

# Review on the Synthesis and Performance for 1,3,4-Oxadiazole-Based Energetic Materials

Yao Du,<sup>[a]</sup> Zhongkai Qu,<sup>[a]</sup> Huanchun Wang,<sup>\*,[a, b, c]</sup> Hu Cui,<sup>[a, c]</sup> and Xuanjun Wang<sup>[a, c]</sup>

**Abstract:** Energetic materials have been widely used in both military and civilian fields. The development of new high-energy materials with improved performance and enhanced stability is critical for promoting future military and space applications. Recently, researchers in the field of energetic materials have paid significant attention to oxadiazole-based energetic compounds, among which 1,3,4-oxadiazole demonstrates moderate energy levels and better stability, owing to the absence of readily cleaved N–O bonds compared with other oxadiazole isomers, such as 1,2,4-oxadiazole and 1,2,5-oxadiazole. Therefore, 1,3,4-oxadiazole is an exceptional explosophoric motif with an efficient compromise between energy and stability, and several outstanding energetic materials have been achieved

based on the combination of 1,3,4-oxadiazole units with various functional groups or rings, such as polynitrobenzene, furazan, pyrazole, and 1,3,4-oxadiazole itself. This review provides an overview of the development of 1,3,4-oxadiazole-based energetic materials during the past few years, outlines their synthesis and energetic performance, and contrasts them with other conventional energetic materials. Owing to the convenience of the synthetic routes and their excellent energetic properties, energetic materials based on the 1,3,4-oxadiazole skeleton may be considered as the next-generation of high-performance energetic materials specifically as heat-resistant explosives or insensitive explosives.

**Keywords:** Energetic materials · 1,3,4-Oxadiazole · Explosives · Thermal stability · Review

## 1 Introduction

As a significant material for the development of the economy and weapons industry, energetic materials used in both military and civilian fields have gained global interest over the past few decades [1–3]. However, traditional energetic compounds, such as trinitrotoluene (TNT) [4–6], hexogen (RDX), octogen (HMX) [7–9], and hexanitrohexaazaisowurtzitane (CL-20) [10–12], cannot meet the requirements of the rapidly developing military and space industry; furthermore, some of these compounds are still faced with several issues, such as high cost [13], high toxicity [14,15], and contamination [16]. Therefore, it is critical to developing new high-energy materials to promote both the development of the weapon industry and social progress. In general, the structure of energetic compounds is composed of the following two parts: an organic skeleton and the energetic groups. The skeleton, the most basic unit, mostly comprises aromatic hydrocarbons or cycloaliphatic amine scaffolds. However, these scaffolds derive their energy only from the oxidation of the carbon backbones, which limits the further increase of energy of these materials [17].


In the continuous search for excellent high-performing energetic materials, energetic materials with a high nitrogen content have been considered as good candidates owing to their high heat of formation, adequate stability, high density, high detonation performance, and advantageous

oxygen balance (OB) [18–20]. Among the heterocyclic skeletons used in energetic materials, potentially useful energetic materials can be demonstrated by nitrogen-rich heterocycles, such as pentazole [21,22], tetrazole [23,24], triazole [25,26], pyrazole [27,28] and oxadiazole [29,30], which release significant energy and nontoxic N<sub>2</sub> during detonation. Unfortunately, despite their high energy content, pentazoles have not been used in practice owing to their poor stability and high sensitivity towards external stimuli [31–33]. Owing to the inherent oxygen atoms in the oxadiazole rings compared to tetrazole, triazole, and pyrazole, the resulting energetic materials not only possess improved density but also demonstrate a better OB. Additionally, oxygen can contribute to a stronger hydrogen bond

[a] Y. Du, Z. Qu, H. Wang, H. Cui, X. Wang  
High-Tech Institute of Xi'an,  
Xi'an, Shaanxi, 710025, China  
\*e-mail: wang-hc12@tsinghua.org.cn

[b] H. Wang  
Shaanxi Engineering Laboratory for Advanced Energy Technology,  
School of Materials Science & Engineering,  
Shaanxi Normal University  
Xi'an, Shaanxi, 710119, China

[c] H. Wang, H. Cui, X. Wang  
Shaanxi Key Laboratory of Special Fuel Chemistry and Material,  
Xi'an, Shaanxi, 710025, China

 Supporting information for this article is available on the WWW under <https://doi.org/10.1002/prep.202000318>

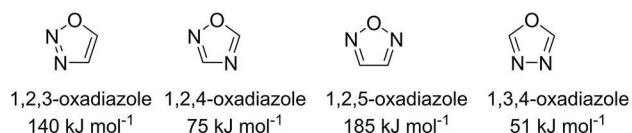
compared to that formed between nitrogen and hydrogen, which favours the closer packing of energetic molecules and leads to higher densities [34]. There are four types of oxadiazole scaffolds: 1,2,3-oxadiazole, 1,2,4-oxadiazole, 1,2,5-oxadiazole, and 1,3,4-oxadiazole (Scheme 1) [35], among which 1,2,5-oxadiazole (also known as furazan) and 1,2,4-oxadiazole have high positive heats of formation, thus are often prioritized in the oxadiazole family for the design of high energetic compounds. Several energetic materials originating from these two isomers have been reported [35–37], for example, the promising TNT substitute bis(1,2,4-oxadiazole)bis(methylene) dinitrate [38]. However, 1,2,3-oxadiazole is unstable and easily reverts to the diazo-ketone tautomer [39]; thus, few studies on it have been conducted. Although 1,3,4-oxadiazole possesses slightly lower energy than 1,2,4-oxadiazole and furazan, the distribution of heteroatoms is more uniform and the absence of readily cleaved N–O bonds in the ring provides better stability, which has allowed its use as an important component in energetic materials. Therefore, a review of the relevant studies regarding 1,3,4-oxadiazole-based energetic compounds can be beneficial to the design and synthesis of novel energetic materials and eventually promote social progress.

This review focuses on 1,3,4-oxadiazole-based energetic materials over the past few years. The related compounds include the following categories: (1) energetic monocyclic 1,3,4-oxadiazoles, (2) energetic alliance of 1,3,4-oxadiazoles and benzene rings, (3) energetic alliance of 1,3,4-oxadiazoles and heterocyclic rings, and (4) poly 1,3,4-oxadiazoles. The synthetic methods for these energetic compounds are summarized, and their physical and detonation properties, such as density ( $\rho$ ), heat of formation (HOF), detonation pressure ( $P$ ), detonation velocity ( $D$ ), sensitivity (IS and FS), and decomposition temperature ( $T_d$ ) are also generalized and compared with other classical energetic materials.

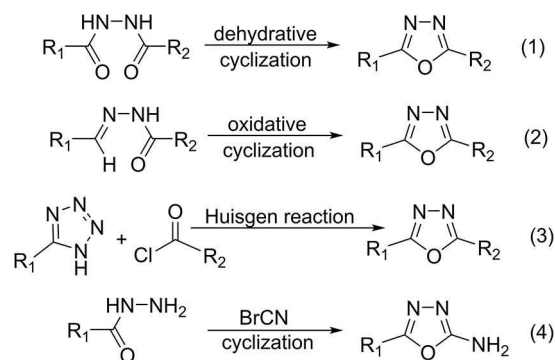
## 2 Synthesis and Energy Characteristics of Monocyclic 1,3,4-Oxadiazoles Based Compounds

### 2.1 Synthesis Principle of 1,3,4-Oxadiazole Ring

Traditionally, the 1,3,4-oxadiazole ring system can be synthesized via the following three routes (Scheme 2) [40]: (1)



**Scheme 1.** The structures and heats of formation for different oxadiazoles.



**Scheme 2.** Synthesis methods for 1,3,4-oxadiazoles.

dehydrative cyclization of 1,2-diacylhydrazines using harsh dehydration reagents [41], (2) oxidative cyclization of *N*-acylhydrazones with the assistance of various oxidizing agents or catalysts [42,43], and (3) the reaction of tetrazoles with electrophiles, also known as the Huisgen reaction [44,45]. Method 1 requires a large quantity of dehydrating agents, such as  $SOCl_2$ ,  $POCl_3$ , and concentrated sulfuric acid [46], while Method 2 needs metal catalysts along with oxidants. Method 3 has been less frequently used than methods 1 and 2, especially on a large scale, which requires careful handling owing to the relative instability and high energy of tetrazole [47]. For 1,3,4-oxadiazole-based energetic materials, oxadiazole heterocyclic scaffolds were generally synthesized using method 1, and the starting materials (2-amino-1,3,4-oxadiazoles) were obtained by the reaction of monohydrazide with cyanogen bromide (generally Scheme 2, Method 4) [48].

