity of IL, it may be due to the increase in the hydrogen bonding and van der Waals' interaction of bulky cation. In addition, the type of anion also affects the viscosity of IL. The [DCA]$^-$ based ILs **15-17** possess lower viscosity than [BH_3CN]$^-$ based ILs (**10**, **13** & **14)** with the same cation. Most of the ILs **8**, **10-13** & **15-16,** have viscosity < 40 mPa·s except the ILs **9**, **14** & **17**. The high viscosity may be attributed to the long hydrocarbon chain length of a cation which lowers the mobility of IL.

Heat of formation and heat of combustion

Heat of formation ($ΔH_f$) and heat of combustion ($ΔH_c$) are noteworthy properties of rocket fuel, and higher the value more efficient is the fuel for space propulsion.[5,46] The experimental $ΔH_c$ of ILs **8-17** was estimated using adiabatic Electro Ceramics Bomb calorimeter. The experiment was performed in triplicate and the average values were noted. As depicted in Table 1, it is observed that ILs have $ΔH_c$ > -6300 $kJ.mol^{-1}$, which is higher than IL, [EMIM][BH_3CN] (-5169 kJ/mol) and UDMH (-1989 $kJ.mol^{-1}$).[44] The $ΔH_c$ is related to the molecular structure of IL, it increases with hydrocarbon chain length of cation as ethyl < allyl < propyl < butyl < pentyl < octyl for the same anion. Within the same imidazolium cation, the [BH_3CN]$^-$ based ILs gives higher $ΔH_c$ than the [DCA]$^-$ based ILs. It is because the [BH_3CN] based ILs liberates an additional

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ILs	Combustion reactions
8.	$C_{10}H_{20}BN_3 + 15.75\ O_2 \longrightarrow 10\ CO_2 + 10\ H_2O + 0.5\ B_2O_3 + 1.5\ N_2$
9.	$C_{13}H_{26}BN_3 + 20.25\ O_2 \longrightarrow 13\ CO_2 + 13\ H_2O + 0.5\ B_2O_3 + 1.5\ N_2$
10.	$C_{10}H_{16}BN_3 + 14.75\ O_2 \longrightarrow 10CO_2 + 8H_2O + 0.5\ B_2O_3 + 1.5N_2$
11.	$C_9H_{16}BN_3 + 13.75\ O_2 \longrightarrow 9CO_2 + 8H_2O + 0.5\ B_2O_3 + 1.5N_2$
12.	$C_{10}H_{18}BN_3 + 15.25\ O_2 \longrightarrow 10CO_2 + 9H_2O + 0.5\ B_2O_3 + 1.5N_2$
13.	$C_{11}H_{20}BN_3 + 16.75\ O_2 \longrightarrow 11\ CO_2 + 10\ H_2O + 0.5\ B_2O_3 + 1.5\ N_2$
14.	$C_{15}H_{28}BN_3 + 22.75\ O_2 \longrightarrow 15\ CO_2 + 114\ H_2O + 0.5\ B_2O_3 + 1.5\ N_2$
15.	$C_{11}H_{13}N_5 + 14.25\ O_2 \longrightarrow 11\ CO_2 + 6.5\ H_2O + 2.5\ N_2$
16.	$C_{12}H_{17}N_5 + 16.25\ O_2 \longrightarrow 12\ CO_2 + 8.5\ H_2O + 2.5\ N_2$
17.	$C_{16}H_{25}N_5 + 22.25\ O_2 \longrightarrow 16\ CO_2 + 12.5\ H_2O + 2.5\ N_2$

Scheme 2. Combustion equations of ILs

product B_2O_3 as confirmed by the powdered XRD analysis (JCPDS 00-006-0297) of combustion residue of IL **11** (Supporting Information, SI-C). Amongst all the ILs, the IL **14** gave highest ΔH_c (-10241 kJ.mol^{-1}) and IL **15** gave lowest ΔH_c (-6325 kJ.mol^{-1}). Thereafter, the ΔH_c values were used to determine the ΔH_f of ILs using combustion reactions (Scheme 2). The combustion products such as CO_2 (ΔH_f = -393.5 kJ.mol^{-1}), H_2O (ΔH_f = -241.8 kJ.mol^{-1}), N_2 (ΔH_f = 0 kJ.mol^{-1}), and B_2O_3 (ΔH_f = -1273.5 kJ.mol^{-1}) were considered for the calculation.[47] The ΔH_f is mainly dependent on the molecular structure of IL. Interestingly, ILs **8-17** have shown positive ΔH_f, and it is higher than IL, [EMIM][BH_3CN], which accomplishes the requirement of rocket fuel.

Specific impulse

The performance of fuel is measured in terms of 'specific impulse (I_{sp})', which is the total impulse per unit of the propellant provided to the system. A high I_{sp} indicates the superior range of a space vehicle for its mission and therefore, it has great importance in designing the rocket engine. The experimental ΔH_f and density of ILs **8-17** were considered to predict the I_{sp}. The theoretical I_{sp} was carried out at 2.4 X 10^6 Pa chamber pressure and 9.8 X 10^4 Pa atmospheric pressure using NASA-CEC-71 code.[48] The maximum I_{sp} was noted by employing the frozen flow condition at optimum oxidizer to fuel ratio (O/F). The theoretical I_{sp} values of ILs were found to be ≥ 227 s. It is very difficult to compare these I_{sp} values with the literature values. It is because various research group used different software codes and conditions for the measurement. The IL **9** has exhibited the highest I_{sp} of 236 s. The demonstrated I_{sp} is higher than the reported IL, [EMIM][BH_3CN] (230 s). Interestingly, the density specific impulse (ρI_{sp}) of ILs were found to be ≥ 296 s.g.cm^{-3}, which is superior than UDMH (292 s.g.cm^{-3}) as given in Table 1.

