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# **Dalton Transactions**

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A series of 1,2,4-oxadiazole-derived energetic compounds were successfully synthesized using the 1,2,4-oxadiazole-3-chloroxime as a versatile starting material. These energetic compounds were fully characterized by NMR spectroscopy, IR spectroscopy, and elemental analysis. The structures of compounds **5**, **6a**, **6c**, **8** and **8a** were determined by single crystal X-ray diffraction. The physicochemical and energetic properties for all synthesized energetic compounds, including density, thermal stability and energetic performance (e.g., detonation velocities and detonation pressures), were investigated. Among these energetic compounds, hydrazinium salts **6b**, **8b** and hydroxylamonium salts **6c**, **8c** exhibit satisfactory calculated detonation performances, which outperforms the commonly used high explosive RDX. Potassium salt **5** shows good detonation performance, high density as well as high sensitivity, making it a potential primary explosive. Compound **9** is a potential candidate for melt-cast explosives due to its remarkable liquid range between melting point ( $T_m = 98$  °C) and decomposition temperature ( $T_d = 208$  °C).

#### Introduction

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Over the past decades, the design and synthesis of new explosive compounds with excellent detonation performance and low sensitivity are important goals in the field of energetic materials.<sup>1</sup> Typical high explosives including cyclo-,1,3,5trimethylene-2,4,6-trinitramine (RDX) and octahydro-1,3,5,7tetranitro-1,3,5,7-tetrazocine (HMX), which are widely used in the military applications as secondary explosives today, lack the low sensitivities of insensitive but lower detonationperforming energetic materials like 2,4,6-triamino-1,3,5trinitrobenzene (TATB), 2,6-diamino-3,5-dinitropyrazine-1oxide (LLM-105), and 2,2-dinitroethene-1,1-diamine (FOX-7).<sup>2</sup> Although there have been numerous attempts to develop potential high quality energetic materials with a fine balance between high detonation level and low sensitivity, an inherent trade-off between high energy and molecular stability makes the discovery and development of high performing energetic materials an interesting but challenging task.<sup>3</sup>

In recent years, nitrogen-rich compounds have received significant interest in the design of new energetic materials. A

variety of new energetic compounds have been designed and synthesized based on versatile nitrogen-rich heterocyclic rings like tetrazoles,<sup>4</sup> 1,2,4-triazoles,<sup>5</sup> 1,2,3-triazoles,<sup>6</sup> pyrazoles,<sup>7</sup> and furazans<sup>9</sup>. Due to the imidazoles.<sup>8</sup> structural characteristics of a large number of energetic N-N, C-N, and N-O bonds in the backbone, these nitrogen-rich energetic compounds usually have the higher nitrogen content, enhanced heats of formation, and superior oxygen balance. Within this context, a number of five- and six-membered nitrogen heterocycles have been considered for the development of new nitrogen-rich energetic materials. Recently, 1,2,4-oxadiazole heterocycles have received growing attentions as the key backbone of energetic nitrogen-rich structures. 1,2,4-oxadiazole has demonstrated its promise for the construction of new high explosives with balanced energy and safety properties. In previous studies, Kayukova et al. 10 reviewed the synthesis of 3,5-substituted 1,2,4-oxadiazoles. Fershtat et al. <sup>11</sup> proposed three synthetic strategies for construction of the 1,2,4-oxadiazole framework. Recently, Klapötke et al. 12,13 demonstrated that the combination of C-C bond bridged 1,2,4-oxadiazoles with different energetic moieties (gem-nitro, trinitromethyl and fluorodinitromethyl) led to a good balance between high detonation performance and low sensitivity for the resulting energetic materials. It is obvious that the great potential of developing new 1,2,4oxadiazole-derived energetic materials has not fully exploited yet. In comparison with single 1,2,4-oxadiazole ring, the coupled heterocyclic ring-based energetic compounds containing the 1,2,4-oxadiazole backbone are expected to have better thermal and molecular stability, higher heats of formation, and superior detonation performance. However,

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the synthetic methods of energetic compounds featuring the coupled heterocyclic frameworks of 1,2,4-oxadiazole and tetrazole or furoxan has not been fully established, and studies on diverse functionalization strategies towards these coupled 1,2,4-oxadiazole-based heterocycles also have great potential to be exploited.

In a continuing effort to develop new energetic compounds with high detonation performance, less sensitivity and ecofriendly feature, in this work our interest focused on the design and synthesis of a series of new 1,2,4-oxadiazole-based energetic compounds with various functionalities. In the synthetic methodology of these new energetic 1,2,4oxadiazoles, 1,2,4-oxadiazole-3-chloroxime demonstrated its promising potential as a versatile platform compound for the efficient construction of the target energetic molecules with various energetic functionalities or in combination with different heterocycles with high heats of formation (i.e., hydroxytetrazole and furoxan). The preparation of several nitrogen-rich 1,2,4-oxadiazole-based energetic salts from was also presented. All the obtained energetic compounds were fully characterized by IR, multinuclear NMR spectroscopy, elemental analysis, and DSC. The structures of part compounds were determined by single crystal X-ray diffraction. The thermal stability, mechanical sensitivities, as well as the theoretical detonation performance for these 1,2,4oxadiazole-based energetic compounds were also investigated or calculated.

