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Nitrato-Functionalized Task-Specific Ionic Liquids as Attractive Hypergolic Rocket Fuels

Yi Wang,[a] Shi Huang,[a] Wenquan Zhang,[a] Tianlin Liu,[a] Xiujuan Qi,[b] and Qinghua Zhang*[a]

Abstract: Hypergolic ionic liquids (HILs) as potential replacements for hydrazine derivatives have attracted increasing interest over the last decade. Previous studies on HILs are mostly concentrated on the anionic innovations of ionic liquids to shorten the ignition delay (ID) time, but few attentions have been paid to the cationic modifications and their structure-property relationships. In this work, we presented a new strategy of cationic functionalization by introducing the energetic nitrato group into the cationic units of HILs. Interestingly, the introduction of oxygen-rich nitrato groups into the cationic structure has obviously improved the combustion performance of HILs with larger flame diameters and duration times. The density-specific impulse (ρI_{sp}) of these novel HILs are all above 279.0 s•g•cm^{-3}, much higher than that of UDMH (215.7 s•g•cm^{-3}). In addition, the densities of these HILs are in range of 1.22-1.39 g•cm^{-3}, which is much higher than that of UDMH (0.79 g•cm^{-3}), showing their higher loading capacity than hydrazine-derived fuels in propellant tank. This promising strategy of introducing nitrato group into the cationic structures has provided a new platform for developing high-performing HILs with improved combustion properties.

Introduction

In the field of aerospace and aviation technologies, propellants have been the subject of intensive research over the past few decades because they are the main power sources in the propulsion systems of missiles and rockets.[1] Nowadays, hydrazine and its methylated derivatives are still widely used as the liquid hypergolic fuels in some bipropellant systems, but their high volatility, toxicity and handling costs are already beyond the need for the ever-growing environmental and safety issues.[2-4] Against this background, there is an urgent and continuing need for exploring new hypergolic fuels as replacements of hydrazine derivatives.

Since 2008, the technical innovations in the field of ionic liquids (ILs) have been attempted for developing safer and more environment-friendly bipropellant fuels. Pioneering studies have demonstrated that using task-specific ionic liquids (TSILs) as replacements for hydrazine derivatives is a viable option for the explorations of new-generation liquid rocket fuels due to their extremely low volatility and excellent hypergolic properties. In the pioneering work, Schneider and co-workers firstly demonstrated that some dicyanamide hypergolic ionic liquids with the allyl and propargyl functionalities can spontaneously ignite rapidly when they are mixed with white fuming nitric acid (WFNA).[5] After that, a number of TSILs with hypergolic properties have been developed and evaluated for potential applications of liquid bipropellant fuels. Shreeve et al. have reviewed on a variety of TSILs with different structures which showed the potential applications for hypergolic fuels.[6] As compared with traditional hydrazine-based fuels, these TSILs as hypergolic fuels exhibit some promising advantages including low vapor toxicity, high thermal stability, low fire hazard and corrosivity, and good thrust control, *etc*.[7] In addition, unlike traditional hydrazine derivatives, the structural designability of TSILs have provided a promising platform towards new hypergolic fuels, in which the cationic or anionic components can be independently designed or modified for a specific need. Thus, the search for new HILs as the substitutes of hydrazine derivatives has become a promising strategy for the development of next-generation hypergolic fuels.

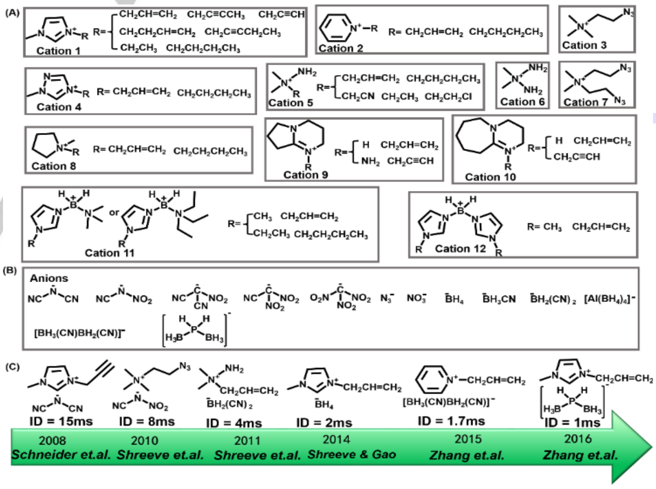

Figure 1. (A) The typical cations for known HILs; (B) the representative anions for known HILs; (C) the evolution of the ignition delay (ID) times of some typical HILs with white fuming nitric acid (WFNA).

By systematically analyzing the cationic and anionic structures of previously reported HILs,[8-26] we have found that the typical cations of known HILs are mainly concentrated on some quaternary ammonium cations (e.g., 1-alkyl-3-methyl-imidazolium,1-alkyl-pyridinium, *N*-methyl-*N*-alkyl-pyrrolidinium, *N*-alkyl-trimethyl-ammonium in Figure 1A), while the anions have undergone a rapid evolution from traditional dicyanamide anion ($[N(CN)_2]^-$)^7 to strongly reducing borohydride-rich anions (e.g., $[BH_4]^-$, $[BH_3CN]^-$, $[Al(BH_4)_4]^-$, $[BH_2(CN)_2]^-$, $[BH_3(CN)BH_2(CN)]^-$ and $[H_2P(BH_3)_2]^-$).[17-25] As a result, the ignition delay (ID) times of

