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Qian Wang, Yanli Shao, and Ming Lu

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$C_8N_{12}O_8$: A Promising Insensitive High-energy-density Material

*Qian Wang, Yanli Shao, Ming Lu**

School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094, China.

ABSTRACT: It is desirable to consider crystal engineering in the research of energetic materials. Herein we report the synthesis, structure and energetic properties of a promising explosive, 1,2-bis(3-(4-nitro-1,2,5-oxadiazol-3-yl)-1,2,4-oxadiazol-5-yl)diazene (**5**). Based on the single-crystal diffraction data, **5** is nearly coplanar and features face-to-face and wavelike crystal stackings, thereby exhibiting an excellent density of 1.92 g cm^{-3}. Meanwhile, the enthalpy of **5** is as high as 962.4 kJ/mol owing to its extensive high-energy N-N, C-N and N-O bonds. Compound **5** featuring such a characteristic demonstrates high thermal stability (T_d = 256 °C), good mechanical sensitivity (IS: 18 J, FS: 220 N), and superior detonation performance (D: 9240 m s^{-1}, P: 37.5 GPa). The combination of advanced performance and desirable security make it a potential replacement for the commonly used explosives RDX and HMX.

Introduction

In the last few decades, accompanied by the extensive demand in the military and civilian fields, the development of high-energy-density materials (HEDMs) has been of broad interest.[1-2]

Preparing safer, cheaper, greener and more powerful energetic materials is a key target for many synthetic and theoretical researchers.[3-4] However, these interrelated requirements are often contradictory to each other, especially energy and safety. Therefore, some suitable strategies are necessary to guide the investigation of new HEDMs.

In the design of modern energetic materials, one of the most acceptable strategies is the crystal engineering. Abundant studies have illustrated that microcosmic structures are closely related to macrocosmic properties in the field of energetic materials.[5-6] In general, there are four types of crystal packing: face-to-face, wavelike, crossing, and mixing (Figure 1).[7] Thereinto, face-to-face and wavelike crystal stackings are the most satisfactory types due to their high crystal densities and good molecular stabilities. For example, 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) with the face-to-face style shows a high density (1.93 g cm^{-3}) and is very insensitive (IS: 50 J, FS: 360 N).[8] Another example, 1,1-diamino-2,2-dinitroethene (FOX-7) has the wavelike stacking, thereby exhibiting an excellent mechanical sensitivity (IS: 60 J, FS: >360 N).[9-10] Unfortunately, TATB and FOX-7 do not have favorable detonation performance due to their negative heats of formation. Their enthalpies are as low as -139.3 kJ/mol and -53.1 kJ/mol, respectively. Thus, their detonation velocities (TATB: 8144 m s^{-1}; FOX-7: 8930 m s^{-1}) are less than the secondary explosive HMX (9144 m s^{-1}). This greatly limits their practical applications.

