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Combining the Furoxanylhydrazone Framework with Various Energetic Functionalities to Prepare New Insensitive Energetic Materials with a 3D-cube Layer Stacking

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Abstract: A series of furoxanylhydrazone-derived energetic compounds including salts and neutral compounds were systematically studied using 3-methyl-4-furoxancarbaldehyde as a versatile starting material. Target compounds present a 3D-cube layer crystal packing style due to the special structure of furoxanylhydrazone and vast hydrogen bonds. This configuration breaks through the limitation of the 2D-plane layer structure. Target compounds, which feature such characteristics, exhibit excellent sensitivities toward impact and friction (IS > 24 J; FS > 180 N) and acceptable energetic performance. Moreover, the detonation velocities and pressures of all ionic compounds (6-9, 11-13) were both increased relative to their corresponding neutral compounds. Compared with 5-(3'-methylfuroxanyl)methyleneamino-tetrazole (10), the sensitivities to impact and friction of its anion salts (11-13) were also lowered to some extent. The structure-property relationship was studied by theoretical calculation, crystal structure analysis and energetic property. It is noted that five types of crystal packing have been analyzed, which may be useful for the further understanding of crystal and chemical phenomena in energetic materials. These desire results demonstrate that this study enriches future prospects for the design of energetic materials.

Introduction

In the past decades, the design and development of high energy density materials (HEDMs) played an important role in civilian and military such as propellants, explosives, pyrotechnics and gas generating agents.¹ The demands of modern HEDMs are getting higher and higher, in addition to high energetic performance (detonation velocity and pressure) and low sensitivity (sensitivity to spark, impact and friction), environmentally friendly decomposition products should be considered.² However, the contradiction between these requirements is often a huge challenge, especially energy and safety, because the enhanced properties come mostly at the expense of molecular stability.3 Therefore, the combination of physics, crystallography and chemistry should be considered to prepare modern HEDMs.⁴ There are four promising routes to obtain modern HEDMs: crystal engineering, constructing energetic metal organic frameworks, designing polynitrogen compounds and forming energetic salts.⁵ As an important crossbranch of chemistry and physics in energetic materials, the design and synthesis of energetic salts have received significant interests due to better detonation performances and stabilities than their precursors.⁶ While the crystal engineering of HEDMs mainly aims to obtain the most stable form to realize the

applications of HEDMs.⁷ Therefore, the combination of the formation of energetic salts and crystal engineering will be worthy of investigation.

As known, furoxan (1,2,5-oxadiazole-2-oxide) 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 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.⁸ Some energetic salts containing furoxan ring and other backbones have been investigated.⁹ There are four known stacking types of classic energetic molecules: face-to-face, wavelike, crossing, and mixing.¹⁰



Figure 1. Several types of 2D-plane and 3D-cube crystal packing.

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Electronic Supplementary Information (ESI) available: [details of any

supplementary information available should be included here]. See



Recently, a 3D-cube layer stacking type has been reported by M. Lu's group, which overcomes the limitation of the 2D-plane layer structure (Figure 1).¹¹ However, the great potential of developing 3D-cube layer stacking in energetic materials has not fully exploited yet. To our best knowledge, few energetic salts based on furoxan-functioned nitrogen-rich heterocycle cations have been reported. With our continuing interest to explore the relation between properties and structures of energetic materials, herein, the reactions of hydrazine groups in nitrogen-rich heterocyclic rings with 3-methyl-4furoxancarbaldehyde are further studied. The synthesis, structure, and energetic performance of 3-(3'-methylfuroxanyl) methyleneamino-4-amino-1,2,4-triazole 5-(3'-(4), methylfuroxanyl)methyleneamino-tetrazole (10) and a series of energetic salts based on furoxanylhydrazone functionalized cation(5-10) and anion (11-13) were reported. Importantly, these crystals of furoxanylhydrazone derivatives exhibit five different 3D-cube layer stacking forms: "Z" shaped, spring shaped, stair shaped, sandwich shaped and face-to-face layer. And the relation between crystal phenomenon and properties of some target compounds were discussed. All these results indicated that the design of furoxan-derived energetic salts and the exploration of their microstructures may open new avenues in the following research on HEDMs.

