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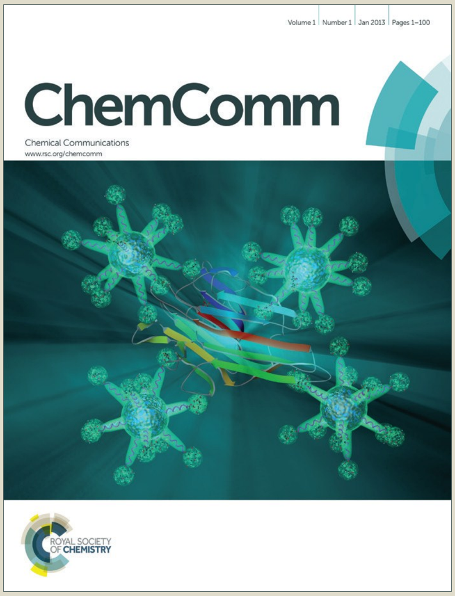

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Exploiting Hydrophobic Borohydride-Rich Ionic Liquids as Faster-Igniting Rocket Fuels†

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A family of hydrophobic borohydride-rich ionic liquids was developed, which exhibited the shortest ignition delay times of 1.7 milliseconds and the lowest viscosity (10 mPa·s) of hypergolic ionic fluids, demonstrating their great potential as faster-igniting rocket fuels to replace toxic hydrazine derivatives in liquid bipropellant formulations.

In the field of space propulsion, the majority of launch vehicles still rely on chemical propellants.[1] In those propulsion systems with pulsing modes of operation and multi-restarts, hypergolic bipropellants are widely used due to their long term reliability and good operability. In this context, rocket scientists are striving for new hypergolic fuel-oxidizer pairs which can meet the increasing requirements of low toxicity, easy handling, as well as desired performance comparable with hydrazine-type fuels.[2,3] Current fuel choices of liquid bipropellants focus more on the hydrazine-type fuels such as methylhydrazine and unsymmetric dimethyl hydrazine (UDMH). Unfortunately, high toxicity, carcinogenic risk, and volatility of hydrazine-type fuels make them environmentally unfriendly, thereby increasing the operation and storage cost. Against this background, the search for more environmentally-friendly hypergolic fuels has been an urgent goal of space science.

In recent years, a new class of ionic fuels, *viz.* hypergolic ionic liquids (HILs), which have negligible vapor pressure, low vapor toxicity and high thermal stability, has emerged as one of frontier fields of rocket propellants.[4-6] Since 2008 when the hypergolicity of some dicyanamide-based ionic liquids were first discovered by Schneider and co-workers,[7] a number of novel HILs with different structures have been developed.[8-11] Typical examples include some imidazolium, pyridinium and hydrazinium salts based on fuel-rich anions such as dicyanamide ($[N(CN)_2]^-$),[12] azide (N_3^-),[13] dicyanoborohydride ($[BH_2(CN)_2]^-$),[14] and borohydride ($[BH_4]^-$)[15] anions, *etc.* Ignition delay (ID) time is an important property in evaluating a bipropellant formulation, which is a reflection of igniting rate of hypergolic fuels. In general, short ID times of a hypergolic fuel are highly desirable. Among the developed HILs, those borohydrogen-rich anion based salts (e.g., $[BH_4]^-$, $[BH_3CN]^-$ and $[Al(BH_4)_4]^-$) exhibited very short ignition delay (ID) times.[15-17] This result is not surprising because these anions have very strong reducing feature in nature, in which the element aluminum or boron serves as an efficient hydrogen carrier. In spite of very short ID times, the majority of these hydride-rich HILs have poor stability to water due to the high reactivity of reducing anions. Thus, the development of new water-stable HILs with very low viscosities and simultaneously ultra-short ID times still remains a challenging task.