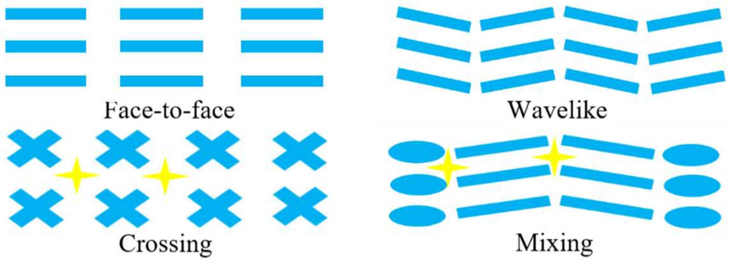
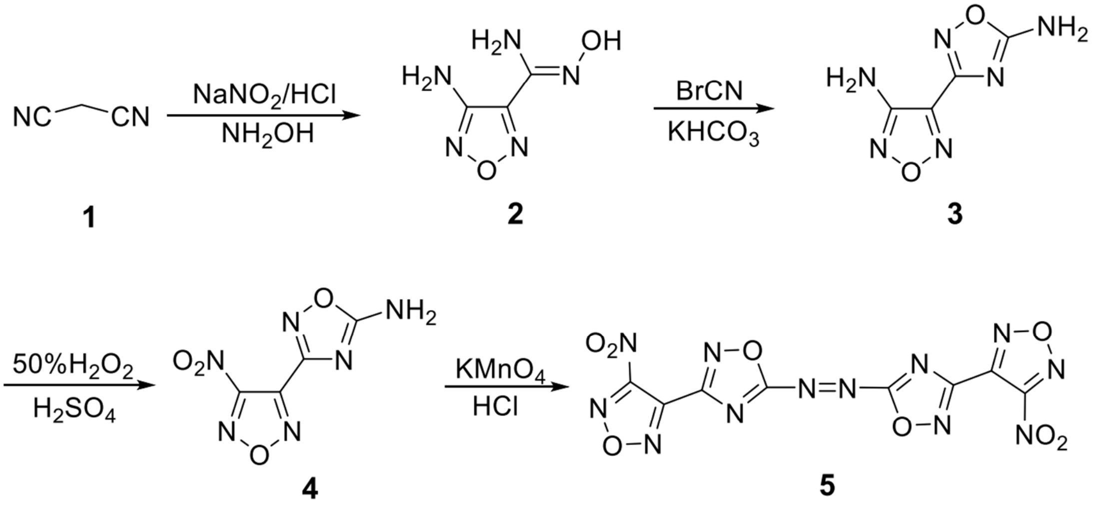


Figure 1. Four types of crystal packing in the field of energetic materials.

To avoid above drawback, an effective strategy is to introduce nitrogen-rich backbones (such as, triazole, tetrazole, and oxadiazole) into the design of HEDMs owing to their high heats of formation.[11-13] With our continuing interest, herein we report the synthesis, structure and energetic performance of 1,2-bis(3-(4-nitro-1,2,5-oxadiazol-3-yl)-1,2,4-oxadiazol-5-yl)diazene (**5**), which shows the face-to-face crystal stacking and a relatively high enthalpy. Furthermore, quantum chemical calculations are employed to better understand the intrinsic structure-property relationship.



Scheme 1. The synthetic pathway of **5**.

Synthesis

The synthetic pathway is shown in Scheme 1. Compounds **1-3** were synthesized according to the literature.[14] Bicyclic compound **4** was obtained by treating **3** with 50% H_2O_2, 98% H_2SO_4 and Na_2WO_4 in high yield (about 85%) (different from the reported method in Ref. 14). Through a direct oxidative coupling reaction of **4**, the target molecule **5** was formed over a period of 4 h at the ambient temperature. Compounds **4** and **5** were well characterized by infrared (IR) and multinuclear nuclear magnetic resonance (NMR) spectroscopy, elemental analysis, differential scanning calorimetry (DSC) and single-crystal X-ray diffraction analysis.

Notably, starting from commercially available material malononitrile, the synthesis process could be divided into four steps. All these reagents used are cheap and the overall yield is as high as 40.33%. The preparation conditions (reaction temperature: -5 - 100 °C and reaction pressure: ambient pressure) are mild. Additionally, the target compound **5** is nonhygroscopic and exhibits a very poor solubility in water. These positive results make it competitive in practical applications.

Structure discussions

In general, the planarity of a molecule is closely related to its crystal packing.[5-7] Compound **4** crystallizes in the monoclinic space *P* 2_1/c with a low density of 1.738 g cm^{-3} at 296K (different from the Ref. 14 (150 K)) (Figure 2). The two oxadiazole rings of **4** are non-coplanar, confirming by the dihedral angle of N4-C3-C1-N2 (-134.85°). Thus, the crystal packing of **4** is not face-to-face or wavelike.

