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Synthesis and characterization of a new family of energetic salts based on guanidinium cation containing furoxanyl functionality

Bo Wu, [a] Zhixin Wang,[a] Hongwei Yang,*[a] Qiuhan Lin,[a,b] Xuehai Ju,[a] Chunxu Lu[a] and Guangbin Cheng*[a]

A new family of energetic salts based on a new guanidinium cation containing furoxanyl functionality, 1-(3'-methylfuroxanyl)methyleneamino guanidinium cation, were synthesized and well characterized by IR and multinuclear NMR spectroscopy, elemental analysis as well as differential scanning calorimetry. The structures of salts **1**, **4**, **5** and **6** were confirmed by single-crystal X-ray diffraction. Most of the salts decompose at temperatures over 180 °C. Furthermore, except for salts **7** and **9**, the remaining energetic salts exhibit low impact sensitivities (15-40 J), friction sensitivities (120-360 N), and are insensitive to electrostatics. The detonation pressure values calculated for these salts range from 19.3 to 27.5 GPa, and the detonation velocities range from 7515 to 8402 m s^{-1}. These results make some energetic salts potential candidates for energetic materials with good thermal stabilities and low sensitivities.

Introduction

In recent years, high nitrogen content energetic compounds offer distinct advantages over conventional carbon-based energetic compounds.[1] These high nitrogen content energetic materials exhibit high enthalpy of formation, which is attributed to a large number of C—N and N—N bonds within their structures. Energetic compounds with high nitrogen, but low hydrogen and carbon content also allow a good oxygen balance to be achieved more easily. They are considered as prime candidates for green energetic materials owing to their main combustion products are molecular nitrogen. Among the most exciting developments of high-energy density materials (HEDMs), high nitrogen energetic salts continue to attract considerable work.[1c, 1g, 1i, 2] Principally, salt-based energetic materials with high nitrogen content often possess advantages over non-ionic molecules since these salts tend to exhibit lower vapor pressures eliminating the risk of exposure through inhalation. Moreover, they possess higher thermal stability than their atomically similar nonionic analogues.

Azoles with energetic substituents such as nitro groups,[3] azido groups[4] and nitramines,[5] are important sources of anions to design and synthesize energetic salts because of the practical and theoretical significance of these unique compounds and the diversity of their properties. Upon elimination of a proton from the *N*H moiety of azole, the highly aromatic azolate anion is formed. The azolate anion pairs with various cations to form azole-based energetic salts with good performance. Among the various cations, the guanidinium cation (amino-, diamino- and triaminoguanidinium cation) is one of the widely used cations to synthesize novel energetic slats.[6] To further enhance the performance of energetic salts based on guanidinium cation, introduce of energetic moieties into guanidinium frame is of great interest. Classical energetic moieties such as nitro-, nitramine- groups, possess strong electron-withdrawing effect, which probably lead to the deprotonation of guanidinium. A *N*-oxide derivative of furazan, furoxan, which has a "latent" nitro group within one side of its ring, is an effective structural unit that is itself an explosive group. The aromatic character of furoxan improves the thermal stability of molecules. By introducing a furoxan ring into energetic molecules, the density can be increased by ca. 0.06-0.08 g cm^{-3}, and the detonation velocity can also be increased by ca. 300m s^{-1}.[7] In the aspect of energetic salts, as shown in Scheme 1, anions containing the furoxan ring and other energetic groups or backbones bearing acidic protons, have been investigated.[8-11] In 2012, Z. Zhou et al. synthesized a series of energetic monoanionic and dianionic salts of 3,4-bis(1*H*-tetrazol-5-yl)furoxan with good thermal stabilities and rather high densities.[8, 9] In the next year, nine

energetic salts based on 4-nitro-3-(5-tetrazolate)furoxan anion were also synthesized and fully characterized by them.[10] These 4-nitro-3-(5-tetrazole)furoxan-based energetic salts with relatively high densities are considered promising. In our previous work, three energetic salts based on furoxanyl functionalized tetrazolate anion were synthesized and well characterized.[11] On the other hand, to the best of our knowledge, few energetic salts based on furoxanyl functionalized cation has been reported in the literature.[12] In the present work, a new family of energetic salts based on a furoxanyl functionalized aminoguanidinium cation (FAG cation) was synthesized. These new energetic ionic salts were well characterized by IR and multinuclear NMR spectroscopy, elemental analysis as well as differential scanning calorimetry (DSC). Their key sensitivity and explosive properties were investigated by experimental and theoretical methods.
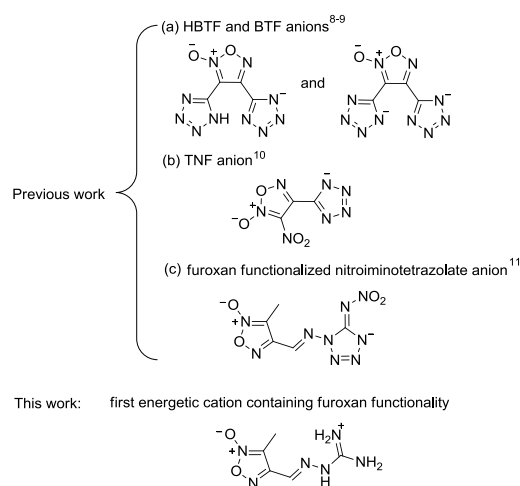

Scheme 1. Energetic ionic salts containing furoxan functionality

Results and discussion

Synthesis

The synthetic pathway to all of the new energetic salts is depicted in Scheme 2. The starting material, 3-methyl-4-furoxancarbaldehyde, can readily be prepared by treatment of crotonaldehyde with sodium nitrite in acetic acid.[13] 1-(3'-methylfuroxanyl)methyleneamino guanidinium salts **1** and **2** were synthesized via the condensation reactions of aminoguanidine hydrochloride and bis(1-aminoguanidinium) sulphate with 3-methyl-4-furoxancarbaldehyde in water solution in high yield of 92% and 90%, respectively. Direct reaction of 1-(3'-methylfuroxanyl)methyleneamino guanidinium chloride (**1**) with disodium 5,5'-azotetrazolate pentahydrate resulted in the formation of salt **3**, which deposited almost immediately in aqueous solution. As known, one of the widely used methods for synthesis of the energetic salts is based on metathesis reactions of the barium salts with sulfates. The driving force of these reactions is the formation of barium sulfate, which has a very low solubility in water and can be easily removed by simple filtration. Herein, energetic salts