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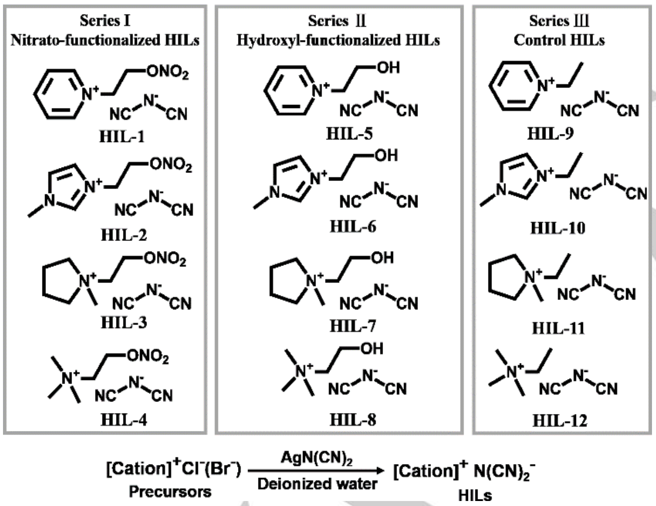
some known HILs with the common oxidizer of white fuming nitric acid (WFNA) have a great breakthrough and the present shortest ID time has reached 1 ms (Figure 1C), [24] which is much shorter than that of unsymmetric dimethyl hydrazine (UDMH) (4.8 ms) under same conditions.[20] These previous studies are mainly focused on the design and synthesis of new hypergolic anions with the aim of shortening the ID times of HILs , however, the cationic modifications have been ignored for a long time. In fact, as an important component of HILs, cationic structure has also very important effect on the combustion properties. Unfortunately, the knowledge of how cationic structure (e.g., quaternary ammonium type substituted functional groups) affecting the hypergolic properties of HILs is still very limited. In this context, studies on the relationships between cationic structures and combustion properties should be strengthened.

It is well known that the essence of spontaneous combustion between HILs and oxidizers is an oxidation-reduction reaction, in which the anionic reaction with oxidizer induces the ignition process of HILs. [27-28] In general, those HILs with fuel-richer anions can exhibit shorter ID times (Figure 1C). In turn, for a given hypergolic anion, it is not clear whether combustion properties of HILs (e.g., ID times, combustion duration) could be significantly influenced by changing oxidation-reduction activity of cations. Herein, we are interested in designing high-performing HILs is by introducing oxygen-rich nitrato group to cations to functionalize their oxidation-reduction activities, which may result in an improved combustion properties.



Scheme 1. Chemical structures and synthetic route of studied HILs.

To verify the feasibility of our designing ideas, here, we first select traditional dicyanamide as the anion, and then try to introduce oxygen-rich nitrato groups into four types of quaternary ammonium cations by two different approaches. One is the direct introduction of nitrato group to form nitrato-functionalized TSILs (Series I in Scheme 1). The other is indirect introduction of nitrato group by hydroxyl-functionalized TSILs (Series II in Scheme 1). Since the hydroxyl group can react with the WFNA to *in-situ* yield the nitrato-functionalized TSILs with an obvious exothermic process, which may also have positive effects on the subsequent igniting process of HILs and thereby improve the ignition and combustion efficiency. In addition, a series of traditional dicyanamide-based HILs as control fuels are synthesized and comparatively studied. In this work, tremendous efforts were made to study three series of TSILs based on nitrato- and hydroxyl-functionalized cations as shown in Scheme 1 (Series I-III), and the detailed comparison of their differences in thermal properties, densities, viscosities, ignition delay times, and combustion duration were particularly emphasized.

Results and Discussion

First, we synthesized three series of dicyanamide-based HILs according to typical metathesis reactions (Series I-III, Scheme 1) The precursors of HIL-1 to HIL-4 were synthesized by literature procedures [23, 29] and the others were purchased from commercial sources. Except HIL-1 and HIL-12 (m.p. 60.0 °C and 96.3°C, respectively), other HILs are viscous liquids at room temperature. Next, the structural identification of all HILs was performed by ^{1}H and ^{13}C NMR spectroscopy and high-resolution mass spectrometer (HRMS). The characterization data supported our structural assignment of as-synthesized TSILs (see ESI). The main physicochemical properties of these TSILs including their thermal properties (T_m and T_d), densities (ρ), viscosities (η), heats of formation ($\Delta_f H$), ignition delay (ID) time, specific impulse (I_{sp}) and density-specific impulse (ρI_{sp}), were measured or calculated (Table 1).

Thermal Properties, Densities, and Viscosities

As one of the most important physicochemical properties, thermal properties of twelve HILs were first investigated. As shown in Table 1, except that HIL-1 and HIL-12 are solids at room temperature, other ten HILs show the low melting points (T_m) of < -40 °C, as determined by differential scanning calorimeter (DSC) analysis. By analyzing the melting points of common HILs (HILs 9-11) and nitrato-/ hydroxyl-functionalized HILs (HILs 2-8), we found that the introduction of nitrato or hydroxyl groups into the HILs' cations has no obvious effects on the melting points of these dicyanamide-based HILs (Table 1), and no definable correlations between functional groups and melting points are observed.

The thermal stabilities of these HILs were also evaluated. For non-functional HILs (HILs 9-12), they all exhibited high thermal stabilities with the decomposition temperatures (T_d) higher than 267 °C. As for these cation-functionalized HILs (HILs 1-8), the introduction of hydroxyl group into the cationic units has no obvious effect on decomposition temperatures (T_d: 248-280 °C for HILs 5-8, Table 1), however, the incorporation of energetic nitrato group gives rise to an obvious decrease of decomposition temperatures (around 200 °C for HILs 1-4, Table 1) (Figure S1). In addition to thermal properties, density is another important parameter for HILs, which directly determines loading capacity of liquid fuels in the propellant tank. In general, a higher density means that more fuels can be packed into rocket fuel tank, thereby affording a higher energy and combustion contribution to

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Table 1. Physicochemical properties of these twelve ionic liquids.

