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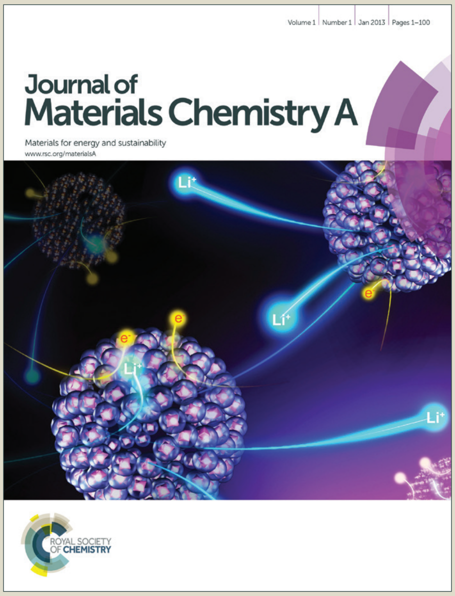

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ARTICLE

Super-Base-Derived Hypergolic Ionic Fuels with Remarkably Improved Thermal Stability

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Two seriels of super-base-derived hypergolic ionic liquid materials were synthesized and are fully characterized by ^{1}H and ^{13}C NMR, IR spectroscopy, and high resolution mass spectrum (HRMS). Their physicochemical properties such as themal property, density, viscosity, heats of formation, specific impulse, and ignition delay time were intensively characterized or calculated. Among fourteen new organic ionic materials, eleven salts are liquids at room temperature, which all exhibit good stability to heat and the expected hypergolic property upon contact with WFNA. The densities of these ionic compounds range from 1.00 to 1.22 g cm^{-3}, and their heats of formation vary between -38.0 and 478.6 kJ mol^{-1}. Surprisingly, most of these new ionic liquids exhibited unexpected thermal stability of > 280 °C, in which the salt **1** gave the T_d value of 310 °C, which is superior to any known hypergolic ionic liquids. As a new class of hypergolic fuels, these novel ionic liquid materials have some unique advantages than traditional propellant fuels like hydrazine and its derivatives, including extremely low vapour pressure, short ID time, and high thermal stability, *etc.*, thereby demonstrating their potential applications as green fuels in liquid bipropellant formulations.

Introduction

Propellants represent an important class of energetic materials in material science.[1] Nowadays, the widely used liquid bipropellants are commonly composed of two components - a fuel and an oxidizer. Of them, the hydrazine derivatives are still the main choice in the liquid rocket engine system.[2] These hydrazine derivatives such as monomethyl hydrazine and unsymmetrical dimethyl hydrazine, are extremely toxic, highly volatile, very sensitive to adiabatic compression (risk of detonation), and difficult to handle, thereby greatly increasing the handling and storage costs. This has resulted in a growing interest in exploring greener alternative fuels that are environmentally friendly while exhibiting excellent properties and performances comparable to hydrazine-based fuels.[3]

Recently, a new class of so-called hypergolic ionic liquids (HILs) has emerged as a hot spot of academic front in the field of propellant materials.[4] As compared to hydrazine and its derivatives, HILs have some unique properties including low volatility, low toxicity, low fire hazard and corrosivity, high energy density, ultrafast ignition delay, and good thrust control, *etc*.[5] Moreover, the designable character of HILs, i.e., the modular design strategy of component ions makes the achievement of an ideal propellant fuel possible, where the property and performance of HILs can be task-specifically customized. In this sense, there are theoretically thousands and millions of HILs with different structures and properties that can be synthesized by proper combinations of the component ions. Thus, the search for new HILs materials and explosion of their potential applications in the bipropellant formulations has become one of the hot topics in the fields of ionic liquids and space propulsion.[3]

In the past several years, a number of interesting HILs materials has been discovered and their applications as the alternative fuels to hydrazine derivatives in the liquid bipropellants have been preliminarily explored.[4, 5-12] For example, Schneider and co-workers reported the hypergolic phenomenon of the series of dicyanamide salts (Figure 1), which is the first report to demonstrate the feasibility of ionic liquid materials as liquid propellant fuels.[13] Moreover, several series of HILs, including the nitrocyanamide-anion based ILs,[14] azide-functionalized liquid salts,[15] dialkyltriazanium-based ILs,[16] dicyanoborate-based ILs,[17] $Al(BH_4)_4^-$-based ILs,[18] borohydride-based ILs,[19] and some others,[20-22] have been reported (Scheme 1). Among these interesting ionic fuels, most of them exhibit very promising properties that meet the requirements of replacing toxic hydrazine derivatives in traditional liquid bipropellant, e.g., higher density, shorter or comparable ignition times, unique greenness due to their low volatility, low toxicity and corrosivity. No doubt that the discovery of HILs has opened a leaf of window for the R&D of propellant materials.

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† Electronic Supplementary Information (ESI) available: the optimized structures of cations and anions for new ionic liquids, the calculation of ΔH_c°, as well as their *Ab initio* computational data are summarized in supporting information. The NMR spectra of fourteen new ionic liquids are also provided in supporting information. See DOI: 10.1039/x0xx00000x

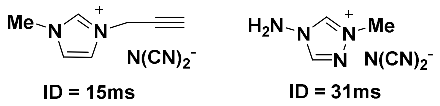
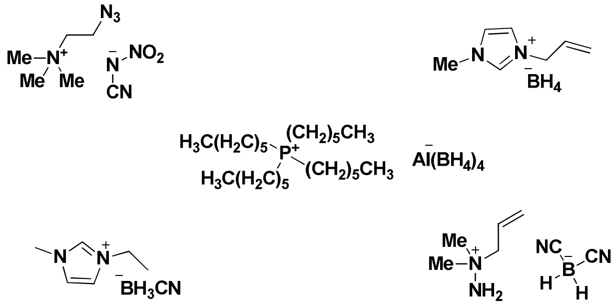


Figure 1. Work of Schneider and co-workers

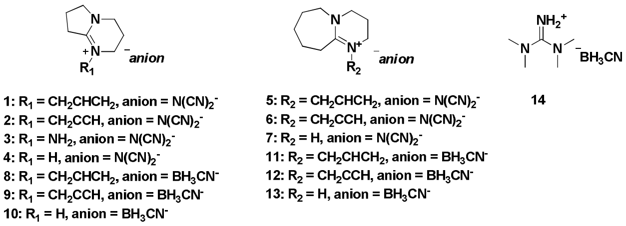


Scheme 1. Inspiring works in the field of HILs

In general, an ideal HIL is expected to possess excellent integrated properties including low volatility and toxicity, high energy density, good thermal stability, low viscosity, short ID times, and high specific impulse, *etc.* But in most cases, it is difficult to simultaneously meet such criteria in one HIL molecule. Among above properties, thermal stability is an important property that is related to the practical application. Unfortunately, most of known HILs exhibited relatively poor thermal stability of < 220 °C. Take the example of the widely studied imidazolium dicyanamide salts, e.g., 1-propargyl-3-methyl-imidazolium dicyanamide ([PMIm]$N(CN)_2$) and 1-allyl-3-methyl-imidazolium dicyanamide ([AMIm]$N(CN)_2$), two ionic salts showed the low decomposition temperature (T_d) values of 144 and 207 °C,[16] respectively. Moreover, for other HILs based on fuel-rich or reducing anions such as borohydride (BH_4^-) and ($Al(BH_4)_4^-$) anions, their thermal decomposition were observed even below 150 °C, i.e., the T_d value of [BMIm]BH_4 is only 99.9 °C.[19] In this regard, the poor thermal stability of most HILs undoubtedly decreased their potential application value as fuels in the bipropellant formulations.

