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Nitrogen-rich tricyclic-based energetic materials

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The chemistry of high-energy-density materials (HEDMs) featuring multiple nitrogen-rich heterocyclic skeletons with energetic fragments has witnessed enormous growth since the process of manufacturing explosives successfully was improved by Alfred Nobel. In particular, the recent surge of interest in HEDMs is because of its wide application in the military and civilian fields. In this review, we provide a systematic introduction to the developments in heterocyclic nitrogen-rich energetic materials with various explosive groups in the form of tricyclic-based compounds. This review summarizes the recent efforts toward new HEDMs based on the synthetic route, crystal behavior and the structure–property relationship. Further studies on new nitrogen-rich heterocycles may be helpful to achieve a more sustainable chemical process, which could make a positive impact of chemistry, not only for HEDMs, but also in other fields.

1 Introduction

With the development of chemical materials, new HEDMs represented by nitrogen-rich polycyclic-based compounds, which play a vital role in controllable storage systems for chemical energy, have obtained widespread application in propellants, explosives, pyrotechnics and gas-generating agents.[1] "Safer, more environmentally friendly, more powerful..." are the keywords in the process of designing HEDMs.[2] The diversified energetic compounds were synthesized to meet the increasing requirement for new energetic materials. However, it is still a challenge to achieve a fine balance between the high energy and low sensitivity of HEDMs because the high energy is primarily at the expense of molecular stability.[3]

It is well known that the history of explosives can be traced back to 220 years BC, when black-powder was invented by

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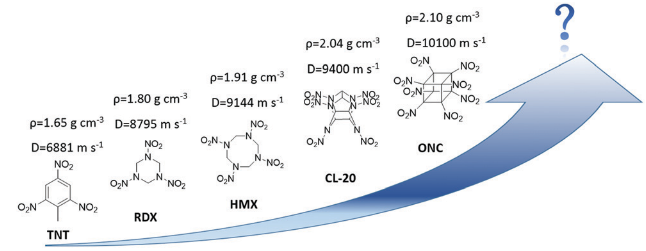

Fig. 1 The developmental course of energetic materials.

mixing flammable charcoal and sulfur with oxidant potassium nitrate by the Chinese.[4] Subsequently, nitroglycerine was developed in the 1860s by Alfred Nobel, the pioneer scientist. The well-known explosive 2,4,6-trinitrotoluene (**TNT**) (Fig. 1) was also first synthesized in 1863, and then applied in components of melt-cast explosives.[5] Then, cyclotrimethylenetrinitramine (**RDX**) was developed with excellent energetic performance during the two world wars.[6] Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (**HMX**), with improved detonation properties, was also discovered in later studies.[7] In 1987, hexanitrohexaazaisowurtzitane (**CL-20**) was first reported, and significant attention was directed to **CL-20** owing to its excellent energetic performance.[8] Furthermore, the continuous work of octanitrocubane (**ONC**) with a high density to 2.1 g cm^{-3} was considered to be a milestone achievement.[9]

However, the incomplete oxidation of all of those traditional explosives (**TNT**, **RDX**, **HMX**, *etc.*) during detonation leads to the significant production of soot, residue, smoke, and other incompletely oxidized toxic residues (CO, NO, *etc.*) owing to the negative oxygen balance of these traditional explosives.[10] As for nitrogen-rich heterocycles (oxadiazole, tetrazole, triazole, pyrazole, imidazole, triazine and tetrazine), they often possess low sensitivity and high energy arising from the large positive heats of formation due to their high nitrogen content and a large number of N–N and C–N bonds, respectively. Moreover, these heterocycles can be functionalized with energetic groups, such as amino, nitro, nitramino, azido, dinitromethyl and trinitromethyl group, thereby extending the design of energetic compounds. Therefore, these heterocycles are promising compounds that fulfill many requirements in the challenging field of energetic materials research. Recently, nitrogen-rich heterocycles have become one of the most exciting scientific discoveries in chemical science. Many derivatives of heterocycles containing two or more rings with excellent performance have sprung up in the field of energetic materials. Although some related reviews concerning this topic have appeared, a systematic review of nitrogen-rich polycyclic-based energetic materials has been rarely reported to the best of our knowledge. In this review, the up-to-date developments of nitrogen-rich tricyclic-based energetic materials that are based on oxadiazole are provided. The attention of this review is not only focused on synthesis strategies and performance, but also on the insight of the relationship of crystal behavior, structure and properties of HEDMs. This contribution may lead to a better understanding of the future design of both energetic materials and other fields.

2 The synthesis and crystal structure of tricyclic-based energetic materials

Unlike the traditionally designed energetic materials, in which the fuel and oxidizing characteristics are the sole factors to determine their performance, nitrogen-rich heterocyclic compounds have some unique properties, such as high heats of formation and significant gas release in the form of environmentally benign nitrogen, and commonly include moieties, such as five-membered azole and six-membered azine rings. Nitrogen-rich heterocycles are at the forefront of high energy materials research and expected to achieve increased performance requirements with reasonable safety. The functionalization of nitrogen-rich heterocyclic compounds with energetic groups (*e.g.*, $-NO_2$, $-NHNO_2$, $-N_3$, $-NH_2$) can increase the

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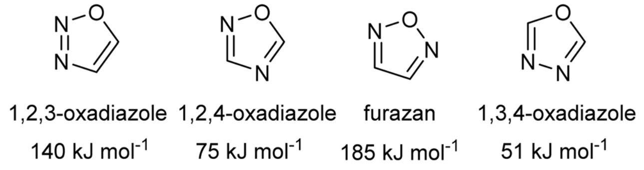


Fig. 2 Four isomers of oxadiazole.

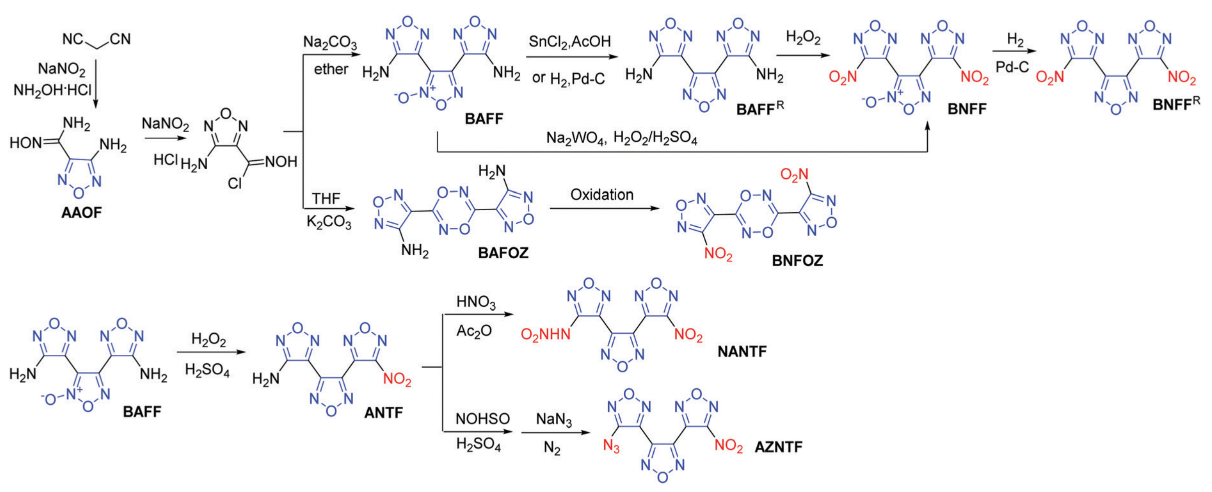
nitrogen content, heats of formation and density, and then improve the detonation performance. Many studies have shown that compounds containing two or more nitrogen-rich heterocycles possess the outstanding energetic property. In this section, the synthesis, properties and structure–property relationship of those tricyclic-based nitrogen-rich heterocyclic compounds based on oxadiazole were investigated.