Results and discussion

Synthesis

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The synthetic pathway is shown in Scheme 1. Compounds **1-3** were synthesized according to the literature.¹² First, the desired

Figure 2. The process of salts (5-9, 11-13) based on Bronsted acid-base reaction.



Figure 3. a) The molecular structure of compound **5**; b) the supramolecular interaction between chloridion and nearby energetic cation; c) the "Z" shaped unit cell contained in **5**; d) the 3D supramolecular structure of **5**. (Green lines represent hydrogen bonds; red ellipsoid indicates furoxanyl framework; blue column presents triazoleyl group, green plot is chloridion).

product 4 can be precipitated from the reaction mixture of 4-3-methyl-4amino-3-hydrazino-1,2,4-triazole and furoxancarbaldehyde with a catalytic amount of hydrochloric acid at 78 °C. Subsequently, the energetic cation salts of 4 were synthesized by means of Bronsted acid-base reaction. When 4 was treated with an equivalent of acid, energetic salts based on furoxanyl functionalized 5, 6 and 7 were prepared. We synthesized protonated salts 8 and 9 by using ammonium dinitramide with hydrochloric acid and 5-nitro-tetrazole, respectively. In addition, in order to systematically study on furoxanyl functionalized derivatives, the compound **10** and its furoxanyl functionalized salts (11-13) were also synthesized. A series of energetic salts from compounds 4 and 10 were prepared by dissolving the neutral compounds in ethanol, followed by the addition of the corresponding Bronsted acid or base (Figure 2). The desired energetic salts were precipitated almost quantitatively with high purities due to the poor solubility of the target ionic molecules.

Single-crystal X-ray analysis

Single crystals of **5**, **7** and cocrystal **8/4** suitable for X-ray diffraction studies were all obtained from methanol by slow evaporation of the solvents at ambient temperature, whereas crystals **10** and **11** were re-crystallized from the hot water solution. The crystallographic data and CCDC numbers of these compounds are summarized in Table S1 (ESI⁺).

Compound **5** crystallizes in the monoclinic space group $P2_1/n$ with four molecules per unit cell (Z = 4) and a calculated density of 1.602 g cm⁻³ based on crystal data. The furoxan ring and triazole ring of **5** are noncoplanar, which is clearly confirmed from torsion angles of C1-C3-C4-N3 (24.5 (4)°) and N2-C3-C4-N3 (-153.0 (3)°) (Figure 3a). The adjacent molecules are interacted with each other through hydrogen bonds (N–H··O) and halogen bonds (N–H··CI) (Figure 3b). The "Z" shaped unit cell is formed through these interactions between two furoxanyl cations and a chloridion (Figure 3c). Then several unit cells arrange side by side to form a layer, finally these layers are further stacked to form the 3D-cube layer stacking type of **5** (Figure 3d).

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Figure 4. a) The molecular structure of compound **7**; b) the supramolecular interaction between perchlorate anion and nearby energetic cation; c) the spring shaped unit cell contained in **7**; d) the 3D supramolecular structure of **7**. (Green lines represent hydrogen bonds; red ellipsoid indicates perchlorate anion; blue column presents furoxanyl functionalized cation.)

Compound **7** belongs to the monoclinic space group $P2_1/c$ with four molecules per unit cell (Z = 4) and a crystal density of 1.745 g cm⁻³. The furoxanyl functionalized cation in compound **7** is nearly coplanar supported by torsion angles (C2-N5-N6-C3, 167.70 (16)° and N7-C4-C3-N6, -6.9 (3°) (Figure 4a). There are abundant intermolecular and intramolecular hydrogen bonds (N–H···O) in compound **7** (Figure 4b). Figure 4c presents a spring shaped layer, which can be interpreted as two adjacent perchlorate anions serving as the connection point of the network. Then, the layers stack into a stratiform structure to form the 3D-cube packing system (Figure 4d). It is notably that abundant hydrogen bonds exist between layers which enhances the strength of crystal packing as well as the stability of explosive crystal.