From the pioneers's works, the thermal stability of HILs was generally determined by the structures of the component ions. In many cases of known HILs, some substituted dialkylimidazolium cations with electron-rich groups like the alkynyl or azido group were always chosen for paring with fuel-rich or reducing anions such as dicyanamide anion. Upon the heating process of HILs with such structures, the deprotonation of C2 position on the imidazole ring is prone to occur and the extricated proton will easily react with the nucleophilic -NCN group of dicyanamide anion, thereby resulting in the rapid decomposition of this kind of HILs. This thermal decomposition mechanism has been demonstrated by multiple, complementary experimental techniques and DFT calculations.[23] This has also shown that the rational design of the structures of component ions is critical for the construction of new HILs materials with excellent integrated properties, especially for their high thermal stability (e.g., new HILs with the T_d values of > 300 °C).

For considerations such as noted above, the design of new cation frameworks suitable for developing thermally stable HILs materials is an interesting and challenging task. It has well-known that the organic super-bases, e.g., 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), have the highly reactive nitrogen atoms in the heterocyclic ring framework, thereby allowing the efficient quaterization to form stable cation structures without chemically active hydrogen atoms. So, starting from these organic-base-derived cations, a number of new organic ionic materials can be synthesized via the pairing with the suitable anions. Nowadays, the studies on super-base-derived ionic liquids are mainly focused on their solvent and electrolyte applications in asymmetric synthesis, fuel cell, and CO_2 capture, *etc.*[24-26] However, it has come to our knowledge that no any studies on super-base-derived HILs have been reported. In our continuing efforts to seek new hypergolic ionic fuels,[3-4, 27] here we designed and synthesized a series of super-base-derived HILs (Scheme 2), which showed unexpected thermal stability superior to any known HILs. In the design of cation frameworks for these new HILs, the protonation strategy of both heterocyclic super-base (i.e., DBU and DBN) and unsaturated aliphatic super-base (i.e., 1,1,3,3-tetramethylguanidine (TMG)) were also used for a comparison purpose. Moreover, the important physicochemical properties of new HILs materials, i.e., melting point, thermal stability, density, viscosity, heats of formation, and hypergolic performance in combination with white fuming nitric acid (WFNA), were measured and studied in detail. As expected, most resulting super-base-derived HILs showed the hypergolic property upon contact with WFNA, thereby endowing them with promising potential as alternative fuels of hydrazine derivatives in the green liquid bipropellant.



Scheme 2. Super-base-derived ionic liquids

Experimental

Chemicals

All the organic solvents used in the study were of analytical grade. 1,8-Diazabicyclo[5.4.0]undec-7-ene (98%), allyl bromide (99%), 1,1,3,3-tetramethylguanidine were purchased from J&K Scientific. 1,5-Diazabicyclo[4.3.0]non-5-ene (99%), 3-bromopropyne (99%) were purchased from Energy Chemical. Sodium cyanoborate (95%) and sodium dicyanamide(96%) was purchased from Aladdin Industrial Inc. All the chemicals were used as received without further purification. Silver dicyanamide was synthesized according to the literature method.[13] NH_2Cl was synthesized according to the literature method.[28]

Synthesis of HILs

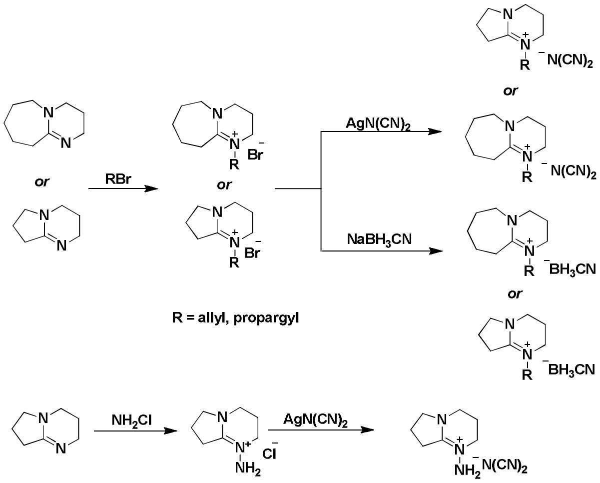


Figure 2. Synthesis of ILs based on DBN or DBU

As described in Figure 2, according to commonly methods for construction of quaternary ammonium salt,[17] allylation and propargylation of organic base can be easily achieved by reaction with relative reagents such as allyl bromide and 3-bromopropyne. After refluxed for about two days, the mixture was workup and the target quaternary ammonium salts were obtained. The diazanium-based IL **3** can be synthesized according to the literature method.[14] DBN and NH_2Cl were added in the mixed solvent of ether and THF at 0 ^oC, then the temperature was raised to r.t. and the mixture was reacted for 24h. After evaporating the solvent and recrystallized from methanol/THF/ether, the DBN derived diazanium salt was obtained. The protonation of organic base can be conveniently achieved by bubbling hydrogen chloride in ether. The subsequent anion metathesis of these quaternary ammonium salts with silver dicyanamide or sodium cyanoborate can efficiently yield the desired ionic liquids with high yields.

General methods for preparing the super-base-derived dicyanamide ($N(CN)_2^-$) salts:

Synthesis of HILs ***1-7****:* 2.45 g 1-allyl-2,3,4,6,7,8-hexahydropyrrolo[1,2-a]pyrimidin-1-ium bromide (10mmol) was dissolved in 20 mL distilled water, and then 1.91 g freshly prepared $AgN(CN)_2$ (11mmol) was subsequently added into the solution. The resulting suspension solution was stirred at room temperature for 12 h. After filtration, water was removed through a rotary vacuum evaporator. The resulting crude product was dissolved in 30 mL CH_2Cl_2 and then 1.5g anhydrous magnesium sulphate was added for drying. After filtration and the removal of the solvent, the ionic liquid **1** was obtained as a light yellow liquid in a yield of 89%. Ionic liquid **2-7** can be readily synthesized via the same procedure. HILs **2-6** are viscous liquid and the salt **7** are white solid at room temperature with high yields of 65-89%.

General methods for preparing the super-base-derived cyanoborohydride (BH_3CN^-) salts:

Synthesis of ionic liquid ***8-14****:* 2.45 g 1-allyl-2,3,4,6,7,8-hexahydropyrrolo[1,2-a]pyrimidin-1-ium bromide (10mmol) was dissolved in 35 mL dichloromethane, and then 0.65g $NaBH_3CN$ (10mmol) was added into the solution. The resulting suspension solution was stirred at room temperature for two days. After filtration and removal of dichloromethane through a rotary vacuum evaporator, the ionic liquid **8** was obtained as a light yellow liquid in a yield of 88%. Ionic liquid **9-14** can be readily synthesized through the same procedure with high yields of 81-89%. Ionic liquids **8**, **9**, **11**, **12**, **14** are viscous liquid and **10**, **13** are white solid at room temperature.