#### **Results and discussion**

#### Synthesis

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Glyoxime and diaminoglyoxime (1) were synthesized according to the literature.<sup>14,15</sup> Diaminoglyoxime (1) and triethylorthoformic could cyclize into 1,2,4-oxadiazole-3carboxyamidoxime (2) which finally formed 1,2,4-oxadiazole-3chloroxime (3) by the chlorination reaction<sup>16</sup>. Subsequently, three different strategies were employed to convert compound 3 to new energetic compounds. First, 3dinitromethyl-1,2,4-oxadizole (6) was readily produced from the nitration of 1,2,4-oxadiazole-3-chloroxime with a mixture of trifluoroacetic acid anhydride (TFAA) in HCCl<sub>3</sub>, followed by treatment with KI in methanol and finally acidification with diluted hydrochloric acid (Scheme 1). Second, 5-(1,2,4oxadiazolyl-3-yl)-1-hydroxytetrazole (8) was prepared by twostep reactions including nucleophile substitution of chlorine with azide and subsequent cyclization in the acidic conditions. 3-[4-(1,2,4-Oxadiazol-3-yl)-2-oxido-1,2,5-oxadiazol-3-yl]-1,2,4oxadiazole (9) was synthesized in one-step reaction through direct cyclization of 1, 2,4-oxadiazole-3-chloroxime in the presence of K<sub>2</sub>CO<sub>3</sub>. Despite 5-(1,2,4-oxadiazolyl-3-yl)-1hydroxytetrazole (8)<sup>17</sup> and 3-[4-(1,2,4-oxadiazol-3-yl)-2-oxido-1,2,5-oxadiazol-3-yl]-1,2,4- oxadiazole (9)18 have been synthesized before, different approaches were used for the synthesis of compound 8 and compound 9, and their energetic



**Scheme 1.** Synthesis of 1,2,4-oxazole derivatives.



**Scheme 2.** Synthetic route to the nitrogen-rich salts derived from 6 and 8 using the corresponding nitrogen-rich bases (ammonia, hydrazine, hydroxylamine).

#### properties are given and discussed.

Preparation of a series of energetic salts from compounds **6** and **8** was accomplished by dissolving the neutral compounds in methanol (or ethanol), followed by the addition of the corresponding nitrogen-rich bases (Scheme 2). Owing to the poor solubility of the target ionic molecules, the desired energetic salts precipitated almost quantitatively with high purities.

#### Single Crystal X-ray Structure Analysis

Single crystals of **5**, **6a**, **6c** and **8a** suitable for X-ray diffraction studies were all obtained from methanol/water by slow evaporation of the solvents at ambient temperature. The single crystal data of four compounds were collected at 173 K. The crystallographic data and CCDC numbers for these compounds are summarized in Table S1 (ESI<sup>+</sup>).

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**Figure 1**. a) the coordination environment of energetic ligand in compound **5**; b) view of the layer structure contained in compound **5**; c) the 3D structure of compound **5** view along [110] direction.

3-Dinitromethyl-1,2,4-oxadizole potassium salt (5) crystallizes in

the triclinic space group P-1 with a high calculated density of 2.066 g cm<sup>-3</sup> based on crystal data. Each energetic ligand is connected to six potassium atoms via K-O bond (Figure 1a), and the bond length of K-O falls in the range of 2.723(2)-2.930(2) Å. In the energetic ligand, the dihedral angel between the plane where gem-dinitromethyl group lies and the oxadiazole ring plane is 89.84°. Each potassium atom is coordinated to six oxygen atoms which are from five different energetic ligands (Figure S1, ESI<sup>+</sup>). This connection mode gives rise to the 3D framework of compound 5. This 3D framework can also been viewed as a pillared layered structure. As shown in Figure 1b, adjacent potassium atoms are connected to each other via oxygen atom to construct the infinite 1D linear structure, and then the nearby 1D linear moieties are connected each other to form the 2D layer structure via nitro groups. Furthermore, the layers are pillared by energetic ligands to construct the 3D framework of compound 5 (Figure 1c). Regular 1D channels are contained in the 3D framework of compound 5 viewed along the [110] direction to further form the same 3D channels.