Figure 5. a) The molecular structure of cocrystal **8/4**; b) the supramolecular interaction between dinitramide anion, compound **4** and energetic cation; c) the stair shaped unit cell contained in **8/4**; d) the 3D supramolecular structure of **8/4**. (Green lines represent hydrogen bonds; red ellipsoid indicates dinitramide anion; blue (yellow) column presents furoxanyl functionalized cation (compound **4**).)



Figure 6. a) The molecular structure of compound $10 \cdot H_2O$; b) the supramolecular interaction of 10; c) the sandwich shaped unit cell contained in 10; d) the 3D supramolecular structure of 10. (Green lines represent hydrogen bonds; blue ellipsoid indicates 10; red column presents water molecule.)

Cocrystal 8/4 (compound 8: compound 4, 1:1) crystallizes in the triclinic space group P-1 consists of two molecules per unit cell (Z = 2) and a calculated density of 1.630 g cm⁻³. All the nonhydrogen atoms in 8/4 are almost in a plane confirmed by the torsion angles (C9-C10-N17-N16, 178.7 (2)° and C10-N17-N16-C11, 171.2 (2)°). The molecular structure is shown in Figure 5, a stair shaped layer structure is constructed by supramolecular interaction between dinitramide anion, compound 4 and 3-(3'methvlfuroxanvl) methyleneamino-4-amino-1,2,4-triazolium cation. And then, the layers are stacked in a face-to-face mode to build the 3D supramolecular structure of cocrystal 8/4. The closed 3D-cube system is held by the inter- and intra-molecular hydrogen bonds between unit cells and layers (green lines in Figure 5b and 5d represent hydrogen bonds), which contributes to low sensitivity to impact and friction.

Compound **10**·H₂O belongs to the monoclinic space group $P2_1/c$ with four molecules per unit cell (Z = 4) and a crystal density of 1.593 g cm⁻³. This molecular structure is also planar confirmed by torsion angles (C2-C4-N3-N4, 179.7 (3)° and C4-N3-N4-C5, -178.0 (3)°) (Figure 6a). The sandwich shaped layer structure was stacked by two **10** molecules and a H₂O molecule due to hydrogen bonds (Figure 6b, 6c). Such layer units are repeated in an infinite stack, which classifies the whole crystal as having a sandwich stacking (Figure 6d). The 3D network of **10** is formed through hydrogen bonding of inter- and intra-molecular. It is notably that the sandwich-type stacking can protect the energy moieties in the interlayer and enhance the molecular stability when encountering external stimuli.¹³

Compound **11**·3H₂O crystallizes in monoclinic $P2_1/n$ space group with a density of 1.421 g cm⁻³, and consists of four molecules per unit cell (Z = 4).As shown in Figure 7, the planar structure is identified by torsion angles (C1-N5-N6-C2, 179.28 (15)° and N5-N6-C2-C3, 179.88 (14)°). The extensive hydrogen bonds between H₂O, ammonium and furoxanyl functionalized anion result in the face-to-face layer stacking. The 3D supramolecular structure of **11** is dominated by an infinite face-to-face arrangement to form a 3D-cube layer stacking (Figure 7d).

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Figure 7. a) The molecular structure of compound $11.3H_2O$; b) the supramolecular interaction of 11; c) the face-to-face layer structure of 11; d) the 3D supramolecular structure of 11. (Green lines represent hydrogen bonds; blue ellipsoid indicates 11; red (blue) pot presents water (ammonium) molecule.)