1-allyl-2,3,4,6,7,8-hexahydropyrrolo[1,2-a]pyrimidin-1-ium dicyanamide (**1**)

Yield, 89%; colourless liquid; ^{1}H NMR (600 MHz, CD_3CN): δ ppm: 2.04-2.09 (m, 2H, CH_2), 2.11-2.16 (m, 2H, CH_2), 2.95 (t, 2H, CH_2), 3.35-3.39 (m, 4H, CH_2), 3.70 (m, 2H, CH_2), 3.99-4.03 (m, 2H, CH_2), 5.28-5.36 (m, 2H, CH_2), 5.83-5.91 (m, 1H, CH); ^{13}C NMR (151 MHz, CD_3CN): δ ppm: 165.47, 131.37, 120.27, 119.15, 55.47, 54.85, 45.05, 42.78, 30.76, 19.31, 18.49; IR (KBr): γ 2971, 2240, 2200, 2139, 1669, 1539, 1446, 1314, 1218, 1092; ESI-HRMS: *m/z* calcd for cation $C_{10}H_{17}N_2$ $[M]^+$: 165.1386; found: 165.1384; *m/z* calcd for anion C_2N_3 $[M]^-$: 66.0098; found: 66.0093; elemental analysis calcd (%) for $C_{12}H_{17}N_5$ (231.30): C 62.31, H 7.41, N 30.28; found: C 62.05, H 7.46, N 30.05.

1-(prop-2-yn-1-yl)-2,3,4,6,7,8-hexahydropyrrolo[1,2-a]pyrimidin-1-ium dicyanamide (**2**)

Yield, 87%; yellow oil; ^{1}H NMR (600 MHz, CD_3CN): δ ppm: 2.07-2.18 (m, 4H, CH_2), 2.83-2.87 (m, 1H, CH_2), 2.99-3.04 (m, 2H, CH_2), 3.37-3.40 (m, 2H, CH_2), 3.48-3.52 (m, 2H, CH_2), 3.70-3.74 (m, 2H, CH_2), 4.23-4.26 (m, 2H, CH_2); ^{13}C NMR (151 MHz, CD_3CN): δ ppm: 165.55, 120.25, 76.24, 75.84, 55.08, 45.06, 42.74, 42.57, 31.00, 19.25, 18.35; IR (KBr): γ 3282, 2242, 2201, 2140, 1702, 1668, 1539, 1314, 1104, 923; ESI-HRMS: *m/z* calcd for cation $C_{10}H_{15}N_2$ $[M]^+$: 163.1230; found: 163.1229; *m/z* calcd for anion C_2N_3 $[M]^-$: 66.0098; found: 66.0093; elemental analysis calcd (%) for $C_{12}H_{15}N_5$ (229.28): C, 62.86; H, 6.59; N, 30.54; found: C 62.43, H 6.65, N 30.29.

1-amino-2,3,4,6,7,8-hexahydropyrrolo[1,2-a]pyrimidin-1-ium dicyanamide (**3**)

Yield, 65%; light yellow oil; ^{1}H NMR (600 MHz, CD_3CN): δ ppm: 2.06-2.13 (m, 4H, CH_2), 3.04 (t, 2H, CH_2), 3.32 (2, 2H, CH_2), 3.55 (t, 2H, CH_2), 3.71 (t, 2H, CH_2), 4.86 (brs, 2H, NH_2); ^{13}C NMR (151 MHz, CD_3CN): δ ppm: 167.71, 117.93, 55.06, 50.55, 42.05, 31.06, 19.91, 18.37; IR (KBr): γ 2964, 2245, 2203, 2142, 1702, 1662, 1312, 1228, 1113, 923; ESI-HRMS: *m/z* calcd for cation $C_7H_{14}N_3$ $[M]^+$: 140.1182; found: 140.1179; *m/z* calcd for anion C_2N_3 $[M]^-$: 66.0098; found: 66.0093; elemental analysis calcd (%) for $C_9H_{14}N_6$ (206.25): C, 52.41; H, 6.84; N, 40.75; found: C 52.00, H 6.89, N 40.42.

2,3,4,6,7,8-hexahydropyrrolo[1,2-a]pyrimidin-1-ium dicyanamide (**4**)

Yield, 83%; colorless oil; ^{1}H NMR (600 MHz, CD_3CN): δ ppm: 1.98-2.02 (m, 2H, CH_2), 2.10-2.15 (m, 2H, CH_2), 2.85 (t, 2H, CH_2), 3.3-3.39 (m, 4H, CH_2), 3.65 (t, 2H, CH_2), 8.44(brs, 1H, NH); ^{13}C NMR (151 MHz, CD_3CN): δ ppm: 165.27, 120.16, 54.15, 42.92, 38.70, 30.70, 18.95, 18.91; IR (KBr): γ 3136, 2974, 2246, 2203, 2142, 1680, 1651, 1595, 1319, 1308; ESI-HRMS: *m/z* calcd for cation $C_7H_{13}N_2$ $[M]^+$: 125.1073; found: 125.1071; *m/z* calcd for anion C_2N_3 $[M]^-$: 66.0098; found: 66.0093; elemental analysis calcd (%) for $C_9H_{13}N_5$ (191.23): C, 56.53; H, 6.85; N, 36.62; found: C 56.12, H 6.89, N 36.33.

1-allyl-2,3,4,6,7,8,9,10-octahydropyrimido[1,2-a]azepin-1-ium dicyanamide (**5**)

Yield, 87%; colourless oil; ^1H NMR (600 MHz, CD_3CN): δ ppm: 1.69-1.79 (m, 6H, CH_2), 2.05-2.10 (m, 2H, CH_2), 2.73-2.78 (m, 2H, CH_2), 3.43 (t, 2H, CH_2), 3.52 (t, 2H, CH_2), 3.62-3.66 (m, 2H, CH_2), 4.11-4.15 (m, 2H, CH_2), 5.23-5.33 (m, 2H, CH_2), 5.85-5.92 (m, 1H, CH); ^{13}C NMR (151 MHz, CD_3CN): δ ppm: 167.66, 131.91, 120.28, 117.65, 55.85, 55.50, 49.61, 47.56, 28.71, 28.69, 26.31, 23.13, 20.26; IR (KBr): γ 2940, 2238, 2199, 2138, 1621, 1528, 1448, 1326, 1197, 1102; ESI-HRMS: *m/z* calcd for cation $C_{12}H_{21}N_2$ $[M]^+$: 193.1669; found: 193.1771; *m/z* calcd for anion C_2N_3 $[M]^-$: 66.0098; found: 66.0093; elemental analysis calcd (%) for $C_{14}H_{21}N_5$ (259.35): C, 64.84; H, 8.16; N, 27.00; found: C 64.20, H 8.24, N 26.72.