To date, no water-stable ionic fuels with ID time of < 2 milliseconds (ms) have been reported. Analyzing the stabilities of previously reported hydrogen-rich anions, i.e., typical $[BH_4]^-$ and $[BH_2(CN)_2]^-$, partial replacement of negatively charged hydrogen atoms with electron-withdrawing cyano group can significantly improve the water stability of resulting HILs. For example, Shreeve and co-workers designed some water-stable dicyanoborohydride ($[BH_2(CN)_2]^-$) HILs.[14] However, decreasing of negatively charged hydrogen content in anionic framework may correspondingly affect the ignition delay performance. Clearly, the strategy of incorporating two cyano groups into anionic framework while retaining the content of negatively charged hydrogen will be highly desirable, since it is likely to achieve the goals of both water stability and short ID times in a HIL molecule. Under the guidance of this principle, here we designed and synthesized a new family of relatively water-stable borohydride-rich HILs, which exhibited hydrophobic characteristic and simultaneously an ultra-short ignition delay time as short as 1.7 ms. In the design strategy of borohydride-rich anion, *viz.* $[BH_3(CN)BH_2(CN)]^-$, one cyano group can serve as a stabilizing ligand to bridge two hydrogen-rich $\{BH_3\}$ and $\{BH_2CN\}$ moieties, while both two cyano groups as electron-withdrawing group play a role in improving the chemical

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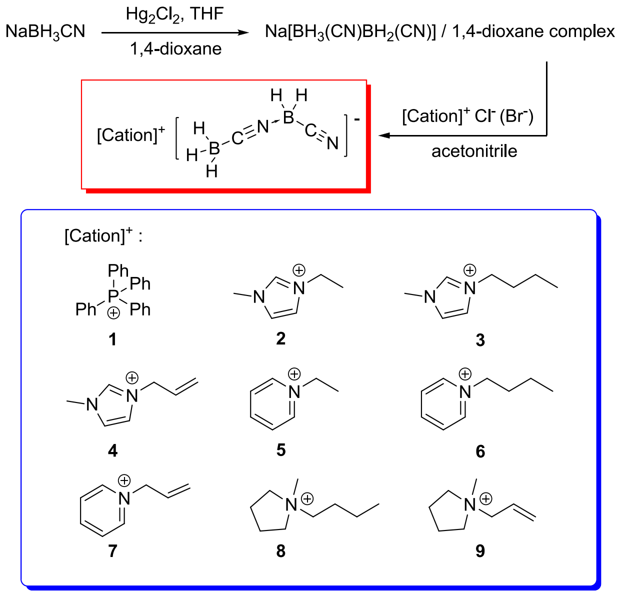

Scheme 1. Synthesis of borohydride-rich ionic liquids based on $[BH_3(CN)BH_2(CN)]^-$ anion.

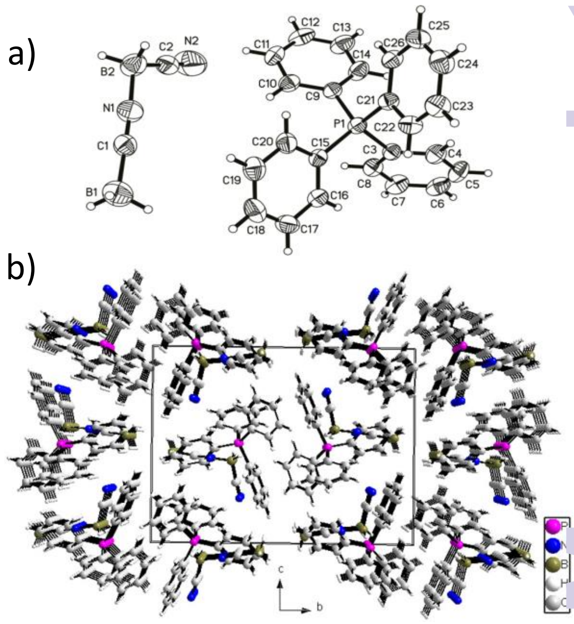

Fig. 1. ORTEP diagram of salt **1**

stability of negatively charged hydrogen atoms. When compared with typical $[BH_2(CN)_2]^-$, this new design strategy demonstrates the smartness and effectiveness of anionic framework, in which the cyano-bridged borohydrogen-rich structure not only increases the content of negatively charged hydrogen but also retains the structural characteristic of two electron-withdrawing groups that can stabilize the reactive $\{BH_3\}$ and $\{BH_2\}$ species.