Moreover, the hydrogen bond and π - π stacking exist among layers and lead to the maximum external stimuli layers sustained.¹⁴

Based on these analyses of crystal structure, furoxanyl functionalized energetic materials own planar structure due to the special structural characteristic of furoxanylhydrazone except compound **5**. In this work, it is interesting to note that five packing styles present 3D-cube layer stacking because of the planar structure molecule, inter- and intramolecular interaction between molecules, unit cells, and layers. The 3D-cube layer stacking can effectively dissipate the external mechanical energy into intermolecular and interlayer slide, avoiding too big potential increases to decay molecules, which leads to high safety.¹⁵ Moreover, all these stacking types may contribute to further understanding and analysis of chemical and physical phenomena in energetic materials.

Physicochemical and energetic properties

To investigate whether 3D-cube layer stacking and formation of energetic salts could improve the properties of energetic materials, their thermal stability, mechanical sensitivities and







Figure 9. DSC plots of compound 10 and its energetic salts 11-13.

detonation performance were evaluated. The thermal stability of all synthesized compounds was obtained by differential scanning calorimetry (DSC) with a linear heating rate of 5 °C min-¹ under a nitrogen atmosphere. All the compounds own acceptable decomposition temperature ($T_{dec} > 160$ °C) due to the extensive hydrogen-bonding interaction. As shown in Figure 8, compound 4 starts to decompose at 208 °C, which is quite a bit higher than its energetic salts. Except for salt 8 (T_{dec} = 175 °C), all other salts of compound 4 decomposed above 190 °C. Interestingly, the decomposition temperature of ammonium salt (11, T_{dec} = 160 °C), hydrazinum salt (12, T_{dec} = 165 °C) and hydroxylammonium salt (13, T_{dec} = 186 °C) are slightly lower than that of neutral compound **10** (T_{dec} = 191 °C) (Figure 9). And the decomposition temperature of cocrystal 8/4 is 189 °C (DSC plot of 8/4 was showed in Supporting Information, Figure S19). The impact sensitivity (IS) and friction sensitivity (FS) were determined using the standard BAM fall hammer and BAM friction tester, respectively.¹⁶ As given in Table 1, all of those compounds in anhydrous powder were very insensitive with low impact sensitivity (> 24 J) and low friction sensitivity (> 280 N). Recently, the relationship between crystal stacking and sensitivity has been widely concerned. External mechanical stimuli on energetic material can lead to a certain degree of shape change of energetic material to store mechanical energy. Hot spots are formed once this energy exceed the limit of the energetic material stored, then decomposition will be activated and trigger final detonation.¹⁷ As known, the stacking modesensitivity relationships of common 2D-plane stackings have been studied through quantum chemical and empirical



Figure 10. Green arrows showing sliding allowed; x and z represent the sliding along right/left and front/back.

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potential calculations. And steric hindrance caused by interlayer sliding is usually thought to be a crucial factor in impact sensitivity.18 However, the stacking mode-sensitivity relationships of 3D-cube layer stacking have rarely been reported. As shown in Figure 10, the aforementioned 3D-cube layer stacking will cause the two-steps slide. First, the sliding is limited to intralayer of 2D plane, which have been reported according to the literature.^{18c} Then, the slide occurs along the layer plane both in front/back and right/left direction, resulting in low sensitivity (4, 6-13, IS > 24 J; FS > 280 N). It is obvious that 3D-cube layer stacking possesses much more sliding orientation relative to 2D-plane stacking.

To better understand the structure-property relationship, twodimensional (2D) fingerprint and Hirshfeld surfaces were employed to analyse the weak interactions and hydrogen bonds of furoxanylhydrazone derivatives. Generally, the sensitivity can be demonstrated by the shape of Hirshfeld surfaces as it represents conjugated molecular structure. Furthermore, the red and blue regions on the Hirshfeld surfaces represent high and low close contact populations, respectively.¹⁹ The molecules of 7 and 8 present an approximately planar structure and a plate shape, and most of the red dots (intermolecular interactions) are located on the surface edges (Fig 11a cf. Fig 11b). O...H and N...H are close contacts, and a pair of spikes at the bottom left of Figure 11c, 11d are the dominant interactions in the 2D fingerprint plots of both 7 and 8, indicating the hydrogen bonds between adjacent molecules and layers in the 3D-cube system. There are many hydrogen-bonding interactions (O...H and N...H contacts, 62.0% for 7 and 57.2% for 8) and π - π interactions exist in 7 and 8 (C...N and N...O contacts, 13.1% for 7 and 10.4% for 8).