### 2.2 Energetic Monocyclic 1,3,4-Oxadiazoles

In contrast to 1,2,4-oxadiazole and 1,2,5-oxadiazole, which constitute several energetic materials through a single ring in combination with various explosophoric groups (e.g., amino, nitro, nitramine, and dinitromethyl functionalities), there are a limited number of energetic materials originating from monocyclic 1,3,4-oxadiazole. Zhang et al. [49] synthesized two zwitterionic energetic compounds (**4** and **6**) consisting of a *gem*-dinitromethyl functional group and an 5-amino-1,3,4-oxadiazole skeleton. Among them, the zwitterionic compound (5-iminio-4,5-dihydro-1,3,4-oxadiazol-2-yl)dinitromethanide (**4**) was synthesized using a four-step synthetic method using commercially available ethyl potassium malonate as the starting material (Scheme 3). Note that the 1,3,4-oxadiazole ring was not formed through the three conventional methods indicated in Scheme 2. Moreover, the amination of **4** with THA (O-tosylhydroxylamine) as an amination agent and the assistance of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) resulted in **6**. In addition to the zwitterionic energetic salts, two routine energetic

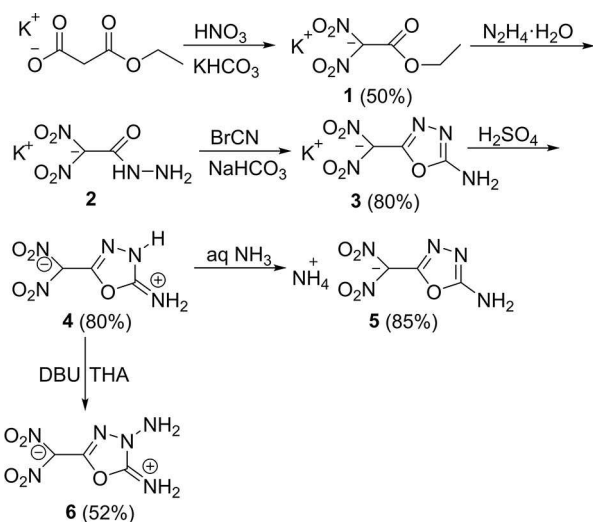
**Table 1.** Physical properties and detonation parameters of energetic materials **3–6**, **10** [49,50].

Compound	$T_d^{[a]}$ [°C]	$\rho^{[b]}$ [g cm <sup>-3</sup> ]	OB <sup>[c]</sup> [%]	HOF <sup>[d]</sup> [kJ mol <sup>-1</sup> ]/[kJ g <sup>-1</sup> ]	$D^{[e]}$ [m s <sup>-1</sup> ]	$P^{[f]}$ [GPa]	IS <sup>[g]</sup> [J]	FS <sup>[h]</sup> [N]
<b>3</b>	235	2.05	3.52	−203.2/−0.89	—	—	10	80
<b>4</b>	138	1.87	4.23	62.0/0.33	8828	34.6	25	120
<b>5</b>	202	1.78	−7.76	−72.2/−0.35	8554	30.1	20	160
<b>6</b>	143	1.87	0	139.1/0.68	8982	35.9	28	128
<b>10</b>	145	1.88	—	−30.3/−0.14	8956	37.1	30	240
FOX-7	220	1.88	0	−130.0/−0.88	8870	34.0	25	340
RDX	204	1.80	0	70.3/0.32	8795	34.9	7.4	120

<sup>[a]</sup> Thermal decomposition temperature. <sup>[b]</sup> Crystal density at 173 K. <sup>[c]</sup> Oxygen balance (based on CO) for  $C_aH_bO_cN_d$ ,  $1600(c-a-b/2)/M_w$ . <sup>[d]</sup> Calculated heat of formation. <sup>[e]</sup> Detonation velocity calculated using EXPLO5 (6.02). <sup>[f]</sup> Detonation pressure calculated using EXPLO5 (6.02). <sup>[g]</sup> Impact sensitivity evaluated using a standard BAM fall-hammer. <sup>[h]</sup> Friction sensitivity evaluated using a BAM friction tester.

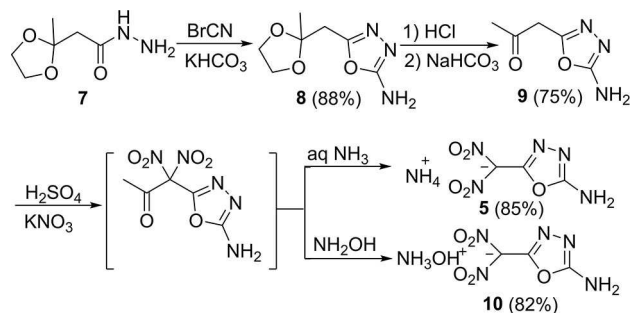
salts (**3** and **5**) were synthesized; **5** has a similar structure to that of **6**.

According to the physical and detonation parameters listed in Table 1, compound **3** exhibits good thermal stability ( $T_d=235$  °C), which is superior to those of the widely used FOX-7 (220 °C) and RDX (204 °C); furthermore, it has a high density of 2.05 g cm<sup>-3</sup> owing to the metal ion, but also exhibits relatively high sensitivities. In addition, the calculated detonation properties of the zwitterionic compounds **4** (8828 ms<sup>-1</sup>, 34.6 GPa) and **6** (8982 ms<sup>-1</sup>, 35.9 GPa) are better than those of the energetic salt **5** (8554 ms<sup>-1</sup>, 30.1 GPa), and can rival those of FOX-7 (8870 ms<sup>-1</sup>, 34.0 GPa). With regard to sensitivity, the zwitterionic compounds **4** and **6** exhibit high sensitivity to friction (**4**: 120 N, **6**: 128 N), but low sensitivity to impact (**4**: 25 J; **6**: 28 J) compared to **5** (FS: 160 N, IS: 20 J). Features such as a high density, good detonation performance, and moderate sensitivity of zwitterionic compounds **4** and **6** make them promising for use as high-performance energetic materials.

**Scheme 3.** Synthesis of zwitterionic energetic materials based on 5-amino-1,3,4-oxadiazole.

In the synthesis route shown in Scheme 3, intermediate **3** is mechanically sensitive, while compound **2** exhibits poor stability and is not suitable for long-term storage [49]. Therefore, this method to synthesize zwitterionic compounds and their salts is not suitable owing to the unstable intermediates posing potential risks during the preparation process. Thus, a safer and more cost-effective route was established [50]; the new method includes the following four steps: cyclization, deprotection, nitration, and neutralization (Scheme 4). Compound **8** was obtained by the acylation of 2-(2-methyl-1,3-dioxolan-2-yl) acetohydrazide (**7**) with cyanogen bromide in a potassium bicarbonate solution, which was then deprotected by hydrochloric acid followed by treatment with sodium bicarbonate to afford compound **9**. After nitrating compound **9** and subsequently neutralizing it with ammonia and hydroxylamine, the final products **5** and **10** were obtained. The new route uses relatively inexpensive raw materials and does not include unstable intermediates, which results in a safer and more cost-effective process.

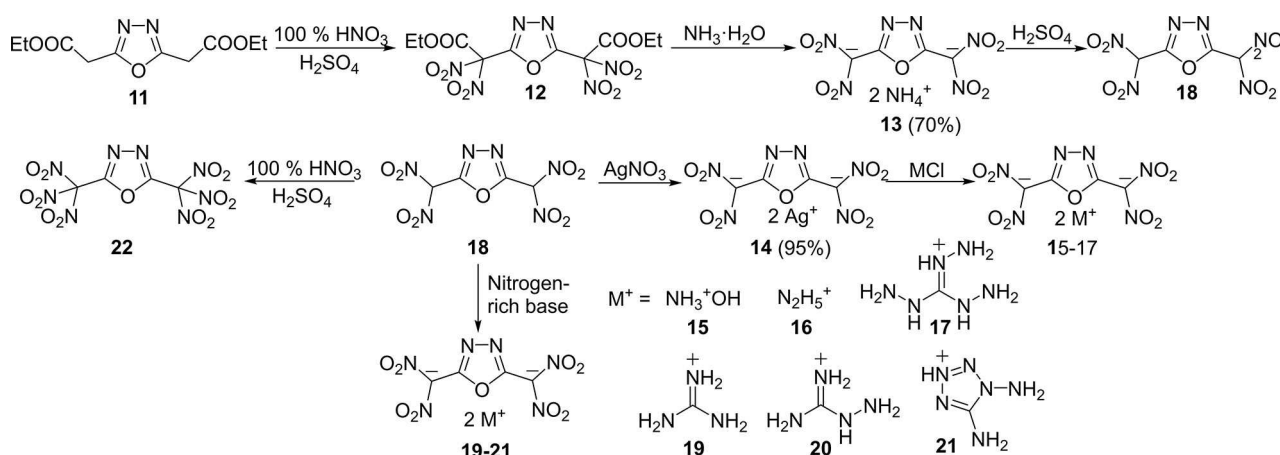
The hydroxylammonium salt **10** has a high density (1.88 g cm<sup>-3</sup>) and better detonation properties ( $D=8956$  ms<sup>-1</sup>,  $P=37.1$  GPa) than those of RDX and FOX-7 and exhibits low mechanical sensitivity (IS=30 J, FS=240 N). The outstanding performance along with the low sensitivity

**Scheme 4.** A new synthesis method for salts based on *gem*-dinitromethyl-functionalized 5-amino-1,3,4-oxadiazolate.

of **10** indicates its potential for use as a novel explosive with good energy–safety balance.

The introduction of a *gem*-polynitromethyl functionality into the heterocyclic skeleton is one of the best methods to increase both the OB value and energy density [51]; a series of energetic materials composed of 1,3,4-oxadiazole and polynitromethyl groups have been designed and synthesized [52]. The starting material, 1,3,4-oxadiazolyl-2,5-diacetic acid diethyl ester (**11**) was easily synthesized based on a previous reference [53] and was nitrated with mixed acid (100 % HNO<sub>3</sub> and 98 % H<sub>2</sub>SO<sub>4</sub>) to form the *gem*-dinitro compound **12** (Scheme 5). Energetic salt **13** was obtained by treating **12** with excess aqueous ammonia, while other nitrogen-rich salts (**13–17** and **19–21**) were synthesized in high yields by two-step procedures including the meta-thesis reaction and acid-base reaction. 2,5-Bis (trinitromethyl)-1,3,4-oxadiazole (**22**) was formed by the nitration of **18** using mixed acid as a nitrating agent.

