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Synthesis, structure and properties of imidazolium-based energetic ionic liquids†

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A series of imidazolium energetic ionic liquids (EILs) **2a**, **3a–f**, and **4a–f** with a nitrooxyethyl or hydroxyethyl side chain in their cations were easily synthesized starting from *N*-methylimidazole *via* quaternization, nitration, and metathesis reactions. The EILs and intermediates were fully characterized by FT-IR, UV/Vis, ESI-MS, ^{1}H NMR, ^{13}C NMR, or elemental analysis. Compounds **3a**, **3b**, and **4b** were further studied through single crystal X-ray diffraction. Solubility experiment shows that all the EILs have good solubilities in most polar solvents. The thermal properties of the EILs were investigated *via* differential scanning calorimetry (DSC) and thermo-gravimetric analysis (TGA). All the EILs have a very wide liquid temperature range over 100 °C. DSC data show that all the energetic compounds are typical ionic liquids with glass transition temperatures from −77 °C to −12 °C and melting temperatures below 100 °C. TGA data indicate that the new ionic liquids possess good thermal stabilities with decomposition temperatures above 165 °C, except for compounds **3d**, **4c**, and **4d**. Generally, the introduction of a nitrooxy group lowered the melting points and decomposition temperatures, but increased the glass transition temperatures of the EILs. The energetic properties of the EILs were further estimated by Kamlet–Jacobs formula. The detonation velocities of ionic liquids **2a** and **4a–f** are 6.84–7.63 km s^{-1}, which are between those of **TNT** and **RDX**. The detonation pressures of ionic liquids **2a**, **3e**, **4a**, **4b**, **4d**, and **4e** are better than that of **TNT**. Besides, energetic data show that the introduction of a nitrooxy group improved the energetic properties of the new ionic liquids.

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Introduction

Ionic liquids, defined as low-melting salts that melt at or below 100 °C, are composed of an organic cation and an inorganic or organic anion.[1] They are of great interest because of their unique chemical and physical properties such as low vapor pressure, non-flammability, high thermal stability, good ionic conductivity, and excellent fluidity and solubility.[2] Initially, ionic liquids were introduced as alternative green reaction media,[3–5] but today they have gradually shown their significant roles in various fields including organic synthesis,[6,7] catalysis,[8–10] analysis,[11] electrochemistry,[12,13] material chemistry,[14,15] energy technology,[16,17] as well as many others.

In the past dozen years, many ionic liquids have been reported to have potentials as green energetic materials.[18–21] Compared with traditional molecular energetic compounds, such as **TNT**, **RDX**, and **HMX**, energetic ionic liquids (EILs) have some intrinsic properties such as low vapour pressures, high thermal stabilities, and low melting points,[22–24] which make them ideal candidates for minimizing or even eliminating hazardous conditions associated with handling, processing and transporting explosive materials.[25] A large number of EILs have been reported based on imidazolium, triazolium, tetrazolium and so on with different energetic anions.[25] However, compared with energetic anions, energetic cations are relatively limited due to the absence of some energetic groups such as –NO_2, –NO, –N_3, –ONO_2 *etc.*[18,26] There has been an interest in exploring new EILs, especially for those containing energetic anions with a wider range and cations with desired energetic groups.[26]

In this study, a series of new imidazolium-based EILs, consisting of different energetic anions and imidazolium cations with a hydroxyethyl or nitrooxyethyl side chain, were designed and easily synthesized. The EILs were fully characterized by FT-IR, UV/Vis, ESI-MS, ^{1}H NMR, ^{13}C NMR, elemental analysis, and/or single crystal diffraction. The influences of the introduction of nitrooxy group on the thermal and energetic properties of the EILs were also investigated.

Results and discussion

Synthesis

A series of energetic alkali metal salts such as potassium 3,5-dinitro-1,2,4-triazolate (**KDNT**),[27,28] potassium picrate (**KP**),[29] potassium 3-nitro-5-oxo-1,2,4-triazolate monohydrate

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† Electronic supplementary information (ESI) available: Data of single crystal diffraction, DSC, and TG-DTG, as well as spectra of UV-Vis, FT-IR, ESI-MS, ^{1}H NMR, and ^{13}C NMR. CCDC 1550835–1550837. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7ra05601j

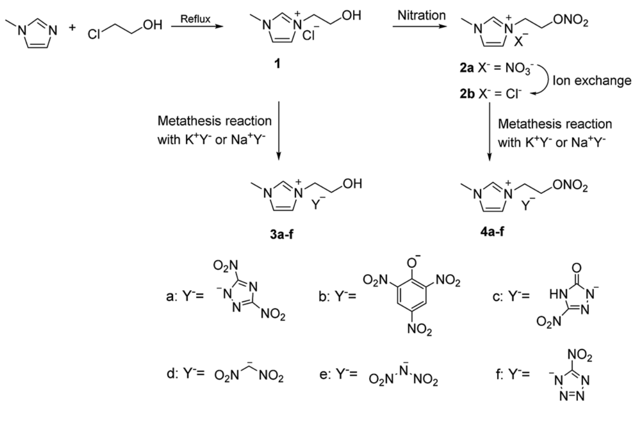
(**KNTO·H$_2$O**),[30] potassium dinitromethanide (**KDNM**),[31] potassium dinitramide (**KDN**),[32] and sodium 5-nitrotetrazolate dihydrate (**NaNT·2H$_2$O**)[33,34] were synthesized according to literature procedures. These energetic alkali metal salts will be used in subsequent metathesis reactions in order to introduce desired energetic anions.

N-Hydroxyethylimidazolium chloride (**1**) was synthesized *via* a quaternization reaction of *N*-methylimidazole with 2-chloroethanol under reflux without solvents (Scheme 1). Subsequent direct metathesis reactions of compound **1** with **KDNT**, **KP**, **KNTO**, **KDNM**, **KDN**, and **NaNT** in acetone successfully gave *N*-hydroxyethylimidazolium EILs **3a–f**.[35] Nitration of compound **1** with fuming nitric acid at a low temperature gave *N*-nitrooxyethylimidazolium nitrate (**2a**) with an energetic nitrooxy group in the side chain. At the same time, the chloride ion in compound **1** was replaced by a nitrate ion. However, direct metathesis reactions of compound **2a** with the alkali metal energetic salts in acetone were unsuccessful. It is probably because that sodium nitrate or potassium nitrate is slightly soluble in acetone, which leads to the presence of few NO^{3-} anions remaining in products. Comparatively, sodium chloride or potassium chloride is insoluble in acetone, indicating that Cl$^-$ anion could be a suitable choice for the metathesis reaction. Ion exchange of compound **2a** with Cl$^-$ type ion exchange resin successfully gave *N*-nitrooxyethylimidazolium chloride (**2b**). Compounds **4a–f** was then readily obtained by metathesis reactions of compound **2b** with **KDNT**, **KP**, **KNTO**, **KDNM**, **KDN**, or **NaNT** in acetone (Scheme 1). The potassium chloride or sodium chloride precipitated was removed by vacuum filtration.

Spectroscopy

EILs **1**, **2a–b**, **3a–f**, and **4a–f** were characterized by UV-Vis, FT-IR, ESI-MS, ^{1}H NMR, ^{13}C NMR, and elemental analysis, of which the data are listed in Experimental section.

The FT-IR spectra were determined in KBr pellets from 4000 to 450 cm^{-1} (see ESI†). All the compounds have the aromatic C–H stretching vibration absorption peak at 3200–3000 cm^{-1} of imidazolium ring, and the aliphatic C–H stretching vibration peak at 3000–2700 cm^{-1} of side chains. Besides, the characteristic IR absorption peaks of 3,5-dinitro-1,2,4-triazolate, picrate, 3-nitro-5-oxo-1,2,4-triazolate, dinitromethanide, dinitramide, and 5-nitrotetrazolate anions are also clearly observed for compounds **2a**, **3a–f**, and **4a–f**.[23,36–39]



Scheme 1 Synthesis of energetic ionic liquids.