Ignition test

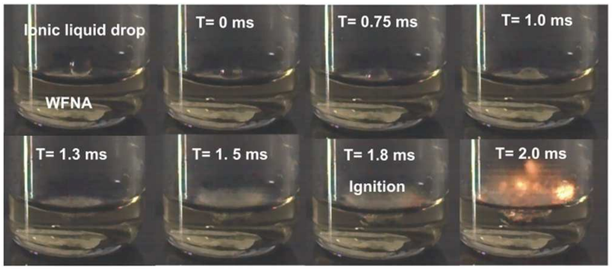

Fig. 3. Hypergolic test of IL **10**.

Ignition delay (ID) is another significant property for measuring the efficiency of liquid rocket fuel. A shorter ID is very desirable for the safe and reliable functioning of the liquid rocket engine.[2] On the contrary, a very high ID can cause the hard start of the engine and increases the possible risk of detonation. Therefore, the ID < 50 ms is the acceptable limit of liquid fuel in bipropellant engines.[3] To measure the precise ignition time of ILs an open cup drop test was performed at atmospheric pressure. Prior to the test, ILs **8-17** were dried in vacuum oven for 3 to 4 days at -760 mmHg & 80 °C. A 500 µl Hamilton syringe was used to drop 10 µl of IL fuel into the pool of cylindrical glass cuvette containing 1000 µl of oxidizer WFNA (HNO_3, 98.40%). The distance between the needle point (where from fuel drop) and oxidizer were kept constant during the ignition test. The sequence of images containing 2500 frame per second (fps) were recorded using Nikon 3700 fps high-speed camera (Fig. 3). The average speed and size of IL drop were measured and found to be 0.6 m/s and 3 mm respectively. The time lapse between initial contact of fuel drop to oxidizer and development of flame was measured. The ID was measured in triplicate and average ID was noted (Table 1).

In this context, the pre-ignition reactions play a vital role. If the amount of heat generated during the pre-ignition reaction is sufficient for taking the fuel to its ignition temperature, then only the ignition will take place. If the pre-ignition reaction fails to generate the required heat then ignition may not take place and only vigorous chemical reactions may be exhibited. Therefore, ID of ILs **8-17** varies from 1.9 to 272 ms. Fig. 1 shows that the pre-ignition reaction of IL **10** commenced at 1.0 ms and shortest ignition at 1.8 ms. ID also depends upon the chemical reactivity of fuel and oxidizer, the chamber pressure, the oxidizer and fuel weight ratio, etc. Even though, same fuel ID can be changed by the quality and purity of fuel and oxidizer. Therefore, it is very difficult to compare with the known literature data. IL **10** exhibited average shortest ID of 1.9 ms and IL **17** showed average longest ID of 272 ms. The ID studies reveal that the nature of cation and anion, both play a decisive role in determining the hypergolicity of IL. From Table 1, it is seen that the [BH_3CN] containing ILs (**8** & **11-14** except **9),** showed relatively shorter ID than dicyanamide based ILs (**15-17)**. It is due to the rapid oxidation of B-H bond with WFNA. For the same anion, the ID varies with nature of hydrocarbon chain of cation, too. The allyl substituted cation with the same anion gives lower ID than methyl substituted

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cation. It is because the allyl group undergoes easy oxidation with WFNA than a methyl group. However, the chain length of alkyl group of cation lowers the ignition delay as allyl < ethyl < propyl < butyl < pentyl < octyl. In summary, ILs **8** and **10-13** exhibit ultra short ID < 5 ms which is comparable with the proven fuel UDMH.

Experimental

Materials and Methods

The chemicals methyl imidazole (Aldrich), allyl imidazole (97%, Across organics), allyl bromide (Aldrich), ethyl bromide (Sigma-Aldrich), 1-chloropropane (98%, Sigma-Aldrich), butyl chloride (Sigma-Aldrich), pentyl chloride (Sigma-Aldrich), 1-chlorobutane (Sigma-Aldrich), diethyl ether (ACS reagent ≥ 99.8%, Sigma-Aldrich), sodium dicyanamide (Aldrich), sodium cyanoborohydride (95%, Alfa Aesar), silver nitrate (Alfa Aesar), ethyl acetate (≥ 99.5%, Merck), methanol (HPLC grade, Merk), acetonitrile and N’N-dimethylformamide (99.8%, Sigma-Aldrich) were used during the synthesis of ILs. All chemicals were used as received without further purification. FT-IR spectra were recorded on model BRUKER ALPHA FT-IR spectrometer with Zn-Se ATR crystal and gold coated mirror. ^{1}H and ^{13}C spectra were recorded in DMSO-d^{6} solvent on a Varian Mercury 500 MHz NMR spectrometer operating at 500 and 126 MHz. Chemical shifts are reported relative to the Me_4Si. The mass spectra were measured using HRMS-ESI (Advion, Model no. 14850) at positive and negative mode (range 10 to 1000 amu).The density and viscosity of ILs were measured by using Anton Paar densitometer and Lovis 2000 M Microviscometer at 25 °C. Hypergolic test of ILs was assessed by Y3-S1 Camera, 3700 fps, Nikon. DSC of ILs was measured by using Q20TA instrument 5, INDIUM as a reference with a heating rate of 10 ˚C min^{-1} and the T_d ILs were measured using Perkin Elmer- simultaneous analyser (STA) 6000 at heating rate of 20 °C.min^{-1}. Moisture analysis was carried out by using UniBloc Moisture Analyzer (Shimadzu, MOC63u) in which, a halogen heater was used during the measurements.