4-10 were prepared from anion exchange of barium 5-nitrotetrazolate, barium 5-nitrotetrazolate-2N-oxide, barium 4-amino-3-(5-tetrazolate)furazan, barium 5-azidotetrazolate, barium 2,4-dinitroimiazolate, barium 5-nitroaminotetrazolate and barium 1,2-bis(4-(tetrazolato)-1,2,5-oxadiazol-3-yl)diazene with bis(1-(3'-methylfuroxanyl)methyleneamino guanidinium) sulphate (**2**) in water.
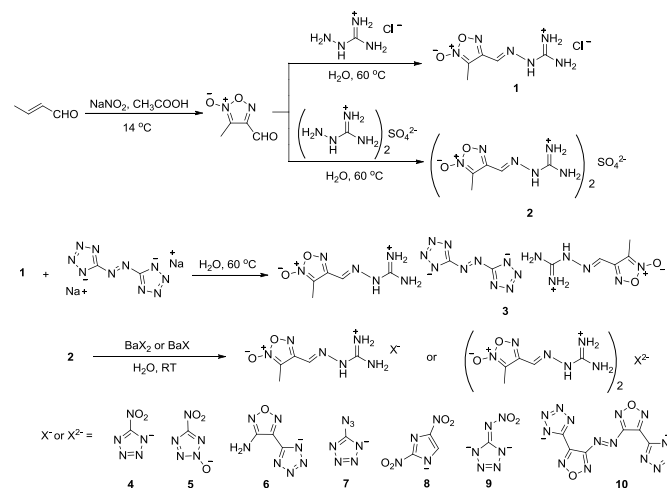
Scheme 2. Synthesis of salts **1-10**.

NMR Spectroscopy

All compounds were characterized by ^{1}H and ^{13}C NMR spectroscopic analysis in [D₆]DMSO. Except for salts **6** and **8**, all of the hydrogen signals arise from the FAG cation. For FAG cation, the proton signals of the methyl group are observed in a range from 2.34-2.37 ppm. The carbon resonance signals of the methyl group are observed between 10.61 and 10.98 ppm. Their proton signals of -CH=N- groups appear at δ = 8.11-8.33 ppm and the corresponding resonance signals of the carbon atoms are observed between δ = 134.84 and 138.28 ppm. In addition, for compounds **1-10**, the proton signals of protonated guanidinium moieties are observed in a range from δ = 7.00 to 8.14 ppm while the corresponding resonance signals of the carbon atoms appear between δ = 156.42 and 159.25 ppm. For salts **4**, **5** and **8**, the proton signals of -NH- group are also observed at δ = ca. 12 ppm. For salts **6** and **8**, the proton signals appearing at δ = 6.55 and 7.71 ppm, are assigned to the amino group and –CH in the imidazole ring, respectively.

The ^{15}N NMR spectra of salts **1**, **4**, **5** and **6** are shown as examples in Figure 1. They were measured in [D₆]DMSO solvent, and chemical shifts are given with respect to CH₃NO₂ as external standard. The assignments are based on the literature values of the similar compounds.[6a, 14] There are five nitrogen signals for the FAG cation and the chemical shifts change little since the interactions between FAG cation and those anions are similar. For FAG cation in **1**, **4**, **5** and **6**, two nitrogen signals of furoxan ring are observed between δ = -6.53 and -6.82 ppm, and between δ = -22.27 and -22.94 ppm, respectively. The nitrogen signals of -CH=N- groups are observed in a range from -53.62 to -55.16 ppm. The nitrogen signals of -NH- groups range from -230.36 to -232.61 ppm. Furthermore, the nitrogen signals of protonated guanidinium moieties are observed

between δ = -301.88 and -304.82 ppm. In the ^{15}N NMR spectra of **4**, **5** and **6**, the other nitrogen signals are from the nitrogen rich anions. Their chemical shift values are in good agreement with these of energetic ionic compounds with the same anions in the literature.[14h, 14i]
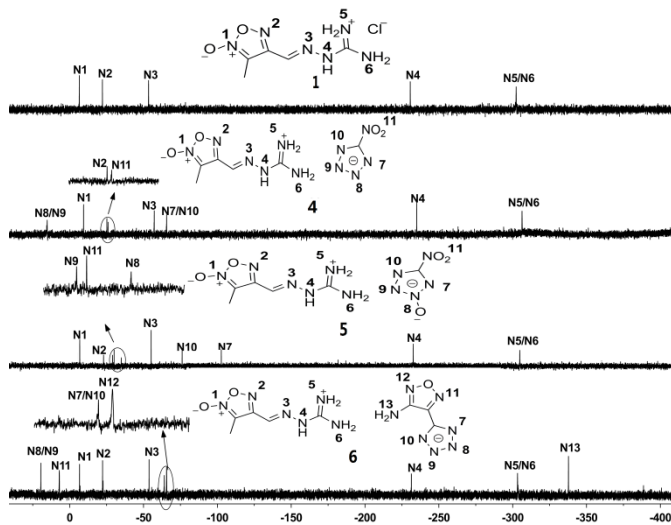

Figure 1. ^{15}N NMR spectrum of compounds **1**, **4**, **5** and **6**

Single-Crystal X-ray Analysis

Single crystals of **1**, **4**, **5** and **6**, suitable for single-crystal X-ray diffraction, were obtained by slow evaporation of aqueous solutions at room temperature and normal pressure. Selected crystallographic data are summarized in Table S2 in the Supporting Information. The structures of **1** and **5** are presented in Figure S1-S4. And the structures of **4** and **6** are shown in Figure 2-5.