The UV-Vis spectra of EILs **1**, **2a–b**, **3a–f**, and **4a–f** were recorded in water by an UV-1800PC ultraviolet and visible spectrophotometer (see ESI†). The maximum UV absorptions of imidazolium cations are obtained at 213–230 nm, and those of anions are found at 285 nm (3,5-dinitro-1,2,4-triazolate), 354 nm (picrate), 344 nm (3-nitro-5-oxo-1,2,4-triazolate), 361 nm (dinitromethanide), 283 nm (dinitramide), and 255–256 nm (5-nitrotetrazolate), respectively. UV-Vis data show that all the compounds have both desired ions.

The ESI-MS spectra of EILs **1**, **2a–b**, **3a–f**, and **4a–f** were also recorded (see ESI†). In ESI-MS positive ion mode, the cationic peaks of compounds **1** and **3a–f** are observed at about 126.9 (1-hydroxyethyl-3-methylimidazolium cation), and those of compounds **2a–b** and **4a–f** are at about 172.0 (1-methyl-3-nitrooxyethylimidazolium cation), indicating the existence of desired imidazolium cations. In ESI-MS negative ion mode, the anionic peaks of compounds **2a**, **3a–f**, and **4a–f** were also detected at 61.8 (nitrate anion), 157.8 (3,5-dinitro-1,2,4-triazolate anion), 227.8 (picrate anion), 128.7 (3-nitro-5-oxo-1,2,4-triazolate anion), 104.6 (dinitromethanide anion), 105.6 (dinitramide anion), and 113.7 (5-nitrotetrazolate anion), respectively. ESI-MS data show that the new energetic salts have both desired cations and anions.

The structures of EILs **1**, **2a–b**, **3a–f**, and **4a–f** were further confirmed by ^{1}H NMR and ^{13}C NMR spectra (see ESI†). ^{1}H NMR data show that the aromatic hydrogen signals of C2–$\underline{H}$ on imidazolium rings were at 8.69–9.27 ppm in DMSO-d$_6$ and disappeared in D$_2$O. This indicated that the C2–$\underline{H}$ on imidazolium rings is acidic, which underwent a H/D exchange reaction in D$_2$O. Besides, the aromatic hydrogen signals of C4–$\underline{H}$ and C5–$\underline{H}$ on imidazolium rings were obtained at 7.34–7.83 ppm. The side chain hydrogen signals of imidazolium cations in EILs **2a–b** and **4a–f** are at 4.78–4.94 ppm (–C$\underline{H}_2$–ONO$_2$), 4.51–4.65 ppm (N–C$\underline{H}_2$–), and 3.78–3.89 ppm (N–C$\underline{H}_3$), while those of imidazolium cations in compounds **1** and **3a–f** are at 5.18–5.23 ppm (–CH$_2$–O$\underline{H}$), 4.22–4.38 ppm (N–C$\underline{H}_2$–), 3.80–3.95 ppm (N–C$\underline{H}_3$), and 3.73–3.96 ppm (–C$\underline{H}_2$–OH). Among the anions of the compounds, only picrate and dinitromethanide anions have hydrogen signals at 8.59 ppm and 8.16 ppm respectively. Besides, ^{13}C NMR spectra display the aromatic carbon signals of imidazolium cation at about 137 ppm (C2), 124 ppm (C5), and 123 ppm (C4). The side chain carbon signals of imidazolium cations in compounds **2a–b** and **4a–f** are at about 71 ppm (–$\underline{C}$H$_2$–ONO$_2$), 47 ppm (N–$\underline{C}$H$_2$–), and 36 ppm (N–$\underline{C}$H$_3$), while those of **1** and **3a–f** are at about 60 ppm (–$\underline{C}$H$_2$–OH), 52 ppm (N–$\underline{C}$H$_2$–), and 36 ppm (N–$\underline{C}$H$_3$). The anions of compounds **2a–b**, **3e** and **4e** without carbon have no carbon signals. The 3,5-dinitro-1,2,4-triazolate anion of **3a** and **4a** has a carbon signal at 163 ppm. The picrate anions of compound **3b** and **4b** have carbon signals at 161–162, 141–142, 126–127, and 125–127 ppm. The 3-nitro-5-oxo-1,2,4-triazolate anions of **3c** and **4c** exhibit carbon signals at about 165 and 160 ppm. The dinitromethanide anions of compounds **3d** and **4d** have a carbon signal at about 123 ppm. The tetrazolate anions of compounds **3f** and **4f** exhibit carbon signals at 167–169 ppm.

Thermal properties

The thermal stabilities of the new energetic compounds were determined by thermogravimetric analysis (TGA) (Fig. 1). The decomposition temperatures obtained from TG data are listed in Table 1. Comparatively, the decomposition temperatures of EILs **3a–f** with a *N*-hydroxyethyl side chain are much higher than those of compounds **4a–f** with a *N*-nitrooxyethyl side chain, when their anions are the same. This indicates that the introduction of a nitrooxy group into the side chains lowered the decomposition temperatures, rendering the corresponding EILs a poorer thermo-stability. Generally, energetic salts **2a**, **3a–f**, **4a–b**, and **4e–f** possess good thermal stabilities, of which the decomposition temperatures are higher than 150 °C. However, EILs **3d** and **4d** with a dinitromethanide anion have the lowest decomposition temperatures at 151 °C and 138 °C. When heated up to 650 °C, a nearly 100% weight loss was observed for compounds **3d–e** and **4e–f**, while compounds **3b** and **4b** with picrate anions had a very high weight residue above 20% (Fig. 1). It is probably because the oxygen-rich dinitromethanide, dinitramide, or 5-nitrotetrazolate anions provide compounds **3d–e** and **4e–f** a better oxygen balance than picrate anion does.

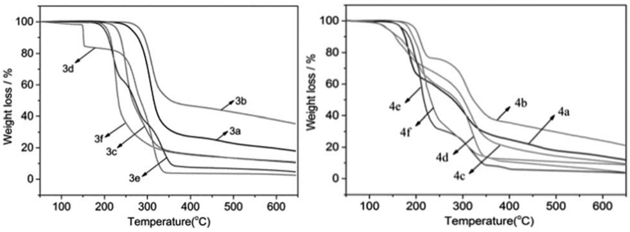


Fig. 1 TG curves of compounds **3a–f** (left) and **4a–f** (right) in argon atmosphere.

Table 1 Physicochemical properties of compounds **2a**, **3a–f** and **4a–f**

Compound	Appearance[a]	T_g[b] (°C)	T_m[c] (°C)	T_d[d] (°C)
2a	l	−51	—	165
3a	s	—	94	263
3b	s	−22	89	283
3c	s	−24	100	231
3d	l	−73	—	151
3e	l	−77	—	200
3f	s	−50	79	207
4a	s	−21	55	169
4b	s	−58	81	198
4c	l	−12	—	139
4d	l	−51	—	138
4e	l	−64	—	171
4f	s	−36	45	185
KDNT[e]	s	—	—	265
KPic[f]	s	—	—	359
KNTO·H_2O[g]	s	—	—	230
KDNM[h]	s	—	—	220
KDN[i]	s	—	—	228
NaNT·$2H_2O$[j]	s	—	—	200

[a] s: solid at r.t., l: liquid at r.t. [b] Glass transition temperature. [c] Melting point. [d] Decomposition temperature. [e] Ref. 28, **KDNT**: potassium 3,5-dinitro-1,2,4-triazolate. [f] Ref. 40, **KPic**: potassium picrate. [g] Ref. 41, **KNTO**: potassium 3-nitro-1,2,4-triazolate-one. [h] Ref. 31, **KDNM**: potassium dinitromethanide. [i] Ref. 42, **KDN**: potassium dinitramide. [j] Ref. 34, **NaNT**: sodium 5-nitrotetrazolate.

DTG curves of the energetic compounds show that compounds **3a**, **3b**, and **3f** have one weight loss process, compounds **2a**, **3c**, **3d** and **4a–d** generally have two weight loss processes, and compounds **3e** and **4e–f** have three weight loss processes (see ESI†). Generally, the first weight loss processes of compounds **4a–f** are surely due to the decomposition of their *N*-nitrooxyethyl side chains, as indicated by the structure and thermo-stability differences between compounds **3a–f** and compounds **4a–f**.