According to their physical properties and detonation parameters (Table 2) [52], the *gem*-polynitromethyl-substituted 1,3,4-oxadiazole derivatives exhibit excellent OB, detonation velocity, and detonation pressure. Among them, compound **22** has the highest OB (39.1 %) owing to its poly nitro groups, which is superior to those of the widely used propellant oxidizing agent ammonium dinitramide (ADN 25.8 %) and ammonium perchlorate (AP + 34.04). Moreover, compound **22** possesses a high crystal density (2.007 g cm<sup>−3</sup> at 150 K) and exhibits good detonation properties ( $D = 8229 \text{ m s}^{-1}$ ,  $P = 29.2 \text{ GPa}$ ), indicating its high potential as a high-energy dense oxidizer for both rocket and missile propellants. Owing to its high density and good heat of formation, dihydroxylammonium salt **15** also exhibits excellent detonation properties ( $D = 9266 \text{ m s}^{-1}$ ,  $P = 38.9 \text{ GPa}$ ), and its detonation velocity is higher than that of HMX ( $D = 9144 \text{ m s}^{-1}$ ,  $P = 39.2 \text{ GPa}$ ), suggesting its potential for use as an environmentally-friendly energetic material. Unexpectedly, 2,5-bis (trinitromethyl)-1,3,4-oxadiazole (**22**) is



**Scheme 5.** Synthesis of 2,5-poly(polynitromethyl)-1,3,4-oxadiazole (**18**, **22**) and their energetic salts (**13–17**, **19–21**).

**Table 2.** Physical properties and detonation parameters of energetic materials **13–22** [52].

Compound	$T_d^{[a]}$ [°C]	$\rho^{[b]}$ [g cm <sup>−3</sup> ]	OB <sup>[c]</sup> [%]	HOF <sup>[d]</sup> [kJ mol <sup>−1</sup> ]/[kJ g <sup>−1</sup> ]	$D^{[e]}$ [m s <sup>−1</sup> ]	$P^{[f]}$ [GPa]	IS <sup>[g]</sup> [J]	FS <sup>[h]</sup> [N]
<b>13</b>	188	1.75	4.9	−297/−0.90	8326	29.4	10	240
<b>15</b>	146	1.89	14.0	−199.5/−0.58	9266	38.9	20	360
<b>16</b>	190	1.84	0	10.3/0.03	8900	36.3	19	80
<b>17</b>	178	1.67	−19.7	442.3/0.91	8510	27.7	28	240
<b>18</b>	86	1.91	23.0	−55.6/−0.20	8967	36.9	3	160
<b>19</b>	235	1.71	−12.1	−273.2/−0.69	8050	25.4	> 40	> 360
<b>20</b>	145	1.65	−15.0	−8.52/−0.02	8055	24.7	> 40	> 360
<b>21</b>	142	1.70	−6.7	989.5/2.07	8623	31.0	11	120
<b>22</b>	102	1.92	39.1	29.4/0.08	8229	29.2	4	240
ADN [54]	159	1.81	25.8	−149.8/−1.21	7860	23.6	3–5	64–72
HMX	280	1.91	0	75.0/0.23	9144	39.2	7.4	120

<sup>[a]</sup> Thermal decomposition temperature (onset) under nitrogen gas (DSC, 5 °C/min). <sup>[b]</sup> Crystal density measured by gas pycnometer (25 °C). <sup>[c]</sup> Oxygen balance (based on CO) for C<sub>a</sub>H<sub>b</sub>O<sub>c</sub>N<sub>d</sub>, 1600(c-a-b/2)/M<sub>w</sub>. <sup>[d]</sup> Calculated heat of formation. <sup>[e]</sup> Detonation velocity calculated using EXPLO5 (6.01). <sup>[f]</sup> Detonation pressure calculated using EXPLO5 (6.01). <sup>[g]</sup> Impact sensitivity. <sup>[h]</sup> Friction sensitivity.

Table 3. Physical property and detonation parameter of TKX-55 (29) [59].

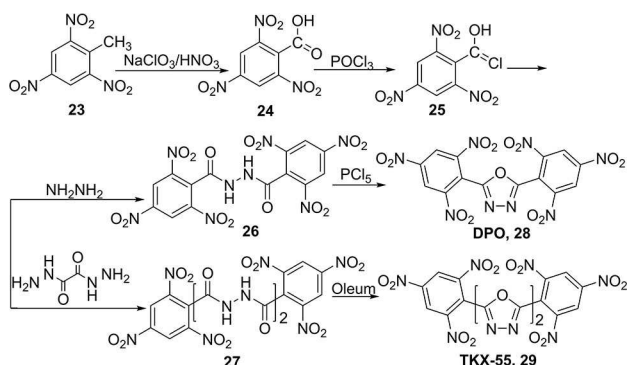
Compound	$T_d^{[a]}$ [°C]	$\rho^{[b]}$ [g cm <sup>-3</sup> ]	OB <sup>[c]</sup> [%]	HOF <sup>[d]</sup> [kJ mol <sup>-1</sup> ]/[kJ gl <sup>-1</sup> ]	$D^{[e]}$ [m s <sup>-1</sup> ]	$P^{[f]}$ [GPa]	IS <sup>[g]</sup> [J]	FS <sup>[h]</sup> [N]	ESD <sup>[i]</sup> [J]
TKX-55 (29)	335	1.83	−57.11	197.6/0.35	8030	27.3	5	> 360	1.0
HNS	318 [62]	1.74	−67.6	78.2/0.17	7612	24.3	5	240	0.8
PYX	360 [57]	1.75	−55.36	43.7/0.07	7757	25.1	10	360	0.5

<sup>[a]</sup> Thermal decomposition temperature. <sup>[b]</sup> Density at 298 K. <sup>[c]</sup> Oxygen balance (based on CO<sub>2</sub>). <sup>[d]</sup> Standard molar enthalpy of formation. <sup>[e]</sup> Detonation velocity. <sup>[f]</sup> Detonation pressure. <sup>[g]</sup> Impact sensitivity. <sup>[h]</sup> Friction sensitivity. <sup>[i]</sup> Electrostatic discharge device (OZM research).

more thermally stable (102 °C vs 86 °C) and less sensitive (4 J, 240 N vs 3 J, 160 N) than its bis(dinitromethyl) analogue (18). The excellent properties of the synthesized compounds demonstrate the advantages of the *gem*-polynitromethyl groups for the development and synthesis of advanced energetic materials.

### 2.3 Energetic Alliance of 1,3,4-Oxadiazoles and Benzene Rings

One of the methodologies adopted for the development of novel heat-resistant explosives is the insertion of functionalities between the two picryl groups to reinforce the conjugated system. For example, 2,2',4,4',6,6'-hexanitrostilbene (HNS) [55], 2,2',4,4',6,6'-hexanitroazobenzene (HNAB) [56] and 2,6-bis(picrylamino)-3,5-dinitropyridine (PYX) [57], are typical thermally stable energetic molecules with two picryl groups connected by a degree of conjugation. 2,5-Bis-(2,4,6-trinitrophenyl)-1,3,4-oxadiazole (DPO, 28) with two picryl moieties linked by 1,3,4-oxadiazole was first synthesized by Dacons and Sitzmann [58]. In 2016, a novel heat-resistant explosive 5,5'-bis(2,4,6-trinitrophenyl)-2,2'-bi(1,3,4-oxadiazole) (TKX-55, 29) was reported by Klapötke [59], in which two picryl moieties are connected by a di(1,3,4-oxadiazole) bridge. The synthetic routes to DPO and TKX-55 are outlined in Scheme 6. Both routes consist of four steps: oxidation, chlorination, condensation, and cyclization. The first step is the oxidation of TNT (23) to 2,4,6-trinitrobenzoic acid (TNBA, 24), and the second one is the chlorination of 24 to

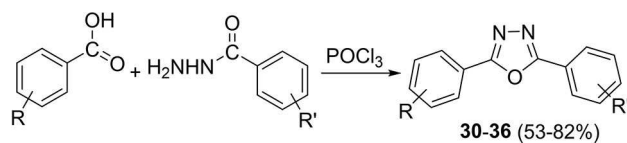


Scheme 6. Synthesis of DPO (28) and TKX-55 (29).

2,4,6-trinitrobenzoyl chloride (25) using POCl<sub>3</sub>. In the third step, 25 reacts with hydrazine and oxalylhydrazine, respectively, forming N,N'-bis(2,4,6-trinitrobenzoyl)hydrazine (26) and N',N'-bis(2,4,6-trinitrobenzoyl)oxalohydrazide (27). In the last step, 1,3,4-oxadiazoles were formed by cyclization. Here, POCl<sub>3</sub> was used as the dehydrating agent in the synthesis of DPO [60] while oleum was used for TKX-55 synthesis [59].

Both DPO and TKX-55 are thermally stable explosives, and the peak decomposition temperature of TKX-55 (335 °C) is lower than that of DPO (343 °C) [61]. Because TKX-55 has a higher density (1.83 g cm<sup>-3</sup>) and HOF than both HNS and PYX (Table 3) [59], it also exhibits better detonation properties ( $D = 8030$  m s<sup>-1</sup>,  $P = 27.3$  GPa). TKX-55 is also friction insensitive ( $IS > 360$  N), and its impact and electrostatic discharge sensitivities are significantly close to those of HNS. Moreover, TKX-55 is practically insoluble in water, which simplifies its isolation and purification. Owing to these advantages, TKX-55 can be widely applied in heat-resistant explosives.