Single X-ray diffraction reveals that ammonium 3dinitromethyl-1,2,4-oxadizole (**6a**) crystallizes in the triclinic space group *P*-1 with a high calculated crystal density of 1.734 g cm<sup>-3</sup>. One ammonium cation and one energetic anion are contained in the asymmetrical unit of compound **6a** (Figure 2a). In the crystal structure of **6a**, each energetic ligand is connected to five adjacent ammonium cations *via* hydrogen bonds of N-H···O (Figure 2b). The distance of N···O is in the range of 2.870(2)-3.087(1) Å, while each ammonium cation is connected to five energetic ligands *via* hydrogen bonds (Figure S2, ESI<sup>+</sup>). A 2D layer structure is constructed by this



**Figure 2**. a) the asymmetrical unit of compound **6a**; b) the supramolecular interaction between energetic anion and adjacent ammoniums; c) the 2D super-molecular structure contained in compound **6a**; d) the 3D super-molecular structure of compound **6a**. Dotted lines represent hydrogen bonds.

supramolecular interaction. And then, the layers are stacked in an AAAA mode to build the 3D supramolecular structure of compound **6a** (Figure 2c).

Hydroxylammonium 3-dinitromethyl-1,2,4-oxadizole (6c) crystallizes in the triclinic space group P-1 with a crystal density of 1.840 g cm<sup>-3</sup> which is higher than that of **6a**. It is interesting that the structure of energetic ligand in 6c is much different to that in compound 5. For instance, the dihedral angel between the plane where gem-dinitromethyl group lies and the oxadiazole ring plane is 74.21° but the dihedral angel is 89.84° in compound 5. In the structure of 6c, each hydroxylammonium cation is interacted with five energetic ligands via strong hydrogen bonds (Figure 3c), i.e., N-H--O and O-H…N. The distances of N…O is in the range of 2.757(2)-3.043(1) Å. And each energetic ligand is connected with five adjacent hydroxylammonium cations via hydrogen bonds (Figure 3a), while the nearby energetic ligands are interacted with each other (Figure 3b) via hydrogen bond of C-H...N and the distance of C…N is 2.989 (2) Å. By virtue of those hydrogen bonds, the 3D supramolecular structure of 6c is constructed (Figure 3d). The very extensive hydrogen bond nets contained in 6c may also explain its higher crystal density (1.840 g cm<sup>-3</sup> of 6c) than that of 6a (1.734 g cm<sup>-3</sup> of 6a).

5-(1,2,4-Oxadiazolyl-3-yl)-1-hydroxytetrazole (8) crystallizes in the orthorhombic space group *Pbca* and one molecule is contained in the asymmetric unit of 8 (Figure 4a). The crystal

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**Figure 3**. a) The supramolecular interaction between energetic anion and adjacent hydroxylammoniums; b) the hydrogen bonds between two nearby energetic anions; c) the supramolecular interaction between hydroxylammonium and nearby energetic anions; d) the 3D supramolecular structure of compound **6c**. Dotted lines represent hydrogen bonds.



Figure 4. a) The molecule structure of compound 8; b) the wave-liked layer structure contained in compound 8; c) the supramolecular interaction between the molecules of compound 8; d) the 3D supramolecular structure of compound 8. Dotted lines represent hydrogen bonds.

density of this compound is 1.689 g cm<sup>-3</sup>. All the non-hydrogen atoms in **8** are almost in a plane (N1-C2-C3-N3=-5.66°). The adjacent molecules are interacted with each other through hydrogen bonds (i.e., O-H···N and C-H···N) (Figure 4c), and the distances of O···N and C···N are 2.578 (2) and 3.224 (2) Å, respectively. Each molecule is interacted with four adjacent molecules. A wave-liked layer is formed through this supramolecular interaction (Figure 4c). These layers are further stacked to form the 3D supramolecular structure of **8** (Figure 4d).

Ammonium 5-(1,2,4-Oxadiazolyl-3-yl)-1-hydroxytetrazolate (8a) crystallizes in the monoclinic space group Cc with one ammonium and one energetic anion contained in the asymmetric unit (Figure 5a). The crystal density of 8a is 1.714 g



Figure 5. a) The molecular structure of compound 8a; b) the supramolecular interaction between energetic anions and ammoniums; c) the supramolecular structure of compound 8a; d) dotted lines represent hydrogen bonds.

cm<sup>-3</sup>. In compound **8a**, each ammonium cation is connected to four adjacent energetic anions *via* hydrogen bonds of N-H···N and N-H···O (Figure S3, ESI<sup>+</sup>). The distances of N···N and N···O are in the range of 2.999 (2)-3.072(2) and 2.892(1)-2.961(1) Å, respectively. Each energetic anion is connected to three nearby ammoniums and two other energetic anions by hydrogen bonds (Figure 5b). The 3D supramolecular structure of compound **8a** is constructed by very strong hydrogen bond interactions (Figure 5c). The existence of these extensive hydrogen bond nets in **8a** may result in the relatively higher density (1.714 g of **8a**) than that of compound **8** (1.689 g cm<sup>-3</sup>).