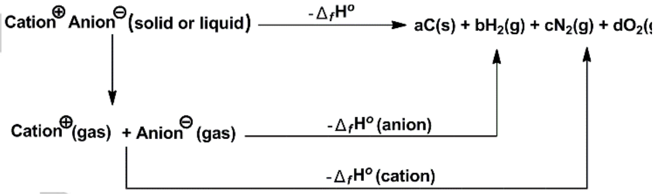
Entry	T_m[a] (°C)	T_d[b] (°C)	OB[c] (%)	ρ[d] (g•cm^{-3})	η[e] (mPa•s)	$\Delta_f H$[f] (KJ•mol^{-1})	ID[g] (ms)	I_{sp}[h] (s)	ρI_{sp}[j] (s•g•cm^{-3})
HIL-1	60.0	186.6	-71.5	1.39	-	237.0	26	233.8	325.0
HIL-2	-50.2	186.8	-67.2	1.30	133.0	169.1	41	226.5	294.5
HIL-3	-49.9	194.1	-89.6	1.22	130.3	68.3	53	243.1	296.6
HIL-4	-50.1	200.9	-78.1	1.22	303.5	50.1	58	234.1	285.6
HIL-5	-48.9	248.2	-109.5	1.21	70.1	115.9	61	252.6	305.6
HIL-6	-50.0	260.8	-103.6	1.19	51.5	64.4	51	246.7	293.6
HIL-7	-49.8	269.1	-130.6	1.13	49.1	-54.7	61	260.4	294.3
HIL-8	-49.9	280.8	-122.4	1.09	51.3	-60.2	62	256.5	279.6
HIL-9	-46.1	267.8	-128.7	1.12	19.7	264.3	33	259.9	291.1
HIL-10	-50.7	316.3	-122.0	1.11	10.9	215.7	30	256.9	285.2
HIL-11	-50.2	308.6	-151.1	1.05	27.2	89.7	47	262.1	275.2
HIL-12	96.3	306.2	-145.5	1.05	-	53.2	-	262.5	275.6
UDMH	-57	64[i]	-159.7	0.79	0.51	53.3	4.8	273.0	215.7

[a] Melting point. [b] Thermal decomposition temperature. [c] Oxygen balance (based on CO) for $C_aH_bO_cN_d$: 1600(c-a-b/2)/M_w; M_w = molecular weight. [d] Density at 25 °C. [e] Viscosity at 25 °C. [f] Heat of formation. [g] Ignition-delay (ID) time with WFNA. [h] specific impulse (Explo5 v6.02. IL/WFNA = 24/76, w/w; isobaric conditions, equilibrium expansion, 7.0 MPa chamber pressure). [i] Boiling point. [j] density-specific impulse.

the propulsion process. Of these ionic liquids, the nitrato-functionalized HILs (HILs 1-4) have relatively higher densities (ranging 1.22 to 1.39 g•cm^{-3}), approximately 15.8~24.1 % higher than non-functional HILs (HILs 9-12) (Table 1). In fact, the densities of four nitrato-functionalized HILs (HILs 1-4, Table 1) are obviously higher than most known dicyanamide-based ionic liquids (around 0.9-1.1 g•cm^{-3}) and unsymmetric dimethyl hydrazine (UDMH) (0.79 g•cm^{-3}),[20] which indicates that nitrato-functionalized HILs have higher loading capacity than traditional hydrazine-based fuels. The high densities of nitrato-functionalized HILs may result from their multiple hydrogen bonds C-H···O between aromatic/aliphatic C-H bonds and nitrato group.[30] With respect to hydroxyl-functionalized HILs (HILs 5-8), because of only one oxygen atom in the molecule, their limited C-H···O hydrogen bonds result in their slightly higher densities than the non-functional HILs (HILs 9-12, Table 1). Due to the additional C-H···O hydrogen bonds in the molecules, these nitrato- and hydroxyl-functionalized HILs (HILs 1-8) exhibited higher viscosities than those non-functional HILs (HILs 9-12). Of these new HILs, these nitrato-functionalized HILs (HILs 1-4) showed the highest viscosities ranging from 130-330 mPa•s owing to their multiple C-H···O hydrogen bonds (Table 1).

Theoretical study

Theoretical calculations were performed by using the Gaussian 09 suite of programs.[31] For these new HILs, geometric optimization and frequency analyses were completed by using the B3LYP functional with the 6-31+G** basis set.[32] Single energy points were calculated at the MP2/6-311++G** level of theory. For all of as-synthesized compounds, the optimized structures were characterized to be true local energy minima on the potential-energy surface without imaginary frequencies. Heats of formation (HOF, $\Delta_f H°$) of ionic liquids were calculated based on a Born–Haber energy cycle (Scheme 2).



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

For all the ionic liquids, calculation of the HOFs was simplified by using Equation (1),[33] in which ΔH_L is the lattice energy of the ionic salts.

$$\Delta_f H° \text{ (ionic liquids, 298K)} = \Sigma\Delta_f H°\text{(cation, 298K)} - \Sigma\Delta_f H°\text{(anion, 298K)} - \Delta H_L \quad (1)$$

For 1:1 salts, considering the nonlinear nature of the cations and anion used, ΔH_L (in kJ/mol) was predicted by using Equation (2), as suggested by Jenkins et al.,[34] in which nM and nX depended on the nature of ions Mp^+ and Xq^-, respectively, and had a value of 6 for nonlinear polyatomic ions.

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

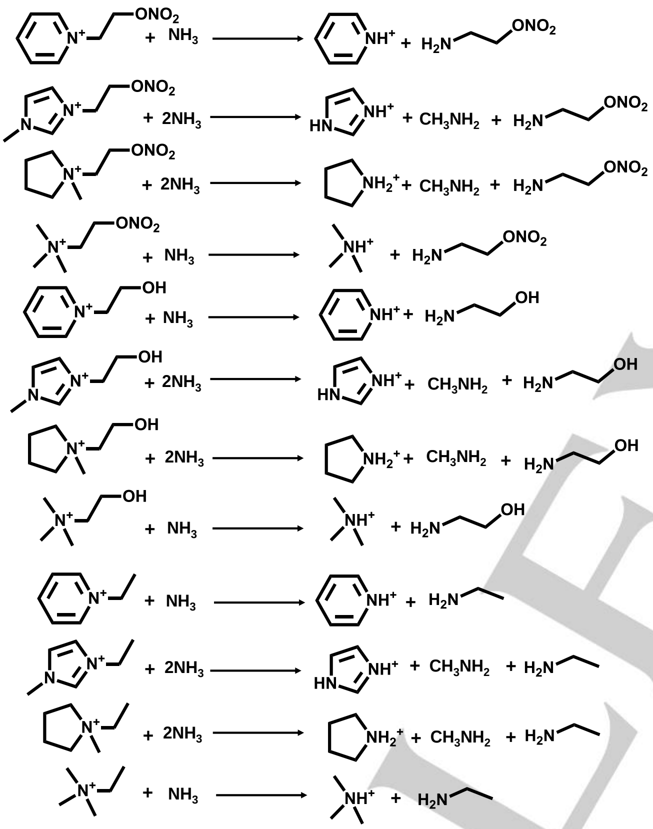
The lattice-potential energy (U_{POT}) was calculated according to Equation (3),[35] in which ρ_m is the density (g•cm^{-3}) and M_m is the chemical formula mass of the ionic material.

