In recent decades, a series of representative synthetic methods for fused energetic materials have been reported, but most of them are still subject to some limitations. In this work, a novel unexpected one-step method for constructing fused tricyclic compounds like 5-amino-6-azido-[3,4',5,6]pyrido[4,3-d][1,2,3]triazine[1,2,5]oxadiazolo-8-oxide (OPTA) and (E)-N-(6-amino-[1,2,5]oxadiazolo[3,4-b]pyrazolo[5,4-d]pyridin-5(4H)-ylidene)nitramide (OPPD) from amino cyanide intermediates has been achieved under the conventional TFA/TFAA/100% HNO3 nitration reaction system. This one-step process that involves at least four steps of reaction is rarely reported in the synthesis of energetic materials. It is worth noting that OPPD is the first example of a fused diazonium primary explosive with higher decomposition temperature ($T_d = 181{\degree}C$), relatively lower sensitivities ($FS = 40 N$, $IS = 5 J$) and greater initiating power ($MPC = 30 mg$) than the most commonly used organic primary explosive DDNP ($T_d = 157{\degree}C$, $FS = 24.7N$, $IS = 1 J$, $MPC = 70 mg$). This work is a giant step forward to advanced green primary explosives and would improve future prospects for the design of fused energetic materials.

Primary explosives are utilized extensively in aerospace, weapons, and industrial explosive device detonation systems because they produce a strong shock wave that causes secondary explosives to detonate.$^{1-3}$ Both organic compounds and inorganic energetic metal complexes have been investigated throughout the evolution of primary explosives in the past centuries.$^{4-6}$ Lead azide (LA) and lead styphnate (LS) are commonly utilized inorganic energetic metal primary explosives, exhibiting superior priming capabilities.$^{7}$ But they have to be replaced with a green explosive because of the severe heavy-metal pollution. The most effective way to move forward in the search for lead-free primary explosives is to find organic substitutes, which can fully remove the environmental risks brought on by heavy metals while yet retaining high priming performances.$^{7} 2$-Diazol-4,6-dinitrophenol (DDNP) is a well-known organic explosive that has been attempted to scale up production.$^1$ However, it is extremely sensitive to impact, friction, and electrostatic discharge as well as having photosensitive nature that causes it to turn dark (due to decomposition) when exposed to light, and other shortcomings limit its further development.$^{18}$

In the review of the development of green primary explosives, azido and diazidometal-free primary explosives are two representative types of organic initiating substances.$^{9-13}$ Zwitterions containing diazoniums have been widely synthesized and studied in the field of energetic materials.$^{14}$ The classical diazonium primary explosive DDNP has been used owing to the strong initiation capability imparted by the diazonium moiety. Numerous metal-free diazonium compounds possessing remarkable energy properties have been synthesized in the past (Fig. 1a).$^{14-17}$ However, the extremely high sensitivities (IS: < 3 J) and low thermal stability ($T_d: <180{\degree}C$) of these diazonium compounds still limit their further application as the primary explosives.$^3$ Moreover, experimental verification of the initiation capability of the reported diazoniums, with the exception of DDNP, has been infrequent (Fig. 1a).$^{14-17}$

The aforementioned problems make it extremely difficult to find metal-free initiating charges for practical applications that have the following qualities: (1) high (tested) initiating capacity; (2) appropriate sensitivity to initiation via non-explosive stimuli; and (3) thermal stability at least at 180 °C (higher thermal stability is needed for specific applications).$^{5,18,19}$ In recent years, there have been a lot of studies focused on the design and synthesis of fused energetic compounds in an effort to achieve high detonation performance and thermodynamic stability.$^{20-26}$ The extensive conjugation system, ring-strain energy, high heat of formation, and polycyclic coplanar structure of the fused...
energetic compounds all contribute to their strong detonation qualities, thermodynamic stability, and low mechanical sensitivity. In recent years, a series of representative synthetic methods for fused energetic materials have been reported (as Fig. 1b). However, most of them are still subject to some limitations, such as unstable, difficult to obtain, highly toxic, and environmentally hazardous reagents and complex synthesis steps.

Herein, two fused [5,6,5], [5,6,6]-tricyclic organic primary explosives OPTA and OPPD were synthesized through three-step reactions. The selective NH₂–CN condensation reaction for constructing fused tricyclic compounds using TFA/TFAA as the catalyst was proposed. The final compounds OPTA and OPPD were characterized by NMR, IR spectra, elemental analysis, DSC and single crystal X-ray diffraction. Moreover, the initiation capacity of primary explosives OPTA and OPPD was also assessed through the initiation tests.