#### Physicochemical and energetic properties

Thermal stability of all compounds were determined via DSC at a heating rate of 5 °C · min<sup>-1</sup> by using approximately 0.7 mg of powdered sample. Compound 6 starts to decompose at 165 °C, which is quite a bit lower than its potassium salt 5 with a decomposition temperature of 170 °C. Interestingly, the thermal decomposition temperatures of ammonium salt (6a, 140 °C), hydrazinum salt (6b, 132 °C) and hydroxylammonium salt (6c, 156 °C) are slightly lower than that of compound 6 (165°C)(Figure 6a). Compound 8 starts to melt at 133 °C and decompose at 143 °C(Figure 6c), and its energetic salts 8a-c demonstrate an enhanced thermal stability (Figure 6b). The DSC curve of compound 9 has two endothermic peaks (Figure 6d). In combination with TG curve, it can be seen that 9 begins to melt at 98 °C and then decompose at 208 °C. Owing to remarkable deviation between  $T_m$  and  $T_d$ , compound **9** can be considered as a potential candidate for melt-cast explosives. The densities of as-synthesized compounds was measured with helium gas pycnometer at 25 °C or calculated. Among them, the densities of 6 (1.85 g cm<sup>-3</sup>), 6b (1.81 g cm<sup>-3</sup>), 6c (1.84 g cm<sup>-3</sup>) and **9** (1.82 g cm<sup>-3</sup>) exceed that of RDX (1.8 cm<sup>-1</sup>).

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For safety testing, the sensitivity of each compound towards impact and friction was measured. The impact sensitivity (IS)

and friction sensitivity (FS) were determined using the standard BAM fall hammer and BAM 10 friction Ditester,



Figure 6. a) DSC plots of compounds 6 and its energetic salts 5, 6a-c; b) DSC plots of energetic salts 8a-c; c) TG and DSC plots of compounds 8; d) DSC plots of compounds 9.

Table 1. Physicochemical and energetic properties of 1,2,4	-oxadiazole-derived energetic compou	nds <b>(5, 6, 6a-c, 8, 8a-c,</b> and <b>9</b> )
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	6	6a	6b	6c	5	8	8a	8b	8c	9	RDX°
Formula	$C_3H_2N_4$	$C_3H_5N_5$	$C_3H_6N_6$	$C_3H_5N_5$	$C_3H_1N_4O_5$	$C_3H_2N_6$	$C_3H_5N_7$	$C_3H_6N_8$	$C_3H_5N_7$	$C_6H_2N_6$	$C_3H_6N_6$
	O <sub>5</sub>	O <sub>5</sub>	O <sub>5</sub>	O <sub>6</sub>	К	O <sub>2</sub>	O <sub>2</sub>	O <sub>2</sub>	O <sub>3</sub>	O <sub>4</sub>	O <sub>6</sub>
M/g mol <sup>-1</sup>	174.07	191.10	206.12	207.10	212.16	154.09	171.12	186.14	187.12	222.12	222.12
ISª/J	4	9	6	6	0.6	6	10	8	8	18	7
FS <sup>b</sup> /N	84	120	144	128	36	72	120	108	96	120	120
N <sup>c</sup> /%	32.2	36.7	40.8	33.8	26.4	54.54	57.30	60.20	52.40	37.84	37.8
$\Omega^d/\%$	-18.4	-29.3	-31.1	-19.3	-11.3	-51.9	-63.1	-68.8	-47.0	-64.8	-21.6
T <sub>m</sub> <sup>e</sup> [°C]	-	-	-	-	-	133	-	-	-	114	-
T <sub>d</sub> f/ °C	165	140	132	156	176	143	174	152	141	214	210
ρ <sup>g</sup> /g cm <sup>−3</sup>	1.85 <sup>n</sup>	1.74 <sup>m</sup>	1.81 <sup>n</sup>	1.84 <sup>m</sup>	2.07 <sup>m</sup>	1.69 <sup>m</sup>	1.72 <sup>m</sup>	1.71 <sup>n</sup>	1.79 <sup>n</sup>	1.82 <sup>n</sup>	1.80
$\Delta_{\rm f} H_{\rm m}^{\rm h}/kJ \ {\rm mol}^{-1}$	-20.57	-29.74	118.82	16.74	-164.44	363	322	478	372	326	70
EXPLO5_V6.02values:											
$-\Delta_{Ex}U^{\circ i}/ kJ kg^{-1}$	5378	4134	4476	4848	3040	4995	4829	5362	3733	4956	6125
T <sub>det</sub> <sup>j</sup> / K	3824	2908	3034	3367	2879	3567	2986	3193	2613	3477	4236
P <sub>CJ</sub> <sup>k</sup> /GPa	32.3	29.4	34.3	35.5	33.4	25.0	28.0	30.4	32.7	26.8	34.9
V <sub>det</sub> <sup>l</sup> /m s <sup>-1</sup>	8527	8301	8843	8793	8880	8037	8576	8929	8913	8043	8748

<sup>a</sup> Impact sensitivity (BAM drop hammer), <sup>b</sup> Friction sensitivity (BAM friction tester), <sup>c</sup> Nitrogen content, <sup>d</sup> Oxygen balance (Ω = (x0–2yC–1/2zH)M/1600, <sup>e</sup> Melting point,

<sup>f</sup> Temperature of decomposition, <sup>g</sup> Density, <sup>h</sup> Calculated energy of formation, <sup>i</sup> Energy of explosion, <sup>j</sup> Explosion temperature, <sup>k</sup> Detonation pressure, <sup>1</sup> Detonation velocity, <sup>m</sup> Crystal density, <sup>n</sup> Measured density (gas pycnometer), <sup>o</sup> Taken from the literature<sup>22</sup>.

