CHEMISTRY
AN ASIAN JOURNAL
www.chemasianj.org

Title: Synthesis and Properties of Azide-functionalized Ionic Liquids as Attractive Hypergolic Fuels

Authors: Zhenyuan Wang, Guangxing Pan, Binshen Wang, Ling Zhang, Weiwei Zhao, Xing Ma, Jichuan Zhang, and Jiaheng Zhang

To be cited as: *Chem. Asian J.* 10.1002/asia.201900364

Link to VoR: http://dx.doi.org/10.1002/asia.201900364

A Journal of
ACES
Asian Chemical Editorial Society

A sister journal of Angewandte Chemie and Chemistry – A European Journal

WILEY-VCH

Chemistry - An Asian Journal 10.1002/asia.201900364

Synthesis and Properties of Azide-functionalized Ionic Liquids as Attractive Hypergolic Fuels

Zhenyuan Wang§[a,b], Guangxing Pan§[a,b], Binshen Wang[a,b], Ling Zhang[a,b], Weiwei Zhao[a,b], Xing Ma[a,b], Jichuan Zhang*[a,b], and Jiaheng Zhang*[a,b,c]

Dedication ((optional))

Abstract: Hypergolic ionic liquids (ILs) have shown a great promise as viable replacements for toxic and volatile hydrazine derivatives as propellant fuels, and hence, have attracted increasing interest over the last decade. To take advantage of the reactivity and high energy density of the azido group, a family of low-cost and easily-prepared azide-functionalized-cation-based ILs, including fuel-rich anions, such as nitrate, dicyanamide, and nitrocyanamide anions, were synthesized and characterized. All the dicyanamide and nitrocyanamide based ILs exhibited spontaneous combustion upon contact with 100% HNO_3. The densities of these hypergolic ILs varied in the range of 1.11-1.29 g·cm^{-3}, and the density-specific impulse, predicted based on Gaussian 09 calculations, was between 289.9 and 344.9 s·g·cm^{-3}. Both these values of two physical properties are much higher than those of unsymmetrical dimethylhydrazine (UDMH). Among the studied compounds, compound IL-3b, i.e., 1-(2-azidoethyl)-1-methylpyrrolidin-1-ium dicyanamide, shows excellent integrated properties including the lowest viscosity (30.9 m·Pas), wide liquid operating range (-70 to 205℃), shortest ignition-delay time (7 ms) with 100% HNO_3, and superior density specific impulse (302.5 s·g·cm^{-3}), suggesting promising application potential as bipropellant formulations.

Introduction

In the technology-intensive aviation and aerospace fields, hypergolic liquid propellants have been a subject of in-depth research over the past decades because of their high specific impulse, excellent ignition with a low ignition-delay (ID) time, and superb thrust control.[1, 2] The current choices of hypergolic liquid propellants are primarily focused on hydrazine and its derivatives, such as monomethyl hydrazine (MMH) and unsymmetrical dimethylhydrazine (UDMH). However, these hydrazine-based fuels are highly toxic due to their volatility and carcinogenic properties, which leads to expensive storage and handling procedures and costly safety precautions.[3-6] Hence, the search for more environment-friendly hypergolic fuels has become a necessity for space science.[7, 8]

In recent years, a novel concept of hypergolic ionic liquids (ILs) has emerged to address the challenges offered by hydrazine derivatives. This is because of their enhanced physico-chemical properties, including extremely low volatility, low toxicity, good thermal stability, high loading density, wide liquid range, short ignition delay, and good thrust control.[9-13] Moreover, the properties of hypergolic ILs can be readily varied and tuned through the modification of the cationic and/or anionic components. Hence, the development of new hypergolic ILs for use as aerospace propellants has attracted significant attention. The hypergolicity of some dicyanamide-based ionic liquids were first discovered by Schneider and co-workers in 2008.[14] Since then, several families of hypergolic ILs with different structures have been reported, including azide (N_3^-),[15, 16] dicyanamide ($[N(CN)_2]^-$),[6, 17-21] nitrocyanamide ($[N(NO_2)CN]^-$),[22, 23] borohydride,[24-38] etc.

The heat of formation (HOF) is one of the crucial characteristics of hypergolic ILs, which is directly related to the number of nitrogen-nitrogen bonds in the molecule. Thus, searching for ILs with a high number of nitrogen-nitrogen bonds should be a promising direction toward the development of new hypergolic ILs.[10, 39] Besides, the design of hypergolic ILs is based on energetic materials. As often as possible, the structures of these materials contain high-energy fragments such as a nitrogen-nitrogen bond, an azido group, or an imidazole or triazole ring, often with unsaturated substituents. It has been found using theoretical calculations that the azido group is highly energetic, adding approximately 280 kJ·mol^{-1} to the energy content of a molecule, which is highly favorable for the design of novel hypergolic ILs.[16, 40] In 2008, Schneider et al. reported the formation of several imidazolium-based azides with saturated and unsaturated side chains.[15] However, when treated with red-fuming nitric acid and N_2O_4, all the liquid azide salts reacted vigorously with copious production of red fumes, but without ignition. Shortly thereafter, Shreeve et al. designed and synthesized some azide-functionalized hypergolic ILs that contain the 2-azido-N,N,N-trimethylethylammonium cation with nitrocyanamide, dicyanamide, dinitramide or azide anion by metathesis reactions.[16] Among these, four hypergolic ILs exhibited hypergolic activity with WFNA, with high values of HOFs ranging from 380 to 894 kJ·mol^{-1}. Interestingly, HOFs of the bis-azido-substitued ILs were nearly twice that of the mono-azido-substituted ones with the same anion, showing significant contribution of the azido group for the HOF of ILs. Besides, the 2-azido-N,N,N-trimethylethylammonium nitrocyanamide exhibited the shortest ID of 8 ms, which is the same as that exhibited by monomethyl-hydrazine. However, 2-azido-N,N,N-trimethylethylammonium nitrocyanamide stayed in the solid state