As shown in Scheme 1, commercially available 4-amino-1,2,5-oxadiazole-3-carbonitrile (1) was used as the starting material. The effort to obtain two final fused tricyclic compounds began with the substitution reaction of compound 1 and malononitrile catalyzed by triethylamine (TEA) to form 2-(amino(4-amino-1,2,5-oxadiazol-3-yl) methyl) malononitrile (2) with geminal-dicyano in a yield of 98.2%. Different alkaline cyclization reagents, sodium azide and hydrazine hydrate, were added to react with dicyano compound 2 to generate furazan-tetrazole and furazan-pyrazole compounds 5-amino-3-(4-amino-1,2,5-oxadiazol-3-yl)-1H-pyrazole-4-carbonitrile (3) and 3-amino-3-(4-amino-1,2,5-oxadiazol-3-yl)-2-(1H-tetrazol-5-yl)propanenitrile (4) (yields, 3: 91.0% and 4: 80.0%), respectively. Later, we originally intended to synthesize the corresponding compound N-(4-(4-nitro-(5-(nitroamino)-1H-pyrazol-3-yl))-1,2,5-oxadiazol-3-yl)nitramide (5) by nitration of 3 according to the reported synthesis route. Several nitration reactions were attempted (100% HNO₃, fuming HNO₃, HNO₃/H₂SO₄), but multiple nitro derivative 5 was not obtained, which may be caused by the lower amino activity on the pyrazole and furan rings. Trifluoroacetic acid (TFA) and trifluoroacetic anhydride (TFAA) were attempted to add in the nitration system (TFA : TFAA : 100% HNO₃ = 1 : 1 : 5, in volume) of 3 to guide the reaction direction and protect the reaction system. The emergence of new products was observed through thin layer chromatography. To our surprise, a fused [5,6,5]-tricyclic energetic compound OPPD (yield: 85.0%) was obtained and further proven by single-crystal X-ray analysis. TFA/TFAA/100% HNO₃ serves as the ring-closing and nitration reagent to promote CN⁺ species to attack the amino group on the furan ring, forming nitrated N–C–N bonded fused-tricyclic compounds. To verify the above analysis, the furozan-tetrazole compound 4 was added in the nitration system of TFA/TFAA/100% HNO₃, and a fused [5,6,6]-tricyclic product OPTA with the azide group was successfully obtained in a high yield of 60.7%. To enhance the energy level of OPTA, the direct nitration of OPTA by using various nitrate systems was attempted to obtain the (E)-6-azido-5-(nitroimino)-4,5-dihydro-[1,2,5] oxadizolo [3′,4′:5,6] pyrido [4,3-d] [1,2,3] triazine 8-oxide (6) with the nitro group. Unfortunately, all attempts have failed, which may be caused by the low reaction activity of amino on the fused ring.

Fig. 1 Representative diazonium metal-free primary explosives (a) and synthetic methods of several fused-ring energetic materials and synthetic strategies in this work (b and c).
The above phenomenon arouses our strong interest in exploring the cyclization reaction mechanism of OPTA and OPPD (as shown in Scheme 2). The TFA/TFAA/100% HNO3 system is usually used for nitration reaction. In the synthesis of OPPD and OPTA, the one-step process involves a condensation–nitration–diazotization–tautomerization reaction and condensation–nitration–elimination–tautomerization reaction under TFA/TFAA/100% HNO3 catalytic conditions, respectively. Under the TFA/TFAA/100% HNO3 system, the CN+ species on pyrazole attacks the anionic nitrogen atom in NH2 to form N–C–N bonded fused intermediate 3-2. Then imine 3-2 undergoes isomerization to generate 3-4. Perhaps due to the presence of HNO2 in nitric acid, the amino intermediate 3-4 further converts the zwitterionic OPPD. Diazotization of the primary amine followed by nitration at the 5-position of the pyridine makes the 2-H of pyrazole more acidic and led to the zwitterionic inner salt OPPD after deprotonation. As for OPTA, the possible mechanism for rationalization of 4 to 4-4 cyclization reaction is similar to that of 3 to 3-4. In this mechanism, the intermediate product 4-4 reacts with the mixed acid to generate an unstable nitramine compound. According to the work of Zhang et al., under the action of hydrogen bonding, the N–H of the tetrazole unit undergoes an electrophilic addition reaction with N=O on the nitro group, generating unstable condensed ring intermediates and rapidly undergoing dehydration elimination reactions, resulting in the formation of a new fused ring intermediate. Then the intermediate may undergo dehydrogenation reaction and azide-tetrazole tautomerization, and irreversibly transforms into the final product OPTA at room temperature.