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respectively. As given in Table 1, the neutral compound **6** shows high sensitivities towards impact and friction with IS value of 4 J and FS value of 84 N, respectively. The potassium salt **5** has higher sensitivities (IS = 0.6 J, FS = 36 N). However, the mechanical sensitivities of the nitrogen-rich salts (**6a-c**) are obviously improved. Especially, the sensitivities of ammonium salt **6a** (IS = 9 J, FS = 36 N) have a obvious reduction compared to their precursor **6**. Similarly, the sensitivities of the nitrogen-rich salts (**6a-c**) are also better than that of neutral compound **8**. Remarkably, formation of the nitrogen-rich salts (**6a-c** and **8a-c**) leads to a significant improvement in mechanical sensitivity, which may be attributed to extensive hydrogenbonding interactions between the cation and the anion in salt. Compound **9** has relative optional sensitivity property with IS value up to 18 J.

The heats of formation of all compounds were calculated (for further details and results refer to the Supporting Information). To estimate the detonation performances of the prepared compounds, selected key parameters were calculated with EXPLO5 (version 6.02)<sup>20</sup> based on calculated heats of formation and experimental densities. The physicochemical and energetic properties of obtained energetic compounds are summarized in Table 1. The detonation pressure of all compounds lie in the range of 25.0 GPa (8) to 35.5 GPa (6c). The calculated detonation velocities for all materials are above 8000 m s<sup>-1</sup>. In despite of **8** and its ionic derivatives 8a-c with lower density, they exhibits good explosive performance because of high positive heats of formation ( $\Delta_f H$ ). In particular, compound **8b** has the  $\Delta_f H$  values of 478 kJ mol<sup>-1</sup>, which are approximately nine times higher than those of RDX (70 kJ g<sup>-1</sup>). The calculated detonation velocity of 6b, 8b, 6c and 8c are higher than the commonly used explosive RDX with the value of 8748 m s<sup>-1</sup>. In comparison to compounds 6 and 8, a marked performance increase of their nitrogen-rich ionic derivatives except for 6a is seen. Potassium salt 5 (8880 m s<sup>-1</sup>) shows good explosive performance due to its high density and high sensitivity, which makes it a potential primary explosive. Compound 9 shows lower detonation velocities and pressures than RDX, despite it has much higher heats of formation and comparable densities.

#### Conclusions

In summary, a series of 1,2,4-oxadiazole energetic compounds were designed and synthesized. In the synthetic strategy, 1,2,4-oxadiazole-3-chloroxime has demonstrated its promise as a versatile starting material for the synthesis of the 1,2,4oxadiazole-derived energetic molecules with various functionalities including *gem*-dinitromehyl group and hydroxytetrazole (or furazan-oxide ring). Three neutral energetic compounds including 3-dinitromethyl-1,2,4oxadizole (6), 5-(1,2,4-Oxadiazolyl-3-yl)-1-hydroxytetrazole (8) 3-[4-(1,2,4-oxadiazol-3-yl)-2-oxido-1,2,5-oxadiazol-3-yl]and 1,2,4-oxadiazole (9) were synthesized, respectively. The corresponding rich-nitrogen energetic salts 6a-c and 8a-c were further prepared. All the as-synthesized energetic compounds were fully characterized by IR, multinuclear NMR spectroscopy, elemental analysis, differential scanning calorimetry, and sensitivity tests towards and act and arrest and pressure were calculated with EXPLO5 (version 6.02). The structures of compounds **5**, **6a**, **6c**, **8** and **8a** were further determined by single crystal X-ray diffraction. The ionic compounds **6a-c** and **8a-c** showed reduced sensitivities as compared to their neutral molecules, in which **6a** and **8a** were much safer to handle since their stability towards friction and impact was considerably increased. The formation of richnitrogen energetic salts from

compounds **6** or **8** showed a positive influence on the detonation performance of as-synthesized compounds, e.g., their detonation velocities and pressures were both increased. Of these 1,2,4-oxadiazole energetic materials, potassium salt **5** has the potential to be used as the primary explosive due to its excellent explosive performance, high density as well as high sensitivity. Compound **9** is a potential candidate for melt-cast explosives due to remarkable deviation between  $T_m$  (98 °C) and  $T_d$  (208 °C). Moreover, both the hydrazinium salts (**6b**, **8b**) and the hydroxylamonium salts (**6c**, **8c**) also exhibited good calculated detonation performances, which outperformed the commonly used high explosive RDX.

#### **Experimental section**

Caution! Although we experienced no explosion in handling these energetic materials, small scale and best safety practices (leather gloves, face shield) are strongly encouraged!