1-(3'-Methylfuroxanyl)methyleneamino guanidinium chloride (**1**) crystallizes in the monoclinic space group $P2_1$ with a cell volume of 480.18(7) Å^3. A density of 1.526 g cm^{-3} was determined from the X-ray crystal structure. As shown in Figure S1, the molecules are in an *E* configuration. The furoxan ring and C=N bonds are in a plane with mean deviation of 0.0143 Å resulting from the presence of large π-conjugation system. The protonated guanidine moiety shows completely planar assembly due to the electron delocalization effect in the moiety. The dihedral angle between the two planes is 8.4°. The bond length of C4-N3 is 1.277(6) Å, which lies in the range of typical C-N double bond length values.[15] Owing to the electron delocalization effect, the C-N bond lengths of the protonated guanidine moiety differ in a range of 1.317(6) Å to 1.337(6) Å, which are closed to those of C—N bonds within the aromatic furoxan ring. All hydrogen bonds observed in the structure of **1** can be considered moderately strong and the details of these hydrogen bonds are summarized in Table S4 (Supporting Information). As depicted in Figure S2, classical hydrogen bonds involving the chloride anion and protonated guanidinium moiety (N5—H5b•••Cl1, N6—H6a•••Cl1, N6—H6b•••Cl1^i, N4—H4a•••Cl1^i, N5—H5b•••Cl1^{ii}, i: 1-x, -0.5+y, -z, ii: 1+x, y, z) are observed. Non-classical hydrogen bond C3—H3a•••Cl1^{ii} are also observed. The D•••A distances of intramolecular

hydrogen bonds, N5—H5b•••N3 and C3—H3a•••O2, are significantly below the sum of van der Waals radii at 2.676(5) and 2.977(8) Å, respectively (rw(N) + rw(N) = 3.10 Å; rw(C) + rw(O) = 3.21 Å).[1f] Furthermore, the D•••A distance of the hydrogen bonds N6—H6b•••O2^{iii} (iii: 1+x, y, -1+z) are significantly below the sum of van der Waals radii at 2.919(6) Å (rw(N) + rw(O) = 3.07 Å).[1f]

1-(3'-Methylfuroxanyl)methyleneamino guanidinium 5-nitrotetrazolate (**4**) crystallizes in the monoclinic space group $P2_1$/c with a cell volume of 1232.65(14) Å^3 and four molecules in the unit cell. The density from the X-ray crystal structure is 1.612 g cm^{-3}. As shown in Figure 2, the furoxan based aminoguanidinium cation is in an *E* configuration. The protonated guanidinium moiety and furoxan ring are planar with mean deviation of 0.0142 and 0.0081 Å, respectively. The dihedral angle between them is 23.7°. The bond lengths of the FAG cation are nearly indentical with that of salt **1**. In the 5-nitrotetrazolate anion, the nitro group is rotated by 11° out of the plane of the tetrazole ring. The C—N and N—N bond lengths in the tetrazolate ring vary from 1.3186(19) to 1.343(2) Å, which are in good agreement with those in 5-nitrotetrazolate based energetic salts.[3b] The crystal structure of **4** is strongly dominated by various hydrogen bonds, illustrated in Figure 3 and the details are gathered in the Supporting Information (see Table S6). The D•••A distances of N9—H9•••N4^i, N10—H10a•••N2^{ii}, N11—H11a•••N1^{iii} and N11—H11b•••N8 (intra-molecular hydrogen bond) (i: 1-x, 1-y, -z; ii: x, -1+y, z; iii: 1-x, -1/2+y, 1/2-z) are below the sum of van der Waals radii at 2.8290(19), 2.988(2), 2.959(2) and 2.657(2) Å, respectively (r$_w$(N) + r$_w$(N) = 3.10 Å).[1f] Furthermore, non-classical intermolecular hydrogen bonds, C4—H4c•••O1^{iii} and C5—H5•••O2^i (i: 1-x, 1-y, -z; iii: 1-x, -1/2+y, 1/2-z), involving the nitro group, methyl group and -CH=N- group are observed.
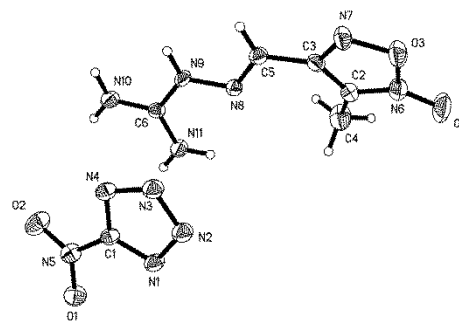

Figure 2. Molecular structure of **4**. Thermal ellipsoids are set to 50% probability. Hydrogen atoms are included but are unlabelled for clarity.
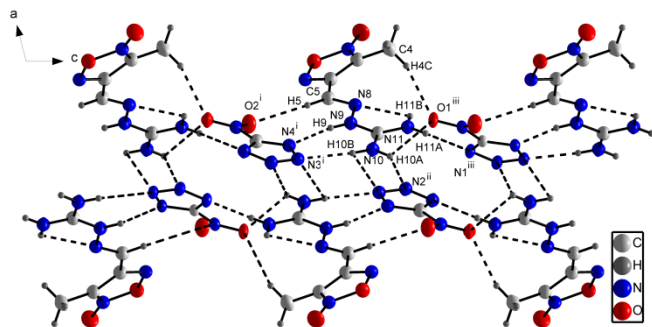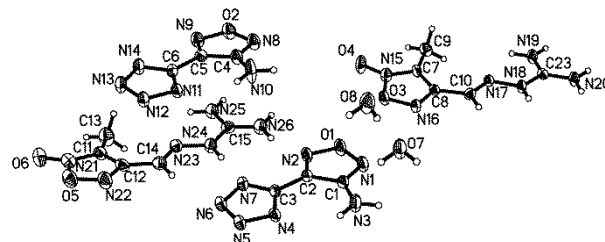
Figure 3. View along the *b* axes in the structure of **4**.