---

[a] Z. Wang, G. Pan, B. Wang, L. Zhang, J. Zhang, W. Zhao, X. Ma, J. Zhang, State Key Laboratory of Advanced Welding and Joining, Harbin Institute of Technology, Shenzhen, 518055, China.
E-mail: jiahengzhang@hit.edu.cn
[b] Z. Wang, G. Pan, B. Wang, L. Zhang, J. Zhang, W. Zhao, X. Ma, J. Zhang, Research Centre of Flexible Printed Electronic Technology, Harbin Institute of Technology, Shenzhen, 518055, China
[c] J. Zhang, Zhuhai Institute of Advanced Technology Chinese Academy of Sciences, Zhuhai, 519000, China

Supporting information for this article is given via a link at the end of the document.((Please delete this text if not appropriate))

10.1002/asia.201900364

in a wide range of room temperatures, which may limit its application scope.

To take advantage of the reactivity and high energy density of the azido group, a series of low-cost, easily prepared, and environment-friendly azide-functionalized cations were designed and synthesized from commercially available materials. Meanwhile, the above mentioned cations were combined with anions that have been previously employed in ionic-liquid-fuel-based hypergolic mixtures, i.e., nitrate, dicyanamide and nitrocyanamide anions, to form a novel family of azide-functionalized hypergolic ILs. These hypergolic ILs exhibited a wide liquid operating range, superb density specific impulse, high density, low viscosity, and simultaneously fast ID times (as short as 7 ms).

Results and Discussion

Synthesis

Some readily available and relatively inexpensive starting materials were used for the synthesis of the ILs via a straightforward three-step procedure as illustrated in Scheme 1. In the first step, the reactions of five types of tertiary amine hydrochlorides (i.e., N,N-diethyl-2-chloroethylanine hydrochloride, N,N-dimethyl-3-chloropropylamine hydrochloride, 2-pyrrolidinoethyl chloride hydrochloride, 2-piperidinoethyl chloride hydrochloride, and 2-morpholinoethyl chloride hydrochloride) with sodium azide complex in water were conducted for the formation of azide substituted tertiary amine. Subsequently, quaternization reactions of azide substituted tertiary amines with MeI led to the formation of azide substituted quaternary ammonium iodides. Finally, fifteen azide-functionalized ILs were generated via metathesis reactions of azide-substituted quaternary ammonium iodides with silver nitrate, silver dicyanamide or silver nitrocyanamide. ^{1}H and ^{13}C NMR spectroscopy, X-ray crystallographic analysis, infrared spectroscopy and elemental analysis were conducted for the characterization of resulting ILs, structures and purities of whom were in good agreement with that expected.

Crystal structure

Single crystals of IL-5a were obtained through slow recrystallization from an ethanol solution, and a suitable crystal was selected for XRD analysis. The structure is shown in Figure 1 and the crystallographic data are summarized in Table S4 in the Supporting Information. The X-ray crystallographic analysis revealed that IL-5a crystallized in the monoclinic *Pbca* space group with the lattice parameters of a=12.2781(7), b=12.6945(7), and c=13.2741(6) Å; α=90°, β=90°, and γ=90°; ρ=1.498 g·cm^{-3} and Z=8. In the structure of the cation, the azide group was connected to the nitrogen atom of morpholine ring through an ethyl group (-CH_2-CH_2-). The cations and anions interacted with each other through electrostatic interactions to form the supramolecular structure of IL-5a.

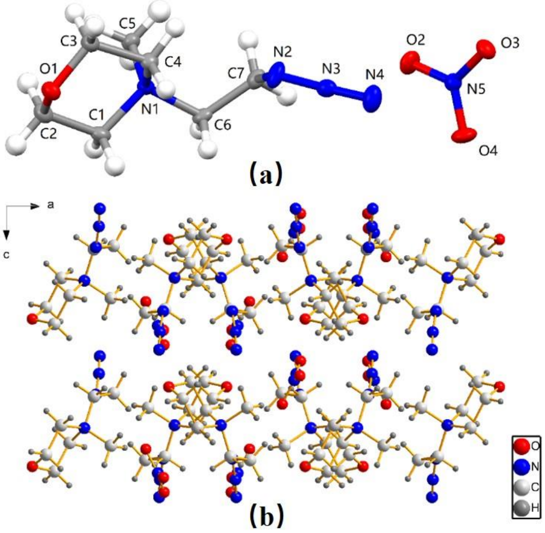
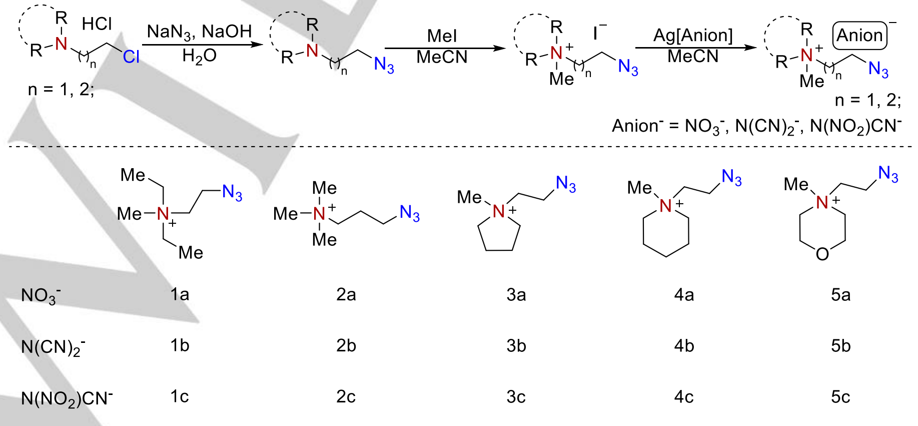


Figure 1. ORTEP diagram of IL-5a.



Scheme 1. Synthesis of the studied ILs.