Among the five-membered rings, oxadiazole attracts wide interest due to its unique characteristic of an intrinsic oxygen atom, which can increase the oxygen content, thus achieving oxygen balance more readily. As shown in Fig. 2, there are four oxadiazole isomers: 1,2,4-oxadiazole, 1,2,5-oxadiazole (furazan), 1,3,4-oxadiazole and 1,2,3-oxadiazole.[3]

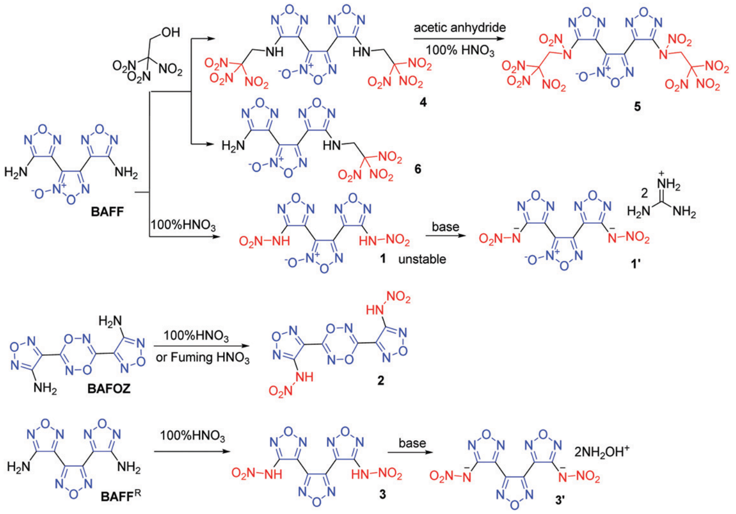
1,2,5-Oxadiazole (furazan) is highly energetic and has potential application in both propellant and explosive formulations owing to its highest positive heat of formation (185 kJ mol^{-1}). Moreover, 1,2,5-oxadiazole-2-oxide (furoxan) is a *N*-oxide derivative of furazan, which has a ''latent'' nitro group within one side of its ring. The density and detonation velocity of the energetic molecule can be increased by *ca.* 0.06–0.08 g cm^{-3} and *ca.* 300 m s^{-1} through introducing a furoxan ring into the molecule, respectively.[11] Therefore, a large amount of polycyclic-based energetic compounds containing furoxan or the furazan ring have been investigated. A wide variety of aminofurazan derivatives and aminofuroxan derivatives are known in the field of energetic materials due to their good stability and high heats of formation.

As shown in Scheme 1, bis(aminofurazano)furoxan (**BAFF**) and bisaminofurazanodioxadiazine (**BAFOZ**) were selectively synthesized *via* 1,3-dipolar cycloaddition of 4-amino-*N*-hydroxy-1,2,5-oxadiazole-3-carbimidoyl chloride, depending on the reaction conditions. Both diamino compounds were oxidized to give dinitro compounds **BNFF** and **BNFOZ** in moderate yield. **BNFF** exhibits a high density (1.90 g cm^{-3}) and detonation velocity (D = 8930 m s^{-1}), which is comparable to traditional explosive **HMX**. Furthermore, the low melting point (110 °C) and relatively high thermal stability of **BNFF** make it easy to cast and process. Subsequently, **BNFF** was treated with H_2/Pd–C to give its deoxygenated product bis(nitrofurazano)furazan (**BNFF^R**).[12] Moreover, the reduction reaction of **BAFF^R** using $SnCl_2$/HCl/AcOH as a reductant and then oxidation using Caro's acid is another synthetic method to achieve **BNFF^R**.[13] Moreover, the oxidation of one amino group of **BAFF** into a nitro group affords (4′-aminofurazan-3′-yl)-(4″-nitrofurazan-3″-yl)furazan (**ANTF**) in a mixture of H_2O_2 and H_2SO_4. To improve the energy of **ANTF**, nitration in HNO_3/Ac_2O and diazotization with nitrosylsulfuric acid in conc. H_2SO_4, followed by treatment with a water solution of sodium azide, were performed to obtain the nitroamino derivatives **NANTF** and azide derivatives **AZNTF**, respectively. However, the performance of these compounds has not been reported.[13]

In a typical procedure, the nitramino compound **3** was obtained by the nitration of **BAFF^R** using 100% nitric acid as the nitrating reagent.[14] The further nitration of **BAFF** and **BAFOZ** with fuming HNO_3 or 100% HNO_3 produced **1** and **2**, respectively. Compound **1** was stable in diethyl ether solution, but decomposed after isolation at room temperature (Scheme 2). To stabilize **1**, the corresponding energetic salt (**1′**) was synthesized by acid–base neutralization reactions. As shown in Fig. 3, the three oxadiazoles are noncoplanar, which is clearly evident from the dihedral angles of two furazan rings (59°) (Fig. 3c). The twist structure may be the cause of the instability of **1**. There are extensive hydrogen bonds in **1′** to improve its stability after the formation of energetic salt. The spiral-shaped layer structure was formed due to hydrogen bonds and the twist structure. Such layer units are repeated



Scheme 1 Synthesis of the C–C bonded tricyclic oxadiazole nitro-derivatives.



Scheme 2 Synthesis of the C–C bonded tricyclic oxadiazole nitramino- and trinitroethyl-derivatives.