1-(3'-Methylfuroxanyl)methyleneamino guanidinium 5-nitrotetrazolate-2*N*-oxide (**5**) crystallizes in the monoclinic space group *P*2$_1$/n with a cell volume of 1252.67(17) Å^3 (Figure S3). The density of is 1.672 g cm^{-3}. For the FAG cation in salt **5**, the atoms in protonated guanidinium moiety and furoxan ring are planar with the mean deviation from their respective plane of 0.0085 and 0.0169 Å, respectively. The dihedral angle between them is 17.9 °. The bond lengths of the C—C, C—N and N—N bonds within the FAG cation are nearly identical with those in salts **1** and **4**. For 5-nitrotetrazolate-2*N*-oxide anion, the atoms in tetrazole ring and *N*-oxide oxygen atom O1 are planar with the mean deviation of 0.0004 Å. The nitro group is rotated by 4.3 ° out of the plane of the tetrazole ring. The bond lengths of the C—N, N—N and N—O bonds are similar to the known values from the literature.[14i] As shown in Figure S4, the crystal structure of **5** is built up by various hydrogen bonds. Classical N—H•••O and N—H•••N hydrogen bonds can be considered strong hydrogen bonds with the D•••A distances of N10—H10a•••O1^i, N10—H10b•••O1^{ii}, N11—11a•••N4^{iii}, N11—H11b•••N8 (i: -1/2-x, -3/2+y, 1/2-z; ii: 1/2+x, 1/2-y, 1/2+z; iii: x, -1+y, z) at 2.930(3), 2.784(3), 2.956(3) and 2.641(3) Å, respectively, which are shorter than the sum of van der Waals radii (r$_w$(N) + r$_w$(O) = 3.07 Å; r$_w$(N) + r$_w$(N) = 3.10 Å).[1f] Additionally, non-classical hydrogen bonds C4—H4a•••O2^{iv} and C5—H5•••O3^v (iv: x, -1+y, z; v: 1/2+x, 1/2-y, 1/2+z) are also observed with D•••A distances of 3.296(3) and 3.398(3) Å, respectively. The details of hydrogen bonds are summarized in Table S8 (Supporting Information).

1-(3'-Methylfuroxanyl)methyleneamino guanidinium 4-amino-3-(5-tetrazolate)furazan (**6**) crystallizes in the monoclinic space group *P*2$_1$/c as a racemic twin. As presented in Figure 4, the asymmetric unit consists of two crystallographically independent 4-amino-3-(5-tetrazolate)furazan anions, two FAG cations as well as two water molecules. The two FAG cations are in an *E* configuration. The protonated guanidinium moiety and furoxan ring within the cation are slightly twisted with the dihedral angles between them of 5.1 ° and 9.9 °. The atoms within either the protonated guanidinium moieties or furoxan ring are planar with mean deviations from their respective plane of 0.0036, 0.0111, and 0.0021, 0.0012 Å, respectively. In two independent 4-amino-3-(5-tetrazolate)furazan anions, the atoms in either tetrazolate anions or furazan rings are planar with mean deviations from their respective plane of 0.0002, 0.0008, and 0.0011, 0.0033 Å, respectively. The tetrazole ring and furazan ring are slightly twisted with the dihedral angles between

them of 5.9 ° and 2.3 °. The exocyclic amine nitrogen atoms (N3, N10) are out of the furazan plane by 0.0359 and 0.0104 Å, respectively. As shown in Figure 5(a), wave-like layer structure of **6** was observed. The perpendicular distance between adjacent sheets is 3.385 Å, which is slightly shorter than the interplanar spacing in graphite (3.4 Å).[1a] Because the asymmetric unit of **6** consists of two independent sets of cations and anions, two different sets of hydrogen bonds are formed for each pair within every single layer (Figure 5(b)). These hydrogen bonds details are summarized in the Table S10 in Supporting Information.

Figure 4. Molecular structure of **6**. Thermal ellipsoids are set to 50% probability. Hydrogen atoms are included but are unlabelled for clarity.

Figure 5. (a) A view of wave-like layer structure of **6**. (b) View of one layer in the structure of **6**.

Thermal Behavior

The decomposition onset temperatures, sensitivities and energetic data for **3–10** are summarized in Table 2. The decomposition onset temperatures (*T*$_{d, onset}$) of salts **3–10** were determined by differential

scanning calorimetry (DSC) at a heating rate of 5 °C min⁻¹. As shown in Table 2, only salts **8** and **10** have a melting process, whereas the other compounds decompose directly. As known, a thermal stability above 180 ℃ is an essential requirement for energetic compounds to adaptation for practical use.[16, 17] Except for compounds **6**, **7** and **9**, which decompose at 151.1, 138.9, and 168.5

°C, respectively, the decomposition onset temperatures of the other energetic ionic compounds are higher than 180 °C. This lower stability may be due to the decrease of hydrogen bonds network. In particular, the most stable energetic ionic compound was **3**, whose decomposition onset temperature is 213 °C.

Table 1. The physicochemical properties of **3–10** compared with 1,3,5-trinitroperhydro-1,3,5-triazine (RDX) and triaminotrinitrobenzene (TATB).

Salts	T_d [a]	d_1[b]/d_2[c]	ΔH_c^o [d]	ΔH_a^o [e]	ΔH_L [f]	ΔH_f^o [g]	IS [h]	FS [i]	ESD [j]	P [k]	D [l]
	[°C]	[g cm⁻³]	[kJ mol⁻¹]	[kJ mol⁻¹]	[kJ mol⁻¹]	[kJ mol⁻¹]	[J]	[N]	[J]	[GPa]	[m s⁻¹]
3	213.0	1.639/-	961.93	788.47	1045.45	704.95	40	360	0.750	19.3	7515
4	184.7	1.700/1.612	961.93	112.01	462.31	611.63	25	280	0.320	26.3	8312
5	193.3	1.718/1.672	961.93	57.84	457.42	562.35	15	120	0.280	27.5	8402
6	151.1	1.670/1.547	961.93	331.55	446.42	847.06	38	360	0.720	23.8	8082
7	138.9	1.641/-	961.93	485.83	459.72	988.04	2	6	0.050	24.7	8212
8	187.1	1.700/-	961.93	-129.87	446.83	385.23	32	300	0.500	24.7	8016
9	168.5	1.659/-	961.93	402.04	1079.2	284.77	6	<120	0.180	20.6	7646
10	184.3	1.696/-	961.93	1200.14	969.83	1192.24	35	320	0.450	21.9	7768
RDX[20]	230	1.82	-	-	-	92.6	7.4	120	0.2[16]	35.2	8977
TATB[17]	350	1.93	-	-	-	-139.7	30-34	-	-	30.5	8176

[a] Decomposition onset temperature. [b] Density from calculation. [c] Density from single crystal structure. [d] Molar enthalpy of the formation of the cation. [e] Molar enthalpy of the formation of the anion. [f] Lattice enthalpy. [g] Molar enthalpy of the formation of salt. [h] Impact sensitivity. [i] Friction sensitivity. [j] Electrostatic discharge sensitivity. [k] Detonation pressure. [l] Detonation velocity.