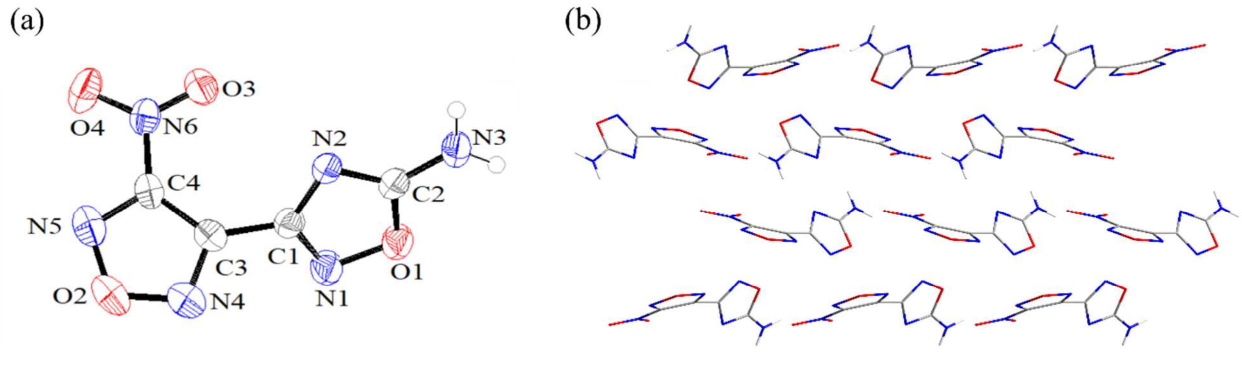


Figure 2. (a) ORTEP representation of molecular structure of **4**. Displacement ellipsoids are shown at 50% probability level. (b) Crystal packing of **4** viewing down the unit cell axis a.

Crystal **5** suitable for single crystal X-ray diffraction was obtained by slow evaporation from dimethyl sulfoxide (DMSO) at room temperature. It crystallizes in the orthorhombic space group *P* bca with a relatively high density of 1.916 g cm^{-3} at 296K (Figure 3). In comparison to **4**, compound **5** is more coplanar, which is evident from the dihedral angles of N3-O2-C3-N6 (179.61°) and N2-C2-C4-N3 (165.72°). The azo double bond of **5** is 1.248 Å, in accord with the general bond distance for N=N (1.20 Å).[15]

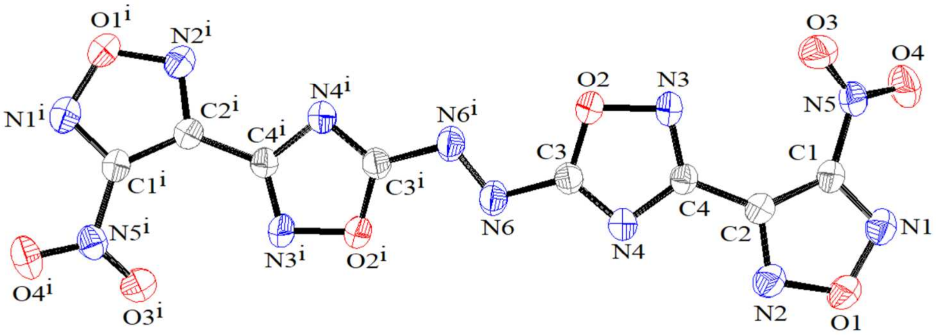


Figure 3. ORTEP representation of molecular structure of **5**. Displacement ellipsoids are shown at 50% probability level.

Further, the crystal packing diagrams of **5** observing from the a-c axes are shown in Figure 4, which reveal the structural details from three directions. Along the b and c axes, the tetracyclic compound **5** features a basic face-to-face stacking. Recent studies indicate that face-to-face stacking often possesses an excellent mechanical performance owing to free interlayer sliding, such as TATB.[16-17] Regarding the a-axis, **5** is wavelike π-stacked which is like the low-sensitivity explosive FOX-7. With such an outstanding crystal performance, it is not surprising that **5** demonstrates desirable energetic properties, such as high density, good impact and friction sensitivities (ρ = 1.92 g cm^{-3}, IS = 18 J, FS = 220 N), which is superior to the benchmark secondary explosive HMX (ρ = 1.91 g cm^{-3}, IS = 7 J, FS = 120 N).