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

$$\Delta_f H(g)C^{+°} = \Delta_f H(g)C° + IE_C \qquad (4)$$

$$\Delta_f H(g)A^{-°} = \Delta_f H\ (g)A° + EA_A \qquad (5)$$

The heats of formation (HOFs) of the ionic salts were obtained by computing the component cations and anions. Specifically, the computation of HOFs for both the cations and anions was performed according to literature methods,[36-37] that is, the gas-phase HOFs of the ions were determined by using Equations (4) and (5) (*IE*=ionization energy; *EA*=electron affinity). In Equations (4) and (5), additional calculations for the corresponding neutral molecules ($\Delta_f H$(g)C° and $\Delta_f H$(g)A° were performed for the atomization reaction $C_aH_bN_cO_d \rightarrow$ aC(g) + bH(g) + cN(g) + dO(g) by using G2 theory. Based on the results from Equation (4), the HOFs of the cations were obtained by using isodesmic reactions. The isodesmic reactions for different cations are shown in Scheme 3.



Scheme 3. Isodesmic reactions for calculating the HOFs of these twelve cations.

The enthalpy of reaction (ΔrH^{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 ionic liquids could be readily extracted.

From Table 1, the $\Delta_f H$ values of these HILs ranged from -60.2 to 237.0 kJ•mol^{-1}, and the $\Delta_f H$ values of nitrato- and hydroxyl-functionalized HILs (HILs 1-8) are generally lower than those of non-functional HILs (HILs 9-12). By using the calculated heats of formation and the experimentally measured densities, the specific impulse (I_{sp}) of these HILs was calculated by virtue of Explo5 v6.02 software. As shown in Table 1, though the specific impulse (I_{sp}) of nitrato-functionalized HILs (HILs 1-4) are slightly lower than hydroxyl-functionalized HILs (HIL 5-8) and common ones (HILs 9-12), their density-specific impulse (ρI_{sp}) are obviously higher than the corresponding hydroxyl-functionalized and common ones owing to their relatively high density. Especially for HIL-1, it has the highest density-specific impulse (ρI_{sp}) value of 325.0 s•g•cm^{-3}, much higher than that of UDMH (215.7 s•g•cm^{-3}), which indicates that HIL-1 has excellent application potential.

Hypergolic Test

As potential liquid propellant fuels, evaluating their hypergolic reactivity with propellant oxidizers is very important since it determines whether these fuels are suitable for practical applications. In general, hypergolic reactivity is estimated by recording the ignition delay (ID) times, which represents the time interval between the initial fuel/oxidizer contact and the start of combustion. Herein, a droplet test with newly prepared 100% HNO_3 (WFNA) as the oxidizer was employed to measure the ID times of these HILs. As an example, a series of high-speed camera (2000 fps) photos of HIL-3 are shown in Figure 2. After the liquid drop of HIL-3 contacted the pool surface of WFNA, it underwent a complex and gradual process, involving a rapid spreading on pool surface of WFNA, the violent reaction with WFNA, spontaneous ignition, the combustion duration and finally a gradual flame-quenching (Figure 2).

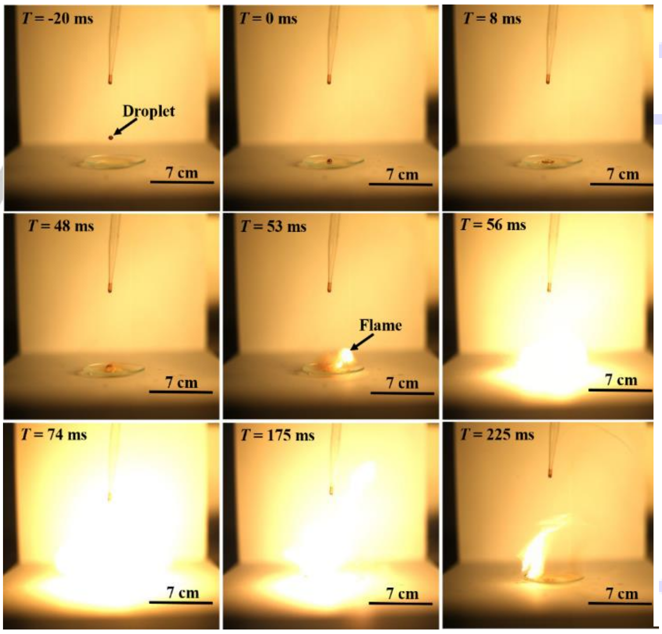


Figure 2. High-speed camera photos that show a spatially resolved ignition event for a droplet of HIL-3 falling into WFNA.

Except for HIL-12, all other HILs (HILs 1-11) can spontaneously ignite upon contact with WFNA, and their ID times are in the range of 26-61 ms (Table 1). Essentially, the spontaneous combustion between hypergolic ionic liquids (HILs) and oxidizers is an oxidation-reduction reaction. Therefore, the reductive activity of anions in HILs usually plays a decisive effect on the ignition delay times (IDs). For most dicyanamide anion-based HILs (Figure S2), their ID times with the oxidizer of WFAN are always longer than 20 ms due to the weak reduction activity of dicyanamide anion. In this work, these nitrato-functionalized dicyanamide HILs also fall within a normal range (26-61 ms). For nitrato-functionalized HILs (HILs 1-4), except that HIL-1 is a solid at room temperature exhibiting an ID time of 26 ms, other HILs as liquid fuels showed a little longer ID times (41-58 ms) than those non-functional HILs (33-47 ms for HILs 9-11), which are probably due to their relatively higher viscosities (Table 1). But for hydroxy-functionalized HILs (HILs 5-8), they did not exhibit the expected shorter ID times by heat-accumulating from the reaction between hydroxy group and WFNA. The main reason is that hydroxy-functionalized HILs could not well contact with WFNA in a very short time due to their high viscosities, and consequently, the heat-accumulating from their reaction is limited (Figure S3). On the whole, the relatively high viscosities of nitrato- and hydroxyl-functionalized HILs (HILs 2-8) make their ID times a little longer than non-functional HILs (HILs 9-11) (Table 1), although the introduction of nitrato and hydroxyl groups increases the oxygen-rich character and even oxygen balance of these ionic liquid fuels (Table 2).