10.1002/asia.201900364

Besides, X-ray diffraction analysis of three iodide precursors with the same cations as IL-1, IL-2, and IL-3 was also conducted. The structures and crystallographic data are summarized in Figure S2 in the Supporting Information.

Thermal properties

The phase transition temperature (T_g/T_m) and thermal decomposition temperature (T_d), determine the liquid operating range, and hence, are the vital parameters for propellant fuels. The values of T_g/T_m and T_d were determined by means of differential scanning calorimetric (DSC) measurements at the heating rate of 5°C·min^{-1}. As shown in Table 1, all the fifteen salts were ionic liquids based on the definition of ionic liquids as the ones having a melting point below 100°C. To become a fuel component of a hypergolic mixture, it is desirable for a compound to exhibit a wide liquid-phase range in order to permit application of the fuel at extreme temperatures. Table 1 shows that most of the ILs (except IL-1a, IL-2b and IL-5a) were liquids at room temperature and their liquid operating ranges were relatively wide (>270°C), which are superior to those of unsymmetrical dimethyl hydrazine (UDMH, 121°C) and 2-azido-N,N,N-trimethylethylammonium nitrocyanamide (217°C).[16] Much the same as most traditional ILs, all of the hypergolic ILs have no boiling point and only undergo an exothermic decomposition upon heating at high temperature.[10] Hence the decomposition temperature (T_d) directly decides the maximum allowable operating temperature of hypergolic ILs. Generally speaking, an ideal T_d value of a hypergolic IL is expected to be over 200°C.[27] It can be seen from Table 1 that T_d values of all these ILs lay within the range of 200.5-211.2°C, showing that they had a high thermal stability. Moreover, the anions were found to have a significant effect on T_d. In the case of the same cation, T_d values of dicyandiamine-based ILs (IL-b series) were the lowest, while the nitrocyanamide-based ILs (IL-c series) possessed the highest values of T_d. In contrast, no definite correlations were observed between cation/anion and the phase transition temperature (T_g/T_m).

Density

In addition to thermal properties, density is another vital parameter for evaluating energy level of the propellant fuels. In general, a fuel with higher density not only allows more fuels to be packed into a given volume of the fuel tank, but also increases the performance through higher I_{sp} values, thereby contributing higher energy and combustion contribution to the propulsion process. Figure 2 and Table 1 show that the densities of all ILs were greater than 1.10 g·cm^{-3}, which are superior to the traditional UDMH (0.79 g·cm^{-3}); thus, suggesting that these new ILs also possess higher loading capacity than the traditional hydrazine-based fuels. Besides, Table 1 shows that anions have a significant effect on the densities. In particular, densities of dicyandiamine-based ILs were in the range of 1.11 to 1.20g·cm^{-3}, which were significantly lower than that for nitrocyanamide-based one (1.19 to 1.29 g·cm^{-3}), while the nitrate-based ILs exhibited the highest densities of all the studied ones (1.20 to 1.31 g·cm^{-3}). On the other hand, in the case of the same anion, the densities of ILs did not exhibit a similar trend.

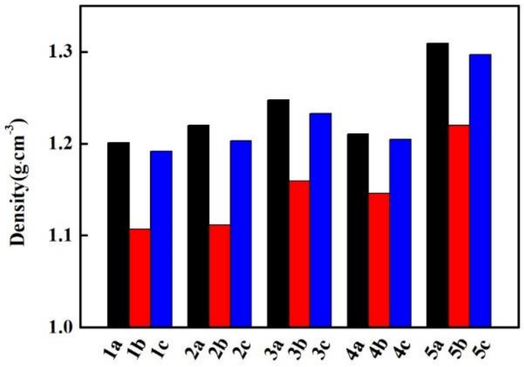
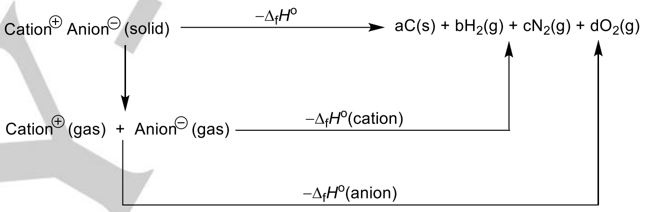


Figure 2. Densities of the studied ILs.



Scheme 2. Born-Haber cycle for the formation of ILs; the number of moles of the respective products are given by a, b, c, and d.

Viscosity and specific impulse

In a bipropellant system, low viscosities can facilitate rapid mass and heat transfer between the fuel and oxidizer in the mixing process; thereby, favoring the inducement of spontaneous initiation and combustion reactions. Therefore, a low viscosity of hypergolic ILs is one of the vital properties that meets the practical application criteria required for well-performing fuels. The viscosities of these azide-substituted ILs are listed in Table 1. The anions also significantly influenced viscosities, and a similar trend the one for densities was found (viscosities: nitrate-based>nitrocyanamide-based>dicyandiamine-based). Among these, IL-3b depicted the lowest viscosity of 30.9 mPa·s, which is lower than those for known azide-functionalized ILs.[10, 21]

The theoretical calculations were performed using the Gaussian 09 suite of programs.[42] Heats of formation (HOF, $\Delta_f H$) of these newly synthesized ILs were calculated based on the Born-Haber energy cycle (Scheme 2) and isodesmic reactions. The computational processes and details are provided in the Supporting Information, while the corresponding results are listed in Table S1-S3. By using the calculated heats of formation and the experimentally measured densities, the values of the specific impulse (I_{sp}) and the density impulse (ρI_{sp}) were calculated with Explo5 v6.02 software.[43] Table 1 shows that the density impulse of all the azide-functionalized ILs were greater than 289 s·g·cm^{-3}, and much higher than that of UDMH (215.7 s·g·cm^{-3}),[20] indicating that these newly synthesized azide-functionalized ILs have excellent application potential.

Table 1. Physicochemical properties of 15 ILs.