As illustrated in Fig. 2, the molecule OPTA belongs to the P21/C space group in the monoclinic crystal system with a crystal density of 1.871 g cm−3 (193 K). Two types of intramolecular hydrogen bonds are present in the crystal structure of OPTA: N12–H12A···N5 (2.1300 Å) and N12–H12B···N9 (2.0600 Å). These hydrogen bonds are produced by nitrogen atoms (N5 or N9) and neighboring amino groups. The crystal structure of compound OPPD belongs to the monoclinic Pna21 space group with a crystal density of 1.805 g cm−3 at 193 K, and each unit cell contains four independent molecules (Fig. 2b). The intra molecular hydrogen bonds of N3–H3···N4 (2.5990 Å) and N3–H3···O2 (2.0000 Å) exist in the crystal structure of OPPD. The fused-ring of OPTA and OPPD shows a nearly flat molecular geometry, which is partly accounts for their high crystal density (Fig. 2c and d). Fig. 2e and f depict two different molecular geometry.

Scheme 1 Synthesis of fused [5,6,5], [5,6,6]-tricyclic energetic molecules OPTA and OPPD.

Scheme 2 The possible formation mechanism for OPTA and OPPD.
types of mixed $\pi-\pi$ stacking modes of OPTA and OPPD, with large layered planar structures present in their mixed stacking. And the distance between the nearest layers of the OPTA crystal stack is 2.1 Å, which is smaller than that of the OPPD (3.9 Å), thereby potentially leading to its higher crystal density.

The densities of the newly synthesized compounds OPTA and OPPD were measured using a gas specific gravity cylinder filled with room temperature helium. The experimental density at room temperature is generally recognized. The experimental densities of compounds OPTA (1.86 g cm$^{-3}$) and OPPD (1.80 g cm$^{-3}$) exceed that of widely used metal-free primary explosive DDNP (1.72 g cm$^{-3}$). Using the Gaussian 09 software, the heat of formation (HOF) of OPTA and OPPD was calculated. Due to the high heat formation of fused [5,6,5], [5,6,6]-tricyclic rings, all of OPTA and OPPD exhibit high positive values of HOF (OPTA: 1076.1 kJ mol$^{-1}$ and OPPD: 1069.7 kJ mol$^{-1}$). With the calculated heat of formation and measured density, the detonation performance including detonation velocity ($D$) and pressure ($P$) of OPTA and OPPD was calculated using EXPLO5 version 6.01 (see ESI Table S1 and ESI Scheme S1†). Not surprisingly, compounds OPTA (8787 m s$^{-1}$, 32.3 GPa) and OPPD (8679 m s$^{-1}$, 31.0 GPa) exhibit much higher detonation velocity and detonation pressure than DDNP (6900 m s$^{-1}$, 24.2 GPa). Compound OPTA even shows high detonation velocity and detonation pressure approaching well-known highly explosive RDX (8795 m s$^{-1}$, 34.9 GPa).

In order to evaluate the risks and ignition efficiency associated with the manufacturing, moving, storing, and common uses/handling of primary explosives, standard BAM techniques were used to ascertain the mechanical sensitivity of each compound. Table 1 shows that compounds OPTA and OPPD have mechanical sensitivities (IS $\geq$ 5 J, FS $\geq$ 60 N) that are suitable for practical usage, better than those of DDNP (IS = 1 J, FS = 24.7 N) and LA (IS: 2.5–4 J, FS: 0.1–1 N). Another crucial characteristic of main explosives is their thermal stability. The thermal stability of OPTA and OPPD was evaluated using differential scanning calorimetry (DSC). With a starting decomposition temperature of 181 °C, compound OPPD exhibits a clear exothermic peak that surpasses those of both DDNP ($T_d = 158$ °C) and the majority of documented diazonium metal-free primary explosives. Compound OPTA has a high decomposition temperature ($T_d = 255$ °C), which is superior to that of RDX ($T_d = 204$ °C) and comparable to that of the widely used inorganic energetic metal-primary explosive lead styphnate (LS) ($T_d = 255$ °C), which is rarely reported in the field of azido metal-free primary explosives.

Appropriate shock sensitivity and the introduction of the azido group or diazonium group make the compounds OPTA and OPPD potential primary explosives. Therefore, detonation tests were carried out to determine the viability of OPTA and OPPD as major explosives. This work evaluates the viability of

![Fig. 2](Image 87x489 to 248x729) The molecular structures of OPTA (a) and OPPD (b); the planar molecular geometries of OPTA (c) and OPPD (d); the crystal stacking structures of OPTA (e) and OPPD (f).

![Fig. 3](Image 326x89 to 530x264) Initiation capability tests for OPTA and OPPD. (a) Initiation capability test apparatus; (b) the blasting caps for tests; (c–f) results for the 5 mm lead plates of OPTA and OPPD.