In addition to DPO and TKX-55 with three nitro groups linked to the benzene rings, a series of 2,5-diaryl-1,3,4-oxadiazoles, including one or two nitro moieties in each benzene skeleton, were also synthesized to explore the effect of the number and position of the energetic groups on the energetic properties [63]. The target energetic compounds 30–36 were prepared by nitro-substituted benzoic acids and nitro-substituted benzohydrazides [64,65] through a cyclization reaction under reflux using phosphorus oxychloride as a cyclodehydrating agent (Scheme 7). The detonation performance for compounds 30–36 generally increases with an increase in the number of nitro groups



For 30, R = 3-NO<sub>2</sub>, R' = 4-NO<sub>2</sub>; For 31, R = 2-NO<sub>2</sub>, R' = 4-NO<sub>2</sub>;  
For 32, R = 2-NO<sub>2</sub>, R' = 3,5-(NO<sub>2</sub>)<sub>2</sub>; For 33, R = 4-NO<sub>2</sub>, R' = 2,4-(NO<sub>2</sub>)<sub>2</sub>;  
For 34, R = 3,5-(NO<sub>2</sub>)<sub>2</sub>, R' = 3,5-(NO<sub>2</sub>)<sub>2</sub>;  
For 35, R = 2,4-(NO<sub>2</sub>)<sub>2</sub>, R' = 3,5-(NO<sub>2</sub>)<sub>2</sub>;  
For 36, R = 2,4-(NO<sub>2</sub>)<sub>2</sub>, R' = 2,4-(NO<sub>2</sub>)<sub>2</sub>.

Scheme 7. Synthesis of energetic compounds 30–36.



(Table 4). Additionally, the density for **DPO** was predicted to be  $1.82 \text{ g cm}^{-3}$ . Notably, **DPO** has the highest density and HOF compared with the other explosives in this series [63], which implies that it possesses the best detonation properties and further indicates its potential use in explosives.

## 2.4 Energetic Alliance of 1,3,4-Oxadiazoles and Heterocyclic Rings

Although 1,3,4-oxadiazole has better stability than its isomers (1,2,4- or 1,2,3-oxadiazoles) owing to the absence of readily cleavable N–O bonds in the ring, 1,3,4-oxadiazole based energetic materials do not exhibit satisfactory energetic properties. To obtain new high energy density materials with excellent properties and to break the energy-stability trade-off in energetic materials, assemblies of 1,3,4-

oxadiazoles with other nitrogen-rich heterocyclic rings were adopted.

In 2015, 3-nitroamino-4-(5-amino-1,3,4-oxadiazol-2-yl) furazan monohydrate (**39**), constituting an assembly of a nitroaminofurazan and the 1,3,4-oxadiazole ring was synthesized by Shreeve et al. [66], and several energetic salts based on it were also prepared; the synthetic routes are presented in Scheme 8. 3-Amino-4-(5-amino-1,3,4-oxadiazol-2-yl)furazan (**38**) was synthesized by the reaction between 4-amino-3-carbohydrazide-furazan (**37**) and cyanogen bromide according to the literature [48], while compound **39** was formed by the nitration of **38** using 100% nitric acid as a nitrating reagent, which exists as a zwitterionic tautomer [66]. However, attempts to transform the amino group bonded to the 1,3,4-oxadiazole ring to a nitroamino group did not succeed despite utilizing a number of nitrating reagents, owing to the low chemical activity of the amino group. The energetic salts **40–48** were synthesized in high yields by simple metathesis reactions of the neutral compound **39** and the corresponding nitrogen-rich bases.

Owing to the combination of the energetic nitroamino moiety of 1,2,5-oxadiazole and 1,3,4-oxadiazole within the same structure, compounds **38–48** exhibit acceptable detonation performances and modest thermal stabilities [66]. The physical properties and detonation parameter values summarized in Table 5 show that all the compounds possess high positive HOF values ranging from 185.3 to  $762.9 \text{ kJ mol}^{-1}$ . Among these compounds, energetic salts **45** and **48** demonstrate prominent detonation performances (for **45**,  $D = 8711 \text{ m s}^{-1}$ ,  $P = 30.6 \text{ GPa}$ ; for **48**,  $D = 8702 \text{ m s}^{-1}$ ,  $P = 30.9 \text{ GPa}$ ), which are comparable to those of RDX. In addition, both salts are also less sensitive to impact and fric-

**Table 4.** Physical properties and detonation parameters of **30–36** [63].

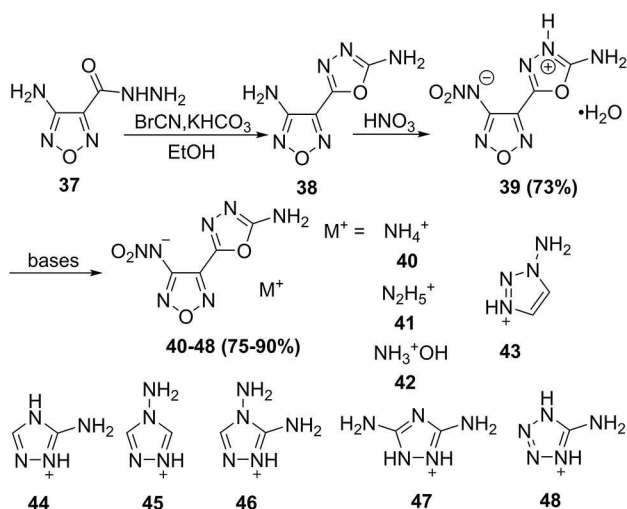
Compound	$\rho^{[a]}$ [g cm <sup>-3</sup> ]	HOF <sup>[b]</sup> [kJ mol <sup>-1</sup> ]/ [kJ g <sup>-1</sup> ]	$D^{[c]}$ [m s <sup>-1</sup> ]	$P^{[d]}$ [GPa]
<b>30</b>	1.56	242/0.78	6109	12.68
<b>31</b>	1.54	263/0.84	6047	12.33
<b>32</b>	1.65	267/0.75	6840	17.37
<b>33</b>	1.60	267/0.75	6654	16.16
<b>34</b>	1.75	256/0.66	7451	22.57
<b>35</b>	1.64	274/0.71	7053	19.28
<b>36</b>	1.65	291/0.75	7103	19.68
<b>DPO</b>	1.82	368/0.75	8175	28.94

[a] Density measured using a gas pycnometer (25 °C). [b] Heats of formation (calcd., gas phase). [c] Detonation velocity calculated using the EXPLO5 program. [d] Detonation pressure calculated using the EXPLO5 program.

**Table 5.** Physical properties and detonation parameters of energetic materials **38–48** [66].

Compound	$T_d^{[a]}$ [°C]	$\rho^{[b]}$ [g cm <sup>-3</sup> ]	HOF <sup>[c]</sup> [kJ mol <sup>-1</sup> ]/ [kJ g <sup>-1</sup> ]	$D^{[d]}$ [m s <sup>-1</sup> ]	$P^{[e]}$ [GPa]	IS <sup>[f]</sup> [J]	FS <sup>[g]</sup> [N]
<b>38</b>	246	1.68	185.3/1.10	7493	20.4	40	360
<b>39</b>	132	1.77	238.2/1.11	8227	28.0	15	120
<b>40</b>	237	1.72	342.2/1.49	8381	27.9	25	240
<b>41</b>	208	1.69	496.1/2.02	8282	28.3	20	240
<b>42</b>	178	1.74	392.4/1.59	8598	31.0	18	160
<b>43</b>	162	1.59	762.9/2.57	7832	23.1	28	360
<b>44</b>	249	1.74	553.3/1.86	8251	26.4	25	360
<b>45</b>	206	1.81	688.8/2.32	8711	30.6	30	360
<b>46</b>	228	1.70	660.2/2.11	8226	25.9	25	360
<b>47</b>	244	1.61	539.1/1.73	7701	21.7	20	240
<b>48</b>	185	1.79	721.7/2.42	8702	30.9	12	160
<b>TNT</b>	295	1.65	-59.4/-0.26	7303	21.3	15	> 353

[a] Temperature of decomposition (onset). [b] Density measured by a gas pycnometer at 25 °C. [c] Calculated molar enthalpy of formation in solid state. [d] Detonation velocity calculated using EXPLO5 (6.01). [e] Detonation pressure calculated using EXPLO5 (6.01). [f] Impact sensitivity. [g] Friction sensitivity.



**Scheme 8.** Synthesis of energetic compounds **38–48**.

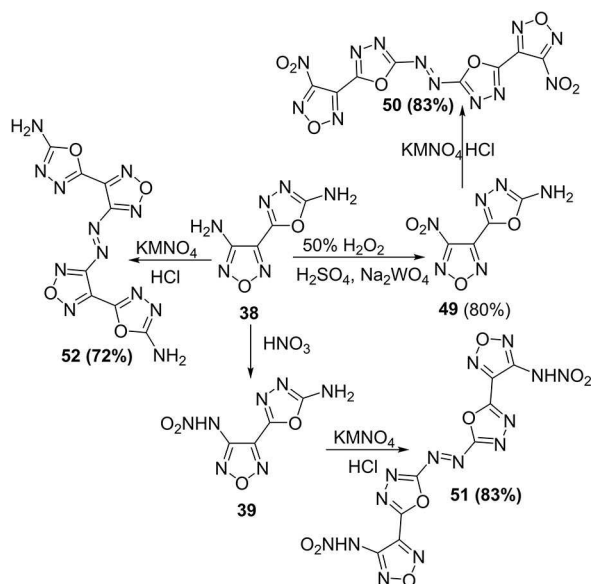
tion than RDX. This simple synthetic method along with the good detonation properties of these new compounds suggests that they have the potential to be applied as energetic materials in the future.