Sensitivities

The sensitivities of the energetic salts **3-10** towards impact, friction, and electrostatic discharge were tested by using standard procedures.[18] As summarized in Table 2, the impact sensitivity values were found to be in the range from 2 (**7**) to 40 J (**3** and **6**). The friction sensitivity values differed in the range from 6 (**7**) to 360 N (**3** and **6**). Based on the classification standard of sensitivities,[19] salts **3** and **6** are classified as less sensitive due to their impact sensitivities of 40 and 38 J ,and friction sensitivity of 360 N. The impact sensitivities of salts **8** and **10** were 32 and 35 J, respectively, which were comparable to that of TATB (30 – 34 J).[17] Salts **4** and **5** were less sensitive to impact and friction than RDX (7.4 J, 120 N)[16] due to their impact sensitivities of 25 and 15 J, and friction sensitivities of 280 and 120 N, respectively. Salts **7** and **9** exhibited high sensitivities towards impact and friction, because of the

presence of azido and nitramine groups within their structures, respectively. As illustrated in Table 2, the electrostatic sensitivities of salts **3** (0.750 J), **6** (0.720 J), **8** (0.500 J) and **10** (0.450 J) were significantly lower than that of RDX (0.200 J).[16] The electrostatic sensitivity values of salts **5** and **9** were 0.280 J and 0.180 J, respectively, which were comparable to that of RDX (0.200 J).[16] In agreement with other reports describing sensitive azide[4] compounds, salt **7** (0.050 J) was sensitive towards electrostatic discharge.

Detonation Parameters

The heat of formation of energetic salts is an important parameter when evaluating the performance of energetic salts. It can be calculated with good accuracy (including the heats of formation of the FAG cation and anions, and the lattice energy of salts). The heats of formation of the cation and anions were calculated by using the Gaussian 09 suite of programs.[21] The

geometric optimization of all the structures and frequency analyses for calculation of heats of formation was carried out by using B3-LYP functional with 6-311+G** basis set.[22] The heat of formation of the furoxanyl fuctionalized guanidinium cation (FAG cation) and anions were computed by using appropriate isodesmic reactions (Supporting information, Scheme S1). The HOF of reference compounds are available either from the experiments or from the high level computing like CBS-4M.[23] The calculated heats of formation of salts **3-10** are summarized in Table 2, and that of the furoxanyl fuctionalized aminoguanidinium cation (FAG cation) is 961.93 kJ mol^{-1}. Energetic salts **3-10** exhibit positive heats of formation. Among them, salt **10** possess the highest at 1192.24 kJ mol^{-1} (RDX: 92.6 kJ mol^{-1}, TATB: -139.7 kJ mol^{-1}). To evaluate the performance of these new salts, the detonation velocity (*D*) and detonation pressure (*P*) were calculated by using the EXPLO5 v6.01 program.[24] As summarized in Table 2, the detonation velocities (*D*) of salts **3-10** are found in the range from 7515 (comparable to TNT, 6881 m s^{-1}) to 8402 m s^{-1} (comparable to TATB, 8176 m s^{-1}). Detonation pressures (*P*) lie in the range of 19.3–27.5 GPa, which is comparable with that of TNT (2,4,6- trinitrotoluene, 19.53 GPa).

Experimental

General Methods

^{1}H, ^{13}C and ^{15}N NMR spectra were recorded on 300 MHz (Bruker AVANCE 300) nuclear magnetic resonance spectrometers operating at 300, 75 and 30 MHz, respectively, by using [D$_6$]DMSO as the solvent and locking solvent unless otherwise stated. Chemical shifts in ^{1}H and ^{13}C NMR spectra are reported relative to dimethyl sulfoxide and those in ^{15}N NMR spectra relative to CH$_3$NO$_2$. The decomposition temperatures were determined by a differential scanning calorimeter (DSC823e instruments) at a heat rate of 5 °C min^{-1}. Infrared (IR) spectra were recorded on a Perkin-Elmer Spectrum BX FT-IR instrument equipped with an ATR unit at 25 °C. Analyses of C/H/N were performed with a Vario EL III Analyzer. The electrostatic sensitivity tests were carried out with an Electric Spark Tester ESD JGY-50 III. The sensitivities towards impact and friction were determined by using a HGZ-1 drophammer and a BAM friction tester.

X-ray crystallography: The data for **1**, **4**, **5** and **6** were collected with a Bruker three-circle platform diffractometer equipped with a SMART APEX II CCD detector. A Kryo-Flex low-temperature device was used to keep the crystals at a constant 173 K during the data collection. The data collection and the initial unit cell refinement was performed by using APEX2 (v2010.3-0). Data Reduction was performed by using SAINT (v7.68A) and XPREP (v2008/2). Corrections were applied for Lorentz, polarization, and absorption effects by using SADABS (v2008/1). The structure was solved and refined with the aid of the programs in the SHELXTL-plus (v2008/4) system of programs. The full-matrix least-squares refinement on F^2 included atomic coordinates and anisotropic thermal parameters for all non-H atoms. The H atoms were included in a riding model. The structure was solved by direct methods with

SHELXS-97 and expanded by using the Fourier technique. The non-hydrogen atoms were refined anisotropically. The hydrogenatoms were located and refined.

Caution: Although we experienced no difficulties in handling these energetic materials, small scale and best safety practices (leather gloves, face shield) are strongly recommended. Manipulation must be carried out in a hood behind a safety shield. Use of leather jacket, conductive equipment is strongly encouraged.

Starting Materials: 3-methyl-4-furoxancarbaldehyde,[13] disodium 5,5'-azotetrazolate pentahydrate,[25] ammonium 5-nitrotetrazolate,[3b] ammonium 5-nitrotetrazolate-2*N*-oxide,[14i] 4-amino-3-(5-tetrazolyl)furazan,[6c] 5-azido-1*H*-tetrazole,[4d] 2,4-dinitro-1,3-imidazole,[26] 5-nitroiminotetrazole[5d, 5e] and 1,2-bis(4-(tetrazole)-1,2,5-oxadiazol-3-yl)diazene[27] were synthesized according to literature procedures.