The thermal properties of compounds **2a**, **3a–f** and **4a–f** were further determined by differential scanning calorimetry (DSC) (see ESI†). The melting points and glass transition temperatures obtained from DSC data are also listed in Table 1. DSC data show that the energetic salts are typical ionic liquids with glass transition temperatures from −77 °C to −12 °C and melting points below 100 °C. Importantly, all the EILs have a very wide liquid temperature range over 100 °C (Table 1). Besides, EILs **3a–c**, **3f**, and **4b** have a melting point from 79 °C to 100 °C and a much higher decomposition temperature from 198 °C to 283 °C, which may be potential choices for melt-cast explosives. Generally, when the anions are the same, the melting temperatures of **3a–f** with a hydroxyethyl side chain are higher than those of **4a–f** with a nitrooxyethyl side chain, while their glass transition temperatures are just the opposite (Table 1). It shows that the introduction of nitrooxy group lowered the melting points, but increased the glass transition temperatures of the ionic liquids.

Compounds **2a**, **3d**, **3e**, **4c**, **4d** and **4e** are liquid at room temperature, of which the secondary heating DSC curves are shown in ESI.† During the secondary heating process, only glass transitions were observed without melting or crystallization. Compounds **3b**, **3c**, **4a**, and **4f** are solid at room temperature, of which the first heating DSC curves and secondary heating DSC curves are quite different (see ESI†). During the first heat process, only melting peaks were observed without glass transition and crystallization peaks. Comparatively, there are no melting peaks in the secondary heating DSC curves, whereas obvious glass transition processes are observed. It is probably because that compounds **3b**, **3c**, **4a**, and **4f** have very slow crystallization rates, of which crystal states could not be formed during the cooling and heating processes. Compounds **3f** and **4b** are solid at room temperature, of which the first and secondary heating DSC curves are different clearly (see ESI†). During the first heating process, only melting peaks were observed, where the glass states of compounds **3f** and **4b** turned into a liquid state. During the secondary heating process, there are glass transition processes at −50 °C and −12 °C, where compounds **3f** and **4b** turned into supercooled liquids. When further heated, compounds **3f** and **4b** crystallized and then melted into a normal liquid.

Solubility

Solubility test shows that all of the salts were soluble in most polar solvents such as acetonitrile, acetone, ethanol, methanol, dimethyl sulfoxide, and water, but insoluble in diethyl ether, petroleum ether, ethyl acetate, and dichloromethane.

Crystal structures

Slow recrystallization of compounds **3a**, **3b**, and **4b** from acetone at room temperature gave crystals suitable for X-ray diffraction analysis. The crystallographic data are summarized in Table 2. Selected bond lengths, bond angles, and some further information about crystal-structure determinations are given in the ESI.† The molecular structures and the packing diagrams of compounds **3a**, **3b**, and **4b** are shown in Fig. 2–4, respectively.

Compound **3a** crystallizes in a triclinic space group $P\bar{1}$ with a density of 1.528 g cm^{-3} and a unit cell volume of 619.95 Å^3 (Table 2). The molecular unit of compound **3a** consists of one 2,5-dinitrotriazolate anion and one 1-hydroxyethyl-3-methylimidazolium cation without coordinated water (Fig. 2). All the atoms of 2,5-dinitrotriazolate anion are almost coplanar. The C–N bonds in the 2,5-dinitrotriazolate ring have nearly same bond lengths of 1.33 Å, showing a conjugation system existed. The bond lengths of N1–C5, N2–C5, N1–C4, and N2–C3 in the imidazolium ring of compound **4b** are 1.32, 1.32, 1.38, and 1.38 Å, respectively. These C–N bonds are much shorter than a classical C–N single bond (1.47 Å), whereas longer than a C=N double bond (1.31 Å), indicating a conjugation existed in the imidazolium ring. Comparatively, the bond lengths of N1–C5 and N2–C5 are shorter than those of N1–C4 and N2–C3, which is consistent with 1,3-disubstituted imidazoliums.[43] There is a strong intramolecular O5–H⋯N3 hydrogen bond with a bond length of 2.07 Å. The crystal structure is formed by intramolecular and intermolecular O–H⋯N hydrogen bonds, π-stack as well as the charge attraction between imidazolium cation and 2,5-dinitrotriazolate anion. The O5–H⋯N3 strong hydrogen bond and the charge attraction between the cation and the anion make compound **3a** have a U-shape layout in the crystal, as shown in Fig. 2.

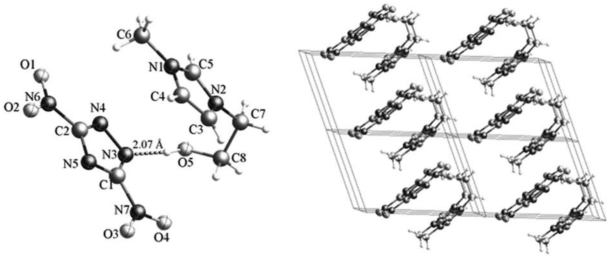


Fig. 2 Molecular structure and packing diagram of compound **3a**.

Compound **3b** crystallizes in a monoclinic space group $P2_1/n$ with a density of 1.552 g cm^{-3} and a unit cell volume of 1520.22 Å^3 (Table 2). The molecular unit of compound **3b** consists of one picrate anion and one 1-hydroxyethyl-3-methylimidazolium cation (Fig. 3). Interestingly, there is no intramolecular hydrogen bond observed although there is a hydroxyl group in compound **3b**. Actually, the three nitro groups of picrate anion are not coplanar. The C2–NO$_2$ has a very big O7–N3–C2–C1

Table 2 Crystal data and structure refinement parameters of compounds **3a**, **3b** and **4b**

Compound	**3a**	**3b**	**4b**
CCDC number	1550836	1550837	1550835
Empirical formula	$C_8H_{11}N_7O_5$	$C_{12}H_{13}N_5O_8$	$C_{12}H_{12}N_6O_{10}$
Formula weight	285.24	355.27	400.28
Temperature [K]	293.15	293.15	293.15
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$
a [Å]	6.7821(4)	14.1861(4)	11.0072(13)
b [Å]	9.5516(6)	7.38696(18)	8.8756(7)
c [Å]	10.3880(5)	15.4711(4)	17.3685(17)
α [°]	94.882(4)	90.00	90.00
β [°]	96.973(4)	110.333(3)	99.588(10)
γ [°]	110.449(5)	90.00	90.00
Volume [Å^3]	619.95(6)	1520.22(7)	1673.1(3)
Z	2	4	4
ρ_{calc} [g cm^{-3}]	1.528	1.552	1.589
μ [mm^{-1}]	1.115	1.154	1.235
F(000)	296.0	736.0	824.0
Crystal size [mm^3]	0.52 × 0.48 × 0.44	0.48 × 0.46 × 0.42	0.46 × 0.38 × 0.32
2θ range [°]	12.29–133.18	10.46–133.18	8.88–133.18
Reflections collected	6297	8196	10 675
Independent reflections/R_{int}	2179/0.0224	2679/0.0273	2913/0.0355
Data/restraints/parameters	2179/0/184	2679/0/229	2913/0/255
Goodness-of-fit on F^2	1.040	1.069	1.112
R_1/wR_2 [$I \geq 2\sigma(I)$]	0.0408/0.1130	0.0479/0.1292	0.0702/0.2069
R_1/wR_2 [all data]	0.0429/0.1152	0.0525/0.1334	0.0813/0.2307
Largest diff. peak/hole [e Å^{-3}]	0.20/−0.22	0.54/−0.34	0.42/−0.33

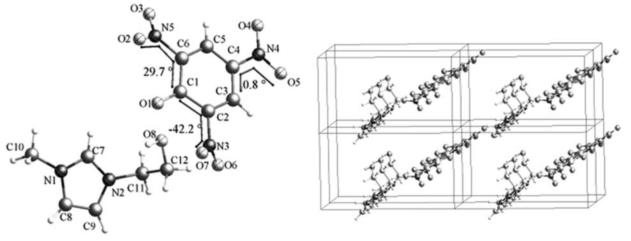


Fig. 3 Molecular structure and packing diagram of compound **3b**.