### Table 1  Physicochemical properties of OPTA and OPPD in comparison with the well-known primary explosives

<table>
<thead>
<tr>
<th>Compound</th>
<th>$T_d$ (°C)</th>
<th>$\rho$ (g cm$^{-3}$)</th>
<th>$\Delta H_f$ (kJ mol$^{-1}$)</th>
<th>$D$ (m s$^{-1}$)</th>
<th>$P$ (GPa)</th>
<th>IS (J)</th>
<th>FS (N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPTA</td>
<td>255</td>
<td>1.86</td>
<td>1076.1</td>
<td>8787</td>
<td>32.3</td>
<td>6</td>
<td>114</td>
</tr>
<tr>
<td>OPPD</td>
<td>181</td>
<td>1.80</td>
<td>1069.7</td>
<td>8679</td>
<td>31.0</td>
<td>5</td>
<td>60</td>
</tr>
<tr>
<td>LA$^b$</td>
<td>315</td>
<td>4.80</td>
<td>450.1</td>
<td>5920</td>
<td>33.8</td>
<td>2.5–4</td>
<td>0.1–1</td>
</tr>
<tr>
<td>LS$^b$</td>
<td>255</td>
<td>3.10</td>
<td>-835.0</td>
<td>5600</td>
<td>—</td>
<td>2.25</td>
<td>1.45</td>
</tr>
<tr>
<td>DDNP$^b$</td>
<td>157</td>
<td>1.72</td>
<td>321.0</td>
<td>6900</td>
<td>24.2</td>
<td>1</td>
<td>24.7</td>
</tr>
</tbody>
</table>

$^a$ Onset decomposition temperature (10 °C min$^{-1}$) from DSC (°C).  
$^b$ Measured density by a gas pycnometer at 25 °C (g cm$^{-3}$).  
$^c$ Heat of formation (kJ mol$^{-1}$).  
$^d$ Calculated detonation velocity (EXPLO5, version 6.01) (m s$^{-1}$).  
$^e$ Calculated detonation pressure (GPa).  
$^f$ Impact sensitivity (J).  
$^g$ Friction sensitivity (N).  

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compounds OPTA and OPPD as primary explosives through a series of initiation tests (Fig. 3). 500 mg of RDX was detonated in this detonation test employing a pyro-technical igniter (Fig. 3a) with OPTA or OPPD serving as the primary explosive (GJB 5891-2006).1,5 A pyrotechnical igniter was used in many detonation tests to explode a lead plate with a thickness of 5.0 mm (Fig. 3a and b). Under the same experimental conditions, OPTA requires at least 70 mg to detonate the lead plate to a diameter of 9.5 mm, while OPPD can detonate to 11.5 mm with the minimum priming charge (MPC) of 30 mg (Fig. 3c and e). The findings demonstrate that OPTA and OPPD can effectively detonate RDX, suggesting that they might make good candidates for future primary explosives that are favorable to the environment. Specifically, OPPD is superior to the well-known DDNP (MPC = 70 mg) as a primary explosive free of metal with an MPC of 30 mg.1,5

Conclusions

In conclusion, fused [5,6,5], [5,6,6]-tricyclic metal-free primary explosives OPTA and OPPD were synthesized by a facile method with yields of 47.6% and 85.9%, respectively. In the synthesis of OPPD and OPTA from amino cyanide intermediates, the one-step process involves a condensation–nitration–diazotization–tautomerization reaction and condensation–nitration–elimination–tautomerization reaction under TFA/TFAA/100% HNO3 catalytic conditions, respectively, which is rarely reported. The final structures of the compounds are thoroughly characterized by the use of elemental analysis, NMR, IR spectra and X-ray diffraction. It is worth noting that the product OPPD would be the first reported fused diazonium metal-free initiating substance in the field of energetic compounds. Fused organic primary explosive OPPD (T_d = 181 °C, D = 8679 m s^-1, P = 31.0 GPa, IS = 5 J, FS = 60 N) exhibits lower sensitivity, better thermal stability, and higher detonation performances than those of DDNP (T_d = 157 °C, D = 6900 m s^-1, P = 24.2 GPa, IS = 1 J, FS = 24.7 N). In addition, the detonation tests prove that OPPD (MPC = 30 mg) has much better initiation capacity than DDNP (MPC = 70 mg) as a novel environment friendly primary explosive candidate. This work demonstrates the promising application of fused diazonium primary explosives, which would accelerate the upgrading of green primary explosives.

Data availability

The data underlying this study are available in the published article and its online ESI.†

Author contributions

Chenghuang Li designed the study, performed the molecular design and carried out the synthesis. Jie Tang performed the structural analysis, and characterization of properties. Hongwei Yang, Chuan Xiao and Guangbin Cheng studied the reaction mechanism and prepared the manuscript. All authors discussed and commented on the manuscript.

Conflicts of interest

The authors declare no competing financial interest.

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