Full Paper

The Unique Synthesis of a Green Metal-Free Primary Explosive: 3,3′-azo-5,5′-diazido-1,2,4-triazole

Cai-jin Lei,[a] Hong-wei Yang,[a] Hua-lin Xiong,[a] and Guang-bin Cheng*[a]

Abstract: The unique synthesis of 3-azido-5-amino-1,2,4-triazole (**1**) and a possible reaction process were described. The target compound 3,3′-azo-5,5′-diazido-1,2,4-triazole (**2**) was obtained by further coupling reaction of compound **1** with potassium permanganate. Compound **2** was well characterized by NMR spectra, IR spectroscopy, elemental analysis, differential scanning calorimetry (DSC), and single crystal X-ray diffraction. The sensitivities towards impact and friction of **2** were characterized by BAM Fallhammer and BAM Friction. Compound **2** exhibited good density (1.68 g cm^{-3}), good thermal stability (193 °C), high heat of formation (1345.1 kJ mol^{-1}/5.468 kJ g^{-1}), excellent detonation performance (26.7 GPa, 8345 m s^{-1}) and acceptable sensitivity (IS = 6 J, FS = 72 N, EDS = 0.224 J). Moreover, compound **2** was tested for its priming ability by detonating RDX. The result indicates that compound **2** could be used as a potential green metal-free primary explosive.

Keywords: high-nitrogen compound · azido · detonation capacity · primary explosive

1 Introduction

Over the past several years, the study of energetic materials such as propellants, explosives and pyrotechnics, has got numerous attentions from researchers due to its important impact on the military and civil aspects [1]. Among them, primary explosives have been widely used in industrial initiation devices [2]. Primary explosives depend on their representatively fast deflagration-to-detonation transition (DDT) upon initiation to detonate a secondary explosive with higher energy but less sensitivity [3–5]. The first substance ever used as a primary explosive was mercury fulminate (MF) in the early 19 century [6]. Then, the famous primary explosives including lead azide (LA) and lead styphnate (LS) have been widely used in civil and military detonator [7]. However, growing concerns over lead contamination stimulate the search for new lead-free primary explosives. During the past decades, the heavy-metal primary explosives such as the copper (I) 5-nitrotetrazolate (DBX-1) have excellent priming ability which may be comparable to lead azide in applications [8]. However, the heavy metal which mainly affects the human health and contaminates the environment is always an important issue in applications. Environmentally acceptable alternatives to toxic lead-based primary explosives are becoming increasingly important for energetic materials [9]. So several heavy-metal-free candidates have been synthesized for the substitution of the heavy-metal primary explosives such as potassium 1,1′-dinitramino- 5,5′-bistetrazolate (K$_2$DNABT) and potassium 4,5-bis(dinitromethyl)-furoxanate (K$_2$BDNMF) [10]. Unfortunately, the initiation ability of potassium-based primary explosive is still relatively weaker than that of lead azide.

Looking back upon the "history tree" of primary explosives (Figure 1), the classic metal-free primary explosives are 2-diazo-4,6-dinitrophenol (DDNP)[11] and tetrazene
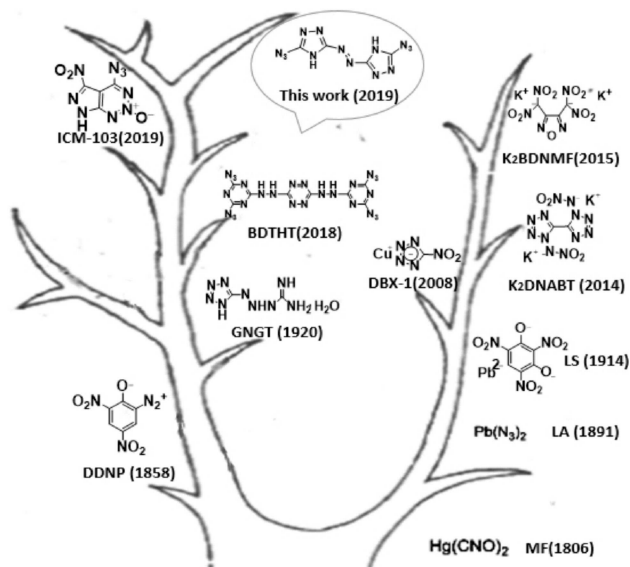
Figure 1. History tree of several representative primary explosive.