Recently, two covalent compounds **50** and **51**, which exhibit remarkable thermal stabilities and have a high endothermic heat of formation owing to the existence of an azo ( $-\text{N}=\text{N}-$ ) moiety were prepared via the oxidative coupling reaction of the unreactive amino groups that were linked to the 1,3,4-oxadiazole rings of (1,3,4-oxadiazolyl)-1,2,5-oxadiazoles via the formation of an azo bridge [67]; the synthetic route is shown in Scheme 9. Compound **49** (5-(4-nitro-1,2,5-oxadiazol-3-yl)-1,3,4-oxadiazol-2-amine) was prepared by the oxidation of **38** using 50%  $\text{H}_2\text{O}_2$ , 98%  $\text{H}_2\text{SO}_4$ , and  $\text{Na}_2\text{WO}_4$ . The amino groups at the 1,3,4-oxadiazole rings for **49** and **39** were easily oxidized under the

action of  $\text{KMnO}_4$  in  $\text{HCl}$  to the azo compounds **50** and **51**, respectively, with high yields (83%). Moreover, the oxidative coupling of **38** by  $\text{KMnO}_4$  in  $\text{HCl}$  provided the corresponding azo compound **52** with an azo group linked to 1,2,5-oxadiazole but not to 1,3,4-oxadiazole [68].

A few essential physical and detonation properties for **49**–**52** were determined to investigate their application prospects (Table 6) [67,68]. The decomposition temperatures for compounds **39** and **49** were 132 and 155 °C, respectively, while their coupling products **51** and **50** did not decompose until 248 and 278 °C, respectively. Notably, 278 °C is the highest known decomposition temperature for furazan-based energetic materials containing nitramino or nitro groups and is higher than that for **52** (233 °C) [68]. Compound **50** also exhibits a high density of  $1.825 \text{ g cm}^{-3}$ , which is higher than that of explosive RDX. In addition, owing to the presence of the azo groups, tetracyclic compounds **50**–**52** present outstanding positive enthalpies ranging from 684.1 to 854.2  $\text{kJ mol}^{-1}$ . Among them, **50** possesses the highest HOF and also exhibit zero-OB. As a result of these excellent properties, **50** demonstrates the best detonation performance of the series ( $D$ :  $8800 \text{ m s}^{-1}$ ,  $P$ : 35.1 GPa), which is comparable to that of RDX ( $D$ :  $8795 \text{ m s}^{-1}$ ,  $P$ : 34.9 GPa). Moreover, the sensitivity values of **50** (IS: 15 J, FS: 220 N) were significantly higher than those of RDX (IS: 7.4 J, FS: 120 N), which further proves its application potential as a secondary explosive.

As previously indicated, the combination of 1,2,5-oxadiazole and 1,3,4-oxadiazole can form energetic compounds with good performances. Similar to 1,2,5-oxadiazole, its N-oxide derivative (furoxan) is also an important explosophore and has drawn considerable attention from the energetic materials community, for example, energetic materials such as 3,4-bis(3-nitrofurazan-4-yl)furoxan [70], bis(1,2,4-oxadiazolyl) furoxan [71], and bis(nitroxymethylisoxazolyl) furoxan [72] with furoxan moiety contained have been found to have melt-castable properties. Moreover, furoxan can possibly increase the density



Scheme 9. Synthesis of energetic compounds **49**–**52**.

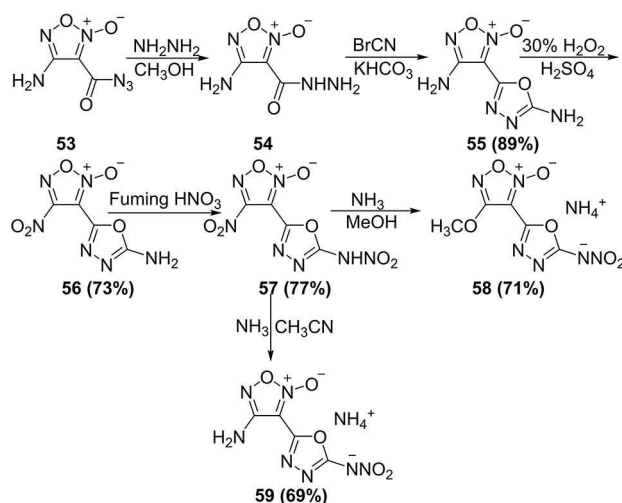
Table 6. Physical properties and detonation parameters of energetic materials **49**–**52** [67,68].

Compound	$T_d^{[a]}$ [°C]	$\rho^{[b]}$ [g cm <sup>-3</sup> ]	OB <sup>[c]</sup> [%]	HOF <sup>[d]</sup> [kJ mol <sup>-1</sup> ]/ [kJ g <sup>-1</sup> ]	$D^{[e]}$ [m s <sup>-1</sup> ]	$P^{[f]}$ [GPa]	IS <sup>[g]</sup> [J]	FS <sup>[h]</sup> [N]
<b>49</b>	155	1.74	−8.08	219.4/1.11	8102	26.9	35	360
<b>50</b>	278	1.82	0	854.2/2.18	8800	35.1	15	220
<b>51</b>	248	1.76	−3.79	786.1/1.86	8409	29.3	3	48
<b>52</b>	233	1.83	9.20	684.1/1.97	8323	27.3	≥ 80	≥ 360
<b>56</b>	150	1.82	0	416.2/1.94	8764	34.0	15	180
<b>57</b>	86	1.88	15.44	436.0/1.68	9258	37.5	8	108
<b>58</b>	158	1.68	−15.33	610.7/2.34	8430	30.1	23	240
<b>59</b>	149	1.72	−13.01	743.4/3.02	8810	33.1	20	220

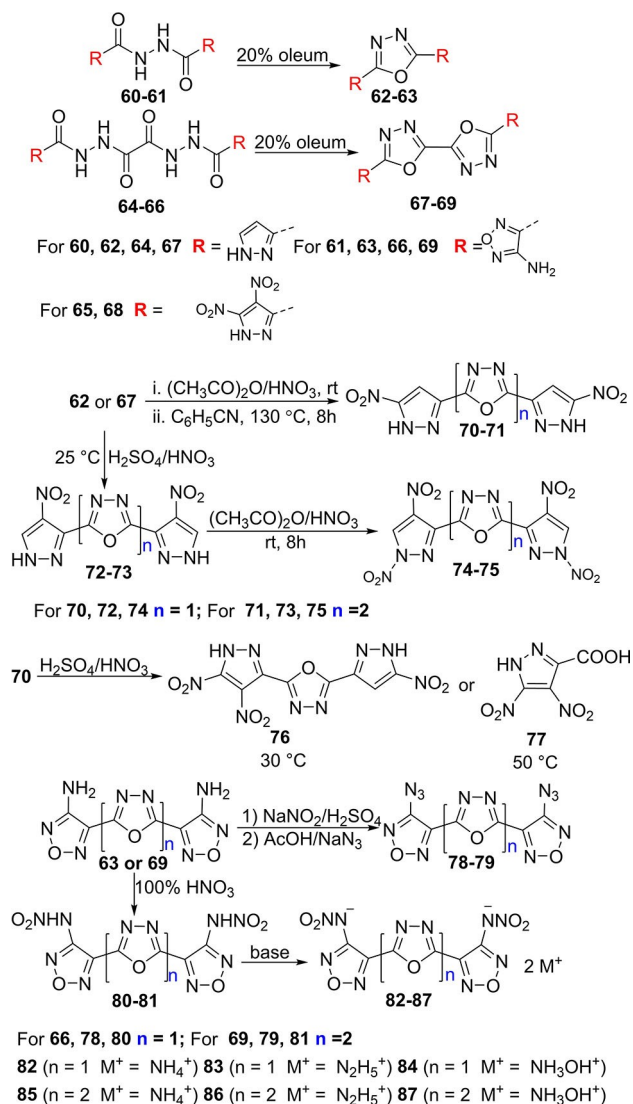
[a] Thermal decomposition temperature (onset) under nitrogen (determined by the DSC exothermal peak, 5 °C/min). [b] The room-temperature (RT) density values converted by the corresponding single-crystal densities using the equation in [69]. [c] Oxygen balance (based on CO) for  $\text{C}_a\text{H}_b\text{O}_c\text{N}_d$ ,  $1600(c-a-b/2)/M_w$ . [d] Calculated molar enthalpy of formation in solid state. [e] Detonation velocity calculated using EXPLO5 (6.01). [f] Detonation pressure calculated using EXPLO5 (6.01). [g] Impact sensitivity. [h] Friction sensitivity.

and heat of formation, thereby improving the energetic performance [73]. Therefore, energetic materials **55–59** based on the combination of furoxan and 1,3,4-oxadiazole structures were also synthesized [74]. The synthetic pathways to these compounds are shown in Scheme 10. The 2-amino-1,3,4-oxadiazole ring was synthesized by the reaction of monohydrazide with cyanogen bromide under alkaline condition, while the intermediate monohydrazide compound **54** was prepared using a modified method based on previous literature [75]. The amino group of furoxan was oxidized to the nitro group by 30%  $\text{H}_2\text{O}_2$  in 98%  $\text{H}_2\text{SO}_4$ , and the amino group of oxadiazole was then nitrated to the nitramino moiety by fuming  $\text{HNO}_3$ , which forms the high-energy explosive **57** with high sensitivity and poor stability. To moderate this defect, the ammonium salt of compound **57** were also synthesized by the authors. Note, the two types of ammonium salts were prepared under different conditions. In methanol, ammonium 3-methoxy-4-(5-nitramino-1,3,4-oxadiazole-yl)furoxan (compound **58**) was formed, while 3-amino-4-(5-nitramino-1,3,4-oxadiazole-yl)furoxan (compound **59**) was obtained in acetonitrile.