Synthesis of 1-(3'-methylfuroxanyl)methyleneamino guanidinium chloride (1)

A solution of aminoguanidine hydrochloride (5.0 mmol, 0.55 g) and 3-methyl-4-furoxancarbaldehyde (6.0 mmol, 0.77 g) in 20 mL H$_2$O was stirred at 60 °C for 12 h. The reaction mixture was cooled to 0 °C and the white precipitate was formed. Then the precipitated solid was filtered off, washed with cold water and dried in vacuo to afford 0.85 g of **1** as a colorless crystalline powder in a yield of 92%. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 12.87 (s, 1H, -N*H*-), 8.39(s, 1H, -C*H*=N-), 8.03 (s, 4H, -N*H$_2$*), 2.37 (s, 3H, -C*H$_3$*). ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 156.8 (-*C*(NH$_2$)=NH$_2$), 154.8 (-*C*ONO), 137.8 (-*C*H=N-), 113.2 (-*C*NO), 10.7 (-*C*H$_3$) ppm. ^{15}N NMR (30 MHz, [D$_6$]DMSO): δ = -6.82 (O*N*O), -22.44 (*N*O), -53.62 (-CH=*N*-), -230.36 (-*N*H-), -301.88 (-*N*H$_2$) ppm. IR (KBr): 3421 (s), 3166 (m), 2953 (w), 2840 (m) 1682 (s), 1616 (vs), 1538 (m), 1501 (w), 1460 (s), 1156 (m), 1038 (w), 1013 (w), 804 (w), 678 (w), 608 (m), 516 (w). Elemental analysis calcd (%) for C$_5$H$_9$ClN$_6$O$_2$ (220.62): C 27.22, H 4.11, N 38.09; found C 27.11, H 4.09, N 37.91.

Synthesis of bis(1-(3'-methylfuroxanyl)methyleneamino guanidinium) sulphate (2)

A solution of bis(1-aminoguanidinium) sulphate (2.5 mmol, 0.62 g) and 3-methyl-4-furoxancarbaldehyde (6.0 mmol, 0.77 g) in 20 mL H$_2$O was stirred at 60 °C for 12 h. The reaction mixture was cooled to 0 °C and the white precipitate was formed. Then the precipitated solid was filtered off, washed with cold water and dried in vacuo to afford 1.05 g of **2** as a colorless crystalline powder in a yield of 90%. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 8.14 (s, 5H, -C*H*=N-, -N*H$_2$*), 2.35 (s, 3H, -C*H$_3$*) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 157.2 (-*C*(NH$_2$)=NH$_2$), 155.0 (-*C*ONO), 136.7 (-*C*H=N-), 113.1 (-*C*NO), 10.7 (-*C*H$_3$) ppm. IR (KBr): 3452 (s), 3386 (s), 3156 (s), 3002 (s), 2171 (vw), 1691 (vs), 1612 (vs), 1459 (s), 1402 (m), 1382 (m), 1322 (w), 1198 (w), 1164 (s), 1082 (vs), 1037 (m), 971 (w), 922 (vw), 859 (w), 798 (w), 743 (w), 671 (w), 597 (w), 536 (w). Elemental analysis calcd (%) for C$_{10}$H$_{18}$N$_{12}$O$_8$S (466.39): C 25.75, H 3.89, N 36.04; found C 25.32, H 3.76, N 37.21.

Synthesis of bis(1-(3'-methylfuroxanyl)methyleneamino guanidinium) 5,5'-azotetrazolate (3)

To a hot solution (~60 °C) of 1-(3'-methylfuroxanyl)methyleneamino guanidinium chloride (**1**) (0.146 g, 0.66 mmol) in 10 mL of water was added a solution of sodium 5,5'-azotetrazolate pentahydrate (0.100 g, 0.33 mmol) in 10 mL of water. The precipitate formed immediately. After 0.5 h later, the precipitate was filtered, washed with H_2O and dried in vacuo. 0.159 g of **3** was afforded as orange solid in a yield of 90%. ^1H NMR (300 MHz, [D_6]DMSO): δ = 8.33 (s, 1H, -CH=N-), 7.68 (s, 4H, -NH_2), 2.37 (s, 3H, -CH_3) ppm. ^{13}C NMR (75 MHz, [D_6]DMSO): δ = 173.65 (C_2N_{10}), 158.03 (-C(NH$_2$)=NH$_2$), 155.30 (-CONO), 136.96 (-CH=N-), 113.24 (-CNO), 10.80 (-CH$_3$) ppm. IR (KBr): 3448 (s), 3308 (m), 3128 (m), 2995 (m), 2857 (m), 2766 (w), 1689 (s), 1659 (vs), 1493 (w), 1450 (s), 1394 (m), 1328 (w), 1195 (w), 1153 (m), 1040 (w), 964 (w), 797 (w), 741 (w), 637 (w), 520 (w). Elemental analysis calcd (%) for $C_{12}H_{18}N_{22}O_4$ (534.42): C 26.97, H 3.39, N 57.66; found C 27.02, H 3.18, N 58.93.

Synthesis of 1-(3'-methylfuroxanyl)methyleneamino guanidinium 5-nitrotetrazolate (4)

Barium hydroxide octahydrate (0.237 g, 0.75 mmol) was added to a stirring aqueous solution of ammonium 5-nitrotetrazolate (0.198 g, 1.5 mmol) in H_2O (15 mL) and the resulting mixture was stirred at 25 °C for 0.5 h. The volume was then reduced to ~5 mL on a rotary evaporator with heating to remove as much ammonia as possible. The pH was subsequently checked (7-8). Meanwhile, 0.350 g (0.75 mmol) of the sulfate salt (**2**) was dissolved in 10 mL of deionized water at room temperature. Then, the barium 5-nitrotetrazolate solution was added dropwise resulting in the formation of a white precipitate. The solution was stirred for 1 h and then filtered. Crystals suitable for X-ray structure determination were obtained by slow evaporation of the resulting solution. 0.417 g of **4** was obtained as colorless needle crystals in a yield of 93%. ^1H NMR (300 MHz, [D_6]DMSO): δ = 11.96 (s, 1H, -NH-), 8.28 (s, 1H, -CH=N-), 7.82 (s, 4H, -NH_2), 2.35 (s, 3H, -CH_3) ppm. ^{13}C NMR (75 MHz, [D_6]DMSO): δ = 170.17 (CNO$_2$), 156.43 (-C(NH$_2$)=NH$_2$), 154.75 (-CONO), 138.30 (-CH=N-), 113.10 (-CNO), 10.62 (-CH$_3$) ppm. ^{15}N NMR (30 MHz, [D_6]DMSO): δ = 18.11 (N8/N9), -6.53 (ONO), -22.32 (NO), -23.11 (NO$_2$), -54.39 (-CH=N-), -62.77 (N7/N10), -232.14 (-NH-), -303.45 (-NH$_2$) ppm. IR (KBr): 3426 (s), 3359 (s), 3188 (m), 2854 (m), 1689 (vs), 1663 (m), 1616 (vs), 1543 (s), 1502 (w), 1452 (s), 1424 (m), 1379 (w), 1322 (m), 1159 (s), 1008 (w), 840 (m), 798 (w), 765 (w), 630 (w), 602 (w), 524 (w). Elemental analysis calcd (%) for $C_6H_9N_{11}O_4$ (299.21): C 24.09, H 3.03, N 51.49; found C 24.22, H 3.8, N 52.93.