General Procedure for Synthesis of Halide Precursor (1-7)

1 mol of 1-R-imidazole was dissolved in 20 mL of dry acetonitrile under N_2 atmosphere. The alkyl halide (1.1 mol) was slowly added into the solution, the reaction mixture was refluxed for 24 to 64 h at 40-80 °C. All the salts were washed by using dry ethyl acetate and recrystallized by using methanol and stored under N_2 atmosphere (Yield: 85-90%).

1-methyl-3-pentyl-imidazolium bromide (1)

Methyl imidazole (0.10 mol, 11.05 g) charged with pentyl bromide (0.11 mol, 13.80 g) 70 °C for 48 h. Yield. 92 %. ^{1}H NMR (500 MHz, [D6]DMSO, 25 °C): δ = 0.83 (t, 3H; $\text{N-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-C}\underline{\text{H}}_3$), 1.15-1.23 (m, 2H; $\text{N-CH}_2\text{-CH}_2\text{-CH}_2\text{-C}\underline{\text{H}}_2\text{-CH}_3$), 1.23-1.33 (m, 2H; $\text{N-CH}_2\text{-CH}_2\text{-C}\underline{\text{H}}_2\text{-CH}_2\text{-CH}_3$) 1.78 (dt, 2H; $\text{N-CH}_2\text{-C}\underline{\text{H}}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$), 3.89 (s, 3H; N-CH_3), 4.21 (t, 2H; $\text{C}\underline{\text{H}}$), 7.83 (t, 1H; $\text{C}\underline{\text{H}}$), 7.90-7.93 (m, 1H; $\text{C}\underline{\text{H}}$), 9.44 ppm (s, 1H; CH); ^{13}C NMR (126 MHz, [D6]DMSO, 25 °C): δ = 14.20, 21.97, 28.05, 29.59, 36.27, 49.11, 122.71, 123.97, 136.99 ppm; FT-IR (BRUKER ALPHA, Zn-Se ATR): ῡ = 3136, 3059, 2943, 2863, 1730, 1628, 1567, 1458, 1377, 1338, 1297, 1240, 1166, 1112, 1035, 841, 750, 617 cm^{-1}.

1-methyl-3-octyl-imidazolium chloride (2)

Methyl imidazole (0.10 mol, 8.76 g) loaded with octyl chloride (0.11 mol, 17.45 g) at 80 °C for 60 h. A yellow coloured product obtained with Yield 87 %; ^{1}H NMR (500 MHz, [D6]DMSO, 25 °C): δ = 0.72 (t, 3H, $\text{N-CH}_2\text{-CH}_2\text{-C}_5\text{H}_{10}\text{-C}\underline{\text{H}}_3$), 1.11- 1.55 (m, 10H, $\text{-CH}_2\text{-CH}_2\text{-C}_5\underline{\text{H}}_{10}\text{-CH}_3$) 1.75 (m, 2H, $\text{N-CH}_2\text{-C}\underline{\text{H}}_2\text{-C}_5\text{H}_{10}\text{-CH}_3$) 3.92 (s, 3H, $\text{N-C}\underline{\text{H}}_3$) 4.25 (t, 2H, $\text{N-C}\underline{\text{H}}_2\text{-CH}_2\text{-C}_5\text{H}_{10}\text{-CH}_3$) 8.06 (s, 1H, $\text{C}\underline{\text{H}}$) 8.16 (s, 1H, $\text{C}\underline{\text{H}}$) 10.00 (s, 1H ,$\text{C}\underline{\text{H}}$); ^{13}C NMR (126 MHz, [D6]DMSO, 25 °C): δ = 14.18, 22.47, 25.96, 28.86, 28.98, 30.06, 31.63, 36.12, 48.95, 122.77, 123.93, 137.33 ppm; FT-IR (BRUKER ALPHA, Zn-Se ATR): ῡ= 3136, 3042, 2924, 2856, 2743, 1665, 1567, 1459, 1377, 1337, 1300, 1170, 1022, 879, 763, 653, 620 cm^{-1}.

1,3-diallyl-imidazolium Bromide (3)

Allyl imidazole (0.80 mol, 8.68 g) charged with allyl bromide (0.088 mol, 10.66 g) at 60 °C for 24 h. A brown coloured viscous product was obtained with Yield: 88%; ^{1}H NMR (500 MHz, [D6]DMSO, 25 °C): δ = 5.01 (d, 4H; $\text{N-C}\underline{\text{H}}_2\text{-CH=CH}_2$), 5.25-5.26 (m, 2H; $\text{N-CH}_2\text{-CH=C}\underline{\text{H}}_2$), 5.27-5.30 (m, 2H; $\text{N-CH}_2\text{-CH=C}\underline{\text{H}}_2$), 5.99-6.07 (m, 2H; $\text{N-CH}_2\text{-C}\underline{\text{H}}\text{=CH}_2$), 8.02 (d, 2H; $\text{C}\underline{\text{H}}$), 9.86 ppm (s, 1H, $\text{C}\underline{\text{H}}$); ^{13}C NMR (126 MHz, [D6]DMSO, 25 °C): δ = 51.23, 120.92, 123.0, 132.20, 136.51 ppm; FT-IR (BRUKER ALPHA, Zn-Se ATR): ῡ = 3126, 3058, 2970, 2853, 1644, 1558, 1422, 1332, 1294, 1157, 993, 938, 833, 747, 625, 558 cm^{-1}.