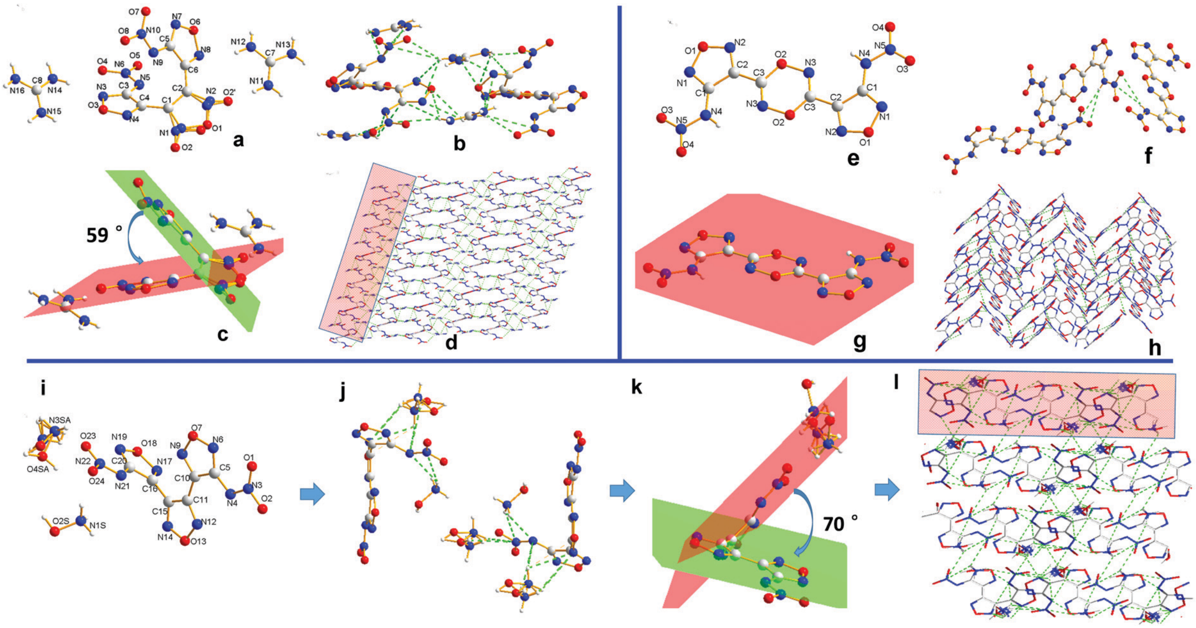


Fig. 3 (a, e and i) Structures; (b, f and j) planarity; (c, g and k) supramolecular interaction; (d, h and l) crystal packing diagram (green lines represent hydrogen bonds) of **1**′, **2**, and **3**′.

in an infinite stack, which classifies the whole crystal as having a spiral-shaped 3D-cube stacking structure (Fig. 3d). In addition, **2** possesses good stability due to its planar structure and intermolecular hydrogen bonding (Fig. 3f and g). One molecule was stacked with another molecular to form an edge-to-face arrangement. Finally, the layers stack into a wave-like packing system (Fig. 3h). Similar to **1**, nitramino compound **3** also has a twist structure confirmed by the dihedral angle of two furazan rings (70°) in energetic salt **3**′ (Fig. 3k). The intramolecular hydrogen bonding also leads to a 3D-cube stacking, as shown in Fig. 3l.

Considering the high energy properties of the nitro and nitramino groups, the synthesis and characterization of a series of *N*-trinitroethylamino compounds that could be functionalized were reported. As shown in Scheme 1, the reaction of trinitroethanol and **BAFF** afforded target products containing one (**6**) and two (**4**) trinitroethyl fragments, respectively. Compound **4** was then treated with 100% nitric acid and acetic anhydride to afford the *N*-nitrated trinitroethylamino derivative **5**.[15]

The three oxadiazole rings are noncoplanar in both compounds **4** and **6**, which was evident from the dihedral angles of

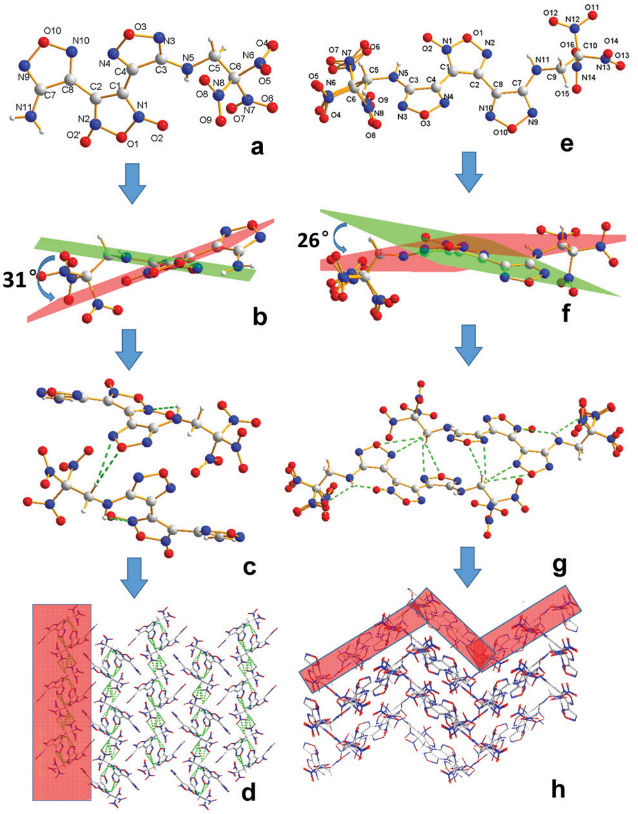


Fig. 4 (a and e) Structures; (b and f) planarity; (c and g) supramolecular interaction; (d and h) crystal packing diagram of **6** and **4**.

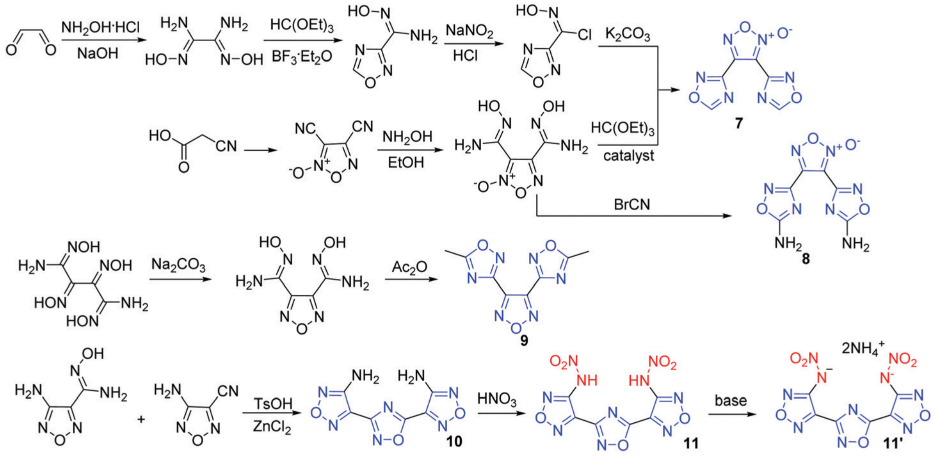
two furazan rings (31°) in **6** and two furazan rings (26°) in **4** (Fig. 4b and f). There are extensive intra- and intermolecular hydrogen bonding interactions in both trinitroethyl compounds to improve their stability (Fig. 4c and d). The hydrogen bonds between the furazan ring and trinitroethyl result in the face-to-face layer stacking of **6** and wave-like layer stacking of **4**. Then, these layers were dominated by an infinite face-to-face arrangement to form a 3D-cube layer stacking (Fig. 4d and h).[16] As shown in Table 1, the trinitroethylnitramino derivatives (**4–6**) possess high detonation velocities (8673–9407 m s^{-1}) and relatively high densities (1.84–1.90 g cm^{-3}), as well as an acceptable impact sensitivity (3.6–21.1 J) compared with the nitro and nitramino compounds, which indicates that these trinitroethyl derivatives might be of interest for future applications as environmentally friendly and nitrogen-rich energetic materials.