Remarkably, the formation of the nitrogen-rich salts (11-13) leads to a significant improvement in mechanical sensitivity compared with that of neutral compound 10. In Figure 12, compound 11 exhibits a more planar shape and red dots (intermolecular interactions) on the surface edges than 10 (Fig 12a cf. Fig 12b). Moreover, these interactions can also be demonstrated by 2D fingerprint plot (Figure 12c, 12d). Compound 11 possesses more O...H and N...H interactions (about 59.3%) than that in 10 (about 50.7%), which indicates stronger hydrogen bonds in 11 results in more stable mechanical stability. C...N and N...O possess 15.9% of total interactions for 10 and 8% for 11 (Figure 12e, 12f), suggesting



Figure 11. Hirshfeld surfaces (a and b), fingerprint plots (c and d) and individual atomic contacts percentage contribution to the Hirshfeld surface (e and f) of 7 and 8, respectively.



Figure 12. Hirshfeld surfaces (a and b), fingerprint plots (c and d) and individual atomic contacts percentage contribution to the Hirshfeld surface (e and f) of **10** and **11**, respectively.

that $\pi-\pi$ interactions exist in both **10** and **11**. In a word, $\pi-\pi$ interactions and multi hydrogen-bonding interactions as well as the 3D-cube packing contribute to the insensitivity of energetic salts.

To further investigate the interactions among target compounds, the non-covalent interaction (NCI) plots of compounds 7, 8, 10 and 11 were performed to analyse the real spatial structure based on electron density.²⁰ As shown in Figure 13, the π - π interactions were abundant in these compounds, which could be easily observed as larger green isosurfaces. Extensive $\pi - \pi$ interactions observed in target compounds result in the low sensitivity of those compounds.

All compounds own positive heats of formation in the rage of 565.9 kJ mol⁻¹ to 1290.1 kJ mol⁻¹ (1.74 kJ g⁻¹ to 3.84 kJ g⁻¹). Based on their heats of formation and measured densities at 298 K, the detonation properties including detonation velocity and pressure were calculated with EXPLO5 (version 6.02²¹). As shown in Table 1, the detonation velocities and pressures are in range from 7058 m s⁻¹ to 8332 m s⁻¹ and 19.9 GPa to 28.5 GPa, respectively. All compounds exhibit higher detonation velocity and detonation pressure than TNT (D = 6881 m s^{-1} , P = 19.5 GPa).

Experimental

Caution: Although we experienced no difficulties in handling these energetic materials, small scale and best safety practices (leather gloves, face shield) are strongly encouraged. All chemical reagents, solvents were obtained by purchase and were used as supplied without further purification.



Figure 13. NCI plots of gradient isosurfaces for 7 (a), 8 (b), 10 (c), 11 (d).

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Table 1. Energetic properties of the title compounds.

Compound	T _d a [°C]	$\Delta_{\rm f} { m H}^{ m b}[k] mol^{-1}/kJ g^{-1}]$	D ^c [m s ⁻¹]	P ^d [GPa]	d ^e [g cm ⁻³]	IS ^f [J]	FS ^g [N]
4	208	686.3/3.06	7058	19.9	1.61	>40	360
6	190	602.4/2.09	7614	24.1	1.62	28	336
7	196	565.9/1.74	8213	28.5	1.75	25	280
8	175	965.3/2.91	8110	24.8	1.64	24	280
9	195	949.4/2.80	8145	27.6	1.63	27	324
10	191	760.2/3.62	7991	23.5	1.60	35	330
11	160	796.6/3.51	8040	23.0	1.61	>40	>360
12	165	930.9/3.84	8270	24.5	1.62	37	360
13	186	856.1/3.54	8332	25.9	1.65	36	336
TNT ^h	295	-67.3/-0.30	6881	19.5	1.65	15	353