#### **General methods**

All chemicals and solvents were obtained from Sigma-Aldrich or Alfa-Aesar and were used as supplied. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded at 298 K using DMSO or D<sub>2</sub>O on Bruker 600AVANCE Spectrometer, operating at 600 and 151 MHz, respectively. The chemical shifts are given relative to tetramethylsilane as external standard. Densities were measured at 25°C using on a Micromeritics Accupycll 1340 gas pycnometer. Elemental analyses were obtained on an Elementar Vario MICRO CUBE (Germany) elemental analyser. The melting and decomposition points were recorded on TGA/DSC Mettler Toledo calorimeter at a scan rate of 5 °C min-<sup>1</sup>. Sensitivity data were determined using a BAM drophammer and a BAM friction tester. Single crystal X-ray diffraction data was collected on an Oxford Xcalibur3 diffratometer with Mo-K $\alpha$  radiation ( $\lambda$ =0.71073 Å) at low temperature. Detonation velocity and detonation pressure data were calculated by program package EXPLO5 (version 6.02).

**I,2,4-oxadiazole-3-carboxyamidoxime (2)** and **1,2,4-oxadiazo-Ie-3-chloroxime(3)** were prepared according to the literature procedures.<sup>16</sup>

**3-dinitromethyl-1,2,4-oxadizole(6).** Compound **3** (0.443 g, 3 mmol) in CHCl<sub>3</sub> (3 mL) was added dropwise to a stirred mixture of trifluoroacetic acid anhydride(2.1 mL) and 100%HNO<sub>3</sub> (1.2 mL), while maintaining the reaction temperature at  $0^{-5}$  °C. After the addition was complete, the ice bath was removed, and the mixture was allowed to warm slowly to room

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temperature. It was stirred for another 2 h, and then poured into ice water (50 mL) and extracted with CHCl<sub>2</sub> (3×20 mL). The organic phases were combined, dried over magnesium sulfate, and then concentrated under vacuum to provide the intermediate 4 as a colorless solid. Compound 4 was dissolved in methanol (10 mL), potassium iodide (0.349 g, 2.1 mmol) in methanol (5 mL) was added dropwise, and the mixture was stirred 3 h at room temperature. The precipitate formed was collected by filtration and washed with methanol (5 mL) and ethyl ether (5 mL) to give 5 (1.12 g, 30.2%) as a light-yellow solid. To the suspension of potassium salt 5(1g, 4.7mmol) in water (20ml) concentrated hydrochloride acid was added dropwise in ice bath. Then extracted with ethyl acetate (3×30mL). The organic phases were combined, dried over magnesium sulfate, and then concentrated under vacuum to provide a yellow liquid. The yellow liquid was dissolved in methanol (5ml) and standed at ambient temperature for a day. The solid formed was collected by filtration and washed with methanol (0.5 mL) and ethyl ether (5 mL) to give 6 (0.27 g, 33%) as a yellow-green solid. <sup>1</sup>H NMR (600 MHz, DMSO-d<sub>6</sub>):  $\delta_{H}$ = 7.09 (1H, s), 9.63 (1H, s) ppm; <sup>13</sup>C NMR (151 MHz, DMSO-d<sub>6</sub>):  $\delta_{\rm C}$  = 122.65, 162.64, 167.31 ppm; IR (KBr): v = 3221, 3128, 3073, 1553, 1521, 1498, 1469, 1428, 1363, 1346, 1271, 1185, 1150, 1103, 1085, 970, 958, 897, 884, 817, 752, 610, 459 cm<sup>-1</sup>; elemental analysis calcd (%) for C<sub>3</sub>H<sub>2</sub>N<sub>4</sub>O<sub>5</sub> (174.07): C 20.70, H 1.16, N 32.19; found: C 20.55, H 1.18, N 32.04.

General procedures for the preparation of energetic salts 6a-c. Ammonia (25 wt% in water, 2.5mmol), hydrazine hydrate (80 wt% in water, 2.1 mmol) or hydroxylamine (50 wt% in water, 2.1 mmol) was added to a solution of 3-dinitromethyl-1,2,4oxadizole 6 (0.348 g, 2 mmol) in methanol (5 mL). After stirring for 2h at ambient temperature, the precipitate was collected by filtration and washed with MeOH and Et<sub>2</sub>O.

#### Ammonium 3-dinitromethyl-1,2,4-oxadizole (6a).

6a (0.248 g, 65%) a light yellow solid. <sup>1</sup>H NMR (600 MHz, DMSO-d<sub>6</sub>):  $\delta_{\rm H}$  = 7.04 (4H, s), 9.57 (1H, s) ppm; <sup>13</sup>C NMR (151 MHz, DMSO-d<sub>6</sub>): δ<sub>C</sub> = 122.64, 162.57, 167.20 ppm; IR (KBr): v = 3212, 3128, 3080, 2859, 1553, 1520, 1498, 1464, 1428, 1360, 1346, 1271, 1185, 1150, 1103, 1085, 970, 958, 897, 884, 817, 752, 610, 460 cm<sup>-1</sup>; elemental analysis calcd (%) for  $C_3H_5N_5O_5$ (191.10): C 18.86, H 2.64, N 36.65; found: C 18.63, H 2.71, N 36.48.