Table 1 Energetic properties of the tricyclic oxadiazole-based energetic compounds

Compd	T_{dec} [°C]	D [m s^{-1}]	P [GPa]	$\Delta_f H$ [kJ mol^{-1}]	IS [J]	FS [N]	d [g cm^{-3}]	Ref.
1′	157	7914	27.1	545	28	360	1.73	15
2	95	8490	32.2	592	<1	32	1.82	12
BNFF	245	8930	—	645	3.1	—	1.90	12
3′	179	8979	36.3	810	8	160	1.80	14
4	167	8935	35.9	923	14.2	240	1.84	15
5	108	9407	40.5	1174	3.6	100	1.90	15
6	169	8673	33.7	840	21.1	300	1.83	15
7	214	8043	26.8	326	18	120	1.82	17
11′	231	8271	27.9	425	16	120	1.71	3
12	184	8480	31.0	493	13	240	1.79	20
BNTFO-IV	146	9503	40.8	579	3	40	1.91	21
BNTFO-I	131	9867	45.0	668	3	35	1.98	21
21	232	7532	20.2	766	22	—	1.56	23
22	215	7528	20.8	1214	18	—	1.57	23

There are two different synthetic routes to compound 3-[4-(1,2,4-oxadiazol-3-yl)-2-oxido-1,2,5-oxadiazol-3-yl]-1,2,4-oxadiazole (**7**) shown in Scheme 3. Compound **7** was synthesized through the direct cyclization of 1,2,4-oxadiazole-3-chloroxime obtained through the oximation, cyclization and chlorination reaction, starting from glyoxal in the presence of K_2CO_3.[17] Another route to **7** was the double cyclization reaction of bis-amidoxime by utilizing trimethyl orthoformate and different calatysts.[18] When bis-amidoxime was reacted with cyanogen bromide, the amino groups were introduced into **7** to form 3,4-bis-(5-amino-1,2,4-oxadiazolyl)furoxan (**8**).[19] The decomposition temperature of **7** (T_{dec} = 214 °C) was increased to 273 °C after the introduction of amino groups. The methyl group was also introduced to the tricyclic oxadiazole backbone shown in Scheme 3. The diaminotetraoxime in aqueous sodium hydroxide was heated to be dehydrated into 3,4-dicarboxamidoxime-furazan. Then, this bis-amidoxime was reacted with acetic anhydride to give 3,4-bis(5-methyl-1,2,4-oxadiazol-3-yl)furazan (**9**). In addition, the formation of 1,2,4-oxadiazole **10** from amidoxime proceeded using $ZnCl_2$ as the Lewis acid. Moreover, nitramino compound **11** was obtained by the treatment of **10** with excess fuming nitric acid.[3] It was found to be unstable in the air, and was treated directly with gaseous ammonia to form salt **11′**. The crystal structure of **11′** is shown in Fig. 5a. A large number of intermolecular hydrogen bonds forms among the furazan rings, water and ammonium ion (Fig. 5b). Furthermore, the triazole ring is slightly twisted out of the indazole plane (Fig. 5c). The crystal packing is dominated by an infinite face-to-face arrangement to form face-to-face-type stacking (Fig. 5d). The multi hydrogen-bonding interactions, as well as the closer layer-by-layer package, contribute to the stability of **11′**.

When bifurazan or trifurazan rings are substituted with nitro groups, such as 4,4′-dinitro-3,3′-bifurazan or the above-mentioned **BNFF**, their far greater stability makes them more favorable for practical applications. As shown in Scheme 4, the chlorination reaction of 3-hydroximoyl-4-aminofuroxan using $NaNO_2$ in concentrated HCl was first attempted to prepare 3-chlorohydroximoyl-4-aminofuroxan, which could undergo dimerization to give a trifuroxan structure (**12**) by treatment with dilute aqueous K_2CO_3 solution. However, the intermediate 3-chlorohydroximoyl-4-aminofuroxan was not obtained in the acid sodium nitrite solution probably due to the diazotization of the amino group in the 4-position of 3-amidoxime-4-aminofuroxan as a starting material. Later, J. M. Shreeve's group reported the synthesis of **12** by protecting the 4-amino group of 3-hydroximoyl-4-aminofuroxan. Then, **12** was



Scheme 3 Synthesis of C–C bonded tricyclic furazan-based 1,2,4-oxadiazole derivatives.

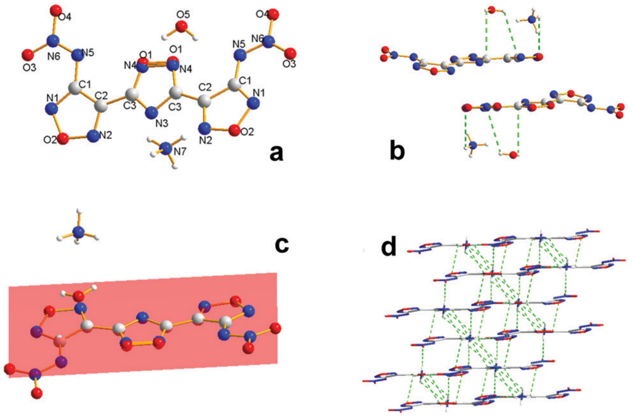
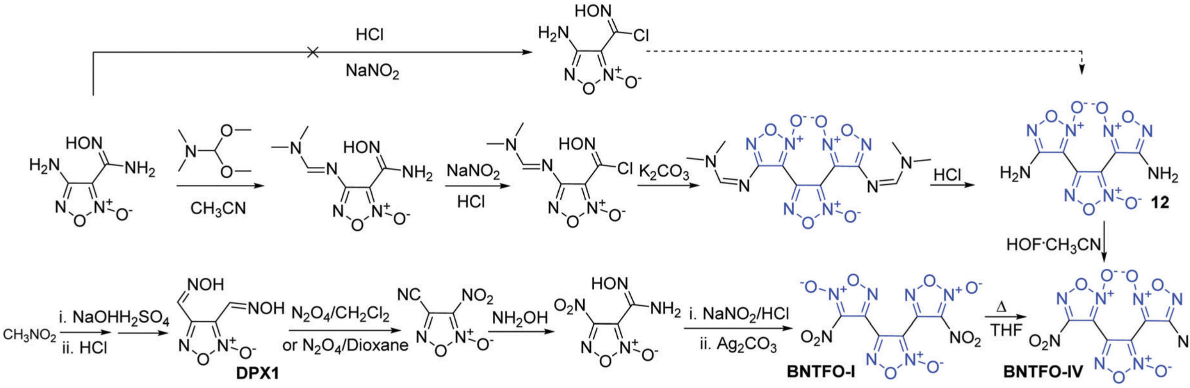


Fig. 5 (a) Structures; (b) planarity; (c) supramolecular interaction; (d) crystal packing diagram of **11′**.