To the best of our knowledge, the anionic crystal structure of $[BH_3(CN)BH_2(CN)]^-$ salts has not been confirmed yet.[18] Thus, in our first attempt a metathesis reaction of $Na[BH_3(CN)BH_2(CN)]$ with tetraphenylphosphonium bromide yielded a water-insoluble solid organic salt with a melting point of 95 °C (Scheme 1, salt **1**). Slow recrystallization of **1** from its ethyl acetate solution afforded colourless prism suitable for X-ray diffraction analysis. The structure is shown in Fig. 1 and the crystallographic data are summarized in Table S6 of ESI†.[19] X-ray crystallographic analysis of **1** showed that it crystallized in monoclinic space group $P2_1/c$, with a calculated density of 1.139 g cm^{-3}. In $[BH_3(CN)BH_2(CN)]^-$ anion, the $\{BH_3\}$ and $\{BH_2CN\}$ species are linked by a cyano bridge, *viz.* C(1)-N(1). The bridged N(1) atom is coordinated to the middle B(2) atom, and the associated B(2)-N(1) bond length is 1.555 Å. The bond angle of triangular N(1)-B(2)-C(2) bonds is up to 109.3°.

After structural confirmation of $[BH_3(CN)BH_2(CN)]^-$ anion through salt **1**, our efforts began to search for new room temperature HILs with this anion. By using asymmetrical organic cations (e.g., 1-allyl-3-methyl-imidazolium and *N*-allyl-pyridium) to replace the bulky tetraphenylphosphonium cation in the metathesis reaction, eight new HILs were obtained with high yields (scheme 1). These HILs were fully characterized by ^1H and ^{13}C NMR, IR spectroscopy, electrospray ionization high resolution mass spectrometry (ESI/HRMS), and elemental analysis. The characterization data support the expected structures and their high purities (See characterization data in ESI†). As expected in our design strategy, all resulting HILs are colorless or light yellow liquids at room temperature while showing high thermal stability, very low viscosities, as well as the hypergolicity upon contact with WFNA (white fuming nitric acid).

Table 1. Properties of the $[BH_3(CN)BH_2(CN)]^-$-based HILs.

IL	T_m/T_g[a] (°C)	T_d[b] (onset) (°C)	ρ[c] (g cm^{-3})	ΔH_f[d] (KJ mol^{-1})	η[e] (mPa·s)	ID[f] (ms)	I_{sp}[g] (s)
1	95	242	1.1606	182.46	-	269.0	133.4
2	-33	240	0.9260	42.18	19	4.3	193.4
3	-30	230	0.9131	15.97	22	3.0	186.4
4	-26	181	0.9348	167.25	17	2.4	199.0
5	-37	261	0.9339	93.88	22	2.0	192.3
6	-32	243	0.9195	66.36	27	2.3	185.4
7	-20	267	0.9412	219.80	10	1.7	197.7
8	-32	245	0.8859	-120.32	25	3.3	182.6
9	-22	166	0.9011	29.11	14	2.1	193.6

[a] Melting point/glass transition temperature. [b] Thermal decomposition temperature (TGA ,onset). [c] Density at 25 °C. [d] Heat of formation. [e] Viscosity at 25 °C. [f] Ignition-delay time with WFNA. [g] Specific impulse (Explo 5 v6.02)