1-allyl-3-ethyl-imidazolium bromide (4)

Allyl imidazole (0.067 mol, 7.31 g) loaded with ethyl bromide (0.074mol, 8.10 g) at 70 °C for 30 h. A yellow coloured product was obtained with Yield. 90 %; ^{1}H NMR (500 MHz, [D6]DMSO, 25 °C): δ = 1.38 (t, 3H; $\text{-CH}_2\text{-C}\underline{\text{H}}_3$) 4.27 (q, 2H; $\text{N-C}\underline{\text{H}}_2\text{-CH}_3$) 4.95 (t, 2H; $\text{N-C}\underline{\text{H}}_2\text{-CH=CH}_2$), 5.98-6.06 (m, 2H; $\text{N-CH}_2\text{-CH=C}\underline{\text{H}}_2$), 5.26-5.31 (m, 2H; $\text{N-CH}_2\text{-CH=C}\underline{\text{H}}_2$) 5.98-6.08 (m, 1H; $\text{N-CH}_2\text{-C}\underline{\text{H}}\text{=CH}_2$), 7.90 (d, 1H; $\text{C}\underline{\text{H}}$), 8.04 (d, 1H; $\text{C}\underline{\text{H}}$), 9.62 ppm (s, 1H; $\text{C}\underline{\text{H}}$); ^{13}C NMR (126 MHz, [D6]DMSO, 25 °C): δ = 15.66, 44.74, 51.10, 122.78, 136.27 ppm; FT-IR (BRUKER ALPHA, Zn-Se ATR): ῡ = 3129, 3057, 2975, 2864, 1643, 1560, 1446, 1424, 1343, 1160, 996, 943, 830, 754, 662, 620, 565 cm^{-1}.

1-allyl-3-propyl-imidazolium bromide (5)

Allyl imidazole (0.10 mol, 11.0 g) loaded with propyl bromide (0.11 mol, 13.80 g) at 70 °C for 48 h. A yellow coloured product was obtained with Yield 92 %; ^{1}H NMR (500 MHz, [D6]DMSO, 25 °C): δ = 0.74 (t, 3H; $\text{N-CH}_2\text{-CH}_2\text{-C}\underline{\text{H}}_3$), 1.77 (m, 2H; $\text{N-CH}_2\text{-C}\underline{\text{H}}_2\text{-CH}_3$), 4.23 (t, 2H; $\text{N-C}\underline{\text{H}}_2\text{-CH}_2\text{-CH}_3$), 4.99 (d, 2H; $\text{N-C}\underline{\text{H}}_2\text{-CH=CH}_2$), 5.24-5.25 (m, 2H; $\text{N-CH}_2\text{-CH=C}\underline{\text{H}}_2$), 5.26-5.29 (m, 2H; $\text{N-CH}_2\text{-CH=C}\underline{\text{H}}_2$), 5.99-6.07 (m, 1H; $\text{N-CH}_2\text{-C}\underline{\text{H}}\text{=CH}_2$), 7.96 (d, 1H; $\text{C}\underline{\text{H}}$), 8.08 (d, 1H; $\text{C}\underline{\text{H}}$), 9.69 ppm (d, 1H; $\text{C}\underline{\text{H}}$);^{13}C NMR (126 MHz, [D6]DMSO, 25 °C): δ = 10.83, 23.36, 50.71, 51.14, 120.63, 122.90, 123.07, 132.35, 136.58 ppm; FT-IR (BRUKER ALPHA, Zn-Se ATR): ῡ = 3128, 3055, 2964, 2876, 1644, 1560, 1448,

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1424, 1344, 1298, 1220, 1161, 1090, 995, 941, 862, 834, 753, 623, 568 cm^{-1}.

1-allyl-3-butyl-imidazolium chloride (6)

Allyl imidazole (0.10 mol, 11.21 g) charged with butyl chloride (0.11 mol, 10.52 g) at 80 °C for 63 h. A viscous yellow coloured product was obtained with Yield: 86 %; ^1H NMR (500 MHz, [D6]DMSO, 25 °C): δ = 0.82 (t, 3H; $-CH_2-CH_2-CH_2-C\underline{H}_3$), 1.19 (dq, 2H; $-CH_2-CH_2-C\underline{H}_2-CH_3$), 1.70-1.80 (m, 2H; $-CH_2-C\underline{H}_2-CH_2-CH_3$), 4.27 (t, 2H; $-C\underline{H}_2-CH_2-CH_2-CH_3$), 4.98 (d, 2H; $-C\underline{H}_2-CH=CH_2$), 5.26 (dq, 1H; $-C\underline{H}_2-CH=CH_2$), 5.27-5.30 (m, 2H; $-CH_2-CH=C\underline{H}_2$), 6.05 (ddt, 1H; $-CH_2-C\underline{H}=CH_2$), 7.99 (t, 1H; $C\underline{H}$), 8.11 (t, 1H; $C\underline{H}$), 9.93 ppm (s, 1H; $C\underline{H}$); ^{13}C NMR (126 MHz, [D6]DMSO, 25 °C): δ = 13.71,19.20, 31.89, 48.91, 51.05, 120.42, 122.93, 123.10, 132.53, 136.85 ppm; FT-IR (BRUKER ALPHA, Zn-Se ATR): ῡ = 3128, 3050, 2959, 2870, 1644, 1560, 1461, 1378, 1331, 1209, 1162, 995, 942, 882, 761, 627, 571, 516 cm^{-1}.