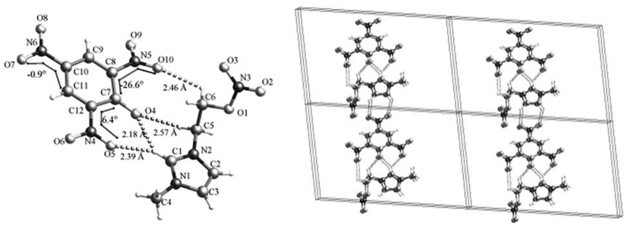


Fig. 4 Molecular structure and packing diagram of compound **4b**.

torsion angle of −42.2° due to the steric hindrances of both O1 and the hydroxyethyl side chain (Fig. 3). The O8–C12 bond length of 1-hydroxyethyl-3-methylimidazolium cation is 1.408 Å, which is much longer than that of O1–C1 (1.241 Å) in picrate anion. The difference originates from the delocalization of the negative charge on the benzene ring. In addition, the π–π conjugation between the nitro group and the aromatic ring results in the C–N bond lengths in picrate anion range from 1.443 to 1.451 Å, which are a little shorter than those of C–N bonds in the imidazolium cation (1.465 and 1.474 Å).

Compound **4b** crystallizes in a monoclinic space group $P2_1/n$ with a density of 1.589 g cm^{-3} and a unit cell volume of 1673.1(3) Å^3 (Table 2). Fig. 4 shows that the molecular unit of compound **4b** consists of one picrate anion and one 1-methyl-3-nitrooxyimidazolium cation without coordinated water. Interestingly, there are no common hydrogen bonds but several intra- and intermolecular C–H⋯O hydrogen bonds formed in the crystal system (Fig. 4). The C1–H on the imidazolium is acidic, which interact with O4 and O5 forming two hydrogen bonds *via* a six-membered ring. The resulting C1–H⋯O4 and C1–H⋯O5 have a hydrogen bond length of 2.18 Å and 2.39 Å, which is significantly shorter than the sum of their van der Waals radii (d_0, 2.72 A°). The bond length of C1–H⋯O4 is a little shorter than that of C1–H⋯O5 probably because that O4 is deprotonated and negatively charged. It is the C1–H⋯O4 and C1–H⋯O5 hydrogen bonds that make the torsion angle of O5–N4–C12–C7 (+6.4°) remarkably smaller than that of O10–N5–C8–C7 (−26.6°). Besides, C5–H and C6–H activated respectively by a quaternary ammonium nitrogen (N2) and a nitrooxy group are reasonable hydrogen bond donors.[44–46] The C5–H⋯O4 (d = 2.57 Å) and C6–H⋯O10 (d = 2.46 Å) hydrogen bonds render imidazolium ring and the nitrooxy group a *gauche* form conformation, as shown in Fig. 4. Furthermore, the C2–H and C3–H on imidazolium ring formed two intermolecular C–H⋯O hydrogen bonds with the two nitro oxygens of picrate in another molecule (Fig. 4). The 2D layer structure is formed by intra- and intermolecular C–H⋯O hydrogen bonds as well as the charge attraction between imidazolium cation and picrate anion, and the 2D layer stacks are parallel to the crystallographic c axis.

Energetic properties

As one of the most important properties of the EILs, density can be calculated by Gaussian software. The molar volume can be calculated with Monte-Carlo method. Furthermore, the density can be readily extracted. Heat of formation is one of the most essential features of the compounds. On the basis of a Born–Haber energy cycle (Scheme 2), the heats of formation of all the EILs can be simplified by the expression shown in eqn (1).

$$\begin{aligned}\Delta H^0_{298}\ (\text{ionic salts, 298 K}) = {} & \sum \Delta H^0_{298}\ (\text{cation, 298 K}) \\ & + \sum \Delta H^0_{298}\ (\text{anion, 298 K}) - \Delta H_\text{L} \qquad (1)\end{aligned}$$

where ΔH_L is the lattice energy of the ionic liquids, which can be predicted by eqn (2) suggested by Jenkins *et al.*

$$\Delta H_\text{L} = U_\text{POT} + [p(n_\text{M}/2 - 2) + q(n_\text{X}/2 - 2)]RT \qquad (2)$$

where n_M and n_X depend on the nature of the ions $\text{M}_p{}^+$ and $\text{X}_q{}^-$, respectively, and are equal to 3 for monatomic ions, 5 for linear polyatomic ions, and 6 for nonlinear polyatomic ions. The equation for lattice potential energy U_POT has the form shown in eqn (3).

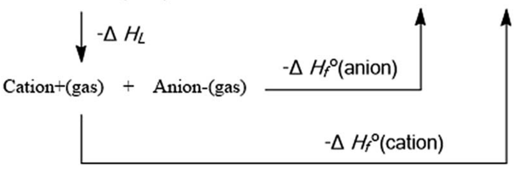
$$U_\text{POT} = \gamma(\rho/M)^{1/3} + \delta \qquad (3)$$

where ρ is the density (g cm^{-1}), M is the chemical formula mass of the ionic liquid (g mol^{-1}). The coefficients γ and δ are obtained from literatures.[47] For MX (1 : 1) salts, γ is 1981.2 kJ mol^{-1} and δ is 103.8 kJ mol^{-1}.

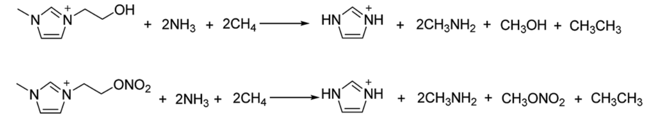
The molar enthalpies of formation of energetic anions are obtained from literatures.[14,23,48] The molar enthalpy of formation of the cation is computed by Gaussian software based on the designed isodesmic reaction (Scheme 3). The enthalpy of reaction ($\Delta H^0_{\text{r}\ 298}$) is obtained by combining the B3LYP/6-31++G** energy differences for the reaction, the scaled zero-point energies, and other thermal factors.

The detonation velocity (D) and detonation pressure (P) of energetic compounds could be predicted by eqn (4) and (5).[49,50]

$$D = 1.01(N\bar{M}^{1/2}Q^{1/2})^{1/2}(1 + 1.30\rho) \qquad (4)$$



Scheme 2 Born–Haber cycle for the formation of energetic ionic liquids.



Scheme 3 Isodesmic reactions of imidazolium cations.

$$P = 1.558\rho^2 N\bar{M}^{1/2}Q^{1/2} \tag{5}$$

The calculated densities, lattice energies, molar enthalpies of formation and detonation parameters of the EILs are listed in Table 3.

As shown in Table 3, the calculated densities of compounds **2a**, **3a–f**, and **4a–f** are from 1.47 to 1.64 g cm^{-3}, which are generally close to their crystal or pycnometric densities. Compounds **2a**, **3a**, **3b**, **3d**, **3e**, **4b**, **4d** and **4e** possess negative heats of formation, which mainly result from the large negative heats of formation of their anions. It is noteworthy that the 5-nitrotetrazolate anion possesses a positive heat of formation of 112.80 kJ mol^{-1} and its salts **3f** and **4f** have a much higher enthalpy of formation than those of other salts. Generally, with the same anions, EILs **4a–f** with an energetic nitrooxy group in their side chains have a higher enthalpy of formation than EILs **3a–f** without a nitrooxy group (Table 3).

When the anions are the same, the detonation velocities and detonation pressures of ionic liquids **4a–f** with a nitrooxyethyl side chain are much higher than those of ionic liquids **3a–f** with a hydroxyethyl side chain (Table 3). It indicates that the introduction of nitrooxy energetic group can improve their energetic properties. The detonation velocities of ionic liquids **2a** and **4a–f** are 6.84–7.63 km s^{-1}, which are between those of **TNT** and **RDX**. The detonation pressures of ionic liquids **2a**, **3e**, **4a**, **4b**, **4d**, and **4e** are better than that of **TNT**. Generally, some of the EILs have good energetic properties which have potentials as new energetic materials.