[a] Thermal decomposition temperature (onset) under nitrogen (determined by the DSC exothermal peak, 5 °C min⁻¹). [b] Heat of formation. [c] Detonation velocity. [d] Detonation pressure. [e] Density determined by gas pycnometer at 25 °C. [f] Impact sensitivity (BAM method). [g] Friction sensitivity (BAM method). [h] Ref.22

Synthesis of 3-(3'-Methylfuroxanyl) methyleneamino-4amino-1,2,4-triazole (4)

A solution of amino-3-hydrazino-1,2,4-triazole (5.0 mmol, 0.57 g) and 3-methyl-4-furoxancarbaldehyde (5.0 mmol, 0.64 g) in 20 ml ethanol, a catalytic amount of hydrochloric acid was added and stirred for 12 h at 60 °C. The reaction mixture was cooled to 0 °C and the white precipitate was formed. Then the precipitated solid was filtered off, washed with cold ethanol and dried in vacuo to afford 1.02 g of 1 as a white powder in a yield of 91%. ¹H NMR (500 MHz, DMSO-d₆): δ (ppm) 8.33 (s, 1H), 8.17 (s, 1H), 6.32 (b, 1H), 5.85 (b, 2H), 2.38 (s, 3H). ¹³C NMR (125 MHz, DMSO-d₆): δ (ppm) 161.2, 155.1, 140. 8, 125.8, 112.0, 9.5. IR (KBr): 3244.91, 2646.85, 1686.73, 1599.82, 1459.39, 1358.60, 1114.58, 993.92, 974.06, 843.52, 816.87, 783.17, 692.04, 644.68 cm⁻¹. C, H, N analysis (%): C₆H₉N₈O₂ (224.08), calculated result: C 32.15, H 3.60, N 49.98; found: C 32.28, H 3.46, N 49.33. Synthesis of 6. A suspension of 4 (5.0 mmol, 1.12 g) in deionized water (15 ml) and nitric acid (5.5 mmol) were mixed in portions. Then the mixture was stirred and then filtered, washed with water and dried in vacuo. 1.19 g of 6 was obtained as a yellow solid in a yield of 83%. ¹H NMR (500 MHz, DMSO-d₆): δ (ppm) 9.68 (s, 1H), 8.92 (s, 1H), 8.37 (s, 2H), 2.40 (s, 3H). ¹³C NMR (125 MHz, DMSO-d₆): δ (ppm) 155.9, 154.9, 150.7, 142.7, 111.8, 11.9. IR (KBr): 3245.75, 3151.45, 2778.65, 2647.03, 1686.24, 1612.26, 1598.29, 1459.79, 1114.85, 994.28, 843.45, 693.44 cm⁻¹. C, H, N analysis (%): C₆H₉N₉O₅ (286.07), calculated result: C 25.18, H 2.82, N 44.05; found: C 25.03, H 2. 71, N 44.38.

Synthesis of 7. A suspension of 4 (5.0 mmol, 1.12 g) in deionized water (15 ml) and perchloric acid (70 wt%, 5.0 mmol) were

mixed in portions. The mixture became clear immediately, then the solution was stirred for another 0.5 h and filtered. The filtrate was left for crystallization at room temperature as a colorless crystalline solid (7), yield, 1.45g, 90%. ¹H NMR (500 MHz, DMSO-d₆): δ (ppm) 8.81 (s, 1H), 8.59 (s, 1H), 6.45 (b, 2H), 2.40 (s, 3H). ¹³C NMR (125 MHz, DMSO-d₆): δ (ppm) 153.3, 148.9, 143.2, 137.9, 111.7, 9.2. IR (KBr): 3363.39, 3099.21, 2706.74, 1693.81, 1592.69, 1461.57, 1087.62, 1063.59, 1036.98, 930.54, 853.10, 776.05, 618.68 cm⁻¹. C, H, N analysis (%): C₆H₉ClN₈O₆ (323.03), calculated result: C 22.27, H 2.49, N 34.62; found: C 22.54, H 2.17, N 34.03.