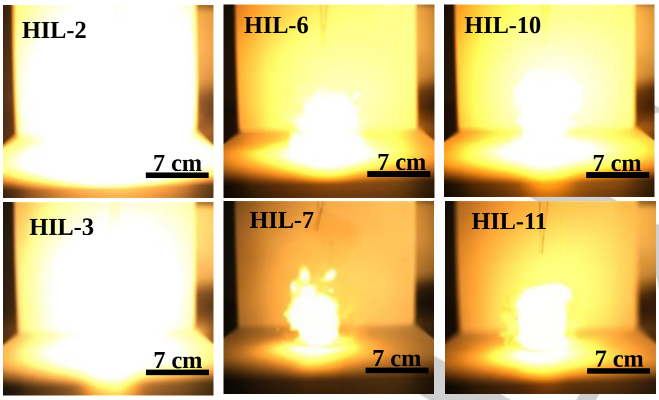


Figure 3. Comparisons of the violent-burning largest brilliant whitish flames of three kinds of HILs.

From the viewpoint of practical applications, the combustion flame and combustion duration times of HILs are also very important aspects, which have long been ignored in previous studies. In this work we are also interested in evaluating the combustion behavior of these HILs. As shown in Figure 3, under same conditions of droplet test, the violent-burning largest brilliant whitish flames of nitrato-functionalized HILs 2 and 3 are obviously larger than those of their analogues, indicating that they can violently burn more efficiently. Further analysis showed that the diameters of largest brilliant whitish flame of those nitrato-functionalized liquid salts (except HIL-1) are much bigger than their hydroxyl-functionalized and non-functional analogues (HIL-2 *vs* HIL-6/HIL-10, HIL-3 *vs* HIL-7/HIL-11, HIL-4 *vs* HIL-8) (Table 2). In addition, under same conditions of droplet test, the combustion durations of nitrato-functionalized HILs (except the solid HIL-1) are also longer than that of other eight HILs (HIL-2 *vs* HIL-6/HIL-10, HIL-3 *vs* HIL-7/HIL-11, HIL-4 *vs* HIL-8) (Table 2). The obvious improvements in both flame size and combustion time can be attributed to the high oxygen-balance character of nitrato-functionalized cations in these HILs (Table 1), thereby promoting their combustion properties including larger brilliant whitish flames and longer combustion duration time.

Table 2. Hypergolic properties of twelve HILs.

Entry	Diameters of violent-burning largest brilliant whitish flame (cm)	Violent combustion duration(ms)[a]
HIL-1	2	18
HIL-2	21	94
HIL-3	18	118
HIL-4	16	68
HIL-5	16	110
HIL-6	7	67
HIL-7	5	92
HIL-8	7	63
HIL-9	15	56
HIL-10	7	72
HIL-11	6	90
HIL-12	-	-

[a]Violent combustion duration (detailed calculation see Figure S4).

Conclusions

In summary, a series of nitrato- and hydroxyl-functionalized HILs were designed and synthesized. Their structures of these TSILs were thoroughly characterized by NMR spectroscopy, electrospray ionization mass spectroscopy (ESI-MS), and elemental analysis. Their physicochemical and hypergolic properties for these HILs including thermal properties, densities, viscosities, heats of formation, specific impulse, ignition delay times, and combustion behavior, were investigated in detail. Of these HILs, the nitrato-functionalized HILs exhibited acceptable ID times (ranging from 26 ms to 58 ms) with the oxidizer of WFNA and obviously improved combustion performance including larger brilliant whitish flames and longer combustion duration times. The nitrato-functionalized HILs exhibit higher density-specific impulse (ρI_{sp}) than those of common HILs and UDMH. In addition, the densities of these nitrato-functionalized HILs are obviously higher than those of non-functional HILs and traditional UDMH. These promising properties and combustion performance of nitrato-functionalized HILs make them a new class of potential candidates for replacements of hydrazine derivatives in the liquid bipropellant formulations. Our studies have demonstrated that the incorporation of oxygen-rich groups into the cationic structures of HILs can open a new avenue to develop high-performing hypergolic fuels.

Experimental Section

Chemicals

These dicyanamide-based hypergolic ionic liquids were synthesized according to typical metathesis reaction (as shown in Scheme 1). Taking HIL-1 as an example, the general synthetic procedure is shown as follow: 1-(2-(nitrooxy)ethyl)pyridin-1-ium bromide (6.07 g, 24.4 mmol) was dissolved in distilled water (60 mL) and freshly prepared $AgN(CN)_2$ salt (5.19 g, 30.0 mmol) was added[38]. The resulting suspension was stirred at RT for 12 h. After simple filtration and removal of water by rotary evaporation, acetonitrile (50 mL) was added to dilute the resulting crude ionic liquid. This acetonitrile solution was cooled in refrigerator for several hours to form flocculent precipitates, then flocculent precipitates were filtrated out and the resulting acetonitrile solution was dried by anhydrous magnesium sulfate. After simple filtration and removal of acetonitrile by rotary evaporation, ionic liquid HIL-1 was obtained as a pale yellow solid in high yield (83 %).

Synthesis of hypergolic ionic liquids

HIL-1: pale yellow solid, 83 % yield; ^{1}H NMR (600 MHz, DMSO-d_6): δ(TMS, ppm): 9.12 (2H, d, J = 6.5), 8.67 (1H, t), 8.22 (2H, t), 5.09-5.04 (4H, m); ^{13}C NMR (151 MHz, DMSO-d_6): δ(TMS, ppm): 146.78, 145.93, 128.63, 119.59, 71.8, 58.22. ESI-HRMS: m/z calcd. for cation $C_7H_9N_2O_3$ $[M]^+$: 169.0608; found: 169.0613; anion calcd. for C_2N_3 $[M]^-$: 66.0098, found: 66.0102; elemental analysis calcd (%) for $C_9H_9N_5O_3$ (235.0705): C 45.96, H 3.86, N 29.78 found: C 46.47, H 4.43, N 29.02.