1-allyl-3-octyl-imidazolium chloride (7)

Allyl imidazole (0.10 mol, 11.13 g) charged with octyl chloride (0.11 mol, 16.80 g) at 80 °C for 64 h. A yellow coloured viscous product was obtained with Yield 75 %; ^1H NMR (500 MHz, [D6]DMSO, 25 °C): δ = 0.83 (m, 3H; $-CH_2-CH_2-C_5H_{10}-C\underline{H}_3$), 1.13-1.34 (m, 10H; $-CH_2-CH_2-C_5\underline{H}_{10}-CH_3$), 1.79 (quin, 2H; $-CH_2-C\underline{H}_2-C_5H_{10}-CH_3$), 4.24 (t, 2H; $-C\underline{H}_2-CH_2-C_5H_{10}-CH_3$), 4.90-4.99 (m, 2 H; $-C\underline{H}_2-CH=CH_2$), 5.28 (dq, 1H; $-CH_2-CH=C\underline{H}_2$), 5.32 (dq, 1H; $-CH_2-CH=C\underline{H}_2$), 6.06 (ddt, 1H; $-CH_2-C\underline{H}=CH_2$), 7.89 (t, 1H; $C\underline{H}$), 8.00 (t, 1H, $C\underline{H}$), 9.74 ppm (d, 1H; $C\underline{H}$); ^{13}C NMR (126 MHz, [D6]DMSO, 25 °C): δ = 14.37, 22.51, 25.97, 28.80, 28.96, 29.88, 31.62, 49.25, 51.15, 120.40, 122.97, 123.07, 132.48, 136.84 ppm; FT-IR (BRUKER ALPHA, Zn-Se ATR): ῡ = 3127, 3045, 2925, 2855, 1644, 1560, 1459, 1374, 1333, 1163, 994, 939, 762, 628, 569 cm^{-1}.

Synthesis of Silver Salt Precursor (Silver Dicyanamide, AgDCA)

It was prepared by drop-wise addition of aqueous solution of $AgNO_3$ (0.12 mol, 20.78 g,) into a saturated solution of equimolar sodium dicyanamide (0.12 mol, 10.89 g,). The resulting white solid was filtered and washed with water. The light sensitive product was dried in an oven over night at 90 °C (Yield: 95%).

Synthesis of ILs 8-14

A solution of sodium cyanoborohydride (1.1 mol) in DMF was drop-wise added in to the salt solution in DMF of **1-7** (10 mL) and stirred at room temperature for 4 h. The precipitate of sodium chloride was decanted by filtration. The filtrate was evaporated under reduced pressure. The isolated product was purified using dichloromethane and dried under high vacuum to form a colourless or yellow liquid.

1-methyl-3-pentyl-imidazolium cyanoborohydride (8)

Yield 92 %; ^1H NMR (500 MHz, [D6]DMSO, 25 °C): δ = -0.00-0.53 (m, 3H; BH3CN), 0.88 (t, 3H; $N-CH_2-CH_2-CH_2-CH_2-CH_3$), 1.22-1.28 (m, 2H; $N-CH_2-CH_2-CH_2-CH_2-CH_3$), 1.29-1.36 (m, 2H; $N-CH_2-CH_2-CH_2-CH_2-CH_3$), 1.82 (quin, 2H; $N-CH_2-CH_2-CH_2-CH_2-CH_3$), 3.89 (s, $N-CH_3$), 4.19 (t, 2H; $N-CH_2-CH_2-CH_2-CH_2-CH_3$), 7.70 (s, 1H; CH), 7.78 (s, 1H; CH), 9.12 ppm (s, 1H, CH); ^{13}C NMR (126 MHz, [D6]DMSO, 25 °C): δ = 14.11, 21.94, 28.06, 29.52, 36.23, 49.33, 122.66, 123.98, 136.89 ppm; FT-IR (BRUKER ALPHA, Zn-Se ATR): ῡ = 3150, 3106, 2948, 2865, 2325, 2224, 2170, 1999, 1666, 1570, 1459, 1377, 1343, 1164, 1126, 1027, 838, 746, 652, 619, 529cm^{-1}; ESI-HRMS: m/z calculated for cation $C_9H_{17}N_2$ $[M]^+$: 153.14; found:153.1390; m/z calculated for anion BH_3CN $[M]^-$: 40.04; found: 40.0371.

1-methyl-3-octyl-imidazolium cyanoborohydride (9)

Yield. 88 %: ^1H NMR (500 MHz, [D6]DMSO, 25 °C): δ = -0.18-0.35 (m, 3H; BH_3CN), 0.71 (t, 3H; $N-CH_2-CH_2-C_5H_{10}-C\underline{H}_3$), 1.10-1.11 (m, 10H; $N-CH_2-CH_2-C_5\underline{H}_{10}-CH_3$) 1.64 (m, 2H; $N-CH_2-C\underline{H}_2-C_5H_{10}-CH_3$), 3.72 (s, 3H; $N-C\underline{H}_3$), 4.02 (t, 2H; $N-C\underline{H}_2-CH_2-C_5H_{10}-CH_3$), 7.54 (s, 1H; $C\underline{H}$), 7.61 (s, 1H; $C\underline{H}$), 8.94 ppm (s, 1H, CH); ^{13}C NMR (126 MHz, [D6]DMSO, 25 °C): δ = 14.34, 22.51, 25.96, 28.79, 28.92, 29.85, 36.23, 49.33, 122.72, 124.05, 136.94 ppm: FT-IR (BRUKER ALPHA, Zn-Se ATR): ῡ = 3148, 3109, 2925, 2856, 2324, 2221, 2165, 1571, 1462, 1378, 1338, 1165, 1124, 1022, 867, 839, 748, 697, 649, 620 cm^{-1}; ESI-HRMS: m/z calculated for cation $C_{12}H_{23}N_2$ $[M]^+$: 195.19; found:195.1855; m/z calculated for anion BH_3CN $[M]^-$: 40.04; found: 40.0380.