The physicochemical properties, including energetic properties and stabilities for **56–59**, were investigated and are listed in Table 6. Among them, compounds **56** and **58** present a good detonation performance (for **56**  $D$ :  $8764 \text{ m} \cdot \text{s}^{-1}$ ,  $P$ : 34.0 GPa; for **58**,  $D$ :  $8430 \text{ m} \cdot \text{s}^{-1}$ ,  $P$ : 30.1 GPa). Compound **57** exhibits the best detonation properties ( $D$ :  $9258 \text{ m} \cdot \text{s}^{-1}$ ,  $P$ : 37.5 GPa) of the series, which are better than those of RDX and comparable to those of HMX. Moreover, the ammonium salts **58** ( $T_d$ :  $158^\circ\text{C}$ , IS: 23 J) and **59** ( $T_d$ :  $149^\circ\text{C}$ , IS: 20 J) display higher stabilities than those of the neutral compound **57** ( $T_d$ :  $86^\circ\text{C}$ , IS: 8 J). The adequate performances of these new compounds make them potential secondary explosives.


 Scheme 10. Synthesis of energetic compounds **56–59**.

Owing to the good balance between the molecular stability and detonation performance of 1,3,4-oxadiazole-based energetic materials, a series of 1,3,4-oxadiazole bridged polynitropyrazoles or furazans with excellent performances were successfully synthesized [76,77]. The synthetic routes to these compounds are shown in Scheme 11. The starting materials **60–61** and **64–66** were prepared according to the method described in the indicated references [78] and their synthetic routes are shown in Scheme S1 of the supporting information. The 1,3,4-oxadiazole derivatives (**62–63** and **67–69**) were formed by the corresponding 1,2-diacylhydrazines by cyclization using 20% oleum. The nitration of compounds **62** and **67** utilizing a mixture of concentrated  $\text{H}_2\text{SO}_4$  and fuming  $\text{HNO}_3$  provided **72** and **73**. Furthermore, compounds **74** and **75** were prepared using the nitrating reagent acetic anhydride and fuming  $\text{HNO}_3$  from


 Scheme 11. Synthesis of energetic compounds **68**, **72–76**, and **78–87**.



**72** and **73**. Compounds **70** and **71** were synthesized through the nitration of **62** and **67**, respectively, in fuming nitric acid/acetic anhydride followed by a thermal rearrangement in benzonitrile. The nitration of **70** and **71** to obtain energetic materials with two C-nitro groups bonded to the pyrazole rings was not successful; however, the tri-C-nitro derivative **76** was obtained from **70** using a fuming  $\text{HNO}_3/98\% \text{H}_2\text{SO}_4$  nitration reagent at  $30^\circ\text{C}$  for 24 h. Moreover, an unexpected ring-open product **77** was obtained through the nitration of **70** using fuming  $\text{HNO}_3/98\% \text{H}_2\text{SO}_4$  at a higher temperature of  $50^\circ\text{C}$ . To pursue more energetic compounds with fully C-nitrated functionalization, 5,5'-bis(3,4-dinitro-1H-pyrazol-5-yl)-2,2'-bi(1,3,4-oxadiazole) (**68**) was also synthesized, but with an improved strategy using four steps (Scheme 11 and S1). The amino groups for compounds **63** and **69** were substituted by azido moieties through diazotization and substitution; thus, azide compounds **78** and **79** were obtained. Moreover, nitroamino-functionalized compounds **80** and **81** were synthesized by the nitration reaction of compounds **63** and **69** using  $100\% \text{HNO}_3$ , and their energetic salts **82–87** were prepared by treating them with different bases. Note, the amine groups for **63** and **69** could not be oxidized to nitro groups, although various oxidizing materials were adopted.

The physicochemical properties of the aforementioned energetic compounds composed of 1,3,4-oxadiazole and polynitropyrazoles or furazans are listed in Table 7. Among the 1,3,4-oxadiazole bridged-polynitropyrazole compounds,

the decomposition temperatures of **72** and **73** are  $338^\circ\text{C}$  and  $368^\circ\text{C}$ , respectively, which are higher than that of the widely used heat-resistant explosive HNS ( $T_d=318^\circ\text{C}$ ). Owing to the weak bond for the N-nitro groups, compounds **74** and **75** exhibit low decomposition temperatures of  $159^\circ\text{C}$  and  $186^\circ\text{C}$ , respectively, while the C-nitrated functionalized compounds **76** and **68** decompose at  $254^\circ\text{C}$  and  $265^\circ\text{C}$ , respectively, which are superior to that of RDX ( $T_d=204^\circ\text{C}$ ). In addition, all the synthesized compounds possess densities higher than  $1.80 \text{ g cm}^{-3}$ , and the density for **68** is the highest ( $1.87 \text{ g cm}^{-3}$ ) among these compounds. In addition, they all have high positive HOF values. After obtaining the density and HOF for these energetic materials, their detonation properties were calculated using EXPLO5. Compounds **74** and **75** possess the highest detonation velocities and pressures (for **74**,  $D=8855 \text{ ms}^{-1}$ ,  $P=34.23 \text{ GPa}$ ; for **75**,  $D=8766 \text{ ms}^{-1}$ ,  $P=33.33 \text{ GPa}$ ), and the detonation properties of **72** ( $D: 8099 \text{ ms}^{-1}$ ,  $P: 27.14 \text{ GPa}$ ) and **73** ( $D: 8054 \text{ ms}^{-1}$ ,  $P: 26.53 \text{ GPa}$ ) are higher than those of HNS ( $D: 7612 \text{ ms}^{-1}$ ,  $P: 24.3 \text{ GPa}$ ). Moreover, **72** and **73** also possess preferable sensitivity ( $\text{IS} > 40 \text{ J}$ ,  $\text{FS} > 360 \text{ N}$ ). These outstanding performances for **72** and **73** suggest their application prospects as heat-resistant explosives. Compound **68** has a low sensitivity to impact and friction ( $\text{IS}=30 \text{ J}$ ,  $\text{FS}=360 \text{ N}$ ), and an excellent detonation performance ( $D=8710 \text{ ms}^{-1}$ ,  $P: 32.75 \text{ GPa}$ ) comparable to RDX, which suggests its promising application potential as an insensitive secondary explosive.

Among the 1,3,4-oxadiazole bridged-furazan compounds, nitroamines **80** and **81** exhibit the lowest decomposition temperatures of  $67^\circ\text{C}$  and  $90^\circ\text{C}$ , respectively, while their ammonium salts **82** ( $T_d=210^\circ\text{C}$ ) and **85** ( $T_d=214^\circ\text{C}$ ) are the most thermally stable compounds among these energetic materials, which are comparable to RDX and FOX-7. Moreover, the tetracyclic compounds present higher thermal stabilities than the analogous tricyclic compounds with the same energetic groups, which can be attributed to the larger conjugated system. With respect to densities, compounds **80** and **81** present the highest densities of  $1.91$  and  $1.92 \text{ g cm}^{-3}$ , respectively, which are comparable to that of HMX. The heats of formation of the bis-1,3,4-oxadiazole-bridged compounds ( $539.6\text{--}1370.2 \text{ kJ mol}^{-1}$ ) are also higher than those of the mono-1,3,4- compounds ( $420.2\text{--}1359.8 \text{ kJ mol}^{-1}$ ) owing to the additional 1,3,4-oxadiazole ring. After obtaining the densities and HOFs for these energetic compounds, their detonation performances were also calculated. The detonation velocities of the nitroamines **80** ( $9211 \text{ ms}^{-1}$ ) and **81** ( $9058 \text{ ms}^{-1}$ ), along with their hydroxylammonium and hydrazine salts ( $8914\text{--}9101 \text{ ms}^{-1}$ ) outperform FOX-7 and RDX. Tricyclic compounds, such as **78** and **82–84**, are less sensitive than RDX and HMX in terms of mechanical sensitivities, while tetracyclic energetic materials present better friction sensitivities than RDX and HMX. The excellent performance and the good mechanical sensitivities make these energetic materials present significant potential as highly energetic insensitive explosives;

**Table 7.** Physical properties and detonation parameters of energetic materials **68**, **72–76**, and **78–87** [76,77].

Compound	$T_d^{[a]}$ [ $^\circ\text{C}$ ]	$\rho^{[b]}$ [ $\text{g cm}^{-3}$ ]	HOF <sup>[c]</sup> [ $\text{kJ mol}^{-1}$ ]/ [ $\text{kJ g}^{-1}$ ]	$D^{[d]}$ [ $\text{m s}^{-1}$ ]	$P^{[e]}$ [ $\text{GPa}$ ]	$\text{IS}^{[f]}$ [ $\text{J}$ ]	$\text{FS}^{[g]}$ [ $\text{N}$ ]
<b>68</b>	265	1.87	602.7/1.34	8710	32.75	30	360
<b>72</b>	338	1.80	521.6/1.79	8099	27.14	>40	>360
<b>73</b>	368	1.80	639.8/1.78	8054	26.53	>40	>360
<b>74</b>	159	1.83	762.1/2.00	8855	34.23	8	150
<b>75</b>	186	1.84	882.4/1.96	8766	33.33	13	220
<b>76</b>	254	1.84	519.4/1.54	8543	31.71	35	>360
<b>78</b>	169	1.76	1359.8/ 4.72	8728	31.2	21.9	280
<b>79</b>	191	1.79	1370.2/ 3.85	8545	29.8	4.9	120
<b>80</b>	67	1.91	711.8/2.18	9211	38.0	-	-
<b>81</b>	90	1.92	793.3/2.01	9058	36.2	6.9	120
<b>82</b>	210	1.82	420.2/1.17	8700	32.2	24.5	360
<b>83</b>	190	1.79	783.5/2.01	8914	33.3	11.0	280
<b>84</b>	169	1.88	553.9/1.41	9101	37.9	17.4	330
<b>85</b>	214	1.87	539.6/1.26	8745	33.1	9.8	240
<b>86</b>	200	1.86	890.2/1.94	8993	34.9	7.7	240
<b>87</b>	186	1.87	680.8/1.48	8926	35.8	6.9	240

[a] Thermal decomposition temperature (onset). [b] Density measured at  $25^\circ\text{C}$ . [c] Heat of formation. [d] Detonation velocity calculated using EXPLO5 (6.01). [e] Detonation pressure calculated using EXPLO5 (6.01). [f] Impact sensitivity. [g] Friction sensitivity.

the outstanding properties of these 1,3,4-oxadiazole-bridged compounds provide new design ideas for novel energetic materials.