#### Hydrazinium 3-dinitromethyl-1,2,4-oxadizole(6b).

6b (0.293 g, 71%) as yellow solid. <sup>1</sup>H NMR (600 MHz, DMSOd\_6):  $\delta_{\text{H}}$  = 7.06 (5H, s), 9.54 (1H, s) ppm;  $^{13}\text{C}$  NMR (151 MHz, DMSO-d<sub>6</sub>): δ<sub>C</sub> =122.65, 162.56, 167.20 ppm; IR (KBr): v = 3245, 3129, 3031, 2977, 2580, 1552, 1522, 1498, 1472, 1374, 1367, 1348, 1296, 1270, 1256, 1184, 1152, 11.3, 1085, 958, 898, 883, 817, 752, 610 cm  $^{\text{-1}}$ ; elemental analysis calcd (%) for  $C_3H_6N_6O_5$ (206.12): C 17.48, H 2.93, N 40.77; found: C 17.25, H 3.03, N 40.48.

#### Hydroxylammonium 3-dinitromethyl-1,2,4-oxadizole(6c).

6c (0.286 g, 69%) as light yellow solid. <sup>1</sup>H NMR (600 MHz, DMSO-d<sub>6</sub>):  $\delta_{\rm H}$  = 7.04 (3H, s), 9.57 (1H, s) ppm; <sup>13</sup>C NMR (151 MHz, DMSO-d<sub>6</sub>):  $\delta_{C}$  = 122.65, 162.57, 167.21 ppm; IR (KBr): v = 3202, 3130, 1552, 1522, 1471, 1426, 1407, 1395, 1366, 1347, 1920, 1271, 1185, 1151, 1103, 1086, 958, 897, 884, 817, 752,

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610 cm<sup>-1</sup>; elemental analysis calcd (%) for  $C_3H_5N_5Q_{fe}$  (207:19) in C 17.40, H 2.43, N 33.82; found: C 17.27, HD2.65, AD33/68. TO3320F 3-[4-(1,2,4-oxadiazol-3-yl)-2-oxido-1,2,5-oxadiazol-3-yl]-1,2,4oxadiazole(9). To a suspension of 3 (0.295 g, 2mmol) in Et<sub>2</sub>O (10 mL) was added dropwise  $K_2CO_3$  (0.157 g, 1.13 mmol) in water (4 mL) for 30 min. After stirring for 2 h at 10 °C, the resulting mother liquid was extracted with ethyl ether (2×20ml). The combined organic layer was dried over MgSO<sub>4</sub>, and concentrated in vacuo to give a white solid (0.098 g, 44%).<sup>1</sup>H NMR (600 MHz, DCCl<sub>3</sub>) :  $\delta_{\rm H}$  = 8.99 (1H, s), 9.03 (1H, s) ppm; <sup>13</sup>C NMR (151MHz, DCCl<sub>3</sub>):  $\delta_{C}$  = 105.59, 144.68, 156.13, 158.23, 166.06, 166.10 ppm; IR (KBr): v = 3118, 1610,1573, 1552, 1532, 1440, 1378, 1367, 1275, 1102, 1093, 1051, 1022, 956, 944, 907, 895, 823, 613 cm<sup>-1</sup>; elemental analysis calcd (%) for C7H4N6O3 (220.15): C 38.19, H 1.83, N 38.18, found: C 38.06, H 1.85, N 38.08.

5-(1,2,4-Oxadiazolyl-3-yl)-1-hydroxytetrazole(8). A solution of sodium azide (1.3 g, 20 mmol) in water (8 mL) was added dropwise to a solution of 3 (2.31 g, 15 mmol) in ethanol (100 mL). The suspension was stirred at room temperature for 20 h and subsequently poured into 2M HCl (400 mL). The clear solution was extracted with ethyl acetate (4×100 mL), the combined organic phases were dried over magnesium sulfate and the solvent was concentrated in vacuum and dry by air flow to 1,2,4-oxadizole-3-azidoxime (7) as a colorless powder (2.08 g, 90%). A solution of 7 (2.08 g, 13.5mmol) in concentrated hydrochloric acid (50 mL) was stirred at room temperature for 12 h. The clear solution was poured on ice and extracted with ethyl acetate (3×100 mL). The combined organic phases were dried over magnesium sulfate and the solvent was solvent was concentrated in vacuum and dry by air flow to yield a colorless powder (1.98 g, 95%). <sup>1</sup>H NMR (600 MHz, DMSO-d<sub>6</sub>):  $\delta_{\rm H}$  = 7.08 (1H, s), 9.9 (1H, s) ppm; <sup>13</sup>C NMR (151 MHz, DMSO-d<sub>6</sub>):  $\delta_{C}$  = 137.95, 156.82, 168.66 ppm; IR (KBr): v = 3120, 1532, 1407, 1351, 1313, 1285, 1257, 1190, 1133, 1098, 1061, 975, 961, 928, 913, 756, 743, 729, 709, 669, 613, 551, 412 cm<sup>-1</sup>;

elemental analysis calcd (%) for  $C_3H_2N_6O_2$  (154.09): C 23.38, H 1.31, N 54.54, found: C 23.29, H 1.36, N 54.38.