synthesized through the chlorination, cyclization and ammoniation starting from the protected 3-hydroximoyl-4-aminofuroxan. Further oxidation reaction of **12** into dinitro compound **BNTFO-IV** using numerous oxidants, such as H_2O_2/H_2SO_4 and H_2O_2/H_2SO_4/Na_2WO_4, was attempted. In addition, he oxidation reaction of diamine **12** into **BNTFO-IV** was successful only using HOF as an oxidant.[20] Another route to **BNTFO** starting from (*E*,*E*)-3,4-bis(oximomethyl)furoxan (**DPX1**) was reported by B. Wang's group. **DPX1** was prepared in high purity by a two-steps reaction from nitromethane (Scheme 4). Furthermore, the oxidation reaction of **DPX1** using N_2O_4 in CH_2Cl_2 or dioxane led to 3-nitro-4-cyanofuroxan, which was then treated with 50% aqueous hydroxylamine in ethanol to give 3-nitro-4-aminoximidofuoxan. **BNTFO-I** was produced through diazotization of 3-nitro-4-aminoximidofuoxan with sodium nitrite in concentrated hydrochloric acid, and subsequent cyclization using Ag_2CO_3 in THF. In an effort to obtain crystals suitable for X-ray diffraction of **BNTFO-I**, the isomer **BNTFO-IV** was formed in some solvents, such as CH_3CN and THF.[21] The crystal structures of **BNTFO-I** and **BNTFO-IV** are shown in Fig. 6a and d. The nitro group is on the inner side of the furoxan ring in **BNTFO-I**, while it is on the outside of the furoxan ring in **BNTFO-IV**. Furthermore, the central furoxan ring is twisted by 53° towards the adjacent ring plane in **BNTFO-I**. The angle between the furoxan rings on both sides is 73°, and the nitro group is twisted out of the adjacent ring plane by 14° (Fig. 6b). Fig. 6c presents a face-to-face layer, which can be interpreted as two adjacent **BNTFO-I** molecules serving



Scheme 4 Synthesis of the C–C bonded tricyclic furoxan derivative.

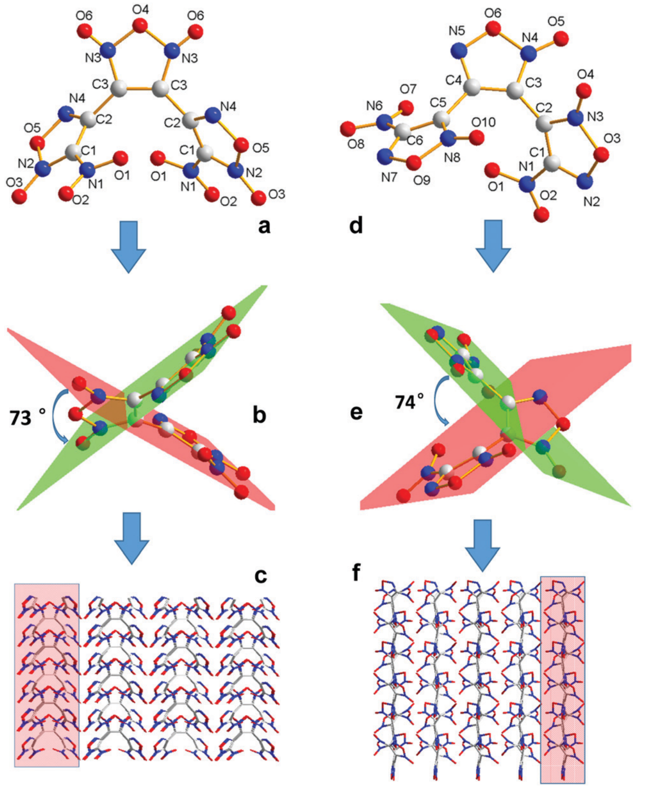


Fig. 6 (a, d) Structures; (b, e) planarity; (c, f) crystal packing diagram of **BNTFO-I** and **BNTFO-IV**.

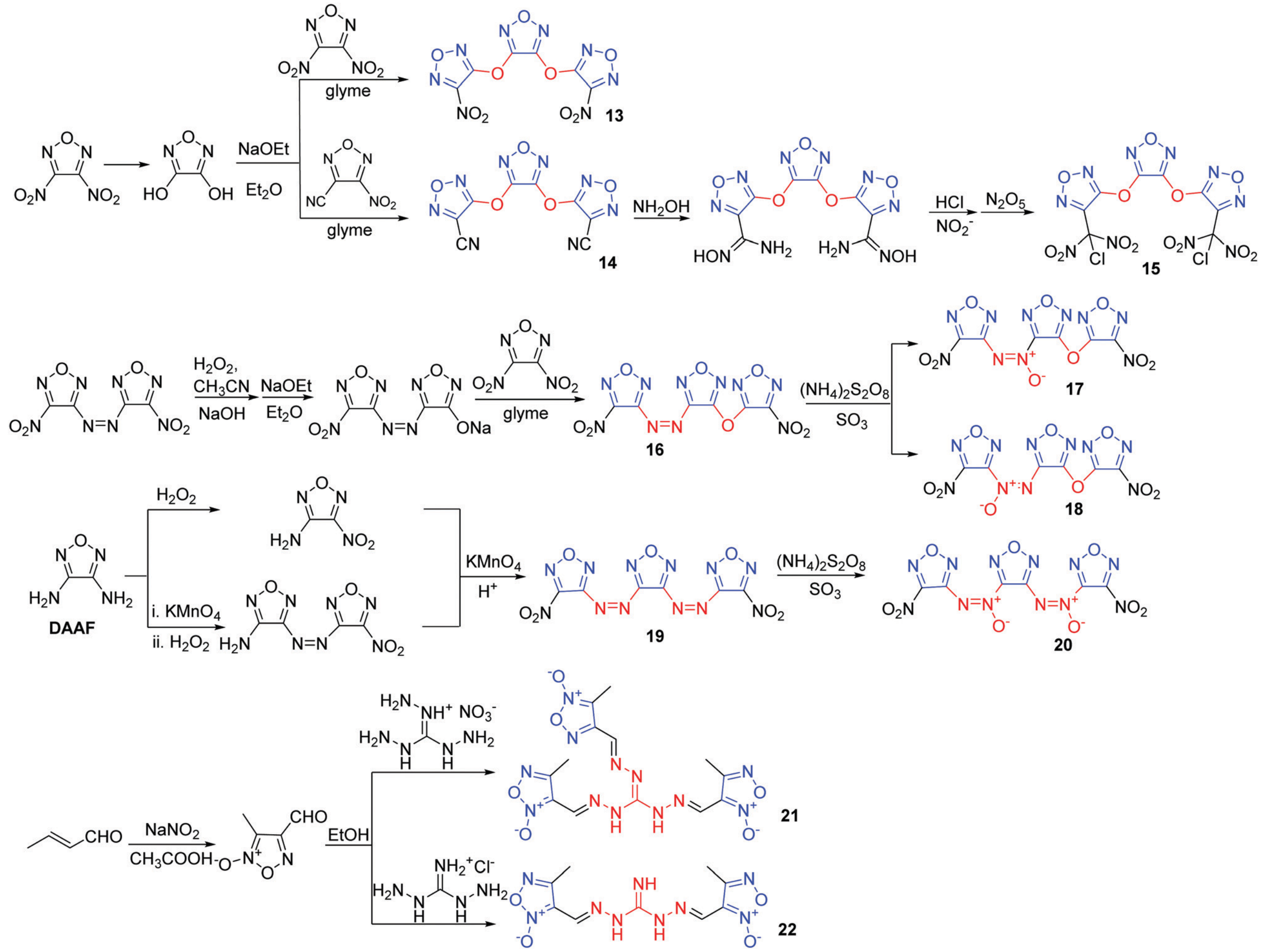
as the connection point of the network. Then, the layers stack into a stratiform structure to form the 3D-cube packing system. It is notable that the sandwich-type stacking can protect the energy moieties in the interlayer, and enhance the molecular stability when encountering external stimuli. The central furoxan ring is twisted by 45.5° and 58.3°, respectively, towards the adjacent ring planes in **BNTFO-IV**. The angle between the furoxan rings on both sides is 74°, and the nitro group is twisted out of the adjacent ring plane by 17.2° and 14.8°, respectively (Fig. 6e). Crystal units are repeated in an infinite stack, resulting in crossing stacking of **BNTFO-IV** because of the twisted molecule. The twist structure and disordered crystal stacking lead to the instability of **BNTFO-IV** with an IS value of 3 J.