1-(prop-2-yn-1-yl)-2,3,4,6,7,8,9,10-octahydropyrimido[1,2-a]azepin-1-ium dicyanamide (**6**)

Yield, 87%; yellow oil; ^1H NMR (600 MHz, CD_3CN): δ ppm: 1.70-1.82 (m, 6H, CH_2), 2.05-2.11 (m, 2H, CH_2), 2.87 (t, 1H, CH), 2.89-2.92 (m, 2H, CH_2), 3.50-3.55 (m, 4H, CH_2), 3.64-3.67 (m, 2H, CH_2), 4.34 (d, 2H, CH_2); ^{13}C NMR (151 MHz, CD_3CN): δ ppm: 167.76, 120.21, 77.19, 75.64, 55.68, 49.57, 47.81, 43.44, 28.93, 28.59, 26.10, 22.79, 20.25; IR (KBr): γ 3268, 2941, 2238, 2198, 2138, 1621, 1525, 1325, 1197, 1103; ESI-HRMS: *m/z* calcd for cation $C_{12}H_{19}N_2$ $[M]^+$: 191.1543; found: 191.1551; *m/z* calcd for anion C_2N_3 $[M]^-$: 66.0098; found: 66.0093; elemental analysis calcd (%) for $C_{14}H_{19}N_5$ (257.33): C, 65.34; H, 7.44; N, 27.22; found: C 64.84, H 7.48, N 26.98.

2,3,4,6,7,8,9,10-octahydropyrimido[1,2-a]azepin-1-ium dicyanamide (**7**)

Yield, 86%; white solid; m.p.: 54.7°C; ^1H NMR (600 MHz, CD_3CN): δ ppm: 1.66-1.75 (m, 6H, CH_2), 1.96-2.00 (m, 2H, CH_2), 2.64-2.66 (m, 2H, CH_2), 3.23-3.30 (m, 2H, CH_2), 3.48 (t, 2H, CH_2), 3.53-3.54 (m, 2H, CH_2), 8.80 (brs, 1H, NH); ^{13}C NMR (151 MHz, CD_3CN): δ ppm: 166.70, 120.07, 54.75, 48.96, 38.55, 33.09, 29.09, 26.64, 24.01, 19.58; IR (KBr): γ 3131, 2941, 2246, 2203, 2142, 1649, 1449, 1324, 1208, 1107; ESI-HRMS: *m/z* calcd for cation $C_9H_{17}N_2$ $[M]^+$: 153.1386; found: 153.1389; *m/z* calcd for anion C_2N_3 $[M]^-$: 66.0098; found: 66.0093; elemental analysis calcd (%) for $C_{11}H_{17}N_5$ (219.29): C, 60.25; H, 7.81; N, 31.94; found: C 60.03, H 7.83, N 31.82.

1-allyl-2,3,4,6,7,8-hexahydropyrrolo[1,2-a]pyrimidin-1-ium cyanotrihydroborate (**8**)

Yield, 88%; light yellow liquid; ^1H NMR (600 MHz, CD_3CN): δ ppm: -0.17-0.32 (m, 3H, BH_3CN), 1.85-1.90 (m, 2H, CH_2), 1.91-1.97 (m, 2H, CH_2), 2.76 (t, 2H, CH_2), 3.17-3.20 (m, 4H, CH_2), 3.49-3.54 (m, 2H, CH_2), 3.82 (dt, 2H, CH_2), 5.08-5.17 (m, 2H, CH_2), 5.62-5.72 (m, 1H, CH); ^{13}C NMR (151 MHz, CD_3CN): δ ppm: 165.31, 131.36, 119.01, 55.36, 54.74, 44.91, 42.66, 30.68, 19.19, 18.38; IR (KBr): γ 2962, 2329, 2219, 2169, 1702, 1669, 1539, 1446, 1313, 1125, 939; ESI-HRMS: *m/z* calcd for cation $C_{10}H_{17}N_2$ $[M]^+$: 165.1386; found: 165.1384; *m/z* calcd for anion CH_3BN $[M]^-$: 39.0395; found: 39.0413; elemental analysis calcd (%) for $C_{11}H_{20}BN_3$ (205.11): C, 64.41; H, 9.83; N, 20.49; found: C 64.01, H 9.89, N 20.33.

1-(prop-2-yn-1-yl)-2,3,4,6,7,8-hexahydropyrrolo[1,2-a]pyrimidin-1-ium cyanotrihydroborate (**9**)

Yield, 85%; light brown oil; ^1H NMR (600 MHz, CD_3CN): δ ppm: -0.26-0.46 (m, 3H, BH_3CN), 1.87-1.98 (m, 4H, CH_2), 2.64 (t, 1H, CH), 2.81 (t, 2H, CH_2), 3.18 (t, 2H, CH_2), 3.28-3.30 (m, 2H, CH_2), 3.50-3.54 (m, 2H, CH_2), 4.04 (d, 2H, CH_2); ^{13}C NMR (151 MHz, CD_3CN): δ ppm: 165.52, 76.22, 75.80, 55.07, 45.05, 42.73, 42.58, 31.00, 19.23, 18.33; IR (KBr): γ 3263, 2971, 2329, 2169, 1668, 1539, 1442, 1313, 1126, 1104; ESI-HRMS: *m/z* calcd for cation $C_{10}H_{15}N_2$ $[M]^+$: 163.1230; found: 163.1229; *m/z* calcd for anion CH_3BN $[M]^-$: 39.0395; found: 39.0413; elemental analysis calcd (%) for $C_{11}H_{18}BN_3$ (203.09): C, 65.05; H, 8.93; N, 20.69; found: C 64.59, H 8.98, N 20.57.

2,3,4,6,7,8-hexahydropyrrolo[1,2-a]pyrimidin-1-ium cyanotrihydroborate (**10**)

Yield, 81%; white solid; m.p.: 54.3°C; ^1H NMR (600 MHz, CD_3CN): δ ppm: -0.05-0.39 (m, 3H, BH_3CN), 1.88-1.92 (m, 2H, CH_2), 2.00-2.05 (m, 2H, CH_2), 2.74 (t, 2H, CH_2),3.24-3.26 (m, 2H, CH_2), 3.29-3.32 (m, 2H, CH_2), 3.56 (t, 2H, CH_2), 8.12 (brs, 1H, NH); ^{13}C NMR (151 MHz, CD_3CN): δ ppm: 164.76, 53.80, 42.55, 38.30, 30.35, 18.58, 18.52; IR (KBr): γ 3333, 3142, 2970, 2335, 2171, 1680, 1588, 1308, 1124, 1083; ESI-HRMS: *m/z* calcd for cation $C_7H_{13}N_2$ $[M]^+$: 125.1073; found: 125.1071; *m/z* calcd for anion CH_3BN $[M]^-$: 39.0395; found: 39.0413; elemental analysis calcd (%) for $C_8H_{16}BN_3$ (165.04): C, 58.22; H, 9.77; N, 25.46; found: C 58.03, H 9.80, N 25.36.