ILs	T_g/T_m[a]	T_d[b]	η[c]	ρ[d]	ID[e]	$\Delta_f H_{salt}$[f]	I_{sp}[g]	ρI_{sp}[h]
	(°C)	(°C)	mPa·s	g·cm^{-3}	ms	kJ·mol^{-1}	s	s·g·cm^{-3}
1a	26.8	204.1	-	1.20	-	113.03	268.3	322.0
1b	<-70	200.5	59.2	1.11	15	309.96	262.6	291.5
1c	<-70	211.2	93.4	1.19	95	406.66	267.8	318.7
2a	<-70	206.5	279.9	1.22	-	59.49	267.4	326.2
2b	3.5	204.2	42.8	1.11	12	258.79	261.1	289.8
2c	<-70	210.5	71.8	1.20	65	355.19	267.0	320.4
3a	<-70	206.2	334.1	1.25	-	110.54	266.4	333.0
3b	<-70	205.0	30.9	1.16	7	307.31	260.8	302.5
3c	<-70	210.2	62.1	1.23	201	405.38	266.1	327.3
4a	<-70	208.2	518.4	1.21	-	91.52	266.0	321.9
4b	<-70	209.0	84.5	1.15	25	285.17	261.0	300.2
4c	<-70	210.5	93.1	1.20	75	383.46	265.8	316.3
5a	95.8	207.0	-	1.31	-	2.25	265.5	347.8
5b	<-70	205.7	310.8	1.22	17	198.39	260.0	317.2
5c	<-70	210.9	404.6	1.30	80	295.24	265.3	344.9

[a] Glass transition temperature (T_g)/melting point (T_m). [b] Decomposition temperature (onset). [c] Viscosity at 25°C. [d] Density at 25°C. [e] Ignition-delay (ID) time with 100% HNO_3. [f] Heat of formation. [g] Specific impulse (Explo5 v6.02) at the optimum oxidizer (100% HNO_3)-to-fuel ratio; isobaric conditions, equilibrium expansion, 7.0 MPa chamber pressure. [h] Density impulse.

Hypergolic test

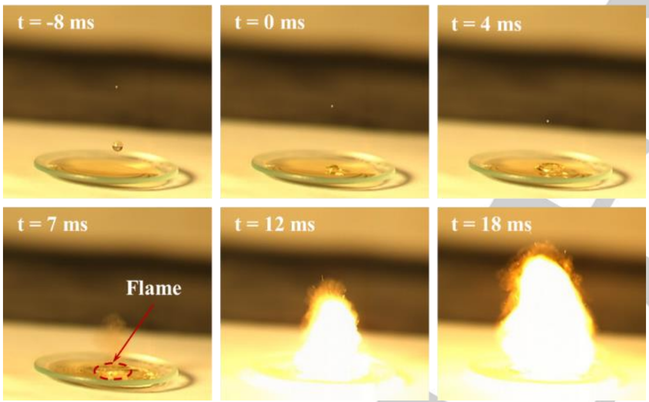


Figure 3. Droplet test recorded for IL-3b with 100% HNO_3.

As potential hypergolic fuels, evaluating the hypergolic reactivity with bipropellant oxidizers is crucial in determining whether the fuel itself is suitable for practical propellant applications. In general, hypergolic reactivity is estimated by recording the ID time, which is defined as the time interval between the instant when the fuel droplet comes into contact with the oxidizer liquid pool surface and the instant when a flame emerges. The shorter ID times can contribute positively towards higher combustion efficiency in the propellant fuels. To investigate the ID times of ILs, a droplet test with newly prepared 100% HNO_3 as oxidizer was performed and the visible ignition was captured using high-speed camera at 2000 fps (each sample was tested three times). Figure 3 shows a representation of the droplet test process performed on IL-3b. Following the contact of IL-3b with 100% HNO_3, a drastic oxidation-reduction reaction occurred immediately, and a hypergolic ignition with a flame kernel was clearly observed after 7 ms.

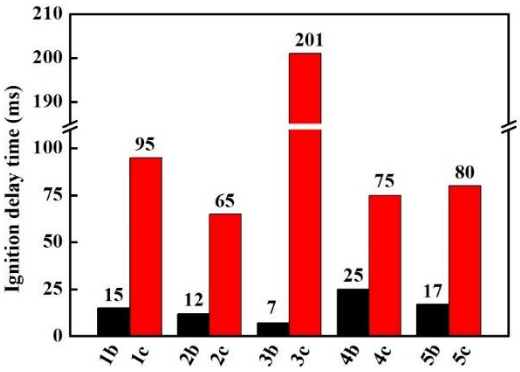


Figure 4. Ignition delay (ID) times of the studied ILs.

The ID times of the newly synthesized ILs are shown in Figure 4 and Table 1 without the nitrate-based ILs (IL-a series), which can not be ignited. In principal, an acceptable time for ignition delay in the real life applications is less than 50 ms.[19] Compared to the traditional hypergolic ILs, such as [BMIm]N(CN)$_2$ (ID=46 ms), five of the synthesized dicyandiamine-based ILs (IL-b series) showed shorter ID times (7-25 ms). Meanwhile, to the best of our knowledge, IL-3b demonstrated the shortest ID time (7 ms) of all the azide-functionalized ILs that have ever been reported. Studies have shown that the fuel-rich anion of an IL plays a decisive role in inducing hypergolicity, while the cation plays a secondary role, i.e., subtly affecting the ID time. By analyzing the factors that might affect the ID time during the hypergolic test, viscosity of the hypergolic IL is one of the most-important factors. The shorter ID times of dicyandiamine-based ILs (IL-b series) may be partly attributed to their relatively lower viscosities than the nitrocyanamide-based ILs (IL-c series), which makes the rapid mixing and an oxidation-reduction reaction between the IL and 100% HNO_3 relatively much easier and faster.