HIL-2: pale yellow liquid, 78 % yield; ^{1}H NMR (600 MHz, DMSO-d_6): δ(TMS, ppm): 9.16 (1H, s), 7.78 (1H, s), 7.70 (1H, s), 4.92 (2H, t), 4.62 (2H, t), 3.89 (3H, s); ^{13}C NMR (151 MHz, DMSO-d_6): δ(TMS, ppm): 137.69, 124.22, 123.24, 119.61, 71.63, 46.76, 36.39. ESI-HRMS: m/z calcd. for cation $C_6H_{10}N_3O_3$ $[M]^+$: 172.0717; found: 172.0713; anion calcd. for C_2N_3 $[M]^-$: 66.0098, found: 66.0103; elemental analysis calcd (%) for $C_8H_{10}N_6O_3$ (238.0814): C 40.34, H 4.23, N 35.28 found: C 40.42, H 4.53, N 35.27.

HIL-3: yellow liquid, 70 % yield; ^{1}H NMR (600 MHz, DMSO-d_6): δ(TMS, ppm): 4.99-4.98 (2H, m), 3.88-3.87 (2H, m), 3.61-3.58 (2H, m), 3.52-3.48 (2H, m), 3.08 (3H, s), 2.11 (4H, s); ^{13}C NMR (151 MHz, DMSO-d_6): δ(TMS, ppm): 119.61, 67.99, 64.59, 60.00, 48.24, 21.37. ESI-HRMS: m/z calcd. for cation $C_7H_{15}N_2O_3$ $[M]^+$: 175.1077; found: 175.1070; anion calcd. for C_2N_3 $[M]^-$: 66.0098, found: 66.0107; elemental analysis calcd (%) for $C_9H_{15}N_5O_3$ (241.1175): C 44.81, H 6.27, N 29.03, found: C 45.40, H 6.26, N 29.53.

HIL-4: pale yellow liquid, 73 % yield; ^{1}H NMR (600 MHz, DMSO-d_6): δ(TMS, ppm): 4.98 (2H, t), 3.82 (2H, t), 3.14 (9H, s); ^{13}C NMR (151 MHz, DMSO-d_6): δ(TMS, ppm): 119.66, 67.34, 62.48, 53.41. ESI-HRMS: m/z calcd. for cation $C_5H_{13}N_2O_3$ $[M]^+$: 149.0921; found: 149.0913; anion calcd. for C_2N_3 $[M]^-$: 66.0098, found: 66.0107; elemental analysis calcd (%) for $C_7H_{13}N_5O_3$ (215.1018): C 39.07, H 6.09, N 32.54, found: C 39.30, H 6.46, N 32.03.

HIL-5: pale yellow liquid, 80 % yield; ^{1}H NMR (600 MHz, DMSO-d_6): δ(TMS, ppm): 8.96 (2H, d, J = 6.3), 8.56 (1H, t), 8.10 (2H, t), 5.19 (1H, s), 4.65 (2H, t), 3.86 (2H, q); ^{13}C NMR (151 MHz, DMSO-d_6): δ(TMS, ppm):146.24, 145.77, 128.40, 119.72, 60.04, 60.74. ESI-HRMS: m/z calcd. for cation $C_7H_{10}NO$ $[M]^+$: 124.0757 found: 124.0750; anion calcd. for C_2N_3 $[M]^-$: 66.0098, found: 66.0101; elemental analysis calcd (%) for $C_9H_{10}N_4O$ (190.0855): C 56.83, H 5.30, N 29.46, found: C 55.68, H 5.39, N 29.52.

HIL-6: pale yellow liquid, 85 % yield; ^{1}H NMR (600 MHz, DMSO-d_6): δ(TMS, ppm): 9.03 (1H, s), 7.66 (1H, s), 7.62 (1H, s), 5.13 (1H, s), 4.20 (2H, t), 3.86 (3H, s), 3.73 (2H, t); ^{13}C NMR (151 MHz, DMSO-d_6): δ(TMS, ppm):137.45, 123.97, 123.30, 119.71, 60.01, 52.40, 36.34. ESI-HRMS: m/z calcd. for cation $C_6H_{11}N_2O$ $[M]^+$: 127.0866; found: 127.0858; anion calcd. for C_2N_3 $[M]^-$: 66.0098, found: 66.0100; elemental analysis calcd (%) for $C_8H_{11}N_5O$ (193.0964): C 49.73, H 5.74, N 36.25, found: C 49.52, H 6.07, N 35.73.

HIL-7: white liquid, 72 % yield; ^{1}H NMR (600 MHz, DMSO-d_6): δ(TMS, ppm): 5.21 (1H, s), 3.83 (2H, s), 3.50-3.49 (4H, m), 3.42-3.40 (2H, m), 3.03 (3H, s), 2.09 (4H, s); ^{13}C NMR (151 MHz, DMSO-d_6): δ(TMS, ppm):119.72, 65.34, 65.04, 56.18, 48.65, 21.60. ESI-HRMS: m/z calcd. for cation $C_7H_{16}NO$ $[M]^+$: 130.1226 found: 130.1211; anion calcd. for C_2N_3 $[M]^-$: 66.0098, found: 66.0103; elemental analysis calcd (%) for $C_9H_{16}N_4O$ (196.1324): C 55.08, H 8.22, N 28.55, found: C 54.45, H 8.39, N 28.06.

HIL-8: white liquid, 78 % yield; ^{1}H NMR (600 MHz, DMSO-d_6): δ(TMS, ppm): 5.24 (1H, s), 3.82 (2H, s), 3.38-3.87 (2H, m), 3.10 (9H, s); ^{13}C NMR (151 MHz, DMSO-d_6): δ(TMS, ppm):119.69, 67.63, 55.73, 53.83, 53.81, 53.79. ESI-HRMS: m/z calcd. for cation $C_5H_{14}NO$ $[M]^+$: 104.1070; found: 104.1087; anion calcd. for C_2N_3 $[M]^-$: 66.0098, found: 66.0100; elemental analysis calcd (%) for $C_7H_{14}N_4O$ (170.1168): C 49.39, H 8.29, N 32.92, found: C 48.98, H 8.65, N 32.62.