1,3-diallyl-imidazolium cyanoborohydride (10)

Yellow coloured product was obtained, Yield 83 %; ^1H NMR (500 MHz, [D6]DMSO, 25 °C): δ = -0.03-0.51 (m, 3H; $B\underline{H}_3CN$), 4.87 (d, 4H; $N-C\underline{H}_2-CH=CH_2$), 5.29-5.34 (m, 2H; $N-CH_2-CH=C\underline{H}_2$), 5.36-5.39 (m, 2H; $N-CH_2-CH=C\underline{H}_2$), 6.02-6.10 (m, 2H; $N-CH_2-CH=C\underline{H}_2$), 7.74 (d, 2H; $C\underline{H}$), 9.15 ppm (d, 1H; $C\underline{H}$); ^{13}C NMR (126 MHz, [D6]DMSO, 25 °C): δ = 51.47, 121.03, 123.05, 131.89, 136.49 ppm; FT-IR (BRUKER ALPHA, Zn-Se ATR): ῡ = 3140, 3105, 2986, 2853, 2324, 2222, 1645, 1561, 1446, 1423, 1331, 1293, 1155, 1126, 992, 943, 839, 745, 628, 598, 558cm^{-1}; ESI-HRMS: m/z calculated for cation $C_9H_{13}N_2$ $[M]^+$:149.11; found:149.1070; m/z calculated for anion BH_3CN $[M]^-$: 40.04; found: 40.0346.

1-allyl-3-ethyl-imidazolium cyanoborohydride (11)

Colourless liquid, Yield 85 %; ^1H NMR (500 MHz, [D6]DMSO, 25 °C): δ = -0.01 - 0.53 (m, 3 H, BH_3CN), 1.43 (t, 3H, $N-CH_2-C\underline{H}_3$), 4.23 (m, 2H, $N-C\underline{H}_2-CH_3$), 4.84 (t, 2H; $N-C\underline{H}_2-CH=CH_2$), 5.33 (m, 2H; $N-CH_2-CH=C\underline{H}_2$), 5.99-6.07 (m, 1H; $N-CH_2-C\underline{H}=CH_2$), 7.66 (d, 1H; $C\underline{H}$), 7.76 (d, 1H; $C\underline{H}$), 9.14 ppm (d, 1H; $C\underline{H}$); ^{13}C NMR (126 MHz, [D6]DMSO, 25 °C): δ = 15.38, 43.15, 51.39, 121.07, 122.61, 122.75, 136.07 ppm; FT-IR (BRUKER ALPHA, Zn-Se ATR): ῡ = 3143, 3106, 2985, 2324, 2222, 2168, 1645, 1563, 1447, 1423, 1388, 1295, 1158, 1125, 1027, 993, 946, 867, 838, 749, 621, 564 cm^{-1}; ESI-HRMS: m/z calculated for cation $C_8H_{13}N_2$ $[M]^+$: 137.11 ; found:137.1065; m/z calculated for anion BH_3CN $[M]^-$: 40.04; found: 40.0401**.**

1-allyl-3-propyl-imidazolium cyanoborohydride (12)

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Yellow coloured product was obtained, Yield: 78 %; ^{1}H NMR (500 MHz [D6]DMSO, 25 °C: δ = -0.00-0.53 (m, 3H; BH_3CN), 0.84 (t, 3H; $N-CH_2-CH_2-C\underline{H}_3$), 1.82 (m, 2H; $N-CH_2-C\underline{H}_2-CH_3$), 4.16 (t, 2H; $N-C\underline{H}_2-CH_2-CH_3$), 4.86 (d, 2H; $N-C\underline{H}_2-CH=CH_2$), 5.29-5.33 (m, 1H; $N-CH_2-CH=C\underline{H}_2$), 5.34-5.37 (m, 1H; $N-CH_2-CH=C\underline{H}_2$), 6.01-6.09 (m, 1H; $N-CH_2-C\underline{H}=CH_2$), 7.69 (d, 1H; $C\underline{H}$), 7.77 (d, 1H; $C\underline{H}$), 9.12 ppm (d, 1H; $C\underline{H}$); ^{13}C NMR (126 MHz, [D6]DMSO, 25 °C): δ = 10.83, 23.28, 50.96, 51.39, 120.86, 122.94, 123.01, 131.99, 136.46 ppm; FT-IR (BRUKER ALPHA, Zn-Se ATR): ῡ = 3141, 3105, 2969, 2969, 2969, 2324, 2222, 2168, 1645, 1562, 1449, 1424, 1387, 1344, 1296, 1159, 1125, 993, 945, 839, 750, 625, 565cm^{-1}; ESI-HRMS: m/z calculated for cation $C_9H_{15}N_2$ [M]$^+$: 151.12 ; found:151.1234; m/z calculated for anion BH_3CN [M]$^-$: 40.04; found: 40.0401.