Synthesis of 1-(3'-methylfuroxanyl)methyleneamino guanidinium 5-nitrotetrazolate-2N-oxide (5)

A similar procedure was followed as that described above for **4**. Ammonium 5-nitrotetrazolate-2N-oxide (0.222 g, 1.5 mmol) was subjected to the method to give 0.449 g of **5** as yellow crystals in a yield of 95%. ^1H NMR (300 MHz, [D_6]DMSO): δ = 11.96 (s, 1H, -

NH-), 8.28 (s, 1H, -CH=N-), 7.82 (s, 4H, -NH_2), 2.36 (s, 3H, -CH_3) ppm. ^{13}C NMR (75 MHz, [D_6]DMSO): δ = 158.64 (CNO$_2$), 156.42 (-C(NH$_2$)=NH$_2$), 154.75 (-CONO), 138.28 (-CH=N-), 113.11(-CNO), 10.61 (-CH$_3$) ppm. ^{15}N NMR (30 MHz, [D_6]DMSO): δ = -6.81 (ONO), -22.94 (NO),, -28.98 (N9), -30.07 (N11), -34.92 (N8), -55.16 (-CH=N-), -76.15 (N10), -102.67 (N7), -232.61 (-NH-), -304.82 (-NH$_2$) ppm. IR (KBr): 3424 (vs), 3239 (m), 3167 (m), 1686 (vs), 1605 (vs), 1548 (m), 1499 (w), 1474 (s), 1424 (s), 1382 (m), 1318 (s), 1229 (w), 1148 (m), 1058 (w), 1035 (w), 1000 (w), 853 (m), 730 (w), 666 (w), 607 (w). Elemental analysis calcd (%) for $C_6H_9N_{11}O_5$ (315.21): C 22.86, H 2.88, N 48.88; found C 21.39, H 2.71, N 50.11.

Synthesis of 1-(3'-methylfuroxanyl)methyleneamino guanidinium 4-amino-3-(5-tetrazolate)furazan (6)

Barium hydroxide octahydrate (0.157 g, 0.5 mmol) was added to a stirring aqueous solution of 4-amino-3-(5-tetrazolyl)furazan (0.153 g, 1 mmol) in 10 mL H_2O. When the mixture was stirred for 0.5 h, the aqueous solution of sulfate salt (**2**) (0.233 g, 0.5 mmol) in 10 mL H_2O was added dropwise resulting in the formation of a white precipitate at room temperature. The solution was stirred for 1 h and then filtered. Crystals suitable for X-ray structure determination were obtained by slow evaporation of the resulting solution. 0.304 g of **6** was obtained as block crystals in a yield of 90%. ^1H NMR (300 MHz, [D_6]DMSO): δ = 8.30 (s, 1H, -CH=N-), 7.86 (s, 4H, -NH_2), 6.55 (s, 2H, -NH_2), 2.35 (s, 3H, -CH_3) ppm. ^{13}C NMR (75 MHz, [D_6]DMSO): δ = 156.91 (-CN$_4$), 156.67 (-C(NH$_2$)=NH$_2$), 154.81 (-CONO), 152.04 (-CNO(CN$_4$)), 141.26 (-CNO(NH$_2$)), 138.13 (-CH=N-), 113.13 (-CNO), 10.64 (-CH$_3$) ppm. ^{15}N NMR (30 MHz, [D_6]DMSO): δ = 19.50 (N8/N9), 7.03 (N11), -6.68 (ONO), -22.27 (NO (FAG cation)), -53.76 (-CH=N-), -64.04 (N7/N10), -65.64 (N12), -231.39 (-NH-), -303.29 (-NH$_2$ (FAG cation)), -337.81 (-NH$_2$ (furazan)) ppm. IR (KBr): 3462 (s), 32.7 (m), 2924 (m), 1701 (m), 1630 (vs), 1614 (w), 1562 (w), 1458 (m), 1433 (w), 1309 (w), 1151 (m), 1038 (w), 986 (w), 888 (w), 671 (w), 547 (w). Elemental analysis calcd (%) for $C_8H_{10}N_{13}O_3$ (337.26): C 28.49, H 3.29, N 53.99; found C 28.21, H 3.22, N 54.67.

Synthesis of 1-(3'-methylfuroxanyl)methyleneamino guanidinium 5-azidotetrazolate (7)

A similar procedure was followed as that described above for **6**. 5-azido-1H-tetrazole (0.111 g, 1.0 mmol) was subjected to the method to give 0.269 g of **6** in a yield of 91%. ^1H NMR (300 MHz, [D_6]DMSO): δ = 8.27 (s, 1H, -CH=N-), 7.86 (s, 4H, -NH_2), 2.35 (s, 3H, -CH_3) ppm. ^{13}C NMR (75 MHz, [D_6]DMSO): δ = 159.04 (N_3CN_4), 156.81 (-C(NH$_2$)=NH$_2$), 154.89 (-CONO), 137.87 (-CH=N-), 113.19 (-CNO), 10.65 (-CH$_3$) ppm. IR (KBr): 3486 (vs), 3443 (s), 2135 (s), 1698 (m), 1678 (m), 1639 (s), 1619 (vs), 1601 (vs), 1552 (w), 1464 (s), 1402 (m), 1379 (m), 1229 (w), 1197 (w), 1172 (w), 1039 (w), 801 (w), 744 (w), 707 (w), 600 (w), 472 (w). Elemental analysis calcd (%) for $C_6H_9N_{13}O_2$ (295.22): C 24.41, H 3.07, N 61.68; found C 25.19, H 3.03, N 62.96.