Conclusions

In summary, 15 novel azide-functionalized-cation-based ILs were designed and synthesized, and 10 of the dicyanamide-based and nitrocyanamide-based ILs exhibited decent hypergolic properties upon contact with 100% HNO_3. The hypergolic ILs displayed excellent physiochemical properties including low melting points, high thermal stability, low viscosities, and unique hypergolic reactivity. Besides, compound IL-3b showed the best integrated properties including the lowest viscosity and the shortest ignition-delay time with 100% HNO_3 among all the azide-functionalized ILs that have been reported to the best of our knowledge. Furthermore, the cost-effective and scale-up advantages of IL-3b highlights its promising potential as a replacement for toxic and volatile hydrazine derivatives.

Experimental Section

Materials

N,N-diethyl-2-chloroethylanine hydrochloride (99%), N,N-dimethyl-3-chloropropylamine hydrochloride (97%), 2-pyrrolidinoethyl chloride hydrochloride (98%), 2-piperidinoethyl chloride hydrochloride (98%), 2-morpholinoethyl chloride hydrochloride (99%), sodium dicyanamide (95%), sodium azide (98%), silver nitrate (99%), and N-methyl-N-nitroso-N-nitroguanidine (99%) were purchased from Aladdin. Silver nitrocyanamide and silver dicyanamide were synthesized using methods reported in previous literatures.[23, 41] All other chemicals and organic solvents were obtained commercially as analytical grade materials and were used as received.

Product characterization

^{1}H and ^{13}C NMR spectra were recorded with a 400 MHz (Bruker AVANCE 400) spectrometer in D_2O. The thermal property measurements of ILs were performed using a TGA/DSC1 and a DSC1 Mettler Toledo calorimeter at a heating rate of 5°C·min^{-1}. The density measurements were performed at 25°C on a Mettler Toledo Densito 30PX densimeter. The elemental analysis was conducted on a Flash EA-1112 elemental analyzer, while the viscosity measurements were performed at 25°C on a Brook field Rheometer DV3T. The ignition photographs of these newly synthesized ILs with the oxidizer of 100% HNO_3 were recorded on an Olympus i-speed 3 camera at 2000 fps.

Synthesis of the ILs

2-Azido-N,N-diethylethan-1-amine: The sodium azide (1.95g, 30 mmol) was added slowly into an aqueous solution of N,N-diethyl-2-chloroethylanine hydrochloride (0.1 mol·L^{-1}, 100 mL, 10 mmol) under stirring at room temperature. The mixture was then heated to 80℃ and stirred overnight. After cooling to room temperature, NaOH was added until the *pH* was equal to 10. Thereafter, the mixture was extracted with CH_2Cl_2 (3V, 80 mL), dried over Na_2SO_4, filtered, and concentrated in a rotary evaporator under vacuum. 2-azido-N,N-diethylethan-1-amine was obtained with a yield of 96.48% (1.37 g).

2-Azido-N,N-diethyl-N-methylethan-1-aminium iodide: An acetonitrile solution of iodomethane (1.5 mol·L^{-1}, 20 mL, 30 mmol) was added dropwise to the ice-cold acetonitrile solution of 2-azido-N,N-diethylethan-1-amine. Then the mixture was stirred and reacted at 0 ° C for 24 h. Afterwards, the solvent and excess iodomethane were removed under reduced pressure, which afforded 2-Azido-N,N-diethyl-N-methylethan-1-aminium iodide in excellent yield (2.63g, 96.13%).

2-Azido-N,N-diethyl-N-methylethan-1-aminium dicyanamide: The $AgN(CN)_2$ (1.76g, 10 mmol) was added into an aqueous solution of 2-azido-N,N-diethyl-N-methylethan-1-aminium iodide, and stirred at room temperature for 24 h without light emission. After filtration and concentration, a colorless liquid of IL-1b (2-azido-N,N-diethyl-N-methylethan-1-aminium dicyanamide) was formed (1.98g, 95.60%). The other ILs were also prepared following the same procedure.

IL-1a: white solid; 88.20% yield; ^{1}H NMR (400 MHz, D_2O) δ 3.85 (t, J=5.8 Hz, 2H), 3.52-3.41 (m, 2H), 3.36 (q, J=7.3 Hz, 4H), 2.98 (s, 3H), 1.27 (t, J=7.3 Hz, 6H); ^{13}C NMR (101 MHz, D_2O) δ 58.31 (s), 57.18 (s), 47.32 (s), 44.18 (s), 7.04 (s); IR (KBr): 3425, 2984, 2396, 2104, 1762, 1384, 826, 553; elemental analysis calcd (%) for $C_7H_{17}N_5O_3$: C 38.35, H 7.82, N 31.94; found: C 38.28, H 7.89, N 31.90.

IL-1b: colorless liquid; 88.66% yield; ^{1}H NMR (400 MHz, D_2O) δ 3.92 (t, J=5.7 Hz, 2H), 3.56-3.48 (m, 2H), 3.43 (q, J=7.3 Hz, 4H), 3.05 (s, 3H), 1.35 (t, J=7.2 Hz, 6H); ^{13}C NMR (101 MHz, D_2O) δ 120.07 (s), 58.41 (s), 57.29 (s), 47.43 (s), 44.27 (s), 7.16 (s); IR (KBr): 3439, 2235, 2138, 1637, 1460, 1312, 526; elemental analysis calcd (%) for $C_9H_{17}N_7$: C 48.41, H 7.67, N 43.91; found: C 48.36, H 7.77, N 43.87.

IL-1c: colorless liquid; 87.96% yield; ^{1}H NMR (400 MHz, D_2O) δ 3.88 (t, J=5.8 Hz, 2H), 3.50-3.43 (m, 2H), 3.38 (q, J=7.3 Hz, 4H), 3.00 (s, 3H), 1.30 (t, J=7.3 Hz, 6H); ^{13}C NMR (101 MHz, D_2O) δ 116.20 (s), 58.34 (s), 57.22 (s), 47.37 (s), 44.21 (s), 7.07 (s); IR (KBr): 3434, 2171, 2107, 1635, 1427, 1266, 1154, 548; elemental analysis calcd (%) for $C_8H_{17}N_7O$: C 42.28, H 7.54, N 43.14; found: C 42.20, H 7.61, N 43.09.