1-allyl-3-butyl-imidazolium cyanoborohydride (13)

Yellow coloured product was obtained, Yield: 80 %; ^{1}H NMR (500 MHz [D6]DMSO, 25 °C): δ = -0.02–0.51 (m, 3H; $B\underline{H}_3CN$), 0.90 (t, 3H; $N-CH_2-CH_2-CH_2-C\underline{H}_3$), 1.27 (dq, 2H; $N-CH_2-CH_2-C\underline{H}_2-CH_3$), 1.79 (m, 2H; $N-CH_2-C\underline{H}_2-CH_2-CH_3$), 4.20 (t, 2H; $N-C\underline{H}_2-CH_2-CH_2-CH_3$), 4.85 (dt, 2H, $N-C\underline{H}_2-CH=CH_2$), 5.30 (dq, 1H; $N-CH_2-CH=C\underline{H}_2$), 5.37 (dq, 1H; $N-CH_2-CH=C\underline{H}_2$), 6.04 - 6.10 (m, 1H; $N-CH_2-C\underline{H}=CH_2$), 7.72 (t, 1H; $C\underline{H}$) 7.81 (t, 1H; $C\underline{H}$), 9.17 ppm (t, 1H; $C\underline{H}$); ^{13}C NMR (126 MHz, [D6]DMSO, 25 °C): δ = 13.71, 19.28, 31.77, 49.20, 51.40, 120.78, 123.00, 123.07, 132.10 ppm; FT-IR (BRUKER ALPHA, Zn-Se ATR): ῡ =3140, 3104, 2962, 2935, 2872, 2323, 2221, 2165, 1645, 1562, 1461, 1424, 1334, 1158, 1125, 993, 945, 867, 841, 750, 625, 571 cm^{-1}; ESI-HRMS: m/z calculated for cation $C_{10}H_{17}N_2$ [M]$^+$: 165.14; found:165.1395; m/z calculated for anion BH_3CN [M]$^-$: 40.04; found: 40.0389.

1-allyl-3-octyl-imidazolium cyanoborohydride (14)

Yellow coloured product was obtained, Yield 83 %; ^{1}H NMR (500 MHz [D6]DMSO, 25 °C): δ = -0.03-0.50 (m, 3H; $B\underline{H}_3CN$), 0.86 (t, 3H; $-CH_2-CH_2-C_5H_{10}-CH_3$), 1.23-1.29 (m, 10H; $N-CH_2-CH_2-C_5\underline{H}_{10}-CH_3$), 1.80 (quin, 2H; $N-CH_2-C\underline{H}_2-C_5H_{10}-CH_3$), 4.18 (t, 2H; $N-C\underline{H}_2-CH_2-C_5H_{10}-CH_3$), 4.85 (dt, 2H; $N-C\underline{H}_2CH=CH_2$), 5.29 (dq, 1H; $N-CH_2CH=C\underline{H}_2$), 5.37 (dq, 1H; $N-CH_2CH=C\underline{H}_2$), 6.02-6.10 (m, 1H; $N-CH_2-C\underline{H}=CH_2$), 7.73 (t, 1H; $C\underline{H}$), 7.82 (t, 1H; $C\underline{H}$), 9.17 ppm (t, 1H; $C\underline{H}$), ^{13}C NMR (126 MHz, DMSO-d_6) δ = 14.39, 22.53, 25.97, 28.77, 28.94, 29.78, 31.62, 49.45, 51.39, 120.65, 123.02 , 123.06, 132.18, 136.51 ppm; FT-IR (BRUKER ALPHA, Zn-Se ATR): ῡ = 3140, 3102, 2926, 2857, 2323, 2221, 2165, 1642, 1562, 1458, 1373, 1337, 1158, 1127, 1025, 992, 944, 866, 752, 629, 568 cm^{-1}; ESI-HRMS: m/z calculated for cation $C_{14}H_{25}N_2$ [M]$^+$: 221.20; found:221.2009; m/z calculated for anion BH_3CN [M]$^-$: 40.04; found: 40.0344.

Synthesis of ILs (15-17)

A solution of salts (1 mol) **3**, **6** and **7** in methanol slowly added into the suspension of silver dicyanamide in methanol The contents were stirred in dark place for 24 h at 30 °C for 24 h. After the stirring, the insoluble silver halide was removed by filtration. The resulting filtrate was evaporated under reduced pressure and dried under vacuum to obtain the yellow or dark red coloured liquid.

1,3-diallyl-imidazolium dicyanamide (15)

Reddish brown coloured product was obtained with Yield: 83%; ^{1}H NMR (500 MHz [D6]DMSO, 25 °C): δ = 4.87 (d, 4H; $N-C\underline{H}_2-CH=CH_2$), 5.27-5.35 (m, 2H, $N-CH_2-CH=C\underline{H}_2$), 5.38 (dd, 2H, $N-CH_2-CH=C\underline{H}_2$), 6.06 (ddt, 2H, $N-CH_2-C\underline{H}=CH_2$), 7.75 (d, 2H; $C\underline{H}$), 9.19 ppm (s, 1H, $C\underline{H}$); ^{13}C NMR (126 MHz, [D6]DMSO, 25 °C): δ = 51.46, 119.57, 120.84, 123.15, 132.08, 136.67 ppm; FT-IR (BRUKER ALPHA, Zn-Se ATR): ῡ = 3137, 3092, 3015, 2225, 2190, 2123, 1645, 1561, 1445, 1423, 1304, 1157, 1105, 991, 942, 903, 842, 745, 663, 624, 599, 557, 520 cm^{-1}; ESI-HRMS: m/z calculated for cation $C_9H_{13}N_2$ [M]$^+$:149.11; found:149.1073; m/z calculated for anion C_2N_3 [M]$^-$: 66.01; found: 66.0104.