1-allyl-2,3,4,6,7,8,9,10-octahydropyrimido[1,2-a]azepin-1-ium cyanotrihydroborate (**11**)

Yield, 89%; light yellow liquid; ^1H NMR (600 MHz, CD_3CN): δ ppm: -0.15-0.29 (m, 3H, BH_3CN), 1.47-1.58 (m, 6H, CH_2), 1.84-1.88 (m, 2H, CH_2), 2.52-2.57 (m, 2H, CH_2), 3.23 (t, 2H, CH_2), 3.31 (t, 2H, CH_2), 3.40-3.46 (m, 2H, CH_2), 3.89-3.96 (m, 2H, CH_2), 4.99-5.13 (m, 2H, CH_2), 5.63-5.72 (m, 1H, CH); ^{13}C NMR (151 MHz, CD_3CN): δ ppm: 167.50, 131.87, 117.46, 55.74, 55.40, 49.50, 47.45, 28.62, 26.21, 23.02, 20.15; IR (KBr): γ 2938, 2326, 2218, 2169, 1621, 1527, 1447, 1328, 1197, 1124; ESI-HRMS: *m/z* calcd for cation $C_{12}H_{21}N_2$ $[M]^+$: 193.1699; found: 193.1771; *m/z* calcd for anion CH_3BN $[M]^-$: 39.0395; found: 39.0413; elemental analysis calcd (%) for $C_{13}H_{24}BN_3$ (233.16): C, 66.97; H, 10.38; N, 18.02; found: C 66.35, H 10.42, N 17.86.

1-(prop-2-yn-1-yl)-2,3,4,6,7,8,9,10-octahydropyrimido[1,2-a]azepin-1-ium cyanotrihydroborate (**12**)

Yield, 85%; light brown oil; ^1H NMR (600 MHz, CD_3CN): δ ppm: -0.18-0.33 (m, 3H, BH_3CN), 1.50-1.60 (m, 6H, CH_2), 1.85-1.90 (m, 2H, CH_2), 2.64 (t, 1H, CH), 2.66-2.70 (m, 2H, CH_2), 3.29-3.34 (m, 4H, CH_2), 3.42-3.47 (m, 2H, CH_2), 4.11 (d, 2H, CH_2); ^{13}C NMR (151 MHz, CD_3CN): δ ppm: 167.72, 77.15, 75.58, 55.67, 49.55, 47.79, 43.43, 28.91, 28.56, 26.07, 22.76, 20.21; IR (KBr): γ 3259, 2940, 2329, 2169, 1620, 1526, 1447, 1328, 1196, 1126; ESI-HRMS: *m/z* calcd for cation

$C_{12}H_{19}N_2$ $[M]^+$: 191.1543; found: 191.1551; *m/z* calcd for anion CH_3BN $[M]^-$: 39.0395; found: 39.0413; elemental analysis calcd (%) for $C_{13}H_{22}BN_3$ (231.14): C, 67.55; H, 9.59; N, 18.18; found: C 67.04, H 9.63, N 18.05.

2,3,4,6,7,8,9,10-octahydropyrimido[1,2-a]azepin-1-ium cyanotrihydroborate (**13**)

Yield, 87%; white solid; m.p.: 46.0°C; ^1H NMR (600 MHz, CD_3CN): δ ppm: -0.15-0.30 (m, 3H, BH_3CN), 1.45-1.56 (m, 6H, CH_2), 1.77-1.79 (m, 2H, CH_2), 2.38-2.44 (m, 2H, CH_2), 3.06-3.09 (m, 2H, CH_2), 3.27 (t, 2H, CH_2), 3.32-3.34 (m, 2H, CH_2), 7.81 (brs, 1H, NH); ^{13}C NMR (151 MHz, CD_3CN): δ ppm: 166.62, 54.76, 48.90, 38.57, 33.26, 28.98, 26.50, 23.87, 19.43; IR (KBr): γ 3132, 2939, 2355, 2333, 2170, 1649, 1585, 1447, 1324, 1123; ESI-HRMS: *m/z* calcd for cation $C_9H_{17}N_2$ $[M]^+$: 153.1386; found: 153.1389; *m/z* calcd for anion CH_3BN $[M]^-$: 39.0395; found: 39.0413; elemental analysis calcd (%) for $C_{10}H_{20}BN_3$ (193.10): C, 62.20; H, 10.44; N, 21.76; found: C 61.93, H 10.50, N 21.69.

bis(dimethylamino)methaniminium cyanotrihydroborate (**14**)

Yield, 85%; colourless liquid; ^1H NMR (600 MHz, CD_3CN): δ ppm: -0.15-0.30 (m, 3H, BH_3CN), 2.72 (s, 12H, CH_3), 6.25 (brs, 2H, NH_2); ^{13}C NMR (151 MHz, CD_3CN): δ ppm: 161.89, 39.80; IR (KBr): γ 3193, 2974, 2325, 2171, 1613, 1565, 1412, 1125, 1063, 873; ESI-HRMS: *m/z* calcd for cation $C_5H_{14}N_3$ $[M]^+$: 116.1188; found: 116.1182; *m/z* calcd for anion CH_3BN $[M]^-$: 39.0395; found: 39.0413; elemental analysis calcd (%) for $C_6H_{17}BN_4$ (156.04): C, 46.18; H, 10.98; N, 35.91; found: C 45.80, H 11.06, N 35.63.

Instrumentation and analysis methods

^1H and ^{13}C NMR spectra were detected by 600 MHz (Bruker AVANCE 600) with CD_3CN as the solvent. Chemical shifts in ^1H and ^{13}C NMR spectra are reported relative to Me_4Si. ESI-HRMS were performed on Shimadzu LCMS-IT-TOF mass spectrometer. Thermal property measurements of ionic liquids were performed on a TA DSC Mettler Toledo calorimeter equipped with an autocool accessory. The densities of ionic liquids were measured at 25 °C on a Micromeritics Accupyc II 1340 gas pycnometer. The viscosity measurements were performed on a Brookfield Rheometer DV3T at 25 °C. Specific impulse data were calculated by Explo5 (version 6.02) software. Ignition photographs of ionic liquids with the oxidizer 100% HNO_3 were recorded on an Olympus *i-speed 3*.

Results and discussion

In this work, fourteen super-base-derived HILs were synthesized, in which eight kinds of quaternized or protonated super-base cations were designed and paired with the cyanoborohydride and dicyanamide anions to form low-melting HILs (Scheme 2, **IL1-14**). Except for three HILs **7**, **10** and **13** that are solids, all other salts are liquids at room temperature. In addition, the anion metathesis of DBN-derived 1-amino-2,3,4,6,7,8-hexahydropyrrolo[1,2-a]pyrimidin-1-ium chloride salts with sodium cyanoborate only gave a very low yield of < 10 wt%. And, the guanidinium-derived dicyanamide salt was obtained as a solid with quite high melting point about 85 °C, which restricts its application as a liquid fuel. Thus, these two products are not listed in Table 1. Surprisingly, as listed in Table 1, fourteen super-base-derived HILs exhibited good hydrolytic stability to the moisture of air (supporting information, Figure S1), although the cyanoborohydride anion was generally thought to slowly decompose in water. For example, under the exposed air conditions without any additional protections, when the cyanoborohydride salt **10** was stored at room temperature for one month, and no detectable chemical degradations were observed, indicating very good stability of these HILs in the air. The strong alkalinity of conjugated super-bases may be responsible to the good stability of these quaternized or protonated salts.