General procedures for the preparation of energetic salts 8a-c. 5-(l,2,4-Oxadiazolyl-3-yl)-1-hydroxytetrazole (0.5 g, 2 mmol) was diluted in EtOH (5 mL) and aqueous ammonia (28 wt% in water), hydrazine hydrate (80 wt% in water) or hydroxylamine (50 wt% in water) (2.1 mmol) was added. After stirring at ambient temperature for 2 h, the precipitate was filtered off and washed with EtOH and Et<sub>2</sub>O.

Ammonium 5-(I,2,4-Oxadiazolyl-3-yl)-1-hydroxytetrazole(8a). 8a (0.229 g, 67%) as white solid. <sup>1</sup>H NMR (600 MHz, DMSO-d<sub>6</sub>):  $\delta_{\rm H}$  = 7.33 (4H, s), 9.75 (1H, s) ppm; <sup>13</sup>C NMR (151 MHz, DMSOd<sub>6</sub>): δ<sub>C</sub> = 134.56, 158.46, 167.49 ppm; IR (KBr): v = 3204, 3197, 3117, 3041, 3033, 2852, 1733, 1688, 1601, 1524, 1455, 1435, 1384, 1341, 1288, 1232, 1175, 1107, 1093, 1012, 973, 961, 945, 901, 755, 713, 693, 613, 584, 411 cm<sup>-1</sup>; elemental analysis calcd (%) for C<sub>3</sub>H<sub>5</sub>N<sub>7</sub>O<sub>2</sub> (171.12): C 21.06, H 2.95, N 57.30, found: C 20.95, H 2.96, N 57.26. 5-(I,2,4-Oxadiazolyl-3-yl)-1-

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hydroxytetrazole(8b). 8b (0.287 g, 77%) as white solid. <sup>1</sup>H

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NMR (600 MHz, DMSO-d\_6):  $\delta_{\rm H}$  = 8.28 (5H, s), 9.67 (1H, s) ppm;  $^{13}\text{C}$  NMR (151 MHz, DMSO-d\_6):  $\delta_{\rm C}$  = 134.49, 158.51, 167.48 ppm; IR (KBr): v = 3321, 3201, 3076, 3025, 2841, 2715, 2625, 1650, 1619, 1584, 1524, 1438, 1409, 1305, 1277, 1235, 1186, 1136, 1105, 1073, 975, 893, 757, 710, 690, 614, 589 cm^{-1}; elemental analysis calcd (%) for C\_3H\_6N\_8O\_2 (186.14): C 19.36, H 3.25, N 60.20, found: C 19.28, H 3.27, N 60.12.

Hydroxylammonium 5-(I,2,4-OxadiazolyI-3-yI)-1-hydroxytetrazole(8c). 8c ( 0.273 g, 73%) as gray-white solid. <sup>1</sup>H NMR (600 MHz, DMSO-d<sub>6</sub>):  $\delta_{H}$  = 7.76 (3H, s), 9.68 (1H, s) ppm; <sup>13</sup>C NMR (151 MHz, DMSO-d<sub>6</sub>):  $\delta_{C}$  = 134.76, 158.35, 167.61 ppm; IR (KBr): v = 3557, 3240, 3035, 2929, 2706, 1606, 1586, 1548, 1527, 1445, 1416, 1387, 1338, 1275, 1241, 1191, 1171, 1112, 1099, 1036, 1014, 899, 759, 714, 617, 411 cm<sup>-1</sup>; <sup>13</sup>C NMR (151 MHz, D<sub>2</sub>O):  $\delta_{C}$  = 135.64, 156.64, 167.18 ppm, elemental analysis calcd (%) for C<sub>3</sub>H<sub>5</sub>N<sub>7</sub>O(187.12): C 19.26, H 2.69, N 52.40, found: C 19.18, H 2.75, N 52.31.

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# Exploiting the Energetic Potential of 1,2,4-Oxadiazole Derivatives:

## Combining the Benefits of 1,2,4-Oxadiazole Framework with Various

## **Energetic Functionalities**

Chao Yan, Kangcai Wang, Tianlin Liu, Hongwei Yang, Guangbin Cheng\*, and Qinghua Zhang\*



A series of energetic compounds based on 1,2,4-oxadiazole framework with various functionalities was synthesized and structurally characterized. Among them, the hydrazinium salt **8b** and hydroxylamonium salt **8c** exhibited satisfactory calculated detonation performances, while compound **9** was a potential candidate for the applications of melt-cast explosives.