Experimental section

Caution

We did not experience any problems in handling these compounds, though some of them were sensitive to shock, heat, or friction. We strongly suggested that they should be synthesized in a very small scale and handled with extreme care using all of the standard safety precautions because of their high nitrogen content and rather high heats of formation.

Materials and methods

All chemical reagents of analytically pure grade were obtained from commercial sources and used as received without additional purification. UV-Vis spectra were recorded by an UV-1800PC ultraviolet and visible spectrophotometer. IR spectra were recorded by using KBr plates in the range 4000–450 cm^{-1} by a Perkin Elmer Spectrum 100 FT-IR spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance III 600 nuclear magnetic resonance spectrometer operating at 600 MHz and 151 MHz, respectively. Meanwhile, a part of ^{1}H NMR spectra were recorded on a Bruker Advance 400 MHz instrument with deuterium oxide (D_2O) as the solvent. All ^{1}H and ^{13}C chemical shifts were reported in ppm relative to tetramethylsilane (TMS). Mass spectra for salts were determined using an electrospray ion source (ESI) in Varian 1200 L high-performance liquid chromatography tandem mass spectrometry (LC-MS). M^+ and M^- were the mass of the cation and anion, respectively. Elemental analyses were performed using a Netsch STA 429 simultaneous thermal analyser. The melting and decomposition points of all the salts were recorded on a Q2000 differential

Table 3 Calculated densities, lattice energies, molar enthalpies of formation and detonation parameters of compounds **2a**, **3a–f** and **4a–f** (298 K)

Compound	ρ_1 (ρ_2)^a (g cm^{-3})	$\Delta_f H_c^{o b}$ (kJ mol^{-1})	$\Delta_f H_a^{o c}$ (kJ mol^{-1})	$\Delta H_L{}^d$ (kJ mol^{-1})	$\Delta_f H_m^{o\ e}$ (kJ mol^{-1})	Q^f (cal g^{-1})	D^g (km s^{-1})	P^h (GPa)
2a	1.53 (1.51)	528.61	−307.90	478.79	−258.08	1697.72	7.53	22.65
3a	1.53 (1.53)^i	481.22	−41.20	455.86	−15.84	1026.08	6.51	16.98
3b	1.59 (1.55)^i	481.22	−108.50	435.54	−62.82	1297.88	6.73	18.60
3c	1.49 (1.47)	481.22	63.90	465.15	79.97	976.51	6.39	16.04
3d	1.48 (1.48)	481.22	−221.70	476.02	−216.50	1021.32	6.42	16.14
3e	1.51 (1.50)	481.22	−162.00	478.33	−159.11	1401.85	7.20	20.57
3f	1.47 (1.47)	481.22	112.80	470.39	123.63	841.00	6.24	15.15
4a	1.59 (1.55)	528.61	−41.20	443.53	43.88	1191.37	7.06	20.50
4b	1.64 (1.59)^i	528.61	−108.50	425.74	−5.63	1339.40	7.12	21.25
4c	1.56 (1.53)	528.61	63.90	451.52	140.99	1244.79	6.93	19.48
4d	1.55 (1.52)	528.61	−221.70	460.75	−153.84	1268.27	7.09	20.34
4e	1.59 (1.54)	528.61	−162.00	462.70	−96.09	1459.08	7.63	23.84
4f	1.54 (1.52)	528.61	112.80	455.98	185.43	1164.08	6.84	18.80
TNT	1.60	—	—	—	−74.50	—	6.84	20.29
RDX	1.81	—	—	—	61.55	—	8.75	34.70

[a] ρ_1: calculated density, ρ_2: pycnometric density. [b] Calculated molar enthalpy of formation of cations. [c] Molar enthalpy of formation of anions. [d] Molar lattice energy. [e] Calculated molar enthalpy of formation of ionic liquids. [f] Detonation heat. [g] Detonation velocity. [h] Detonation pressure. [i] Single crystal density.

scanning calorimeter (DSC) from TA Instruments at a scan rate of 10 °C min^{-1}. Thermal decomposition of the salts up to 650 °C in argon (flow rate 30 mL min^{-1}) were performed by a Perkin Elmer Pyris 1 thermal gravimetric analysis (TGA) at a heating rate of 10 °C min^{-1}.

Synthesis of ionic liquids

1-(2-Hydroxyethyl)-3-methylimidazolium chloride (1). A mixture of 1-methylimidazole (5.2 g, 63.5 mmol) and 2-chloroethanol (5.2 g, 64.0 mmol) was added into a 100 mL two-necked round-bottomed flask that was fitted with a reflux condenser. The mixture was stirred at 80 °C for 20 h, to which 10 mL anhydrous ethanol was then added. The resulting mixture was poured into 100 mL cold ethyl acetate and cooled to room temperature. After decanting the ethyl acetate layer, the crude product was washed with diethyl ether (3 × 10 mL) and dried in vacuum overnight to give compound **1** as fairly hygroscopic white crystals (9.1 g, 55.9 mmol, 88% yield). UV-Vis (H_2O) λ_{max}: 227 nm; ^{1}H NMR (600 MHz, D_2O), δ 7.59 (d, J = 2.4 Hz, 1H, C5–H), 7.54 (d, J = 2.4 Hz, 1H, C4–H), 4.38 (t, J = 4.8 Hz, 2H, N–CH_2–), 3.96 (t, J = 4.8 Hz, 2H, –CH_2–OH), 3.95 (s, 3H, N–CH_3); ^{13}C NMR (151 MHz, D_2O), δ 136.25 (C2), 123.70 (C5), 122.59 (C4), 59.96 (–CH_2–OH), 51.72 (N–CH_2–), 36.02 (N–CH_3); FT-IR (KBr) ν: 3411.3, 3156.4, 3111.2, 2958.9, 2886.2, 1635.5, 1574.8, 1450.2, 1357.6, 1167.8, 1068.8, 944.9, 870.8, 841.3, 753.7, 651.2 cm^{-1}; ESI-MS m/z (%): 126.9 (M^+, 100).

1-Methyl-3-(2-nitrooxyethyl)imidazolium nitrate (2a). Compound **1** (2.4 g, 15.0 mmol) was added in small portions to a two-necked round-bottomed flask containing fuming nitric acid (10 mL, 240.0 mmol) and cooled by a water-ice bath to maintain the temperature below 10 °C. After addition, the reaction mixture was stirred for 1 h at 10–15 °C and then for 6 h at room temperature. The mixture was poured into 150 mL cold diethyl ether. After stirring for 2 h, the diethyl ether layer was decanted. The crude product was washed with diethyl ether (3 × 10 mL) and dried in vacuum overnight to obtain **2a** as a colorless liquid (3.0 g, 12.8 mmol, 85% yield). UV-Vis (H_2O) λ_{max}: 226 nm; ^{1}H NMR (600 MHz, D_2O), δ 8.69 (s, 1H, C2–$\underline{H}$), 7.42 (t, J = 1.8 Hz, 1H, C5–$\underline{H}$), 7.34 (t, J = 1.8 Hz, 1H, C4–$\underline{H}$), 4.78 (t, J = 4.2 Hz, 2H, –$C\underline{H_2}$–ONO_2), 4.51 (t, J = 4.2 Hz, 2H, N–$C\underline{H_2}$–), 3.78 (s, 3H, N–$C\underline{H_3}$); ^{13}C NMR (151 MHz, D_2O) δ 136.68 (C2), 124.65 (C5), 122.54 (C4), 70.85 (–$\underline{C}H_2$–ONO_2), 46.51 (N–$\underline{C}H_2$–), 35.75 (N–$\underline{C}H_3$); FT-IR (KBr) ν: 3153.9, 3110.2, 2968.7, 2853.0, 1642.4, 1577.9, 1565.6, 1377.5, 1282.6, 1171.6, 1036.7, 1005.4, 895.9, 848.0, 826.3, 754.9, 707.8, 623.4 cm^{-1}; ESI-MS m/z (%): 172.0 (M^+, 100), 61.8 (M^-, 100). Anal. calcd for $C_6H_{10}N_4O_6$: C 30.78, H 4.30, N 23.93; found C 30.74, H 4.31, N 23.91.