All the new HILs are fully characterized by ^1H and ^{13}C NMR, IR spectroscopy, and electrospray ionization mass spectrometry (ESI/MS). The characterization data support the structures of new ILs (see experimental section and supporting information, Figure S2-S29). The physicochemical properties of all the new HILs (**1–14**) (Scheme 2), including their phase-transition temperatures (T_m or T_g), thermal decomposition temperatures (T_d, loss weight 5%), viscosities (η) and densities (ρ), were determined by differential scanning calorimetry (DSC), micro VISC viscometer, and gas pycnometry, respectively. The heats of formation, heats of combustion of HILs, and specific impulse (I_{sp}) were calculated with the Gaussian 09 and Explo5 (version 6.02) software, respectively. Their ID times were obtained by droplet tests (Table 1).

Table1. Physicochemical properties of fourteen new ionic liquids

IL	T_m[a] °C	T_d[b] °C	ρ[c] g/cm^3	η[d] mPa·s	ΔH_f[e] kJ/mol	ΔH_c[f] kJ/mol	ID[g] ms	I_{sp}[h] s
1	6.2	310	1.12	46.4	+305.0	-7456.3	27	162.5
2	<-70	301	1.14	121.7	+478.6	-7344.1	37	174.8
3	1.40	296	1.19	80.1	+305.3	-5847.4	40	169.1
4	11.4	249	1.15	193.1	+212.2	-5611.4	100	157.7
5	<-70	293	1.11	289.0	+287.8	-8797.7	95	160.8
6	1.6	266	1.13	725.5	+460.2	-8684.3	51	171.5
7	54.7	266	1.22	-	+175.3	-6933.1	72	154.3
8	0.8	232	1.00	87.4	+88.8	-7912.1	79	175.5
9	0.7	284	1.03	332.8	+261.9	-7799.3	67	188.1
10	54.3	263	1.02	-	-5.4	-6065.7	92	173.8
11	<-70	233	1.01	523.8	+71.9	-9253.7	115	172.5
12	-51.3[i]	258	1.02	2043.0	+244.4	-9140.5	59	183.3
13	46.0	283	1.06	-	-38.0	-7391.8	137	168.5
14	<-70	205	1.04	255.5	+5.1	-6219.2	576	174.7

[a] Melting point. [b] Decomposition temperature. [c] Density at 25 °C. [d] Viscosity at 25 °C. [e] Heat of formation. [f] Heat of isobaric combustion. [g] Ignition delay time. [h] Specific impulse (Explo5 v6.02). [i] Glass transition temperature.

Thermal Property, Density and Viscosity

Thermal property is one of the most important properties for the HILs, especially considering their practical applications as green propellant fuels. In general, an ideal HIL is expected to have the safe and stable liquid operating range between -40 and 200 ºC. Thus, the thermal properties of fourteen new HILs were firstly measured and studied. As shown in Table 1, four HILs (**2**, **5**, **11**, **14**) showed very low melting points of < -70 ^{o}C while three HILs (**7**, **10**, **13**) had the relatively high melting points of 54.3 ºC, 54.7 ºC, and 46.0 ºC, respectively. The high melting points of above three HILs may be explained by that the relatively stronger hydrogen bond interactions between the protonated cations with anions result in the close packing of ions and thus give higher melting point. Moreover, six HILs (i.e., **1**, **3**, **4**, **6**, **8**, **9**) showed a melting point between 0 ^{o}C and room temperature, in which **4** gave a relatively high melting point of 11.4 ^{o}C, perhaps due to the presence of amino group in the cation structure.

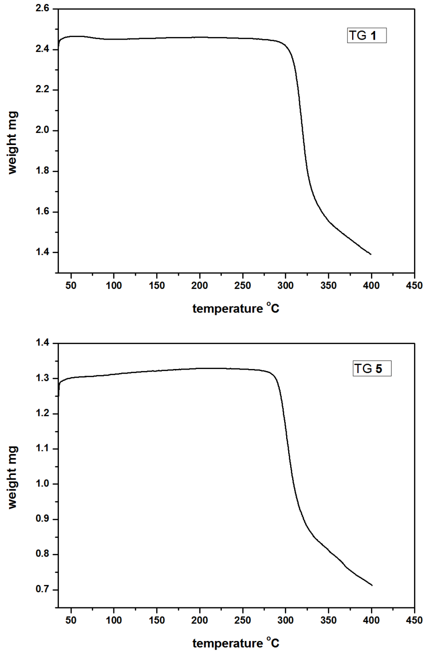


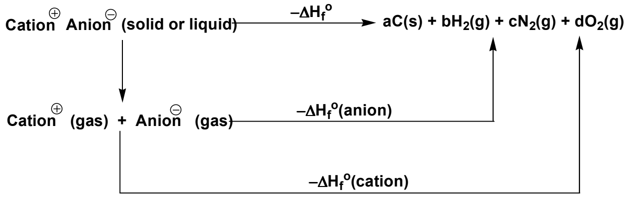
Figure 3. TG graph of ionic liquid **1** and **5**

In addition to the T_m and T_g, more efforts have been put into the study of their thermal stabilities. As shown in Table 1, all the new ILs showed good decomposition temperature of > 200 ^{o}C, which was determined by the temperature point for losing 5 wt% sample weight during thermal analysis. Of these, the salt **1** gave the highest T_d value of 310 ^{o}C that is superior to any known HILs, while **14** showed the lowest thermal stability of 205^{o}C. As compared to the developed HILs reported previously (most of their T_d values vary from 100-200 ^{o}C), there is no doubt that the thermal stability of these super-base-derived HILs were remarkably improved, in particular those dicyanamide salts based on the skeletons of DBU and DBN. Perhaps it is just the special structure of super-base cation responsible for the high thermal stability of these HILs. As mentioned above, it has been demonstrated that the C2 hydrogen atom of the imidazole ring are prone to extricate and subsequently induce the degradations of dicyanamide or cyanoborohydride anions, which is therefore responsible to the low thermal stability of imidazolium-based HILs. By contrast, the quaternized DBN or DBU skeletons exhibited higher chemical inertness than traditional imidazolium cations due to the lacking of active hydrogen atoms in the structures, thereby explaining the remarkably improved thermal stability of the resulting HILs. This is also proven by the comparison results from Table 1. For example, for those HILs without N-H bonds in the cation, they exhibited better thermal stability. Moreover, with the same cation structures, most dicyanamide salts were more stable than those cyanoborohydride-based ones (**1**, **2**, **5**, **6** & **8**, **9**, **11**, **12**), except that **4**, **7** showed lower T_d values than **10**, **13**. For those protonated cations, the structure and alkalinity of super-base substrates also resulted in the difference, e.g., among five protonated HILs, **14** gave the lowest T_d value of 205 ^{o}C, probably due to the relatively weak alkalinity and reactive NH_2 groups of the TMG structure. Different from the quaternized DBN- or DBU-derived HILs, the protonated cations favoured the degradations of dicyanamide anion than cyanoborohydride anion, which may be attributed to different decomposition mechanism of two different series of anionic salts.