### 3 Synthesis and Energy Characteristics of Poly 1,3,4-Oxadiazoles Structures

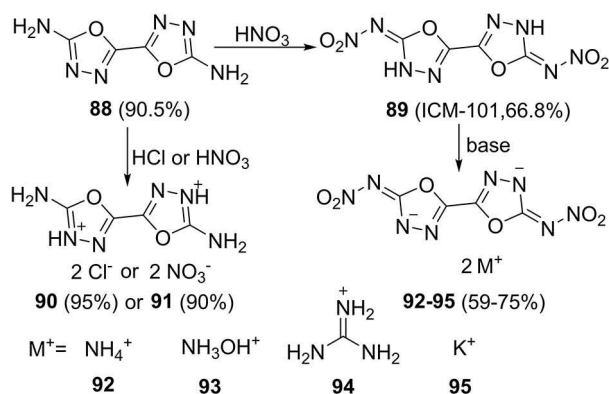
Owing to the thermal stability and energetic property of the 1,3,4-oxadiazole unit, poly 1,3,4-oxadiazole structures were introduced to researchers. The first representative of the energetic structures consisted of two 1,3,4-oxadiazole rings connected by the C–C bond; 2,2'-bi(1,3,4-oxadiazole)-5,5'-dinitramide (ICM-101, **89**) was synthesized by a practical two-step reaction from commercially-available reagents (Scheme 12 and S2) [79,80]. The reaction between oxalyl dihydrazide and cyanogen bromide in the presence of potassium bicarbonate yields the [2,2'-bi(1,3,4-oxadiazole)]-5,5'-diamine (**88**) in a high yield of 90.5%. Subsequently, the nitration reaction of **88** with fuming nitric acid yields ICM-101. The diprotonated chloride (**90**) and di-

nitrate salts (**91**) were obtained from HCl and HNO<sub>3</sub> upon aiming to recrystallize low soluble **88** from these concentrated mineral acids. Additionally, four nitrogen-rich salts (**92–95**) were synthesized in methanol by treating **89** with corresponding bases.

As shown in Table 8, ICM-101 exhibits an ultra-high density of 1.99 g cm<sup>-3</sup> and possesses a decent decomposition temperature of 210 °C. In addition, ICM-101 presents an outstanding detonation performance ( $D = 9481 \text{ m s}^{-1}$ ,  $P = 41.9 \text{ GPa}$ ), which is comparable to that of CL-20 and higher than those of HMX and RDX. The excellent physical properties and detonation performance coupled with its straightforward preparation make ICM-101 a possible high-performing energetic material. In addition to the outstanding ICM-101, its energetic salts also exhibit good performance. Among them, the diammonium salt (**92**) and dihydroxylammonium salt (**93**) possess significantly better detonation parameters than those of RDX.

Note, 1,3,4-oxadiazole ring-based energetic materials have significant potential for use as secondary or heat-resistant explosives. For example, compounds **50**, **74**, **75**, and **68** exhibit good detonation properties, thus can be considered as promising candidates for replacing the widely used explosive RDX. Surprisingly, compound **89**, also referred to as ICM-101, exhibits an excellent detonation performance comparable to that of CL-20, which makes ICM-101 have the potential for use as a high-performance energetic material. Moreover, owing to the high stability of the 1,3,4-oxadiazole ring, several heat-resistant explosives comprised of 1,3,4-oxadiazole and a benzene ring or pyrazole ring (DPO, TKX-55, **72**, and **73**) were prepared, and their thermal stabilities were significantly improved by the formed conjugated systems.

As previously indicated, the introduction of a *gem*-polynitromethyl functionality, such as that of the dinitromethyl and trinitromethyl groups, into the heterocyclic rings is beneficial to the OB and energy density; energetic compounds comprised of bi(1,3,4-oxadiazole) and polynitromethyl were synthesized [81]. The raw material, 2,2'-bi(1,3,4-oxadiazole)-5,5'-diacetic acid diethyl ester (**97**) was synthesized by a two-step procedure according to the literature [53]. Then, compound **98** was obtained by the hydrolysis of **97** in the presence of NaOH, followed by acidification with aqueous HCl. The trinitromethyl compound **99** was obtained by the nitration of **98** with a mixture of HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>; the nitration of **97** with a mixture of 100% HNO<sub>3</sub> and 96% H<sub>2</sub>SO<sub>4</sub> resulted in compound **100**. Moreover, dinitromethyl energetic salts were synthesized by simple deprotonation and metathesis reactions starting from **100**. Among these salts, guanidinium (**103**), daminoguanidinium (**104**), and triaminoguanidinium (**105**) salts were prepared by the reaction of silver salt **102** with the corresponding chloride salts, while the other salts were synthesized by the neutralization reaction of strong bases with the weak acidic compound **98**. The synthesis routes for these energetic compounds are listed in Scheme 13.

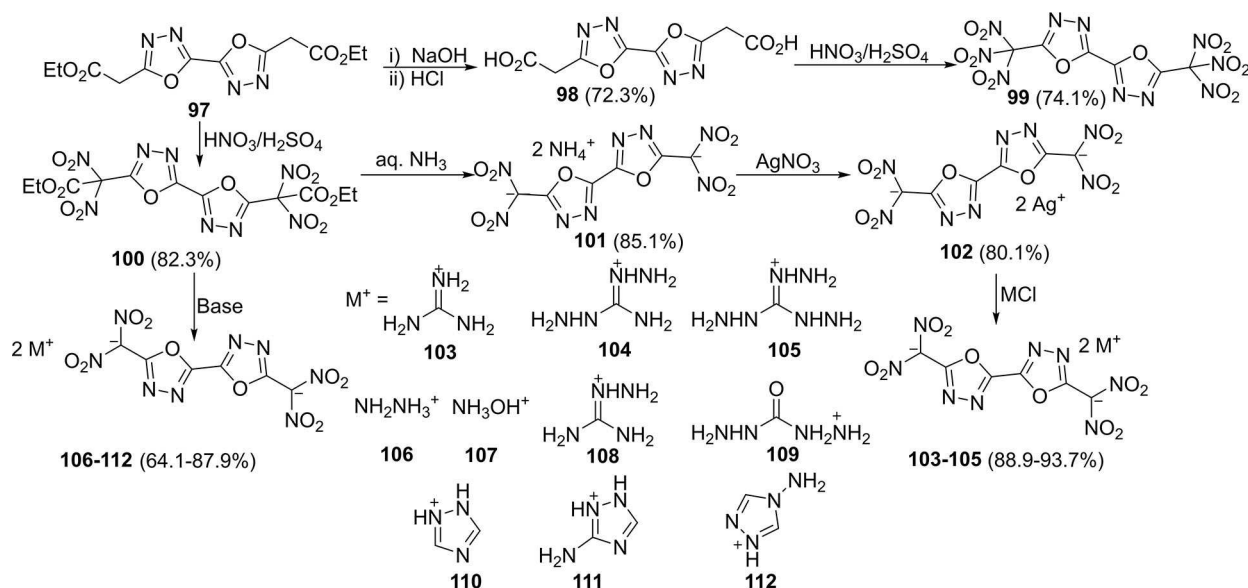


Scheme 12. Synthesis of energetic compounds **88–95** [79,80].

Table 8. Physical properties and detonation parameters of energetic materials **88**, **89** and **92–95** [79,80].

Compound	$T_d^{[a]}$ [°C]	$\rho^{[b]}$ [g cm <sup>-3</sup> ]	HOF <sup>[c]</sup> [kJ mol <sup>-1</sup> ]/ [kJ g <sup>-1</sup> ]	$D^{[d]}$ [m s <sup>-1</sup> ]	$P^{[e]}$ [GPa]	$IS^{[f]}$ [J]	$FS^{[g]}$ [N]
<b>88</b>	310	1.93	77.4/0.46	–	–	> 40	> 360
<b>89</b>	210	1.99	166.8/0.65	9481	41.9	5	60
<b>92</b>	197	1.95	–71.8/–0.25	9225	34.9	10	360
<b>93</b>	160	1.92	70.2/0.22	9186	34.1	4	120
<b>94</b>	260	1.79	–59.9/–0.16	8027	24.8	40	360
<b>95</b>	260	2.04	–382.7/ –1.14	7567	23.3	5	288
<b>ε-CL-20</b>	215	2.04	365.4/0.83	9455	46.7	4	48

[a] Thermal decomposition temperature (onset). [b] Density measured at 25 °C. [c] Heat of formation. [d] Detonation velocity calculated using EXPLO5 (6.01). [e] Detonation pressure calculated using EXPLO5 (6.01). [f] Impact sensitivity. [g] Friction sensitivity.



Scheme 13. Synthesis of energetic compounds **99**, **101** and **103–112** [81].