IL-2a: colorless liquid; 88.07% yield; ^{1}H NMR (400 MHz, D_2O) δ 3.50 (t, J=6.4 Hz, 2H), 3.46-3.38 (m, 2H), 3.14 (s, 9H), 2.16-2.03 (m, 2H); ^{13}C NMR (101 MHz, D_2O) δ 64.08 (s), 53.14-52.72 (m), 47.83 (s), 22.28 (s); IR (KBr): 3427, 2955, 2401, 2102, 1763, 1379, 825, 554; elemental analysis calcd (%) for $C_6H_{15}N_5O_3$: C 35.12, H 7.37, N 34.13; found: C 35.09, H 7.46, N 34.07.

IL-2b: colorless liquid; 88.02% yield; ^{1}H NMR (400 MHz, D_2O) δ 3.51 (t, J=6.4 Hz, 2H), 3.48-3.40 (m, 2H), 3.15 (s, 9H), 2.17-2.05 (m, 2H); ^{13}C NMR (101 MHz, D_2O) δ 120.08 (s), 64.12 (s), 53.18-52.77 (m), 47.84 (s), 22.32 (s); IR (KBr): 3454, 2241, 2135, 1644, 1485, 1310, 526; elemental analysis calcd (%) for $C_8H_{15}N_7$: C 45.92, H 7.23, N 46.86; found: C 45.82, H 7.28, N 46.90.

IL-2c: colorless liquid; 87.89% yield; ^{1}H NMR (400 MHz, D_2O) δ 3.51 (t, J=6.4 Hz, 2H), 3.48-3.40 (m, 2H), 3.15 (s, 9H), 2.18-2.04 (m, 2H); ^{13}C NMR (101 MHz, D_2O) δ 116.21 (s), 64.05 (s), 53.12-52.70 (m), 47.79 (s), 22.26 (s); IR (KBr): 3424, 2172, 2108, 1631, 1427, 1270, 1153, 547; elemental analysis calcd (%) for $C_7H_{15}N_7O$: C 39.43, H 7.09, N 45.98; found: C 39.32, H 7.17, N 45.88.

IL-3a: colorless liquid; 88.28% yield; ^{1}H NMR (400 MHz, D_2O) δ 3.94 (t, J=5.5 Hz, 2H), 3.66-3.45 (m, 6H), 3.09 (s, 3H), 2.22 (s, 4H); ^{13}C NMR (101 MHz, D_2O) δ 65.18 (s), 61.99 (s), 48.17 (s), 45.31 (s), 21.07 (s); IR (KBr): 3433, 2983, 2398, 2138, 1762, 1371, 826, 555; elemental analysis calcd (%) for $C_7H_{15}N_5O_3$: C 38.70, H 6.96, N 32.24; found: C 38.64, H 7.03, N 32.20.

IL-3b: colorless liquid; 88.30% yield; ^{1}H NMR (400 MHz, D_2O) δ 3.96 (t, J=5.5 Hz, 2H), 3.69-3.49 (m, 6H), 3.11 (s, 3H), 2.24 (s, 4H); ^{13}C NMR (101 MHz, D_2O) δ 120.09 (s), 65.23 (s), 62.03 (s), 48.23 (s), 45.34 (s), 21.11 (s); IR (KBr): 3457, 2241, 2132, 1642, 1462, 1309, 933, 529; elemental analysis calcd (%) for $C_9H_{15}N_7$: C 48.85, H 6.83, N 44.31; found: C 48.79, H 6.90, N 44.31.

IL-3c: colorless liquid; 88.12% yield; ^{1}H NMR (400 MHz, D_2O) δ 3.92 (t, J=5.6 Hz, 2H), 3.64-3.41 (m, 6H), 3.08 (s, 3H), 2.20 (s, 4H); ^{13}C NMR (101 MHz, D_2O) δ 116.21 (s), 65.17 (s), 61.97 (s), 48.14 (s), 45.30 (s), 21.04

(s); IR (KBr): 3424, 2172, 2111, 1635, 1434, 1274, 1155, 546; elemental analysis calcd (%) for $C_8H_{15}N_7O$: C 42.66, H 6.71, N 43.53; found: C 42.62, H 6.78, N 43.49.

IL-4a: colorless liquid; 88.17% yield; ^{1}H NMR (400 MHz, D_2O) δ 3.95 (t, J=5.5 Hz, 2H), 3.69-3.52 (m, 2H), 3.52-3.32 (m, 4H), 3.13 (s, 3H), 2.01-1.80 (m, 4H), 1.79-1.57 (m, 2H); ^{13}C NMR (101 MHz, D_2O) δ 62.02 (s), 61.33 (s), 48.21 (s), 44.11 (s), 20.43 (s), 19.54 (s); IR (KBr): 3432, 2967, 2405, 2141, 1760, 1375, 822, 556; elemental analysis calcd (%) for $C_8H_{17}N_5O_3$: C 41.55, H 7.41, N 30.28; found: C 41.49, H 7.44, N 30.25.

IL-4b: colorless liquid; 88.19% yield; ^{1}H NMR (400 MHz, D_2O) δ 3.93 (t, J=5.7 Hz, 2H), 3.62-3.52 (m, 2H), 3.50-3.31 (m, 4H), 3.11 (s, 3H), 1.98-1.82 (m, 4H), 1.77-1.57 (m, 2H); ^{13}C NMR (101 MHz, D_2O) δ 120.04 (s), 62.06 (s), 61.36 (s), 48.29 (s), 44.14 (s), 20.46 (s), 19.58 (s); IR (KBr): 3464, 2233, 2138, 1638, 1465, 1304, 529; elemental analysis calcd (%) for $C_{10}H_{17}N_7$: C 51.05, H 7.28, N 41.67; found: C 51.01, H 7.37, N 41.62.