Density is one of the important indicators for evaluating the energy property of the propellant fuels. In general, the fuels with higher density means that more fuels can be packed into the rocket fuel tank, thereby giving higher energy and combustion contribution to the propulsion process. In this work, the densities of fourteen HILs were measured and ranged from 1.00 to 1.22 g·cm^{-3} (Table 1), which was much higher than hydrazine and its derivatives. It seemed that the dicyanamide salts showed slightly higher densities (**1-7**, 1.11-1.22 g·cm^{-3}) than those cyanoborohydride-based salts (**8-14**, 1.00-1.06 g·cm^{-3}). Among them, the salt **7** gave the highest density of 1.22 g·cm^{-3}, while the salt **8** had the lowest density of 1.00 g·cm^{-3}. The high density indicated that these new HILs as potential fuels have higher energy performance than hydrazine and its derivatives. Moreover, the viscosities of these new HILs were also measured at 25^{o}C and listed in Table 1. Their viscosities ranged from 46.4 to ~2043 mPa·s, in which **1**, **3**, **8** gave relatively lower viscosities than other salts. Among them, the salt **1** gave the lowest viscosity of 46.4 mPa·s, which was comparable to those imidazolium dicyanamide salts. From Table 1, with the same substitutes and anions, DBN-based HILs showed much lower viscosities than DBU-based salts (e.g., **1**&**5**, **8**&**11**, **2**&**6**, **9**&**12**), which might be attributed to the bulky structure of DBU with larger cycle than DBN and thus more difficulty in the ionic mobility. In addition to the cation structure, the anions may also play an important role in determining the viscosities of HILs. It seemed that the dicyanamide-based HILs showed relatively lower viscosity than those cyanoborohydride salts. For allyl substituted DBN-based HILs, the dicyanamide salts gave lower viscosities than those cyanoborohydride salts. Moreover, the substituent structures also showed obvious influence on the viscosity, e.g., the replacement of propargyl with the allyl in cation resulted in an obvious increase in their viscosities (Table1). Obviously, the viscosities of these new HILs are determined by a series of influence factors such as the structures of anion/cation, substituent, and functional groups, *etc*.

Theoretical Calculations

The heats of formation (ΔH_f) and heats of combustion (ΔH_c) of the HILs as fuels, which are directly related to their structures, are also very critical for evaluating its energy level. Thus, the ΔH_f and ΔH_c values of fourteen HILs were calculated. It should be noted that all the calculations were performed with the Gaussian 03 (Revision D.01) suite of programs.[29] The geometric optimization of the structures were carried out by using the B3LYP functional with the 6-31+G** basis set,[30] and single energy points were calculated at the MP2/6-311++G** level. For all the compounds, their optimized structures were characterized to be true local-energy minima on the potential-energy surface without imaginary frequencies. Heats of formation (HOF, $\Delta H_f{}^{\circ}$) of all the ionic liquids are calculated based on a Born–Haber energy cycle (Scheme 3).



Scheme 3. Born–Haber cycle for the formation of ionic compounds; the number of moles of the respective products are given by *a*, *b*, *c*, and *d*.

For all the ionic salts, calculation of HOFs can be simplified by equation (1):[31]

$$\Delta H_f{}^{\circ}\ (\text{ionic salts, 298K}) = \Sigma\Delta H_f{}^{\circ}(\text{cation, 298K}) + \Sigma\Delta H_f{}^{\circ}(\text{anion, 298K}) - \Delta H_L \qquad (1)$$

in which ΔH_L is the lattice energy of the ionic salts. For 1:1 salts and considering the nonlinear nature of the cations and anions used, ΔH_L (kJ mol^{-1}) can be predicted by equation (2) suggested by Jenkins *et al*.:[32]

$$\Delta H_L = \text{UPOT} + [p(n_M/2 - 2) + q(n_X/2\text{-}2)]RT \qquad (2)$$

in which n_M and n_X depend on the nature of the ions $M_p{}^{+}$ and $X_q{}^{-}$, respectively, and have a value of 6 for nonlinear polyatomic ions. The equation for lattice potential energy U_{POT} has the form shown in equation (3):[33]

$$U_{POT}\ (\text{kJ mol}^{-1}) = 1981.2(\rho_m/M_m)\ 1/3 + 103.8 \qquad (3)$$

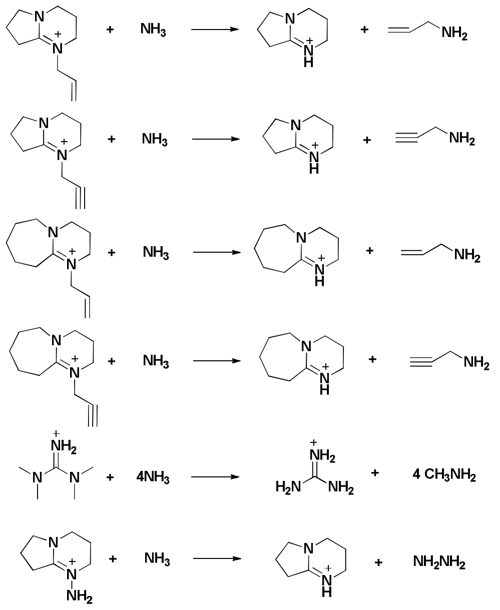
in which ρ_m is density (g·cm^{-3}) and M_m is the chemical formula mass of the ionic material.

For all the super-base-derived ionic salts, their heats of formation (HOF) were obtained by computing the component cation and anion respectively. Specifically, the computation of the HOF for both cations and anions can be readily achieved according to the reported methods,[34] i.e., the gas phase HOF of ions can be determined using equ 4 and 5, respectively. In equ. 4 and 5, additonal calclulations for the corresponding neutral molecules ($\Delta H_{f(g)C}{}^{o}$ and $\Delta H_{f(g)A}{}^{o}$) were carried out for the atomization reaction $C_aH_bN_cO_dB_e \rightarrow$ a C(g) + b H(g) + c N(g) + d O(g) + e B(g) using the G2 theory. In combination with the equ 4, the HOFs of cations were obtained by using the method of isodesmic reactions. The isodesmic reactions for seven different cations are shown in Scheme 4.

$$\Delta H_{f\,(g)C}{}^{+o} = \Delta H_{f\,(g)C}{}^{o} + IE_C \qquad (4)$$

$$\Delta H_{f\,(g)A}{}^{-o} = \Delta H_{f\,(g)A}{}^{o} + EA_A \qquad (5)$$

The enthalpy of reaction ($\Delta_r H^o{}_{298}$) is obtained by combining the MP2/6-311++G** energy difference for the reaction, the scaled zero-point energies, and other thermal factors. As a result, the heats of formation of all the ionic liquids synthesized in this work can be readily extracted. The heats of combustion (HOC, $\Delta H_c{}^{\circ}$) were calculated as the difference of the HOFs ($\Delta H_f{}^{\circ}$) between the products and reactants on the basis of combustion equations. The combustion equations of fourteen HILs are shown in the supporting information. By using the calculated heats of formation and the experimentally measured densities, the specific impulse of these new hypergolic ionic liquids was calculated by using Explo5 v6.02.



Scheme 4. Isodesmic reactions for calculating the HOFs of seven super-base-derived cations.