HIL-9: pale yellow liquid, 75 % yield; ^{1}H NMR (600 MHz, DMSO-d_6): δ(TMS, ppm): 9.10 (2H, d, J = 5.7 Hz), 8.60 (1H, t), 8.16 (2H t), 4.63 (2H, q), 1.55 (3H, t); ^{13}C NMR (151 MHz, DMSO-d_6): δ(TMS, ppm):145.84, 144.99, 128.54, 119.58, 56.88, 16.73. ESI-HRMS: m/z calcd. for cation $C_7H_{10}N$ $[M]^+$: 108.0808; found: 108.0799; anion calcd. for C_2N_3 $[M]^-$: 66.0098, found: 66.0102; elemental analysis calcd (%) for $C_9H_{10}N_4$ (174.0905): C 62.05, H 5.79, N 32.16, found: C 61.82, H 5.76, N 31.78.

HIL-10: pale yellow liquid, 82 % yield; ^{1}H NMR (600 MHz, DMSO-d_6): δ(TMS, ppm): 9.09 (1H, s), 7.73 (1H, t), 7.64 (1H, t), 4.19 (2H, q), 3.85 (3H, s), 1.42 (3H, t); ^{13}C NMR (151 MHz, DMSO-d$_6$): δ(TMS, ppm):136.84, 124.10, 122.50, 119.70, 44.88, 36.30, 15.58. ESI-HRMS: m/z calcd. for cation $C_6H_{11}N_2$ $[M]^+$: 111.0917; found: 111.0907; anion calcd. for C_2N_3 $[M]^-$: 66.0098, found: 66.0100; elemental analysis calcd (%) for $C_8H_{11}N_5$ (177.1014): C 54.22, H 6.26, N 39.52, found: C 54.03, H 6.80, N 39.38.

HIL-11: colorless liquid, 80 % yield; ^{1}H NMR (600 MHz, DMSO-d$_6$): δ(TMS, ppm): 3.46-3.36 (6H, m), 2.97 (3H, s), 2.09 (4H, m), 1.28 (3H, t); ^{13}C NMR (151 MHz, DMSO-d$_6$): δ(TMS, ppm):119.16, 63.04, 58.53, 46.97, 21.18, 8.56. ESI-HRMS: m/z calcd. for cation $C_7H_{16}N$ $[M]^+$: 114.1277; found: 114.1267; anion calcd. for C_2N_3 $[M]^-$: 66.0098, found: 66.0103; elemental analysis calcd (%) for $C_9H_{16}N_4$ (177.1014): C 59.97, H 8.95, N 31.08, found: C 59.79, H 8.87, N 30.74.

HIL-12: white solid, 83 % yield; ^{1}H NMR (600 MHz, DMSO-d$_6$): δ(TMS, ppm): 3.34 (2H, q), 3.02 (9H, s), 1.26 (3H, t); ^{13}C NMR (151 MHz, DMSO-d$_6$): δ(TMS, ppm):119.58, 61.39, 52.08, 52.06, 52.03, 8.52. ESI-HRMS: m/z calcd. for cation $C_5H_{14}N$ $[M]^+$: 88.1121; found: 88.1111; anion calcd. for C_2N_3 $[M]^-$: 66.0098, found: 66.0100; elemental analysis calcd (%) for $C_7H_{14}N_4$ (154.1218): C 54.52, H 9.15, N 36.33, found: C 53.88, H 9.29, N 35.69.

Instrumentation and analysis methods

^{1}H and ^{13}C NMR spectra were recorded on Bruker 600 AVANCE spectrometer (600 and 151 MHz, respectively) with internal standard (^{1}H NMR: DMSO at 2.50 ppm; ^{13}C NMR: DMSO at 39.52 ppm). High resolution mass spectra were performed on Shimadzu LCMS-IT-TOF mass spectrometer using electrospray ionization (ESI). Elemental analysis was performed on Flash EA-1112 elemental analyzer. Thermal property measurements were performed on TGA/DSC1 and DSC1 Mettler Toledo calorimeter equipped with auto cool accessory. Densities were measured on a Micromeritics Accupyc II 1340 gas pycnometer at 25 °C. Viscosity measurements were performed on a Brook field Rheometer DV3T at 25 °C. Ignition photographs of these HILs with the oxidizer of 100% HNO_3 were recorded on an Olympus i-speed 3.

Acknowledgements

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Keywords: propellant fuel • hypergolic ionic liquids • nitrato-functionalization • structure-property relationship • combustion performance