1-allyl-3-butyl-imidazolium dicyanamide[45] (16)

Brown coloured product was obtained with Yield 78 %; ^{1}H NMR (500 MHz [D6]DMSO, 25 °C): δ = 0.90 (t, 3H, $N-CH_2-CH_2-CH_2-C\underline{H}_3$), 1.23-1.31 (m, 2H, $N-CH_2-CH_2-C\underline{H}_2-CH_3$), 1.79 (m, 2H; $N-CH_2-C\underline{H}_2-CH_2-CH_3$), 4.20 (t, 2H; $N-C\underline{H}_2-CH_2-CH_2-CH_3$), 4.84-4.86 (m, 2H, $N-C\underline{H}_2-CH=CH_2$), 5.30 (dq, 1H; $N-CH_2-CH=C\underline{H}_2$), 5.37 (dq, 1H; $N-CH_2-CH= C\underline{H}_2$), 6.02-6.10 (m, 1H; $N-CH_2-C\underline{H}=CH_2$), 7.73 (d, 1H, $C\underline{H}$), 7.82 (t, 1H, $C\underline{H}$), 9.21 ppm (s, 1H; $C\underline{H}$); ^{13}C NMR (126 MHz, [D6]DMSO, 25 °C): δ = 13.70, 19.28, 31.78, 49.18, 51.39, 119.57, 120.73, 123.02, 132.11, 136.53 ppm; FT-IR (BRUKER ALPHA, Zn-Se ATR): ῡ = 3137, 3094, 2961, 2935, 2874, 2225, 2190, 2123, 1645, 1562, 1461, 1446, 1424, 1303, 1160, 992, 944, 901, 844, 751, 662, 636, 623, 520 cm^{-1}; ESI-HRMS: m/z calculated for cation $C_{10}H_{17}N_2$ [M]$^+$:165.14; found:165.1388; m/z calculated for anion C_2N_3 [M]$^-$: 66.01; found: 66.0111.

1-allyl-3-octyl-imidazolium dicyanamide[45] (17)

Brown coloured product was obtained with Yield 80 %; ^{1}H NMR (500 MHz [D6]DMSO, 25 °C): δ = 0.85 (m, 3H; $N-CH_2-CH_2-C_5H_{10}-C\underline{H}_3$), 1.21-1.29 (m, 10H; $N-CH_2-CH_2-C_5\underline{H}_{10}-CH_3$), 1.80 (quin, 2H; $N-CH_2-C\underline{H}_2-C_5H_{10}-CH_3$), 4.18 (t, 2H; $N-C\underline{H}_2-CH_2-C_5H_{10}-CH_3$), 4.85 (d, 2H; $N-C\underline{H}_2-CH=CH_2$), 5.29 (dq, 1H, $N-CH_2-CH=C\underline{H}_2$), 5.37 (dq, 4H, $N-CH_2-CH=C\underline{H}_2$) 6.06 (ddt, 1H; $N-CH_2-C\underline{H}=CH_2$), 7.73 (t, 1H, $C\underline{H}$) 7.82 (t, 4H; $C\underline{H}$), 9.18 ppm (s, 1H; $C\underline{H}$); ^{13}C NMR (126 MHz, [D6]DMSO, 25 °C): δ = 14.38, 22.53, 25.97, 28.77, 28.93, 29.78, 31.62, 49.44, 51.39, 119.56, 120.65, 123.05, 132.15, 136.53 ppm; FT-IR (BRUKER ALPHA, Zn-Se ATR): ῡ = 3138, 3093, 2926, 2857, 2227, 2191, 2125, 2563, 1458, 1305, 1160, 992, 943, 901, 754, 629 cm^{-1}; ESI-HRMS: m/z calculated for cation $C_{14}H_{25}N_2$ [M]$^+$:221.20; found:221.2012; m/z calculated for anion C_2N_3 [M]$^-$: 66.01; found: 66.0108.

Conclusions

A new series of imidazolium-based ILs **8-17** have been designed and synthesized with good yields. The investigation has helped in resolving the problem of hydrolytic stability of hypergolic IL fuels. The hydrophobic properties of the $[BH_3CN]^-$ based ILs were found to vary with different -allyl or n-alkyl substituents of the cation. All the ILs are found to be liquid at

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room temperature, hypergolic with WFNA and exhibit positive ΔH_f. The ILs **8** & **10-13** exhibit the ultrafast ID < 5 ms and fulfils the requirement of new fuel. The IL **11** has acceptable viscosity of 16.62 mPa·s and density of 0.95 $g.cm^{-3}$ at 25 °C which is comparable with known hypergolic IL fuel. ILs **15-17** showed high density > 0.99 $g.cm^{-3}$ among the developed ILs. Amongst all the ILs, the IL **10** can be considered as the most suitable candidates for the bipropellant formulation. Therefore distinctive properties of ILs viz. superior ID, water stability, high density, liquideous over wide temperature range, acceptable viscosity, and high ΔH_f make them interesting equivalents as fuels for space propulsion. In addition, these new ILs may find extensive scope in industrial applications such as energy storage, separation technique, as a solvent for chemical reactions, catalysis and absorption of CO_2.

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