Surprisingly, **BNTFO-I** has a measured density of 1.98 g cm^{-3}, which is slightly higher than that of **BNTFO-IV** (1.91 cm^{-3}) due to smaller dihedral angles between the furoxan rings and nitro groups, as well as relatively closer 3D network, which results in the higher detonation performance of **BNTFO-I** (D = 9867 m s^{-1}, P = 45.0 GPa) and **BNTFO-IV** (D = 9503 m s^{-1}, P = 40.8 GPa).

Apart from the abovementioned C–C bonded tricyclic oxadiazole derivatives, a series of zero-hydrogen nitrofurazans containing an oxy, azo and azoxy bridge have also been synthesized. As shown in Scheme 5, dinitrofurazan was hydrolyzed in aqueous acetonitrile alkali, followed by acidification with hydrochloric acid to give 3,4-dihydroxyfurazan. 3,4-Dihydroxyfurazan was then converted to the bisalt by treatment with sodium ethoxide in ether. When dinitrofuran and 3-cyano-4-nitrofurazan were subjected to the bisalt in glyme, the desired trifurazan oxy-bridged compounds **13** and **14** were obtained, respectively. The addition reaction of compound **14** with hydroxylamine led to pure aminoximidofurazan compound in a high yield. Then, the chloroximidofurazan compound is obtained by diazotization of aminoximidofurazan using sodium nitrite in concentrated hydrochloric acid. Finally, 3,4-bis(3-chlorodinitromethylfurazan-4-oxy)furazan **15** was formed through the oxidation of chloroximidofurazan using N_2O_5 in chloroform.[22] Encouraged by this, another trifurazan ether containing the azo bridge (**16**) was also synthesized from 3,3′-nitro-4,4′-azoxyfurazan following the same synthetic route to **14**. Successful oxidation of **16** into **17**, accompanied by the formation of a very slight amount of **18**, was finally achieved utilizing ammonium persulfate in oleum. 3-Nitro-4-amino-furazan and 3-nitro-3′-amino-4,4′-azoxyfurazan were readily prepared through the oxidation reaction of **DAAF** using H_2O_2 and $KMnO_4$, respectively. Then, the oxidative coupling reaction of nitro-4-amino-furazan and 3-nitro-3′-amino-4,4′-azoxyfurazan was completed to give the product **19**. Finally, the oxidation reaction of azo-bridged compound **19** to azoxy-bridged compound was performed to give a mixture of positional isomers of **20** *via* nonselective attack at four nitrogen atoms of both azo bridges. To the best of our knowledge, the energetic performances of these azoxy-bridged or oxy-bridged furazan derivatives have not been reported.

In addition, the guanidine bridge was introduced to trioxadiazole rings by the reaction of hydrazine groups with 3-methyl-4-furoxancarbaldehyde (Schemes 2–4). Starting from 3-methyl-4-furoxancarbaldehyde, the treatment of 1,3-diaminoguanidine monohydrochloride and triaminoguanidine nitrate salts led to the desired 1,3-bis-(3-methylfuroxan-4-methyleneamino)guanidine (**22**) and 1,2,3-tris-(3-methylfuroxan-4-methyleneamino)guanidine (**21**) in a high yield, respectively.[23] As for compound **21**, the three furoxan rings are planar, which was clearly confirmed by the planarity of **21** (Fig. 7c). The crystal packing is dominated by an infinite face-to-face arrangement to form face-to-face-type stacking (Fig. 5c). Furthermore, a large number of intermolecular hydrogen bonds form among the furoxan rings, solvent molecule and guanidine. The distance between the two adjacent molecules of **21** is less than 4.0 Å (3.33 Å, Fig. 7d), suggesting that two of the molecules are in the range of π–π interactions and in closer packing. Hence, the face-to-face-type stacking of molecules in **21** is connected through hydrogen bonds and π–π interactions, forming a 3D net structure. Furthermore, the π–π interactions, multi-intramolecular hydrogen-bonding interactions, as well as the closer layer-by-layer package, contribute to the stability of **21** (IS = 22 J, T_{dec} = 232 °C).

Much attention has been recently focused on the relationship of the crystal behavior and sensitivity. External mechanical stimuli can lead to the shape change of the energetic material to some extent to store the mechanical energy. Once this energy exceeds the limit of the energetic material, many hot spots will form, resulting in decomposition and final detonation of the energetic materials. The steric hindrance caused by layer



Scheme 5 Synthesis of oxy, azo, azoxy and guanidine-bridged tricyclic oxadiazole derivatives.

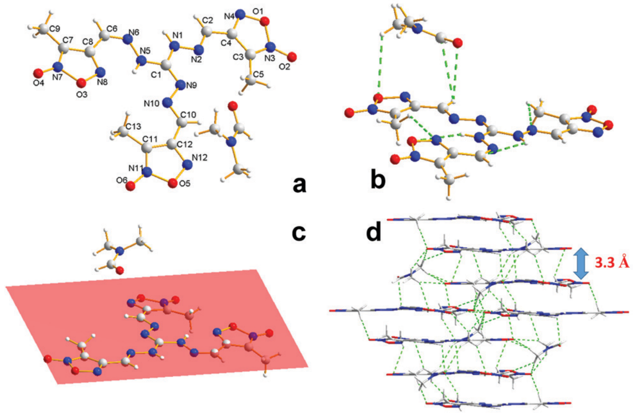


Fig. 7 (a) Structures; (b) planarity; (c) supramolecular interaction; (d) crystal packing diagram of **21**.

sliding in the crystal is usually thought to be a crucial factor influencing the impact sensitivity of the energetic materials. Herein, five crystal packing types were employed to understand the effects of the crystal structure on the sensitivity of the target compounds. As shown in Fig. 8, there are five known stacking types of classic energetic molecules: face-to-face, wavelike, crossing, mixing and 3D-cube.[24] These stacking types will lead to different steric hindrances when interlayer or intralayer sliding happens (Fig. 8).[25] The face-to-face stacking (**11′** and **21**) causes the easiest slide, as it occurs along the molecular plane, resulting in very low impact sensitivity. The sliding of wavelike stacking is limited to the front/back direction, with much less sliding orientation relative to face-to-face stacking. As for crossing and mixing stacking, sliding along any orientation is strongly forbidden, implying very high impact sensitivity. It is noteworthy that the 3D-cube layer stacking will cause the two-steps slide. First, the sliding is limited to a one-line intralayer, and then the easiest slide occurs along the layer plane, resulting in low sensitivity. For example, compounds **6** and **1′** with a 3D-cube layer stacking have relatively low sensitivities (**1′**, IS = 28 J, FS = 360 N; **6**, IS = 21 J, FS = 300 N) among the furazan derivatives. However, compounds **BNTFO-I** and **BNTFO-IV** with a 3D-cube layer stacking still exhibit very high sensitivity with an IS value up to 3 J, suggesting that the sensitivity mechanism is very complicated, and any factor considered alone will be insufficient.