[1] G. P. Sutton. *Rocket Propulsion Elements* 2nd ed., Wiley, New York, **1956**.
[2] Y. Zhang, H. Gao, Y. -H. Joo, J. M. Shreeve, *Angew. Chem. Int. Ed.* **2011**, *50*, 9554-9562; *Angew. Chem.* **2011**, *123*, 9726‑9734.
[3] J. Tian, Q. Zhang, *Chin. J. Energy Mater.* **2014**, *22*, 580-581.
[4] Q. Zhang, J. M. Shreeve, *Chem. Eur. J.* **2013**, *19*, 15446-15451.
[5] S. Schneider, T. Hawkins, M. Rosander, G. Vaghjiani, S. Chambreau, G. Drake, *Energ. Fuel.* **2008**, *22*, 2871-2872.
[6] Q. Zhang, J. M. Shreeve, *Chem. Rev.* **2014**, *114*, 10527-10574.
[7] E. Sebastiao, C. Cook, A. Hub, M. Murugesu, *J. Mater. Chem. A* **2014**, *2*, 8153-8173.
[8] P. D. McCrary, P. A. Beasley, O. A. Cojocaru, S. Schneider, T. W. Hawkins, J. P. L. Perez, B. W. McMahon, M. Pfeil, J. A. Boatz, S. L. Anderson, S. F. Son, R. D. Rogers, *Chem. Commun.* **2012**, *48*, 4311-4313.
[9] J. P. L. Perez, B. W. McMahon, S. Schneider, J. A. Boatz, T. W. Hawkins, P. D. McCrary, P. A. Beasley, S. P. Kelley, R. D. Rogers, S. L. Anderson, *J. Phys. Chem. C* **2013**, *117*, 5693-5707.
[10] P. D. McCrary, P. S. Barber, S. P. Kelley, R. D. Rogers, *Inorg. Chem.* **2014**, *53*, 4770-4776.
[11] J. P. L. Perez, B. W. McMahon, J. Yu, S. Schneider, J. A. Boatz, T. W. Hawkins, P. D. McCrary, L. A. Flores, R. D. Rogers, S. L. Anderson, *ACS Appl Mater. Interfaces*, **2014**, *6*, 8513-8525.
[12] R. Fareghi-Alamdari, F. Ghorbani-Zamani, M. Shekarriz, *Energ. Fuel.* **2015**, *30*, 551-559.
[13] H. Gao, Y. -H. Joo, B. Twamley, Z. Zhou, J. M. Shreeve, *Angew. Chem. Int. Ed.* **2009**, *48*, 2792-2795; *Angew. Chem.* **2009**, *121*, 2830-2833.
[14] Y. -H. Joo, H. Gao, Y. Zhang, J. M. Shreeve, *Inorg. Chem.* **2010**, *49*, 3282-3288.
[15] Y. Zhang, J. M. Shreeve, *Angew. Chem. Int. Ed.* **2011**, *50*, 935-937; *Angew. Chem.* **2011**, *123*, 965-967.
[16] S. Schneider, T. Hawkins, Y. Ahmed, M. Rosander, L. Hudgens, J. Mills, *Angew. Chem. Int. Ed.* **2011**, *50*, 5886-5888; *Angew. Chem.* **2011**, *123*, 6008-6010.
[17] Q. Zhang, P. Yin, J. Zhang, J. M. Shreeve, *Chem. Eur. J.* **2014**, *20*, 6909-6914.
[18] D. Chand, J. Zhang, J. M. Shreeve, *Chem. Eur. J.* **2015**, *21*, 13297-13301
[19] K. Wang, Y. Zhang, D. Chand, D. A. Parrish, J. M. Shreeve, *Chem. Eur. J.* **2012**, *18*, 16931-16872.
[20] S. Li, H. Gao, J. M. Shreeve, *Angew. Chem. Int. Ed.* **2014**, *53*, 2969-2672; *Angew. Chem.* **2014**, *126*, 3013-3016.
[21] W. Zhang, X. Qi, S. Huang, J. Li, Q. Zhang, *J. Mater. Chem. A* **2015**, *3*, 20664-20672.
[22] S. Huang, X. Qi, W. Zhang, T. Liu, Q. Zhang, *Chem. Asian J.* **2015**, *10*, 2725-2732.
[23] T. Liu, X. Qi, S. Huang, L. Jiang, J. Li, C. Tang, Q. Zhang, *Chem. Commun.* **2016**, *52*, 2031-2034.
[24] W. Zhang, X. Qi,; S. Huang, J. Li, C. Tang, J. Li, Q. Zhang, *J. Mater. Chem. A* **2016**, *4*, 8978-8982.
[25] V. K. Bhosale, P. S. Kulkarni, *Propellants Explos. Pyrotech.* **2016**, *41*, 1013-1019.
[26] V. K. Bhosale, P. S. Kulkarni, *New J. Chem.* **2017**, *41*, 1250-1258.
[27] T. Litzinger, S. Iyer, *Energ. Fuel.* **2011**, *25*, 72-76.
[28] D. Bedrov, O. Borodin, *J. Phys. Chem. B* **2010,** *114,* 12802-12810.
[29] R. Shan, S. E. Howlett, E. E. Knaus, *J. Med. Chem.* **2002**, *45,* 955-961.
[30] W. Drake, S. Bolden, J. Dailey, M. J. McQuaid, D. Parrish, *Propellants Explos. Pyrotech.* **2012**, *37*, 40-51.
[31] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, Mennucci, B. 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. Montgomery, 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 and D. J. Fox, Gaussian 09, (Revision A. 02), Gaussian, Inc., Wallingford, CT **2009**.

[32] Parr, R. G. W. Yang, *Density Functional Theory of Atoms and Molecules*, Oxford University Press, New York, **1989**.

[33] L. A. Curtiss, K. Raghavachari, G. W. Trucks, J. A. Pople, *J. Chem. Phys.* **1991**, *94*, 7221.

[34] H. D. B. Jenkins, D. Tudela, L. Glasser, *Inorg. Chem.* **2002**, *41*, 2364-2367.

[35] S. Bastea, L. E. Fried, K. R. Glaesemann, W. M. Howard, P. C. Souers, P. A. *Vitello, Cheetah 5.0 User's Manual, Lawrence Livermore National Laboratory*, Livermore, **2007**.

[36] H. D. B. Jenkins, H. K. Roobottom, J. Passmore, L. Glasser, *Inorg. Chem.* 1999, **38**, 3609-3620.

[37] B. M. Rice, E. F. C. Byrd, W. D. Mattson, *In Structure and Bonding, High Energy Density Materials* (Ed.: T. M. Klapotke), Springer, Berlin, **2007**, p. 153.

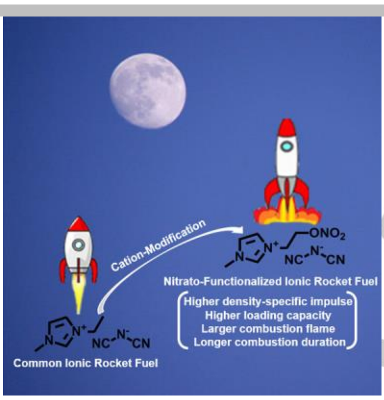
[38] D. R. MacFarlane, S. A. Forsyth, J. Golding, G. B. Deacon, *Green Chem. 2002,* **4**, 444-448.

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

Layout 1:

FULL PAPER

A series of nitrato-functionalized hypergolic ionic liquids were synthesized, which exhibited improved comprehensive performances including higher densities, higher density-specific impulse, larger combustion flames and longer violent combustion durations upon contact with the oxidizer of WFNA.



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Nitrato-Functionalized Task-Specific Ionic Liquids as Attractive Hypergolic Rocket Fuels