IL-4c: colorless liquid; 88.03% yield; ^{1}H NMR (400 MHz, D_2O) δ 3.92 (t, J=5.6 Hz, 2H), 3.65-3.51 (m, 2H), 3.50-3.28 (m, 4H), 3.10 (s, 3H), 1.97-1.76 (m, 4H), 1.75-1.50 (m, 2H); ^{13}C NMR (101 MHz, D_2O) δ 116.22 (s), 61.99 (s), 61.29 (s), 48.22 (s), 44.08 (s), 20.39 (s), 19.51 (s); IR (KBr): 3469, 2174, 2105, 1635, 1429, 1269, 1154, 547; elemental analysis calcd (%) for $C_9H_{17}N_7O$: C 45.18, H 7.16, N 40.98; found: C 45.12, H 7.23, N 40.93.

IL-5a: white solid; 88.11% yield; ^{1}H NMR (400 MHz, D_2O) δ 4.16-3.91 (m, 6H), 3.76-3.67 (m, 2H), 3.66-3.47 (m, 4H), 3.28 (s, 3H); ^{13}C NMR (101 MHz, D_2O) δ 62.91 (s), 60.34 (s), 47.49 (s), 43.97 (s); IR (KBr): 3429, 2959, 2400, 2117, 1764, 1382, 825, 555; elemental analysis calcd (%) for $C_7H_{15}N_5O_4$: C 36.05, H 6.48, N 30.03; found: C 36.01, H 6.59, N 29.95.

IL-5b: colorless liquid; 88.04% yield; ^{1}H NMR (400 MHz, D_2O) δ 4.13-3.94 (m, 6H), 3.76-3.67 (m, 2H), 3.66-3.48 (m, 4H), 3.27 (s, 3H); ^{13}C NMR (101 MHz, D_2O) δ 120.08 (s), 62.94 (s), 60.37 (s), 47.58 (s), 44.01 (s); IR (KBr): 3455, 2237, 2137, 1638, 1473, 1309, 1128, 881, 529; elemental analysis calcd (%) for $C_9H_{15}N_7O$: C 45.56, H 6.37, N 41.32; found: C 45.53, H 6.46, N 41.23.

IL-5c: colorless liquid; 87.93% yield; ^{1}H NMR (400 MHz, D_2O) δ 4.12-3.91 (m, 6H), 3.73-3.66 (m, 2H), 3.64-3.46 (m, 4H), 3.25 (s, 3H); ^{13}C NMR (101 MHz, D_2O) δ 116.25 (s), 62.89 (s), 60.32 (s), 47.47 (s), 43.96 (s); IR (KBr): 3489, 2174, 2115, 1633, 1438, 1271, 1128, 550; elemental analysis calcd (%) for $C_8H_{15}N_7O_2$: C 39.83, H 6.27, N 40.64; found: C 39.77, H 6.35, N 40.59.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (21703218), the Shenzhen Science and Technology Innovation Committee (JCYJ20151013162733704), Economic, Trade and Information Commission of Shenzhen Municipality through the Graphene Manufacture Innovation Center [201901161514] and the Thousand Talents Plan (Youth).

Keywords: Hypergolic • Propellant • Azide-functionalized • Ionic liquids • Ignition delay time

Author Contributions

§These authors contributed equally.

Notes

The authors declare no competing financial interest.

[1] S. G. Kulkarni, V. S. Bagalkote, S. S. Patil, U. P. Kumar and V. A. Kumar, *Propellants, Explosives, Pyrotechnics: An International Journal Dealing with Scientific and Technological Aspects of Energetic Materials* **2009**, *34*, 520-525.

[2] Y. Ishikawa and M. J. McQuaid, *J. Mol. Struct. THEOCHEM* **2007**, *818*, 119-124.

[3] W. Daimon, Y. Gotoh and I. Kimura, *J. Propul. Power* **1991**, *7*, 946-952.

[4] O. d. Bonn, A. Hammerl, T. M. Klapötke, P. Mayer, H. Piotrowski and H. Zewen, *Z. Anorg. Allg. Chem.* **2001**, *627*, 2011-2015.

[5] S. Pichon, L. Catoire, N. Chaumeix and C. Paillard, *J. Propul. Power* **2005**, *21*, 1057-1061.

[6] P. D. McCrary, P. A. Beasley, S. A. Alaniz, C. S. Griggs, R. M. Frazier and R. D. Rogers, *Angew. Chem. Int. Ed.* **2012**, *124*, 9922-9925.

[7] H. Kang, J. Won, S. W. Baek and S. Kwon, *Combust. Flame.* **2017**, *181*, 149-156.

[8] X. Weng, C. Tang, J. Li, Q. Zhang and Z. Huang, *Combust. Flame.* **2018**, *194*, 464-471.

[9] Q. Zhang and J. n. M. Shreeve, *Chem. Eur. J.* **2013**, *19*, 15446-15451.

[10] Q. Zhang and J. n. M. Shreeve, *Chem. Rev.* **2014**, *114*, 10527-10574.

[11] E. Sebastiao, C. Cook, A. Hu and M. Murugesu, *J. Mater. Chem. A* **2014**, *2*, 8153-8173.

[12] B. Wang, L. Qin, T. Mu, Z. Xue and G. Gao, *Chem. Rev.* **2017**, 117, 7113-7131.

[13] K. Wang, Y. Zhang, D. Chand, D. A. Parrish and J. n. M. Shreeve, *Chem. Eur. J.* **2012**, 18, 16931-16937.

[14] S. Schneider, T. Hawkins, M. Rosander, G. Vaghjiani, S. Chambreau and G. Drake, *Energ. Fuel.* **2008**, *22*, 2871-2872.

[15] S. Schneider, T. Hawkins, M. Rosander, J. Mills, G. Vaghjiani and S. Chambreau, *Inorg. Chem.* **2008**, *47*, 6082-6089.

[16] Y.-H. Joo, H. Gao, Y. Zhang and J. n. M. Shreeve, *Inorg. Chem.* **2010**, *49*, 3282-3288.