General procedures for preparation of energetic salts 8-9.

A suspension of **4** (5.0 mmol, 1.12 g) in deionized water (15 ml) was stirred at ambient temperature while an energetic acid was added. The reaction mixture was stirred for another 1 h at 60-70 °C. Then, the precipitate for **8** and **9** was filtered and dried in air.

Synthesis of 8. Ammonium dinitramide (5.0 mmol, 0.62 g) and 1ml 1M hydrochloric acid were added to suspension, 1.47g of **8** was obtained as a white solid in a yield of 89%. ¹H NMR (500 MHz, DMSO-d₆): δ (ppm) 8.51 (s, 1H), 8.42 (s, 1H), 6.20 (b, 2H), 2.39 (s, 3H). ¹³C NMR (125 MHz, DMSO-d₆): δ (ppm) 157.0, 155.2, 153.3, 137.2, 110.2, 9.2. IR (KBr): 3334.36, 3120.50, 1690.48, 1582.70, 1501.58, 1459.66, 1170.54, 1109.42, 1002.10, 851.44, 663.82 cm⁻¹. C, H, N analysis (%): C₆H₈N₁₂O₆ (337.21), calculated result: C 21.82, H 2.44, N 46.66; found: C 21.53, H 2.17, N 46.88. **Synthesis of 9.** 5-nitrotetrazole (5.0 mmol, 0.58 g) was added to suspension, 1.49 g of **9** was obtained as a yellow solid in a yield of 88%. ¹H NMR (500 MHz, DMSO-d₆): δ (ppm) 12.79 (s, 1H),

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9.78 (b, 1H), 8.81 (s, 1H), 8.36 (s, 1H), 2.40 (s, 3H). ¹³C NMR (125 MHz, DMSO-d₆): δ (ppm) 162.3, 156.7, 154.5, 153.2, 145.0, 107.1, 9.2. IR (KBr): 3367.23, 1606.80, 1565.05, 1491.75, 1456.22, 1375.15, 1174.54, 1060.06, 1022.16, 821.87, 636.21 cm⁻¹. C, H, N analysis (%): C₇H₉N₁₃O₄ (338.08), calculated result: C 24.86, H 2.38, N 53.84; found: C 24.55, H 2.17, N 54.21.

Synthesis of 10. A solution of 5-hydrazino-tetrazole (5.0 mmol, 0.50 g) and 3-methyl-4-furoxancarbaldehyde (5.0 mmol, 0.64 g) in 20 ml ethanol, a catalytic amount of hydrochloric acid was added and stirred for 12 h at 60 °C. The reaction mixture was cooled to 0 °C and the white precipitate was formed. Then the precipitated solid was filtered off, washed with cold ethanol and dried in vacuo to afford 0.98 g of 10 as a white powder in a yield of 91%. ¹H NMR (500 MHz, DMSO-d₆): δ (ppm) 15.68 (b, 1H), 12.48 (s, 1H), 8.08 (s, 1H), 2.39 (s, 3H). ¹³C NMR (125 MHz, DMSO-d₆): δ (ppm) 154.8, 153.6, 131.9, 111.6, 9.3. IR (KBr): 2979.00, 2843.10, 1634.53, 1598.18, 1533.51, 1458.11, 1376.73, 1155.11, 1043.36, 848.99 cm⁻¹. C, H, N analysis (%): C₅H₆N₈O₂ (210.06), calculated result: C 28.58, H 2.88, N 53.32; found: C 28.64, H 2.37, N 53.77.

General procedures for the preparation of energetic salts 11-13.