Thermal, physical and hypergolic properties of eight room temperature HILs (**2**-**9**) were studied in detail. From Table 1, it is seen that the HILs **2**-**9** exhibited very wide liquid operating ranges of wider than 200 °C, in which **5** gave the lowest glass transition temperature (T_g) of -37 °C and **7** showed the highest thermal decomposition temperature (T_d, onset) of 267 °C, respectively. Density and viscosity are another two important physical properties. In general, high fuel density can contribute effectively to small tankage and therefore reduce the structural weight and aerodynamic drag of vehicle. From Table 1, eight room temperature HILs (compounds **2**-**9**) displayed the densities of 0.89-0.94 g cm^{-3}, which was comparable to dicyanoborohydride and borohydride HILs (approximately 0.9-1 g cm^{-3}) but much higher than hydrazine-type fuels (e.g., 0.793 g cm^{-3} of UDMH),[16] indicating their higher loading capacity than hydrazine-type fuels. Low viscosity of propellant fuels is highly desirable for the mass transfer requirements during fuel pumping, pressurization, ignition and combustion processes. Ionic fuels **2**-**9** exhibited impressive low viscosities of less than 30 mPa·s, in which **7** gave the lowest viscosity (10 mPa·s) of known HILs to date, highlighting their promising potential as novel fuels in rocket engines.

Interestingly, this new family of HILs displayed unexpected water immiscibility (Fig. S2, ESI†). This promising property not only facilitates the synthesis and purification of salts but also can efficiently relieve the hygroscopic problem during the storage, transport, and operating processes. It has been demonstrated that the exact association of water molecules to the anions of ionic liquids can be considered as a reliable indicator for the immiscibility of ionic liquids with water.[20,21] In order to gain a deep insight into the water immiscibility of these new HILs, the interaction energy (E_{inter}) of four different borohydride-containing anions (i.e., $[BH_3(CN)BH_2(CN)]^-$, $[BH_2(CN)_2]^-$, $[BH_3CN]^-$, and $[BH_4]^-$) with water molecule was calculated. The optimized structures of four different anion/water systems were given in Fig. S1 (ESI†). The results showed that the calculated E_{inter} values of four anions with water molecule were −5.1 kcal mol^{-1} of $[BH_3(CN)BH_2(CN)]^-/H_2O$, -6.1 kcal mol^{-1} of $[BH_2(CN)_2]^-/H_2O$, -7.5 kcal mol^{-1} of $[BH_3CN]^-/H_2O$, and −8.6 kcal mol^{-1} of $[BH_4]^-/H_2O$, respectively (Table S1, ESI†), which indicated $[BH_3(CN)BH_2(CN)]^-$ exhibit much weaker interactions with water molecule than other three borohydride-containing anions. Considering that a few $[BH_2(CN)_2]^-$-based HILs (-6.1 kcal mol^{-1} of anion/H_2O E_{inter}), e.g., 1-allyl-1-methylpyrrolidinium dicyanoborate,[15] have exhibited the immiscible characteristic in water, the hydrophobicity of new $[BH_3(CN)BH_2(CN)]^-$ HILs (−5.1 kcal mol^{-1} of anion/H_2O E_{inter}) could be justified by their weaker anionic interaction energy with water than that of $[BH_2(CN)_2]^-$. These can shed light on the hydrophobic nature of these new borohydride-rich HILs.

Heats of formation (ΔH_f) of rocket fuels, which are directly related to their structures, are very critical for evaluating their energy level. Thus, the ΔH_f values of nine HILs were also calculated (Table 1). The computation details are provided in the Supporting Information. From Table 1, except for salt **8**, other seven HILs had positive heats of formation, in which **7** gave the highest ΔH_f value of 219.80 kJ mol^{-1}. It seems that the allyl-substituted imidazolium and pyridinium based HILs (e.g., **4** and **7**) showed relatively higher ΔH_f values than that of other HILs, while the pyrrolidine based ones showed the lowest ΔH_f values (**8** and **9**). By using the calculated heats of formation and experimental densities of new HILs, their specific impulses (I_{sp}) were calculated. In general, the I_{sp} value of a desired HIL is expected to be comparable with that of UDMH (198 s).[16] In this study, eight room temperature HILs (**2**-**9**) showed the calculated I_{sp} values ranging from 182.6 to 199.0 s. Of these **4** and **7** exhibited high I_{sp} values of 199.0 s and 197.7 s, respectively, which were higher or comparable to that of UDMH (198 s), demonstrating their potential applications as promising replacements of hydrazine derivatives.