[17] Y. Jin, B. Wang, W. Zhang, S. Huang, K. Wang, X. Qi and Q. Zhang, *Chem. Eur. J.* **2018**, *24*, 4620-4627.

[18] Y. Yuan, Y. Zhang, L. Liu, N. Jiao, K. Dong and S. Zhang, *RSC Adv.* **2017**, *7*, 21592-21599.

[19] V. K. Bhosale and P. S. Kulkarni, *New J. Chem.* **2017**, *41*, 1250-1258.

[20] Y. Wang, S. Huang, W. Zhang, T. Liu, X. Qi and Q. Zhang, *Chem. Eur. J.* **2017**, *23*, 12502-12509.

[21] R. Fareghi-Alamdari, F. Ghorbani-Zamani and N. Zekri, *RSC Adv.* **2016**, *6*, 26386-26391.

[22] H. Gao, Y. H. Joo, B. Twamley, Z. Zhou and J. n. M. Shreeve, *Angew. Chem. Int. Ed.* **2009**, *48*, 2792-2795.

[23] L. He, G. H. Tao, D. A. Parrish and J. n. M. Shreeve, *Chem. Eur. J.* **2010**, *16*, 5736-5743.

[24] Y. Zhang, H. Gao, Y. H. Joo and J. n. M. Shreeve, *Angew. Chem. Int. Ed.* **2011**, *50*, 9554-9562.

[25] Q. Zhang, P. Yin, J. Zhang and J. n. M. Shreeve, *Chem. Eur. J.* **2014**, *20*, 6909-6914.

[26] S. Huang, X. Qi, W. Zhang, T. Liu and Q. Zhang, *Chem. Asian J.* **2015**, *10*, 2725-2732.

[27] W. Zhang, X. Qi, S. Huang, J. Li and Q. Zhang, *J. Mater. Chem. A* **2015**, *3*, 20664-20672.

[28] T. Liu, X. Qi, S. Huang, L. Jiang, J. Li, C. Tang and Q. Zhang, *Chem. Commun.* **2016**, *52*, 2031-2034.

[29] S. Schneider, T. Hawkins, Y. Ahmed, M. Rosander, L. Hudgens and J. Mills, *Angew. Chem. Int. Ed.* **2011**, *123*, 6008-6010.

[30] S. Li, H. Gao and J. n. M. Shreeve, *Angew. Chem. Int. Ed.* **2014**, *53*, 2969-2972.

[31] D. Chand, J. Zhang and J. n. M. Shreeve, *Chem. Eur. J.* **2015**, *21*, 13297-13301.

[32] W. Zhang, X. Qi, S. Huang, J. Li, C. Tang, J. Li and Q. Zhang, *J. Mater. Chem. A* **2016**, *4*, 8978-8982.

[33] T. Liu, J. Qi, B. Wang, Y. Jin, C. Yan, Y. Wang and Q. Zhang, *Chem. Eur. J.* **2018**.

[34] X. Li, H. Huo, H. Li, F. Nie, H. Yin and F.-X. Chen, *Chem. Commun.* **2017**, *53*, 8300-8303.

[35] X. Li, C. Wang, H. Li, F. Nie, H. Yin and F.-X. Chen, *J. Mater. Chem. A* **2017**, *5*, 15525-15528.

[36] V. K. Bhosale and P. S. Kulkarni, *Propellants Explos. Pyrotech.* **2016**, *41*, 1013-1019.

[37] N. Jiao, Y. Zhang, L. Liu, M. S. Jean'ne and S. Zhang, *J. Mater. Chem. A* **2017**, *5*, 13341-13346.

[38] N. Jiao, Y. Zhang, H. Li, L. Liu and S. Zhang, *Chem. Asian J.* **2018**, 13, 1932-1940.

[39] P. D. McCrary, G. Chatel, S. A. Alaniz, O. A. Cojocaru, P. A. Beasley, L. A. Flores, S. P. Kelley, P. S. Barber and R. D. Rogers, *Energ. Fuel.* **2014**, *28*, 3460-3473.

[40] H. Gao, C. Ye, C. M. Piekarski and J. n. M. Shreeve, *J. Phys. Chem. C* **2007**, *111*, 10718-10731.

[41] Y. Zhang, H. Gao, Y. Guo, Y. H. Joo and J. n. M. Shreeve, *Chem. Eur. J.* **2010**, *16*, 3114-3120.

[42] Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr. , J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian Inc., Wallingford CT, **2009**.

[43] M. Suceska, Explo5 6.02 program, Zagreb, Croatia, **2014**.

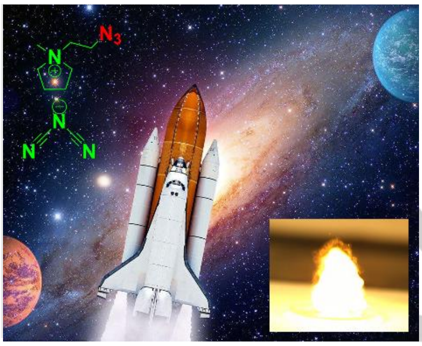
Entry for the Table of Contents (Please choose one layout)

Layout 1:

FULL PAPER

Text for Table of Contents

Alternative hypergolic fuels: A family of novel azide-functionalized-cation-based hypergolic ionic liquids were designed and synthesized from cost-effective materials. These ionic liquids displayed excellent properties including low melting points, high thermal stability, low viscosities, and unique hypergolic reactivity, demonstrating their promise as potential alternative hypergolic fuels to toxic and volatile hydrazine derivatives.



*Zhenyuan Wang, Guangxing Pan, Binshen Wang, Ling Zhang, Weiwei Zhao, Xing Ma, Jichuan Zhang, and Jiaheng Zhang**

Page No. – Page No.

Synthesis and Properties of Azide-functionalized Ionic Liquids as Attractive Hypergolic Fuels