Pretreatment of Amberlite 717

Amberlite 717 was immersed in distilled water for 24 h and filtered. Then the resin was immersed in brine for another 24 h in order that all OH^- was replaced by Cl^-. At last, the resin was washed by deionized water several times until there were no precipitations formed in the filtrate by addition of a silver nitrate solution.

1-Methyl-3-(2-nitrooxyethyl)imidazolium chloride (2b). Anion exchange resin (40 g) was added into a two-necked round-bottomed flask containing compound **2a** (10.3 g, 44.0 mmol) in 10 mL water and 40 mL methanol. Then the mixture was stirred at room temperature for 12 h. The resin was removed by vacuum filtration, giving a colorless filtrate. The solvent was removed by a rotary evaporator to yield **2b** as a slight yellow solid (9.0 g, 43.4 mmol, 99%). ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.19 (s, 1H, C2–$\underline{H}$), 7.81 (t, J = 1.8 Hz, 1H, C5–$\underline{H}$), 7.74 (t, J = 1.8 Hz, 1H, C4–$\underline{H}$), 4.94 (t, J = 4.8 Hz, 2H, –$C\underline{H_2}$–ONO_2), 4.62 (t, J = 4.8 Hz, 2H, N–$C\underline{H_2}$–), 3.88 (s, 3H, N–$C\underline{H_3}$); ^{13}C NMR (151 MHz, D_2O) δ 136.91 (C2), 123.85 (C5), 122.53 (C4), 71.22 (–$\underline{C}H_2$–ONO_2), 46.51 (N–$\underline{C}H_2$–), 35.79 (N–$\underline{C}H_3$).

General procedures for the preparation of energetic ionic liquids 3a–f and 4a–f

Compounds **1** or **2b** was dissolved in acetone, and then one equivalent of **KDNT**, **KP**, **KNTO·H_2O**, **KDNM**, **KDN**, or **NaNT·$2H_2O$** was added. The precipitation of white chloride salts was observed intermediately and the resulting slurry was stirred at room temperature for 24 h. After removal of the precipitation by vacuum filtration, the solvent was evaporated *via* a rotary evaporator. The resulting crude product was dissolved in acetone to remove the residual chloride salts by vacuum filtration, the filtrate was evaporated, and then the residue was washed twice with Et_2O.

1-(2-Hydroxyethyl)-3-methylimidazolium 3,5-dinitro-1,2,4-triazolate (3a). Slightly yellow solid, yield: 93.5%. UV-Vis (H_2O) λ_{max}: 214, 285 nm; ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.08 (s, 1H, C2–H), 7.72 (t, J = 1.8 Hz, 1H, C5–H), 7.69 (t, J = 1.8 Hz, 1H, C4–H), 5.18 (t, J = 4.8 Hz, 1H, –CH_2–O$\underline{H}$), 4.22 (t, 2H, J = 4.8 Hz, N–$C\underline{H_2}$–), 3.87 (s, 3H, N–$C\underline{H_3}$), 3.73 (q, J = 4.8 Hz, 2H, –$C\underline{H_2}$–OH); ^{13}C NMR (151 MHz, DMSO-d_6) δ 163.32 (–$\underline{C}$–NO_2), 137.26 (C2), 123.80 (C5), 123.11 (C4), 59.79 (N–$\underline{C}H_2$–), 52.09 (–$\underline{C}H_2$–OH), 36.12 (N–$\underline{C}H_3$); FT-IR (KBr) ν: 3395.3, 3149.2, 2854.6, 2755.1, 1555.6, 1538.6, 1503.4, 1413.3, 1390.0, 1385.6, 1300.5, 1100.4, 1049.6, 850.8, 836.5, 771.2, 651.4, 605.6 cm^{-1}; ESI-MS m/z (%): 126.9 (M^+, 100), 157.7 (M^-, 100), 316.8 (32); anal. calcd for $C_8H_{11}N_7O_5$: C 33.69, H 3.89, N 34.38; found C 33.65, H 3.90, N 34.37.

1-(2-Hydroxyethyl)-3-methylimidazolium picrate (3b). Yellow solid, yield: 97.9%. UV-Vis (H_2O) λ_{max}: 221, 354 nm; ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.10 (s, 1H, C2–$\underline{H}$), 8.61 (s, 2H, picrate), 7.73 (t, J = 1.8 Hz, 1H, C5–$\underline{H}$), 7.70 (t, J = 1.8 Hz, 1H, C4–$\underline{H}$), 4.23 (t, J = 4.8 Hz, 2H, N–$C\underline{H_2}$–), 3.88 (s, 3H, N–$C\underline{H_3}$), 3.74 (t, J = 4.8 Hz, 2H, –$C\underline{H_2}$–OH); ^{13}C NMR (151 MHz, D_2O) δ 162.13 (picrate C1′), 140.79 (picrate C2′ C6′), 136.37 (C2), 127.09 (picrate C4′), 126.65 (picrate C3′ C5′), 123.61 (C5), 122.48 (C4), 59.84 (–$\underline{C}H_2$–OH), 51.55 (N–$\underline{C}H_2$–), 35.74 (N–$\underline{C}H_3$); FT-IR (KBr) ν: 3417.7, 3155.8, 3086.3, 2959.6, 2894.5, 2824.6, 1630.7, 1611.8, 1563.3, 1496.8, 1483.1, 1438.6, 1369.5, 1334.6, 1277.7, 1163.7, 1081.1, 937.5, 907.9, 795.9, 746.0, 704.0, 651.4, 621.8 cm^{-1}; ESI-MS m/z (%): 126.8 (M^+, 100), 227.7 (M^-, 100); anal. calcd for $C_{12}H_{13}N_5O_8$: C 40.57, H 3.69, N 19.71; found C 40.62, H 3.58, N 19.65.

1-(2-Hydroxyethyl)-3-methylimidazolium 3-nitro-5-oxo-1,2,4-triazolate (3c). Orange solid, yield: 94.1%. UV-Vis (H_2O) λ_{max}: 230, 344 nm; ^{1}H NMR (400 MHz, D_2O) δ 7.49 (d, J = 2.0 Hz, 1H, C5–$\underline{H}$), 7.43 (d, J = 2.0 Hz, 1H, C4–$\underline{H}$), 4.30 (t, J = 4.8 Hz, 2H, N–C$\underline{H}_2$–), 3.91 (t, J = 4.8 Hz, 2H, –C$\underline{H}_2$–OH), 3.89 (s, 3H, N–C$\underline{H}_3$); ^{13}C NMR (151 MHz, DMSO-d_6) δ 165.31 ($\underline{C}$=O), 160.56 ($\underline{C}$–NO_2), 137.42 (C2), 123.74 (C5), 123.13 (C4), 59.80 (–$\underline{C}H_2$–OH), 52.06 (N–$\underline{C}H_2$–), 36.10 (N–$\underline{C}H_3$); FT-IR (KBr) ν: 3362.5, 3251.5, 3153.7, 3110.2, 2966.7, 2841.5, 2791.4, 1699.3, 1656.1, 1592.2, 1576.5, 1544.2, 1508.7, 1424.7, 1383.3, 1312.7, 1167.9, 1117.6, 1050.0, 1015.0, 848.8, 812.0, 776.8, 746.8, 619.6 cm^{-1}; ESI-MS m/z (%): 126.9 (M^+, 100), 128.7 (M^-, 100), 258.8 (38); anal. calcd for $C_8H_{12}N_6O_4$: C 37.50, H 4.72, N 32.80; found C 37.34, H 4.86, N 32.65.