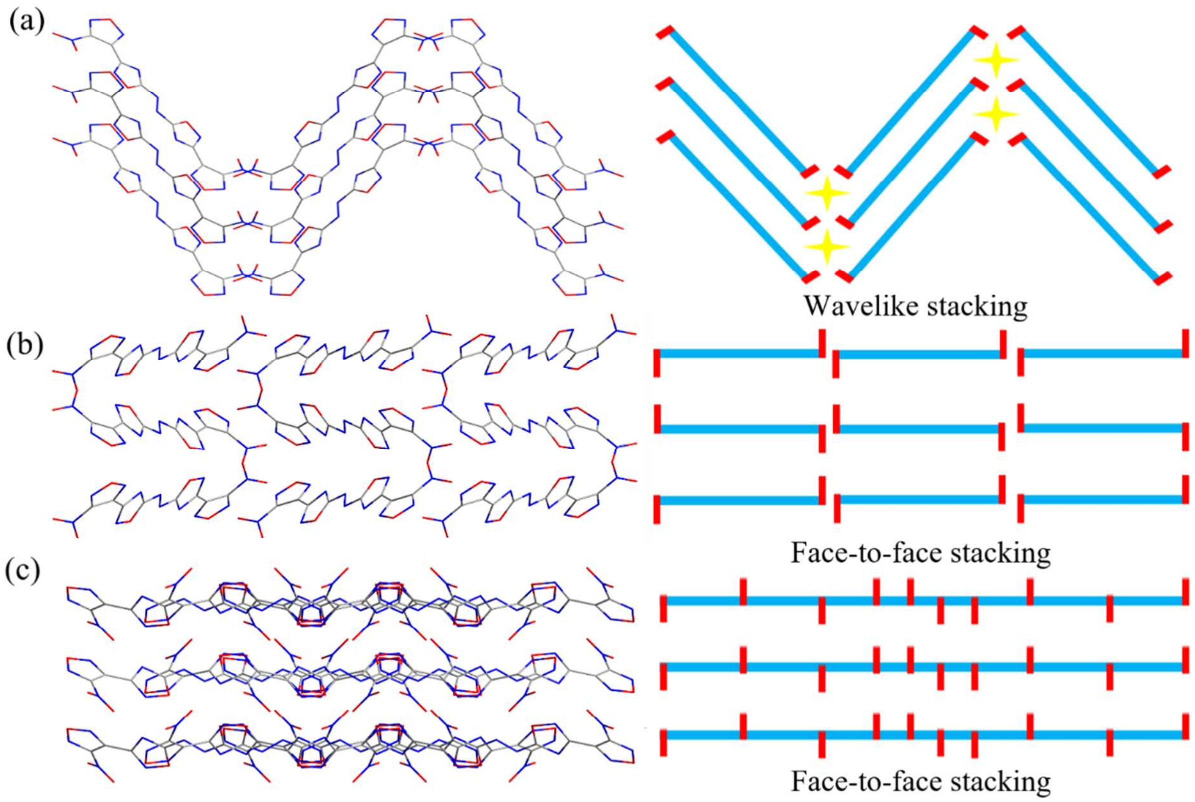


Figure 4. (a) Crystal packing of **5** viewing down a-axis and its simplified drawing. (b) Crystal packing of **5** viewing down b-axis and its simplified drawing. (c) Crystal packing of **5** viewing down c-axis and its simplified drawing (Blue line: oxadiazole rings; Red line: NO_2; Yellow star: hot spot).

Energetic properties

In addition to crystal analysis, its physical properties (such as thermal stability, density, and detonation performance) were also measured (Table 1). The thermal stability is an important physical factor of safety level. The melt point and decomposition temperature of **5** were confirmed by DSC at a scan rate of 5 °C min^{-1}. Compound **5** melts at 157 °C and has a high decomposition point at 256 °C, which is higher than RDX (204 °C).

Table 1. Physiochemical properties of **4-5**, HMX, RDX, TNT, FOX-7, and TATB.