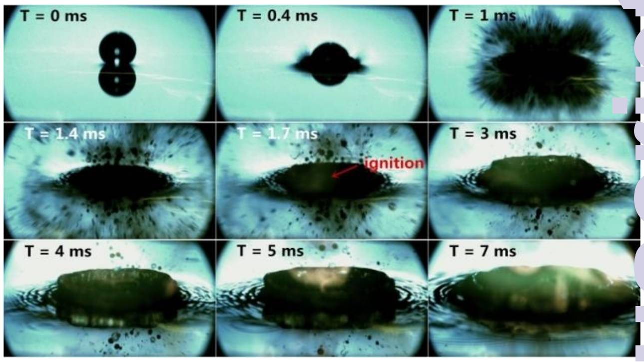

Fig. 2. The droplets tests recorded of HIL **7** with WFNA captured by high speed camera phaton v12 with a long scope microscope; sampling rate is 7000 fps, i.e., the time interval between two frames is 0.143 ms.

Short ID times can contribute positively to high combustion efficiency of propellant fuels. In order to accurately measure the ID times, a droplets test was performed. A high speed camera phaton v12 with a long scope microscope was used to capture the pictures for the process of the ionic liquid drop dropping down into an oxidizer pool. The shadow images (7000 fps) for a D = 1.8 mm ionic liquid drop of HIL **7** were shown in Fig. 2. From Fig. 2, upon the drop contact the oxidizer surface at T = 0 ms, it merged with the pool liquid and a mixing layer was formed, in which liquid phase oxidation-reduction reaction was expected to occur. When sufficient gas products were accumulated in the mixing layer, micro-explosion happened, as shown by the picture for T = 0.4 ms. At the same time, the liquid phase reaction released significant amount of heat, which vaporized the fuel and oxidizer mixture. If the temperature of gas phase reactant mixture increased to sufficiently high, ignition happened and a flame kernel was initiated as shown by the picture for T = 1.7 ms.

During the drop tests of eight HILs **2**-**9**, vigorous ignition took place, with ultra-short ID times of less than 5 ms. Among them, the ID time of **7** was as short as 1.7 ms, which is faster than all known HILs, demonstrating its superior hypergolic activity. When compared to those $[BH_2(CN)_2]^-$ and $[BH_4]^-$-based HILs, these $[BH_3(CN)BH_2(CN)]^-$ HILs showed very competitive ID times. For example, with the same cation of $[AMIm]^+$ (1-allyl-3-methyl-imidazolium), the ID times of three HILs $[AMIm][BH_3(CN)BH_2(CN)]$, $[AMIm][BH_2(CN)_2]$ and $[AMIm][BH_4]$ were 2.4 ms, 8 ms, and 2 ms, respectively. This indicates that our design strategy of borohydride-rich using cyano-bridged $[BH_3(CN)BH_2(CN)]^-$ anion is very successful to achieve both improved water stability and short ID times. Analyzing the factors of determining these HILs' ultra-short ID times, in addition to high content of negatively charged hydrogen in the anion, the low viscosity is another important factor. Clearly, with same cation structure, those HILs with relatively lower viscosities (e.g., **4**, **7** and **9**) exhibited shorter ID times, which could be explained by low viscosity making rapid mixing and oxidation-reduction reaction between HIL and oxidizer much easier and faster.

In conclusion, a new family of borohydride-rich HILs was synthesized, which showed highly hypergolic feature with WFNA as oxidizer. These novel HILs possessed superior physical properties and hypergolic performance than most reported hydrogen-rich HILs, e.g., better water stability, lower viscosities and faster igniting rate. More interestingly, these new HILs exhibited a promising characteristic of water immiscibility due to low E_{inter} values between ILs' anion and water molecule. With the decomposition temperatures and specific impulses as high as 267 ^{o}C and 199 s respectively, their viscosities as low as 10 mPa·s, and ID times as short as 1.7 ms, these novel borohydride-rich HILs are promising choices of hypergolic fuels to date to replace toxic hydrazine-type fuels in the bipropellant formulations.

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