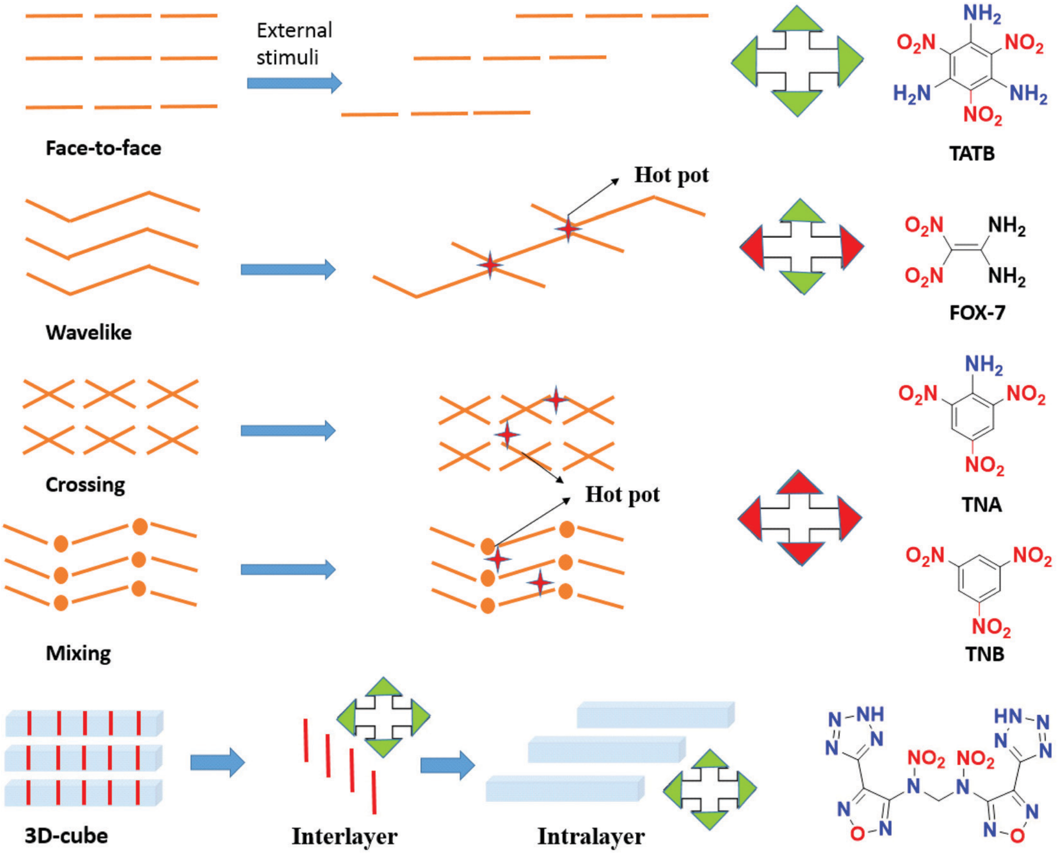


Fig. 8 Representative energetic compounds and their diverse crystal stacking (arrows showing sliding allowed (green arrows) and unallowed (red arrows)).

3 Conclusion

It is attractive and challenging to achieve a fine balance between energy and safety in the field of HEDMs. Therefore, the in-depth study in the design and syntheses of new HEDMs especially for nitrogen-rich tricyclic-based energetic materials is growing in interest among chemical researchers. Up to now, there are four promising routes to modern HEDMs: crystal engineering, constructing energetic metal organic frameworks, designing polynitrogen compounds and forming energetic salts. In fact, molecular design is the most commonly used method to achieve the balance through the combination of stable skeletons with high energy units through suitable linkages. In this review, we outline the major synthetic strategies, energetic properties and crystal behavior of a series of nitrogen-rich heterocycles. By summarizing these research studies, the main routes to design high-energy and low-sensitivity heterocyclic compounds are as follows: (1) cyclization reactions of oxime or hydrazide to construct different oxadiazole forms; (2) the change of performance can be realized by introducing a bridge, such as imine, hydrazine, azo, triazene, tetrazene, azoxy, oxy, alkoxy, alkyl and bisnitramino-methylene linkage; (3) a close layer-by-layer structure features can improve the density and stability of energetic material; (4) forming energetic salts with abundant hydrogen bonds will greatly improve stability compared to the neutral compound.

The numerous works on the synthesis and study of tricyclic-based energetic materials in recent years reveal that this field is of major interest to the chemical community. We believe that the wide use of ecofriendly polycyclic-based energetic materials can help achieve a positive impact of chemistry on our society. The authors hope that more new powerful and strategic energetic materials may appear in the literature in the future.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

1 (*a*) J. P. Agrawal and R. D. Hodgson, *Organic Chemistry of Explosives*, John Wiley & Sons Ltd, Copyright, 2007; (*b*) X. Mei, H. Yang, X. Li, Y. Li and Y. Cheng, Study of some low temperature gas-generating compositions, *Propellants, Explos., Pyrotech.*, 2015, **40**, 526–530.

2 (*a*) J. Tang, D. Chen, G. Zhang, H. Yang and G. Cheng, A green primary explosive: Design, synthesis and testing, *Synlett*, 2019, 885–892; (*b*) M. H. V. Huynh, M. D. Coburn, T. J. Meyer and M. Wetzler, Green primary explosives: 5-Nitrotetrazolato-N^2-ferrate hierarchies, *Proc. Natl. Acad. Sci. U. S. A.*, 2006, **103**, 10322–10327; (*c*) M. H. V. Huynh, M. A. Hiskey, T. J. Meyer and M. Wetzler, Green primaries: Environmentally friendly energetic complexes, *Proc. Natl. Acad. Sci. U. S. A.*, 2006, **103**, 5409–5412.

3 (*a*) J. Ma, G. Cheng, X. Ju, Z. Yi, S. Zhu, Z. Zhang and H. Yang, Amino-nitramino functionalized triazolotriazines: a good balance between high energy and low sensitivity, *Dalton Trans.*, 2018, **47**, 14483–14490; (*b*) T. M. Klapotke, P. C. Schmid, S. Schnell and J. Stierstorfer, 3,6,7-Triamino-[1,2,4]triazolo[4,3-*b*][1,2,4]triazole: A non-toxic, high-performance energetic building block with excellent stability, *Chem. – Eur. J.*, 2015, **21**, 9219–9228; (*c*) H. Wei, C. He, J. Zhang and J. M. Shreeve, Combination of 1,2,4-oxadiazole and 1,2,5-oxadiazole moieties for the generation of high-performance energetic materials, *Angew. Chem., Int. Ed.*, 2015, **54**, 9367–9371.

4 P. Yin and J. M. Shreeve, Chapter four-nitrogen-rich azoles as high density energy materials: Reviewing the energetic footprints of heterocycles, *Adv. Heterocycl. Chem.*, 2017, **121**, 89–131.

5 J. Wilbrand, Notiz über trinitrotoluol, *Ann. Chem. Pharm.*, 1863, **128**, 178–179.

6 T. L. Davis, *In the chemistry of powder and explosives II*, John Wiley & Sons Inc., New York, 1943.

7 P. W. Cooper, *In explosives engineering*, Wiley-VCH, New York, 1996.

8 M. P. Nadler, R. A. Nissan, W. P. Norris, D. J. Vanderah and R. Y. Yee, Polynitropolyaza caged explosives, Report NWC TP 7020 (Part 7), Naval Weapons Center 1989.