Ammonia (25 wt% in water, 5.0 mmol), hydrazine hydrate (80 wt% in water, 5.0 mmol) or hydroxylamine (50 wt% in water, 5.0 mmol) was added to a solution of 12 (5.0 mmol, 1.05 g) in methanol (5 ml). After stirring for 2h at ambient temperature, the precipitate was collected by filtration and washed with MeOH.

11 (White solid), 0.77 g, in a 65% yield. ¹H NMR (500 MHz, DMSO-d₆): δ (ppm) 8.54 (s, 1H), 3.85 (b, 2H), 2.36 (s, 3H). ¹³C NMR (125 MHz, DMSO-d₆): δ (ppm) 160.4, 154.9, 126.5, 111.8, 9.4. IR (KBr): 2948.71, 2873.79, 1600.62, 1497.03, 1458.21, 1417.63, 1377.53, 1315.01, 1167.15, 1126.71, 1013.91, 912.35, 844.59, 652.51 cm⁻¹. C, H, N analysis (%): C₅H₉N₉O₂ (227.09), calculated result: C 26.43, H 3.99, N 55.49; found: C 26.03, H 4.12, N 55.16.

12 (White solid), 0.82 g, in a 68% yield. ¹H NMR (500 MHz, DMSO-d₆): δ (ppm) 8.64 (s, 1H), 7.67 (b, 1H), 2.36 (s, 3H). ¹³C NMR (125 MHz, DMSO-d₆): δ (ppm) 155.4, 124.4, 111.8, 99.5, 9.4. IR (KBr): 3333.91, 3207.81, 2875.64, 2466.28, 1607.80, 1508.74, 1382.40, 1134.25, 949.15, 651.83 cm⁻¹. C, H, N analysis (%): C₅H₁₀N₁₀O₂ (242.10), calculated result: C 24.80, H 4.16, N 57.83; found: C 24.53, H 4.55, N 57.19.

13 (White solid), 0.87 g, in a 71% yield. ¹H NMR (500 MHz, DMSO-d₆): δ (ppm) 8.68 (s, 1H), 8.44 (s, 1H), 7.07 (b, 9H), 2.35 (s, 3H). ¹³C NMR (125 MHz, DMSO-d₆): δ (ppm) 160.4, 154.9, 126.5, 111.8, 9.4. IR (KBr): 3029.23, 2881.47, 2682.16, 1581.63, 1490.34, 1452.35, 1376.14, 1163.03, 893.65, 845.44, 653.00 cm⁻ ¹. C, H, N analysis (%): $C_5H_9N_9O_3$ (243.08), calculated result: C 24.69, H 3.73, N 51.84; found: C 24.38, H 3.55, N 51.99.

Conclusions

56 A new series of energetic salts and neutral compounds containing furoxanylhydrazone with a 3D-cube layer stacking 58 were designed and synthesized based on 3-methyl-4-59 furoxancarbaldehyde. All target compounds were well 60

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characterized by NMR spectra, IR spectroscopy and differential scanning calorimetry (DSC). The structures of compounds 5,47, 8, 10 and 11 were further determined by single crystal X-ray diffraction. All ionic compounds 6-9 and 11-13 showed a positive influence on the detonation performance, such as detonation velocities and pressures relative to their corresponding neutral compounds. Compared with 10, the anion salts (11-13) exhibit increases of exceeding 5 J and 6 N in impact and friction sensitivity due to more hydrogen bonds in 3D-cube layer stacking system, respectively. Furthermore, the combination of experimental results, theoretical calculations and crystal structure analysis was employed to better understand the structure-property relationship. All these desire results demonstrate that a 3D-cube layer stacking structure features can improve impact, and friction stability of energetic material. And these different crystal stacking forms would contribute to further understanding of chemical and physical phenomena in energetic materials. Therefore, the combination of energetic salts and crystal engineering could be a promising strategy for design of energetic materials.

Conflicts of interest

There are no conflicts to declare.

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Combining the benefits of furoxan framework with various energetic functionalities

We provide a new series of energetic salts and neutral compounds containing furoxanylhydrazone with a 3D-cube layer stacking.