Compound	**4**	**5**	RDX[k]	HMX[k]	TNT[l]	FOX-7[l]	TATB[l]
T_m[a] [°C]	–	157	–	–	81	–	–
T_d[b] [°C]	89	256	204	280	295	274	324
ρ[c] [g cm^{-3}]	1.74	1.92	1.80	1.91	1.65	1.89	1.93
N+O[d] [%]	74.7	75.5	81.1	81.1	60.8	81.1	69.8
OB_{co}[e] [%]	-8.1	0	0	0	-18.6	0	-18.6
ΔH_f[f] [kJ mol^{-1}]	269.8	962.4	70.3	70.4	-59.4	-53.1	-139.3
D[g] [m s^{-1}]	8155	9240	8795	9144	7303	8930	8144
P[h] [GPa]	27.3	37.5	34.9	39.2	21.3	34.0	31.2
IS[i] [J]	35	18	7	7	15	60	50
FS[j] [N]	360	220	120	120	>353	>360	360

[a] Melting point. [b] Thermal decomposition temperature (onset) under nitrogen (determined by the DSC exothermal peak, 5 °C min^{-1}). [c] X-ray densities at 296K and the corresponding RT Values using the equation ($\rho_{298k}=\rho_T/(1+a_v(298-T_0))$; $a_v=1.5\times10^{-4}$ K^{-1}). [d] Content of nitrogen and oxygen. [e] Oxygen balance [%] Based on CO for CaHbNcOd: OB[%]=1600×(d-a-b/2)/M_W. [f] Calculated molar enthalpy of formation in solid state. [g] Detonation velocity. [h] Detonation pressure. [i] Impact sensitivity. [j] Friction sensitivity. [k] Ref. [3]. [l] Ref. [10].

Interestingly, nitro-based compound **5** does not have intra- and intermolecular hydrogen bonds, however, it still has such a remarkable thermal behavior. The single crystal data indicates two possible explanations, trigger bond dissociation enthalpy (TBDE) and noncovalent interaction analysis (NCI).[18-19] The TBDE represents the lowest energy to break the first chemical bond during thermal decomposition, in this case, calculations show that the C-nitro bond is the weakest. The TBDE of **5** is as high as 295.6 kJ mol^{-1}, which significantly outperforms the powerful explosive RDX (152.8 kJ mol^{-1}). Meanwhile, the NCI plots were evaluated by using Multiwfn[20] (Figure 5). Compound **5** shows edge-to-face π-π stackings between two independent molecules, thereby increasing the thermostability and the density.

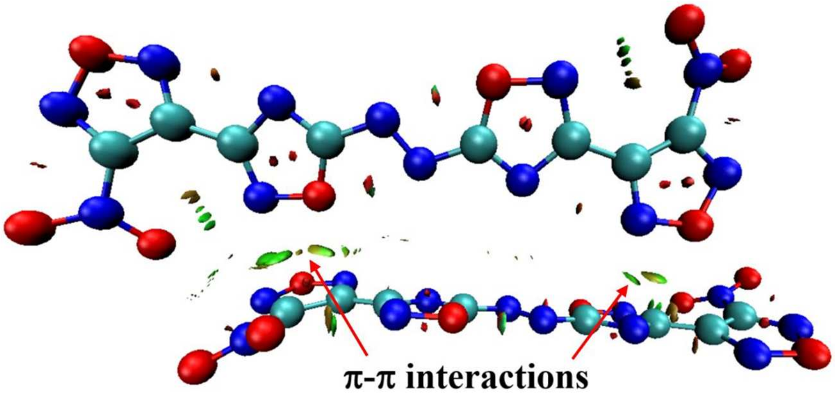


Figure 5. Noncovalent interaction analysis, including hydrogen bonds (no signal in this case) and π-π interactions for **5** (blue, strong attraction; green, weak interaction; and red, strong repulsion).