Synthesis of 1-(3'-methylfuroxanyl)methyleneamino guanidinium 2,4-dinitro-1,3-imidazolate (8)

A similar procedure was followed as that described above for **6**. 2,4-dinitro-1,3-imidazole (0.158 g, 1.0 mmol) was subjected to the method to give 0.315 g of **8** in a yield of 92%. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 11.99 (s, 1H, -N*H*-), 8.28 (s, 1H, -C*H*=N-), 7.79 (s, 4H, -N*H$_2$*), 7.71 (s, 1H, C*H*), 2.36 (s, 3H, -C*H$_3$*) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 156.50 (-*C*(NH$_2$)=NH$_2$), 155.52 (-O$_2$N*C*N$_2$), 154.79 (-*C*ONO), 148.32 (-O$_2$N*C*NC), 138.20 (-*C*H=N-), 131.64 (*C*H), 113.12 (-*C*NO), 10.63 (-*C*H$_3$) ppm. IR (KBr): 3565 (m), 3501 (s), 3440 (s), 3394 (s), 3132 (w), 3008 (w), 2917 (w), 1697 (s), 1599 (vs), 1516 (vs), 1470 (s), 1452 (s), 1398 (w), 1303 (s), 1224 (m), 1152 (m), 1041 (w), 1000 (w), 870 (w), 838 (w), 760 (w), 660 (w), 607 (w). Elemental analysis calcd (%) for C$_8$H$_{10}$N$_{10}$O$_6$ (342.23): C 28.08, H 2.95, N 40.93; found C 28.66, H 2.82, N 41.38.

Synthesis of bis(1-(3'-methylfuroxanyl)methyleneamino guanidinium) 5-nitroiminotetrazolate (9)

A similar procedure was followed as that described above for **6**. 5-nitroiminotetrazole (0.130 g, 1.0 mmol) was subjected to the method to give 0.459 g of **9** in a yield of 92%. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 8.11(s, 1H, -C*H*=N-), 7.00 (s, 4H, -N*H$_2$*), 2.34 (s, 3H, -C*H$_3$*) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 160.25 (-*C*=N-NO$_2$), 159.25 (-*C*(NH$_2$)=NH$_2$), 155.95 (-*C*ONO), 134.84 (-*C*H=N-), 113.32 (-*C*NO), 10.98 (-*C*H$_3$) ppm. IR (KBr): 3470 (s), 3386 (s), 3148 (m), 2934 (m), 2855 (w), 1695 (m), 1611 (vs), 1500 (w), 1455 (s), 1394 (m), 1378 (m), 1301 (w), 1201, (w), 1158 (m), 1076 (w), 1037 (w), 801 (w), 602 (w), 530 (w). Elemental analysis calcd (%) for C$_{11}$H$_{18}$N$_{18}$O$_6$ (498.38): C 26.51, H 3.64, N 50.59; found C 27.15, H 3.59, N 52.06.

Synthesis of bis(1-(3'-methylfuroxanyl)methyleneamino guanidinium) 1,2-bis(4-(tetrazolato)-1,2,5-oxadiazol-3-yl)diazene (10)

A similar procedure was followed as that described above for **6**. 1,2-Bis(4-(tetrazole)-1,2,5-oxadiazol-3-yl)diazene (0.302 g, 1.0 mmol) was subjected to the method to give 0.570 g of **10** in a yield of 85%. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 8.27 (s, 1H, -C*H*=N-), 7.74 (s, 4H, -N*H$_2$*), 2.36 (s, 3H, -C*H$_3$*) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 156.69 (-*C*(NH$_2$)=NH$_2$), 156.07 (-*C*N$_4$), 154.83 (-*C*ONO), 151.30 (-*C*NO(CN$_4$)), 150.43 (-*C*NO(N$_2$)), 137.99 (-*C*H=N-), 113.20 (-*C*NO), 10.62 (-*C*H$_3$) ppm. IR (KBr): 3454 (vs), 2964 (w), 2821 (w), 1693 (s), 1614 (vs), 1551 (m), 1516 (m), 1455 (s), 1416 (m), 1386 (w), 1154 (m), 1082 (w), 1040 (w), 1002 (w), 867 (w), 807 (w), 598 (w). Elemental analysis calcd (%) for C$_{16}$H$_{18}$N$_{26}$O$_6$ (670.48): C 28.66, H 2.71, N 54.32; found C 29.02, H 2.69, N 55.81.

Conclusions

A new series of nitrogen-rich energetic salts based on furoxanyl fuctionalized guanidinium cation (FAG cation) were prepared and well characterized with NMR and IR spectra, differential scanning calorimetry (DSC) and elemental analysis. Single crystal X-ray measurements were accomplished for salts **1**, **4**, **5** and **6**. According to the DSC results, Except for the salts **6**, **7** and **9**, the decomposition onset temperatures ($T_{d, onset}$) of the remaining energetic salts are higher than 180 ℃. In particular,

the most stable salt was **3**, which decomposed at 213 ℃. Its decomposition onset temperature is higher than that of RDX (T_d = 205 °C). The impact sensitivity values of salts **3**-**10** lie in the range between 2 and 40 J. Except for salts **7** and **9**, the other salts were less sensitive to impact and friction than RDX (7.4 J, 120 N). All salts possess positive heats of formation, whose values lie in the range from 284.77 to 1192.24 kJ mol^{-1}. With the EXPLO5 v6.01 program, the detonation pressures and velocities were calculated. For energetic salts **3**-**10**, calculated detonation pressures and velocities ranged from 19.3 to 27.5 GPa and 7515 to 8402 m s^{-1}, respectively. Salt **5** had a detonation pressure and velocity of 27.5 GPa and 8402 m s^{-1}, respectively, which was higher than that of TATB (D, 8176 m s^{-1}). Based on these results, some energetic salts based on the FAG cation have the potential to be candidates for energetic materials with good thermal stabilities and low sensitivities.

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Notes and references

^{a} School of Chemical Engineering, Nanjing University of Science and Technology, Xiaolingwei 200, Nanjing, P. R. China, E-mail: hyang@mail.njust.edu.cn (H. Yang); gcheng@mail.njust.ed.cn (G. Cheng).
^{b} School of Materials Science & Engineering, Beijing Institute of Technology, 5 South Zhongguancun Street, Beijing, P. R. China.

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