As shown in Table 1, the ΔH_f values of fourteen HILs ranged from -38.0 to 478.6 kJ mol^{-1}, in which the HIL **2** gave the highest ΔH_f value, i.e., 478.6 kJ mol^{-1}. Of these, except for **10**, **13** and **14** (-5.4, -38.0, and 5.1 kJ mol^{-1}, respectively), the ΔH_f values of all other HILs are higher than that of UDMH (48.3 kJ mol^{-1}) (Table 1).[2, 9] By contrast, most dicyanamide-based salts showed relatively higher ΔH_f values than those of cyanoborohydride-based HILs. Two propynyl-functionalized dicyanamide salts (i.e., **2** and **6**) gave the high ΔH_f values of > 460 kJ mol^{-1}, mainly due to the presence of some energetic bonds (like C-N, $C\equiv N$, $C\equiv C$ and C=N bonds) in their molecular frameworks. The ΔH_c values of new HILs ranged from -5611.4 kJ mol^{-1} to -9253.7 kJ mol^{-1}, suggesting that all of them can release much more energy than that of UDMH (-1979 kJ mol^{-1}) in the combustion processes.[2, 9] This is also very beneficial to improve the combustion performance of the liquid bipropellant formulations. Moreover, specific impulse (I_{sp}) is another important parameter for an propellant fuel, which is absolutely critical to the design of liquid rocket engine. By virtue of Explo5 v6.02 software, the specific impulse of new HILs were calculated, and their values varied from 154.3 to 188.1 s, in which eight HILs (i.e., **2**, **6**, **8**, **9**, **10**, **11**, **12**, and **14**) exhibited a higher I_{sp} value (> 170 s) than that of [BMIm]N(CN)$_2$ (164 s).[7] Of these, IL **9** gave the highest I_{sp} value of 188.1 s, which was very close to that of UDMH (199 s). The density impulse is the product of density and specific impulse (measure of energy content). The density impulse values for all the new HILs ranged from 173.4 to 201.2 s·g/cm^3. The relatively low volumetric specific impulse values can be attributed to the low densities (ca. 1.0-1.2 g·cm^{-3}). Among them, IL **3** gave the highest density impulse value of 201.2 s·g/cm^3, which was much higher than that of UDMH (157.2 s·g/cm^3).[2, 9]

Hypergolic Test

As a new class of hypergolic fuels, there is no doubt that the hypergolicity is very important for evaluating their uses. In previous literatures, the evaluation of the hypergolic behaviour and ignition delay time (ID time) of the fuels can be achieved by recording the time interval between the initial contact of fuel/oxidizer and the start of combustion.

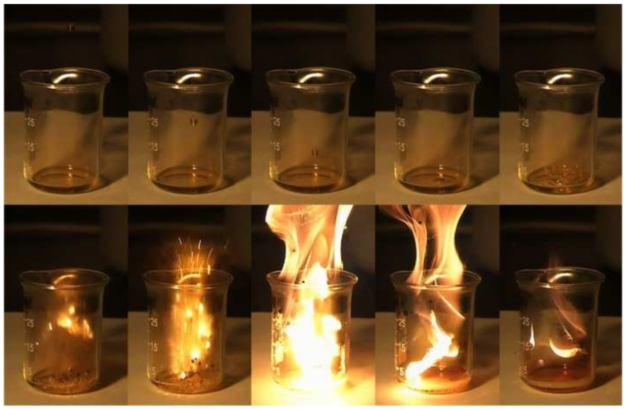


Figure 4. A droplet of ionic liquid **1** falling into 100% HNO3.

In this work, the newly prepared 100% HNO_3 was used as the oxidizer to test the hypergolicity and ID time of new HILs. The ionic liquid sample (about 20 mg) was dropped into a 25 mL glass beaker containing 100% HNO_3 (2 mL). A high-speed camera operating at 1000 frames s^{-1} was used to record the ID times. When the ionic liquid drop came into the contact with 100% HNO_3, spontaneous combustion immediately took place. In this work, all the super-base-derived HILs showed the hypergolic phenomenon upon the contact with 100% HNO_3, suggesting that they all have the potentials as the hypergolic fuels in the bipropellant formulations. Of these, the HIL **1** gave the best ignition delay performance during the hypergolic test, i.e., its ID time was as short as 27 ms, which was shorter than that of traditional [BMIm]N(CN)$_2$ (47 ms).[11] Moreover, the IL **2** also exhibited a second fastest ID time of 37 ms. Among many influence factors, the viscosity may significantly affect the ID times through the mass transfer between the fuels and the oxidizer. During ignition test, low-viscosity HILs can mix with the oxidizer much easier and faster, thereby facilitating the shorter ID times. Herein, the shorter ID times of **1**, **2** may be partly attributed to their relatively lower viscosities than other HILs. In addition to the viscosity, it seems that the ID time is also related to some other factors, e.g., the type of anion or cation, the size of droplet, and even the quality of the oxidizer and fuels. Thus, the accuracy and reproducibility of the ID times also depends on several factors. From Table 1, it can be found that the structures of both cations and anions had obvious effects on the ID times. For example, with the same anion and under same ignition conditions, those HILs containing fuel-rich groups like the allyl- and vinyl in the cations showed relatively shorter ID times. This is also demonstrated in the literature that the ID times of HILs were shortened by incorporating the allyl or vinyl substituents into the cation frameworks. Moreover, with the same anion, DBN-based salts showed relatively shorter ID times than those of DBU-based ILs, which might be explained by the lower viscosity of the former. As compared to cation effect, the choices of anion types seemed to have a dominant influence in determining their hypergolicity and ID times. When compared to those cyanoborohydride salts, it was obvious that the dicyanamide-based HILs gave shorter ID times, perhaps due to their higher viscosities of the former. Of all new HILs, **1** and **2** showed relatively good integrated properties, including relatively low viscosities, short ID times, and in particular their good thermally stability. On the whole, the discovery of these super-base-derived HILs has provided a new strategy for solving the poor thermal stability problem of traditional HILs, which can inspire researchers to search for new ionic fuels with excellent thermal stability.

Conclusions

In conclusion, fourteen super-base-derived ionic fuels have been designed and synthesized, which have been found to be hypergolic with WFNA. Of these new HILs, eleven salts are liquids at room temperature and all of them exhibit good hydrolytic stability to moisture in the air. Surprisingly, some kinds of new HILs, in particular those derived from DBU and DBN frameworks, showed unexpected thermal stability of > 280 ^oC, in which the salt **1** gave the T_d values of 310 ^oC. To the best of our knowledge, this is the highest thermal stability report that is superior to any known HILs. Moreover, two new HILs possessed relatively high loading densities, acceptable viscosities, and short ID times of < 50 ms, thereby demonstrating their potential applications as green thermally-stable fuels in formulating the liquid bipropellants.

Acknowledgements

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Notes and references

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Super-Base-Derived Hypergolic Ionic Fuels with Remarkably Improved Thermal Stability

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Two series of super-base-derived hypergolic ionic liquids were synthesized, which all exhibit good hydrolytic stability to heat and expected hypergolic property upon contact with WFNA.