Density is an important physical factor of energy level. The density of **5** was measured by using single crystal analysis at 296K and converted into the corresponding RT values using the equation ($\rho_{298k}=\rho_T/(1+a_v(298-T_0))$; $a_v=1.5\times10^{-4}$ K^{-1}).[21] Tetracyclic compound **5** shows a remarkable density at 1.92 g cm^{-3} (a measured density of 1.9151 g cm^{-3} determined by a gas pycnometer), which is higher than that of HMX and FOX-7 (1.91 cm^{-3} and 1.89 cm^{-3}, respectively). This value is due to its prominent crystal packing (Figure 4), extensive noncovalent interactions between molecules (Figure 5) and high packing coefficient. Its packing coefficient was evaluated by PLATON and is up to 74.3%, which is slightly lower than TATB (78.1%).

Another physical factor of energy level is heat of formation. Generally, higher heats of formation always result in better detonation performance. The enthalpy of **5** was calculated based on compatible isodesmic reactions by using Gaussian09[22] program (more details in the Supporting information). As anticipated, due to the existence of extensive high-energy N-N, C-N and N-O bonds, **5** exhibits a high positive enthalpy at 962.4 kJ/mol (a calculated enthalpy of 903.86 kJ/mol determined by the bomb calorimetry), greatly superior to FOX-7 (-53.1 kJ/mol) and TATB (-139.3 kJ/mol). With the enthalpy and calculated density in hand, the detonation performance was determined by using EXPLO5.[23] As for detonation velocity, the value of **5** (9240 m s^{-1}) remarkably exceeds HMX (9144 m s^{-1}) and FOX-7 (8930 m s^{-1}). In terms of detonation pressure, the value of **5** is observed at 37.5 GPa, which is slightly lower than HMX (39.2 GPa) while transcends RDX (34.9 GPa) and FOX-7 (34.0 GPa). Furthermore, on the basic carbon monoxide (CO), **5** exhibits an oxygen balance value of 0%, equal to HMX (0%) and FOX-7 (0%).

The mechanical sensitivity of **5** was measured to evaluate its safety to external stimuli.[24] The IS and FS of **5** are estimated to be 18 J and of 220 N, respectively. These values are much higher than those of HMX (IS: 7 J, FS: 120 N) and comparable to TNT (IS: 15 J, FS: >353 N), which further suggests its promising application potential.

To obtain a better understanding of good mechanical properties, the two-dimensional (2D)-fingerprint of crystal and the associated Hirshfeld surfaces were employed to show the intermolecular interactions.[25] Generally, block-shaped surfaces contributes more efficiently to face-to-face π–π stacking and lead to lower IS. These noncovalent interactions are attributed by red spots on the Hirshfeld surfaces.[26] As for **5**, the molecule presents a nearly planar structure and a plate shape (Figure 6a). At the same time, most red dots locate on the surface edges. With respect to those red dots on the plate faces, they denote π–π stacking, such as C-N and O-C interactions (about 22.8%) (Figure 6b, 6c). The N-N interactions is about 20.7%, which demonstrates the weak interactions between molecules. Moreover, the ratio of N-O interactions is as high as 39.4%, which reflects in high percentage of interlayer contact, thereby improving the mechanical stability.