9 M. Zhang, P. E. Eaton and R. Gilardi, Hepta- and Octanitrocubanes, *Angew. Chem., Int. Ed.*, 2000, **39**, 401–404.

10 Y. Qu and S. P. Babailov, Azo-linked high-nitrogen energetic materials, *J. Mater. Chem. A*, 2018, **6**, 1915–1940.

11 C. Zhang, Computational investigation of the detonation properties of furazans and furoxans, *THEOCHEM*, 2006, **765**, 77–83.

12 (*a*) T. K. Kim, J. H. Choe, B. W. Lee and K. Chung, Synthesis and characterization of BNFF Analogues, *Bull. Korean Chem. Soc.*, 2012, **33**, 2765–2768; (*b*) H. Huang, Y. Shi, Y. Liu and J. Yang, 1,2,4,5-Dioxadiazine-functionalized [N–NO$_2$]− furazan energetic salts, *Dalton Trans.*, 2016, **45**, 15382–15389.

13 (*a*) Y. Zhang, C. Zhou, B. Wang, Y. Zhou, K. Xu, S. Jia and F. Zhao, Synthesis and characteristics of bis(nitrofurazano)furazan (BNFF), an insensitive material with high energy-density, *Propellants, Explos., Pyrotech.*, 2014, **39**, 809–814; (*b*) A. A. Astrat'ev, A. I. Stepanov, V. S. Sannikov and D. V. Dashko, Synthesis and some chemical characteristics of 4″-nitro-3,3′:4′,3″-ter-1,2,5-oxadiazol-4-amine, *Russ. J. Org. Chem.*, 2016, **52**, 1194–1202.

14 Y. Tang, C. He, L. A. Mitchell, D. A. Parrish and J. M. Shreeve, Small cation-based high-performance energetic nitraminofurazanates, *Chem. – Eur. J.*, 2016, **22**, 11846–11853.

15 (*a*) Q. Yu, H. Yang, X. Ju, C. Lu and G. Cheng, The synthesis and study of compounds based on 3,4-bis(aminofurazano)furoxan, *ChemistrySelect*, 2017, **2**, 688–696; (*b*) A. DeHope, P. F. Pagoria and D. Parrish, New polynitro alkylamino furazans, 16th New Trends in Research of Energetic Materials, Proceedings of the Seminar, Pardubice, Czech Republic (Part 1), 2013, pp. 130–136.

16 (*a*) Q. Sun, S. Chen, X. Li, Q. Lin and M. Lu, 3D-Cube Layer Stacking: A promising strategy for high-performance insensitive energetic materials, *Cryst. Growth Des.*, 2017, **17**, 6105–6110; (*b*) J. Tang, H. Yang, H. Xiong, W. Hu, C. Lei and G. Cheng, Combining the furoxanylhydrazone framework with various energetic functionalities to prepare new insensitive energetic materials with 3D-cube layer stacking, *New J. Chem.*, 2020, **44**, 5895–5902; (*c*) J. Tang, P. Yang, H. Yang, H. Xiong, W. Hu and G. Cheng, A simple and efficient method to synthesize high-nitrogen compounds: Incorporation of tetrazole derivatives with N5 chains, *Chem. Eng. J.*, 2020, **386**, 124027.

17 C. Yan, K. Wang, T. Liu, H. Yang, G. Cheng and Q. Zhang, Exploiting the energetic potential of 1,2,4-oxadiazole derivatives: combining the benefits of a 1,2,4-oxadiazole framework with various energetic functionalities, *Dalton Trans.*, 2017, **46**, 14210–14218.

18 (*a*) L. L. Fershtat, I. V. Ananyev and N. N. Makhova, Efficient assembly of mono- and bis(1,2,4-oxadiazol-3-yl)furoxan scaffolds via tandem reactions of furoxanylamidoximes, *RSC Adv.*, 2015, **5**, 47248–47260; (*b*) E. C. Johnson, E. J. Bukowski, J. J. Sabatini, R. C. Sausa, E. F. C. Byrd, M. A. Garner and D. E. Chavez, Bis(1,2,4-oxadiazolyl)furoxan: A promising melt-castable eutectic material of low sensitivity, *ChemPlusChem*, 2019, **84**, 319–322.

19 T. S. Hermann, T. M. Klapotke, B. Krumm and J. Stierstorfer, Synthesis, characterization and properties of ureido-furazan derivatives, *J. Heterocycl. Chem.*, 2018, **55**, 852–862.

20 C. He, H. Gao, G. H. Imler, D. A. Parrishc and J. M. Shreeve, Boosting energetic performance by trimerizing furoxan, *J. Mater. Chem. A*, 2018, **6**, 9391–9396.

21 (*a*) L. Zhai, F. Bi, Y. Luo, N. Wang, J. Zhang and B. Wang, New strategy for enhancing energetic properties by regulating trifuroxan configuration: 3,4-bis(3-nitrofuroxan-4-yl)furoxan, *Sci. Rep.*, 2019, **9**, 4321–4329; (*b*) T. M. Klapotke, D. G. Piercey and J. Stierstorfer, The facile synthesis and energetic properties of an energetic furoxan lacking traditional "Explosophore" moieties: (*E*,*E*)-3,4-bis(oximomethyl)furoxan (DPX1), *Propellants, Explos., Pyrotech.*, 2011, **36**, 160–167.

22 (*a*) L. Zhai, X. Fan, B. Wang, F. Bi, Y. Lia and Y. Zhu, A green high-initiation-power primary explosive: synthesis, 3D structure and energetic properties of dipotassium 3,4-bis(3-dinitromethylfurazan-4-oxy)furazan, *RSC Adv.*, 2015, **5**, 57833–57841; (*b*) A. B. Sheremetev, V. O. Kulagina, N. S. Aleksandrova, D. E. Dmitriev and Y. A. Strelenko,

Dinitro trifurazans with oxy, azo, and azoxy bridges, *Propellants, Explos., Pyrotech.*, 1998, **23**, 142–149.

23 B. Wu, H. Yang, Q. Lin, Z. Wang, C. Lu and G. Cheng, New thermally stable energetic materials: synthesis and characterization of guanylhydrazone substituted furoxan energetic derivatives, *New J. Chem.*, 2015, **39**, 179–186.

24 (*a*) J. Tang, G. B. Cheng, S. H. Feng, X. Zhao, Z. C. Zhang, X. H. Ju and H. W. Yang, Boosting performance and safety of energetic materials by polymorphic transition, *Cryst. Growth Des.*, 2019, **19**, 4822–4828; (*b*) P. Yin, L. A. Mitchell, D. A. Parrish and J. M. Shreeve, Energetic N-nitramino/N-oxyl-functionalized pyrazoles with versatile π–π stacking: structure–property relationships of high-performance energetic materials, *Angew. Chem., Int. Ed.*, 2016, **55**, 14409–14411.

25 Y. Ma, A. Zhang, C. Zhang, D. Jiang, Y. Zhu and C. Zhang, Crystal packing of low-sensitivity and high-energy explosives, *Cryst. Growth Des.*, 2014, **14**, 4703–4713.