The trinitromethyl compound **99** has a slightly lower detonation performance ( $D=8764\text{ m}\cdot\text{s}^{-1}$ ,  $P=33.2\text{ GPa}$ ) than that of RDX ( $D=8795\text{ m}\cdot\text{s}^{-1}$ ,  $P=34.9\text{ GPa}$ ). However, it presents poor thermal stability ( $T_d=98.5^\circ\text{C}$ ) owing to the trinitromethyl group within **99**, which can't meet the requirements for the practical use of energetic materials. Compared with **99**, energetic salts featuring dinitromethyl present better thermal stabilities, and the decomposition temperatures for these salts (**101**, **103–112**) are in the range of 133.0 to 250.3 °C. In particular, compounds **103** and **112** possess higher decomposition temperatures (250.3 and 205.8 °C) than that of RDX (204 °C). Moreover, the calculated detonation pressure and detonation velocity for these energetic salts range from 24.2 to 34.5 GPa and from 7978  $\text{m}\cdot\text{s}^{-1}$  and 8770  $\text{m}\cdot\text{s}^{-1}$ , respectively. Among these energetic salts, the hydroxylammonium salt **107** exhibits the best detonation performance with a detonation velocity of 8770  $\text{m}\cdot\text{s}^{-1}$  and a detonation pressure of 34.5 GPa, which is similar to that of the majority of energetic hydroxylammonium salts [35,82,83]. In addition, compound **107** also has low sensitivities ( $IS=20\text{ J}$ ,  $FS=240\text{ N}$ ,  $ESD=0.33\text{ J}$ ). Therefore, the hydroxylammonium salt **107** herein is the most promising potential candidate for energetic materials.

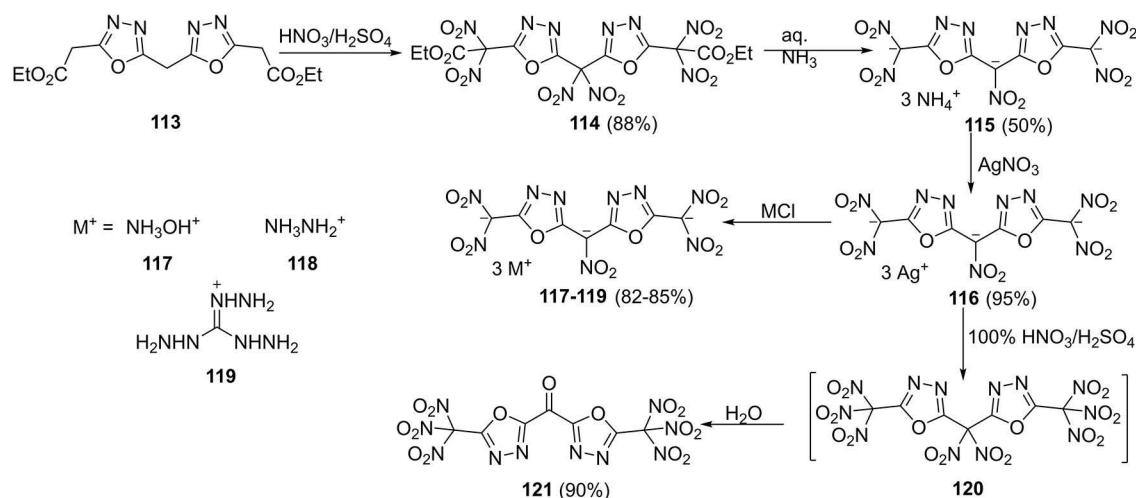
In addition to the simple C–C bonded bi(1,3,4-oxadiazole)-based energetic materials, energetic compounds based on nitromethane-bridged bis(1,3,4-oxadiazoles) were also synthesized (Scheme 14) [84]. The starting material diethyl 2,2'-(methylenedibis(1,3,4-oxadiazole-5,2-diyl))diacetate (**113**) was synthesized according to the method available in the literature [53] and was treated with a mixture of 100% HNO<sub>3</sub> and 98% H<sub>2</sub>SO<sub>4</sub>, which resulted in dinitromethylene-bridged intermediate **114** with a high yield of 88%. Note, the unstable dinitromethylene group of **114** was converted

to a mononitromethylene group via an aminolysis reaction with an excess of aqueous ammonia to form triammonium salt **115**, while the nitrogen-rich trianionic energetic salts (**117–119**) were prepared using two consecutive metathesis reactions. Note, the nitration of **116** led to the production of ketone **121**, which arose from the hydrolysis of intermediate gem-dinitro bridged derivative **120**.

The physical and detonation properties of the new trianionic salts **115**, **117–119**, and ketone **121** were investigated, and the related parameters are provided in Table 9. As shown in the table, the onset decomposition temperatures for trianionic salts range from 168 to 180 °C, which are higher than that of ADN. Ketone **121** has the worst thermal stability among these new energetic materials, as it begins to decompose at only 108 °C. Considering the detonation performance, compound **118** exhibits the highest detonation velocity of 8821  $\text{m}\cdot\text{s}^{-1}$ , which is higher than that of RDX. Compounds **117** and **121** present slightly lower detonation velocities and lower detonation pressures than RDX. However, **121** is relatively sensitive ( $IS=4\text{ J}$ ,  $FS=60\text{ N}$ ) to impact and friction. Therefore, the relatively low stability (thermal stability and sensitivity) of ketone **121** may affect its further application. By comprehensively considering the energetic properties of these new energetic compounds, compounds **117** and **118** may be promising candidates as RDX substitutes owing to the combination of a good detonation performance and low sensitivity.

## 4 Summary and Prospect

Unlike other oxadiazole isomers such as 1,2,4-oxadiazole and 1,2,5-oxadiazole, 1,3,4-oxadiazole is an excellent ex-



Scheme 14. Synthesis of energetic compounds 115, 117–119 and 121 [84].

Table 9. Physical properties and detonation parameters of energetic compounds 99, 101, 103–112, 115, 117–119 and 121 [81] [84].

Compound	$T_d^{[a]}$ [°C]	$\rho^{[b]}$ [g cm <sup>-3</sup> ]	HOF <sup>[c]</sup> [kJ mol <sup>-1</sup> ]/ [kJ g <sup>-1</sup> ]	$D^{[d]}$ [m s <sup>-1</sup> ]	$P^{[e]}$ [GPa]	IS <sup>[f]</sup> [J]	FS <sup>[g]</sup> [N]	ESD <sup>[h]</sup> [J]
99	98.5	1.90	231.0/0.53	8764	33.2	10	160	0.20
101	200.8	1.80	-126.2/ -0.33	8407	31.1	12	180	0.23
103	250.3	1.72	-146.1/ -0.31	7978	25.1	40	360	0.69
104	180.9	1.63	341.4/0.65	8001	24.2	40	340	0.68
105	187.6	1.71	538.7/0.97	8484	28.1	31	300	0.56
106	196.8	1.77	193.8/0.47	8577	32.0	8	120	0.16
107	160.2	1.85	-30.0/ -0.07	8770	34.5	20	240	0.33
108	190.8	1.70	80.8/0.16	8095	25.7	31	320	0.58
109	184.5	1.76	88.7/0.17	8431	29.8	25	280	0.37
110	133.0	1.80	372.8/0.77	8270	28.8	25	280	0.38
111	198.6	1.83	406.8/0.79	8455	30.1	17	220	0.30
112	205.8	1.84	589.0/1.15	8601	31.8	16	200	0.29
115	174	1.74	-501.6/ -1.10	8042	26.7	28	240	-
117	180	1.87	-695.2/ -1.38	8561	33.2	33	360	-
118	168	1.87	-295.6/ -0.59	8821	33.7	38	240	-
119	171	1.65	408.7/0.57	8188	24.7	40	160	-
121	108	1.89	60.3/0.13	8665	32.7	4	60	-
TATB	324	1.94	-154.2/ -0.60	8114	31.2	50	-	-

[a] Decomposition temperature from DSC (5 °C min<sup>-1</sup>). [b] Density measured at 25 °C. [c] Calculated molar enthalpy of formation. [d] Detonation velocity calculated using EXPLO5 (6.01). [e] Detonation pressure calculated using EXPLO5 (6.01). [f] Impact sensitivity. [g] Friction sensitivity. [h] Sensitivity against electrostatic discharge.

phosphoric unit that demonstrates high stability while maintaining a relatively high energy level. Therefore, 1,3,4-oxadiazole has increasingly attracted the attention of researchers in the field of energetic materials, and several energetic materials have been achieved using 1,3,4-oxadiazole as building blocks. In this review, we provide a comprehensive summary of the developments in the synthesis and performance of energetic materials incorporating 1,3,4-oxadiazole over the past few years. In most cases, the 1,3,4-oxadiazole ring was obtained through the simple dehydrative cyclization of 1,2-diacylhydrazines, and the explosophore groups connected to the 1,3,4-oxadiazole ring were mostly amino, nitroamino, and polynitromethyl groups. Energetic materials composed of a 1,3,4-oxadiazole backbone and different heterocycles or benzene rings with energy-rich functionalities bonded to these rings were also prepared, which were either linked directly or through various heteroatom bridges such as azo and nitromethane.

Considering the overall performance and applicability of the energetic materials, 1,3,4-oxadiazole-based energetic compounds appear to be superior to other congeneric compounds. Energetic materials with even better detonation performances, high stabilities, and convenient synthesis approaches could be achieved by integrating multiple fields of organic, inorganic, structural, physical, and theoretical chemistry. As a benign candidate for energetic material explosophoric units, 1,3,4-oxadiazole may promote the application and industrialisation of novel high-performing energetic materials.

## Acknowledgements

The authors acknowledge financial support from the National Natural Science Foundation of China (22005337).



## Data Availability Statement

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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Manuscript received: December 8, 2020

Revised manuscript received: February 28, 2021

Version of record online: April 23, 2021