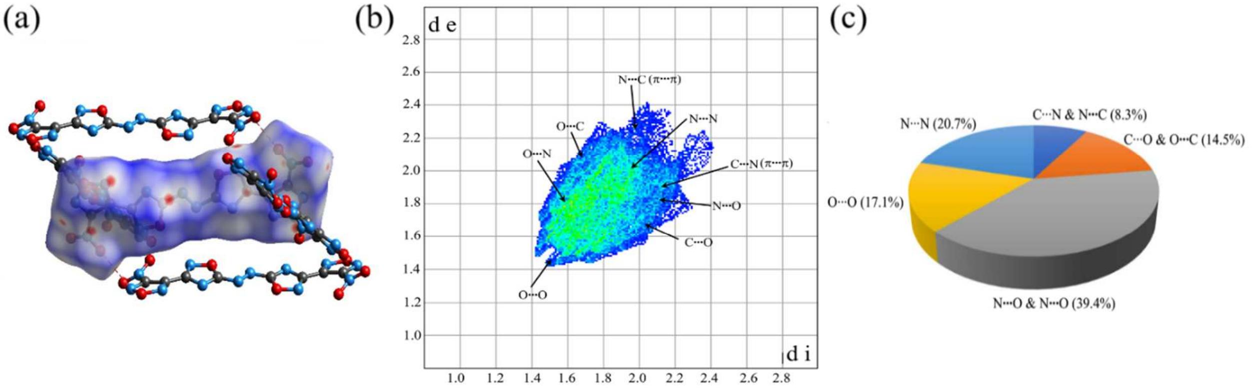


Figure 6. (a) Hirshfeld surfaces calculation of **5** (white, distance d equals the van der Waals distance; blue, d exceeds the van der Waals distance; red, d is less than van der Waals distance). (b) Two-dimensional fingerprint plots in crystal stacking for **5** as well as the associated Hirshfeld surfaces. (c) The individual atomic contact percentage contribution to the Hirshfeld surface.

Conclusion

In conclusion, a promising energetic compound featuring face-to-face and wavelike crystal stackings was prepared. TBDE, NCI analysis and the Hirshfeld surfaces analysis were studied to better understand its intrinsic structure-property relationship. Tetracyclic compound **5** exhibits excellent thermostability (T_d = 256 °C), desirable detonation performance (D: 9240 m s^{-1}, P: 37.5 GPa) and moderate mechanical sensitivity (IS: 18 J, FS: 220 N). Additionally, the preparation of

5 is within four steps from commercially available reagents in high overall yields. All these positive contributions highlight its potential application as a next-generation energetic material.

ASSOCIATED CONTENT

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AUTHOR INFORMATION

Corresponding Author

*Ming Lu, Email: luming@mail.njust.edu.cn.

Present Addresses

†If an author's address is different than the one given in the affiliation line, this information may be included here.

Author Contributions

Q. Wang and M. Lu designed the study. Q. Wang performed most of the reactions. Y. Shao synthesized part of the precursor. Q. Wang finished the DFT calculations. Q. Wang and Y. Shao prepared the manuscript.

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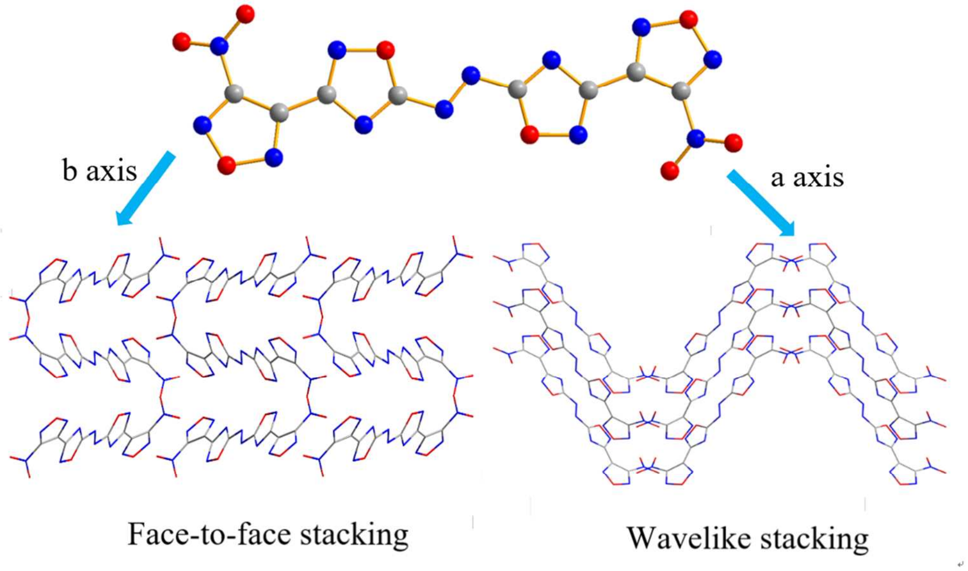

A promising energetic compound featuring face-to-face and wavelike crystal stackings was prepared. This compound exhibited high crystal density, excellent thermal stability, high detonation velocity, and good sensitivities, which makes it a potential insensitive high-energy-density Material.