1-(2-Hydroxyethyl)-3-methylimidazolium dinitromethanide (3d). Yellow viscous liquid, yield: 91.5%. UV-Vis (H_2O) λ_{max}: 214, 361 nm; ^{1}H NMR (400 MHz, D_2O) δ 7.42 (d, J = 1.2 Hz, 1H, C5–$\underline{H}$), 7.36 (d, J = 1.2 Hz, 1H, C4–$\underline{H}$), 4.23 (t, J = 4.8 Hz, 2H, N–C$\underline{H}_2$–), 3.84 (t, J = 4.8 Hz, 2H, –C$\underline{H}_2$–OH), 3.80 (s, 3H, N–C$\underline{H}_3$); ^{13}C NMR (151 MHz, DMSO-d_6) δ 137.32 (C2), 123.73 (C5), 123.11 (C4), 122.58 ($\underline{C}H(NO_2)_2$), 59.75 (N–$\underline{C}H_2$–), 52.01 (–$\underline{C}H_2$–OH), 36.11 (N–$\underline{C}H_3$); FT-IR (KBr) ν: 3372.3, 3148.9, 3110.8, 2957.9, 2884.9, 1638.1, 1570.6, 1462.9, 1413.9, 1365.3, 1300.4, 1170.5, 1079.8, 1003.1, 946.5, 842.3, 784.5, 747.2, 692.2, 650.5 cm^{-1}; ESI-MS m/z (%): 126.9 (M^+, 100), 104.6 (M^-, 100); anal. calcd for $C_7H_{12}N_4O_5$: C 36.21, H 5.21, N 24.13; found C 36.18, H 5.23, N 24.11.

1-(2-Hydroxyethyl)-3-methylimidazolium dinitramide (3e). Slightly yellow liquid, yield: 98.8%. UV-Vis (H_2O) λ_{max}: 221, 283 nm; ^{1}H NMR (400 MHz, D_2O) δ 8.75 (s, 1H, C2–$\underline{H}$), 7.51 (d, J = 1.6 Hz, 1H, C5–$\underline{H}$), 7.45 (d, J = 1.6 Hz, 1H, C4–$\underline{H}$), 4.33 (t, J = 4.0 Hz, 2H, N–C$\underline{H}_2$–), 3.92 (t, J = 4.0 Hz, 2H, –C$\underline{H}_2$–OH), 3.91 (s, 3H, N–C$\underline{H}_3$); ^{13}C NMR (151 MHz, DMSO-d_6) δ 137.26 (C2), 123.79 (C5), 123.11 (C4), 59.79 (–$\underline{C}H_2$–OH), 52.09 (N–$\underline{C}H_2$–), 36.11 (N–$\underline{C}H_3$); FT-IR (KBr) ν: 3429.4, 3156.3, 3116.5, 2960.5, 2888.1, 1633.1, 1573.5, 1565.7, 1519.9, 1434.8, 1358.7, 1337.8, 1186.6, 1068.6, 1013.0, 828.4, 759.2, 651.7, 622.8 cm^{-1}; ESI-MS m/z (%): 126.9 (M^+, 100), 105.6 (M^-, 100); anal. calcd for $C_6H_{11}N_5O_5$: C 30.91, H 4.76, N 30.03; found C 30.99, H 4.62, N 30.17.

1-(2-Hydroxyethyl)-3-methylimidazolium 5-nitrotetrazolate (3f). Slightly yellow solid, yield: 93.2%. UV-Vis (H_2O) λ_{max}: 221, 256 nm; ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.11 (s, 1H, C2–$\underline{H}$), 7.74 (t, J = 1.8 Hz, 1H, C5–$\underline{H}$), 7.70 (t, J = 1.8 Hz, 1H, C4–$\underline{H}$), 5.23 (t, J = 4.8 Hz, 1H, –CH_2–O$\underline{H}$), 4.24 (t, J = 4.8 Hz, 2H, N–C$\underline{H}_2$–), 3.89 (s, 3H, N–C$\underline{H}_3$), 3.74 (q, J = 4.8 Hz, 2H, –C$\underline{H}_2$–OH); ^{13}C NMR (151 MHz, D_2O) δ 167.54 (–$\underline{C}$–NO_2), 136.29 (C2), 123.54 (C5), 122.40 (C4), 59.74 (–$\underline{C}H_2$–OH), 51.52 (N–$\underline{C}H_2$–), 35.68 (N–$\underline{C}H_3$); FT-IR (KBr) ν: 3410.6, 3153.6, 3114.0, 2960.1, 2881.4, 1631.7, 1574.2, 1564.5, 1542.1, 1437.5, 1416.0, 1384.7, 1355.5, 1341.1, 1169.2, 1072.9, 868.1, 838.0, 763.1, 671.8, 652.4, 623.7 cm^{-1}; ESI-MS m/z (%): 126.8 (M^+, 100), 113.8 (M^-, 100), 228.7 (43); anal. calcd for $C_7H_{11}N_7O_3$: C 34.86, H 4.60, N 40.65; found C 34.75, H 4.56, N 40.55.

1-Methyl-3-(2-nitrooxyethyl)imidazolium 3,5-dinitro-1,2,4-triazolate (4a). Slightly yellow solid, yield: 96%. UV-Vis (H_2O) λ_{max}: 225, 285 nm; ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.17 (s, 1H, C2–$\underline{H}$), 7.81 (t, J = 1.8 Hz, 1H, C5–$\underline{H}$), 7.74 (t, J = 1.8 Hz, 1H, C4–$\underline{H}$), 4.94 (t, J = 4.8 Hz, 2H, –C$\underline{H}_2$–ONO_2), 4.63 (t, J = 4.8 Hz, 2H, N–C$\underline{H}_2$–), 3.89 (s, 3H, N–C$\underline{H}_3$); ^{13}C NMR (151 MHz, DMSO-d_6) δ 163.32 (–$\underline{C}$–NO_2), 137.64 (C2), 124.19 (C5), 123.16 (C4), 71.61 (–$\underline{C}H_2$–ONO_2), 46.70 (N–$\underline{C}H_2$–), 36.33 (N–$\underline{C}H_3$); FT-IR (KBr) ν: 3156.2, 3096.6, 2904.4, 1644.3, 1539.1, 1487.8, 1378.4, 1346.8, 1282.5, 1204.7, 1170.2, 1113.8, 1026.0, 894.5, 856.9, 843.1, 769.0, 756.1, 711.0, 652.5, 627.4 cm^{-1}; ESI-MS m/z (%): 172.0 (M^+, 100), 157.8 (M^-, 100). Anal. calcd for $C_8H_{10}N_8O_7$: C 29.10, H 3.05, N 33.93; found C 29.04, H 3.09, N 33.87.

1-Methyl-3-(2-nitrooxyethyl)imidazolium picrate (4b). Yellow solid, yield: 97%. UV-Vis (H_2O) λ_{max}: 216, 354 nm; ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.16 (s, 1H, C2–$\underline{H}$), 8.59 (s, 2H, picrate), 7.79 (t, J = 1.8 Hz, 1H, C5–$\underline{H}$), 7.72 (t, J = 1.8 Hz, 1H, C4–$\underline{H}$), 4.92 (t, J = 4.8 Hz, 2H, –C$\underline{H}_2$–ONO_2), 4.61 (t, J = 4.8 Hz, 2H, N–C$\underline{H}_2$–), 3.88 (s, 3H, N–C$\underline{H}_3$); ^{13}C NMR (151 MHz, DMSO-d_6) δ 161.32 (picrate C1′), 142.29 (picrate C2′ C6′), 137.64 (C2), 125.71 (picrate C4′), 124.69 (picrate C3′ C5′), 124.19 (C5), 123.16 (C4), 71.61, (–$\underline{C}H_2$–ONO_2), 46.69 (N–$\underline{C}H_2$–), 36.33 (N–$\underline{C}H_3$); FT-IR (KBr) ν: 3165.2, 3140.5, 3099.0, 3047.6, 2990.2, 2894.2, 1633.0, 1559.1, 1492.1, 1434.1, 1384.0, 1364.6, 1335.0, 1308.0, 1277.4, 1160.4, 1076.3, 1037.2, 890.4, 856.4, 788.6, 766.0, 710.0, 652.6 cm^{-1}; ESI-MS m/z (%): 172.0 (M^+, 100), 227.8 (M^-, 100). Anal. calcd for $C_{12}H_{12}N_6O_{10}$: C 36.01, H 3.02, N 21.00; found C 35.95, H 3.06, N 20.95.

1-Methyl-3-(2-nitrooxyethyl)imidazolium 3-nitro-5-oxo-1,2,4-triazolate (4c). Orange liquid, yield: 86%. UV-Vis (H_2O) λ_{max}: 225, 344 nm; ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.27 (s, 1H, C2–$\underline{H}$), 7.83 (t, J = 1.8 Hz, 1H, C5–$\underline{H}$), 7.75 (t, J = 1.8 Hz, 1H, C4–$\underline{H}$), 4.94 (t, J = 4.8 Hz, 2H, –C$\underline{H}_2$–ONO_2), 4.65 (t, J = 4.8 Hz, 2H, N–C$\underline{H}_2$–), 3.89 (s, 3H, N–C$\underline{H}_3$); ^{13}C NMR (151 MHz, DMSO-d_6) δ 164.82 ($\underline{C}$=O), 159.88 ($\underline{C}$–NO_2), 137.81 (C2), 124.17 (C5), 123.17 (C4), 71.69 (–$\underline{C}H_2$–ONO_2), 46.65 (N–$\underline{C}H_2$–), 36.29 (N–$\underline{C}H_3$); FT-IR (KBr) ν: 3361.8, 3251.7, 3148.4, 3101.8, 2842.2, 2791.3, 1698.5, 1648.3, 1578.2, 1543.6, 1509.9, 1423.4, 1384.1, 1132.0, 1282.9, 1171.7, 1117.6, 1049.4, 1014.7, 896.6, 849.2, 777.0, 747.2, 709.0, 621.9 cm^{-1}; ESI-MS m/z (%): 172.0 (M^+, 100), 128.7 (M^-, 100). Anal. calcd for $C_8H_{11}N_7O_6$: C 31.90, H 3.68, N 32.55; found C 31.83, H 3.73, N 31.52.

1-Methyl-3-(2-nitrooxyethyl)imidazolium dinitromethanide (4d). Brown liquid, yield: 91%. UV-Vis (H_2O) λ_{max}: 213, 361 nm; ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.17 (s, 1H, C2–$\underline{H}$), 8.16 (s, 1H, C$\underline{H}(NO_2)_2$), 7.80 (t, J = 1.8 Hz, 1H, C5–$\underline{H}$), 7.73 (t, J = 1.8 Hz, 1H, C4–$\underline{H}$), 4.93 (t, J = 4.8 Hz, 2H, –C$\underline{H}_2$–ONO_2), 4.62 (t, J = 4.8 Hz, 2H, N–C$\underline{H}_2$–), 3.88 (s, 3H, N–C$\underline{H}_3$); ^{13}C NMR (151 MHz, DMSO-d_6) δ 137.68 (C2), 124.18 (C5), 123.79 ($\underline{C}H(NO_2)_2$), 123.16 (C4), 71.63 (–$\underline{C}H_2$–ONO_2), 46.67 (N–$\underline{C}H_2$–), 36.30 (N–$\underline{C}H_3$); FT-IR (KBr) ν: 3148.8, 3100.7, 3061.7, 2959.7, 2899.3, 1632.7, 1591.5, 1541.4, 1487.4, 1467.1, 1440.2, 1412.4, 1384.0, 1305.4, 1280.7, 1220.2, 1123.2, 1086.7, 1020.1, 1004.9, 893.7, 861.8, 787.5, 750.6, 707.6, 692.3, 666.5 cm^{-1}; ESI-MS m/z (%): 172.0 (M^+, 100), 104.6 (M^-, 100). Anal. calcd for $C_7H_{11}N_5O_7$: C 30.33, H 4.00, N 25.27; found C 30.24, H 4.06, N 25.20.

1-Methyl-3-(2-nitrooxyethyl)imidazolium dinitramide (4e). Yellow liquid, yield: 96%. UV-Vis (H_2O) λ_{max}: 223, 283 nm; ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.15 (s, 1H, C2–$\underline{H}$), 7.79 (t, J = 1.8 Hz, 1H, C5–$\underline{H}$), 7.72 (t, J = 1.8 Hz, 1H, C4–$\underline{H}$), 4.93 (t, J =

4.8 Hz, 2H, $-C\underline{H}_2-ONO_2$), 4.62 (t, $J = 4.8$ Hz, 2H, $N-C\underline{H}_2-$), 3.88 (s, 3H, $N-C\underline{H}_3$); ^{13}C NMR (151 MHz, DMSO-d_6) δ 137.61 (C2), 124.14 (C5), 123.13 (C4), 71.56 ($-\underline{C}H_2-ONO_2$), 46.68 ($N-\underline{C}H_2-$), 36.29 ($N-\underline{C}H_3$); FT-IR (KBr) ν: 3156.1, 3117.5, 2967.8, 2916.8, 1643.0, 1577.5, 1564.1, 1517.5, 1434.0, 1338.3, 1282.9, 1184.4, 1009.4, 895.6, 847.0, 757.0, 708.9, 623.1 cm^{-1}; ESI-MS m/z (%): 172.0 (M^+, 100), 105.6 (M^-, 100). Anal. calcd for $C_6H_{10}N_6O_7$: C 25.91, H 3.62, N 30.21; found C 25.81, H 3.69, N 30.15.

1-Methyl-3-(2-nitrooxyethyl)imidazolium 5-nitrotetrazolate (4f). Brown solid, yield: 97%. UV-Vis (H_2O) λ_{max}: 217, 255 nm; ^1H NMR (600 MHz, D_2O) δ 8.73 (s, 1H, C2–$\underline{H}$), 7.45 (t, $J = 1.8$ Hz, 1H, C5–$\underline{H}$), 7.37 (t, $J = 1.8$ Hz, 1H, C4–$\underline{H}$), 4.81 (t, $J = 4.8$ Hz, 2H, $-C\underline{H}_2-ONO_2$), 4.54 (t, $J = 4.8$ Hz, 2H, $N-C\underline{H}_2-$), 3.81 (s, 3H, $N-C\underline{H}_3$); ^{13}C NMR (151 MHz, DMSO-d_6) δ 169.2 ($-\underline{C}-NO_2$), 137.64 (C2), 124.17 (C5), 123.16 (C4), 71.60 ($-\underline{C}H_2-ONO_2$), 46.70 ($N-\underline{C}H_2-$), 36.34 ($N-\underline{C}H_3$); FT-IR (KBr) ν: 3156.2, 3114.9, 2968.6, 2912.2, 2853.0, 1643.2, 1564.9, 1536.5, 1435.3, 1412.0, 1384.6, 1313.8, 1282.9, 1171.4, 1024.7, 896.0, 837.5, 755.0, 707.3, 672.5, 623.6 cm^{-1}; ESI-MS m/z (%): 172.0 (M^+, 100), 113.7 (M^-, 100). Anal. calcd for $C_7H_{10}N_8O_5$: C 29.38, H 3.52, N 39.15; found C 29.34, H 3.56, N 39.12.

Conclusions

A series of imidazolium-based energetic salts with a hydroxyethyl or nitrooxyethyl side chain were easily synthesized and characterized through NMR, IR, MS, UV/Vis, elemental analysis (EA), DSC, TGA, and/or single crystal X-ray diffraction. DSC analysis shows that the energetic salts are all typical ionic liquids with a wide liquid temperature over 100 °C. TGA data show that the EILs possess good thermal stabilities with decomposition temperatures above 165 °C, except for compounds **3d**, **4c**, and **4d**. Besides, compounds **3a–c**, **3f**, and **4b** have a melting temperature from 79 °C to 100 °C and a much higher decomposition temperature from 198 °C to 283 °C, which may be suitable choices for melt-cast explosives. The calculated detonation velocities of ionic liquids **2a** and **4a–f** are 6.84–7.63 km s^{-1}, which are between those of **TNT** and **RDX**. The calculated detonation pressures of ionic liquids **2a**, **3e**, **4a**, **4b**, **4d**, and **4e** are better than that of **TNT**. Data show that the introduction of the nitrooxy group lowered the melting points and decomposition temperatures, while increased the glass transition temperatures, and improved the energetic properties of the EILs. Solubility experiment shows that all the EILs have a good solubility in most polar solvents. Generally, these EILs have good stabilities and energetic properties, which could be applied as potential energetic materials.

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