[a] C.-j. Lei, H.-w. Yang, H.-l. Xiong, G.-b. Cheng
School of Chemical Engineering
Nanjing University of Science and Technology
Xiaolingwei 200, Nanjing, Jiangsu (P. R. China)
*e-mail: hyang@mail.njust.edu.cn

(GNGT) [12]. However, due to the poor pressure resistance, the tetrazene (GNGT) has gradually been eliminated in practical applications. Up to now, 2-diazo-4,6-dinitrophenol (DDNP) remains to be the mainly metal-free primary explosive in applications [11]. Recently, environmental problems force the development of new generation of green primary explosives, which not only requires good thermal stability, mechanical insensitivity and better performance, but also has an environmentally friendly synthesis and detonation process to decrease environmental pollution [13–15].

The green primary explosives show several features including (1) insensitive to light and humidity; (2) thermal decomposition temperature at least above 180 °C; (3) Stable chemical structure and long-term storage; (4) free of toxic metals: lead, mercury, barium, silver, antimony, cadmium, etc.; (5) free of toxic perchlorate; (6) ease and safety of synthesis [16].

In recent years, two metal-free compounds 3,6-bis-(2-(4,6-diazido-1,3,5-triazine-2-yl)-hydrazinyl)-1,2,4,5-tetrazine (BDTHT)[17] and 6-nitro-7-azido-pyrazole[3,4-d][1,2,3]triazine-2-oxide (ICM-103) [18] were synthesized. Two compounds can detonate the RDX successfully and the initiation ability of them are comparable to Pb(N$_3$)$_2$. The results make them promising replacements of Pb(N$_3$)$_2$ as green primary explosives. Despite of good detonation capacity, there still are some drawbacks such as low thermal stability to ICM-103 and long steps with low yield to BDTHT. Therefore, seeking the newly green metal-free primary explosives may become the main research in future.

Herein, we introduce the unique synthesis and the characterization of 3,3′-azo-5,5′-diazido-1,2,4-triazole with good yield through a facile three-step reaction. Particularly, this compound may be a green metal-free primary explosive through initiation ability which can be compared with Pb(N$_3$)$_2$.

2 Experimental Section

Caution! All triazole, tetrazole and azide compounds are energetic materials. They should be handled in small scale. Experimental operation should be carried out behind blast shields and with proper protective equipment.

2.1 General Methods

^{1}H, ^{13}C NMR and ^{15}N NMR spectra were recorded on nuclear magnetic resonance spectrometer operating at 300 and 500 MHz, respectively. The d_6-DMSO was selected as locking solvents. The decomposition temperatures were determined on a DSC at a heating rate of 5 °C min^{-1}. Infrared (IR) spectra were obtained on a Perkin-Elmer Spectrum BX FT-IR instrument equipped with an ATR unit at 25 °C. Sensitivity towards impact, friction and electrostatic discharge

was determined using a BAM friction tester and a BAM Fall-hammer. The impact sensitivity test was conducted according to the PRC GJB 5891.22-2006. The friction sensitivity test was conducted according to the PRC GJB 5891.24-2006. The electrostatic discharge sensitivity test was conducted according to the PRC GJB 5891.27-2006. The grain size of three sensitivity measurements is 100 meshs. Density of the compound was determined at room temperature by employing a gas pycnometer.

2.2 X-ray Crystallography

The data for **2**·4H$_2$O was collected with a Bruker three-circle platform diffractometer equipped with a SMART APEXII CCD detector. A Kryo-Flex low-temperature device was used to keep the crystals at a constant temperature of 100 K during the data collection. The data collection and the initial unit cell refinement were performed using APEX2 (v2010.3-0). Data reduction was performed using SAINT (v7.68 A) and XPREP (v2008/2). Corrections were applied for Lorentz, polarization, and absorption effects using SADABS (v2008/1). The structure was deduced and refined with the aid of the programs in the SHELXTL-plus (v2008/4) system of programs. All non-hydrogen atoms were refined. All hydrogen atoms were located and refined.

2.3 Syntheses

5-Hydrazinotetrazolium chloride was synthesized according to the literature procedure [19]. Then, according to the relevant literature, we originally intended to synthesize compound **1′** by reacting 5-hydrazinotetrazolium chloride with cyanogen bromide in aqueous HCl solution at room temperature [20]. Interestingly, 5-hydrazinotetrazolium chloride was readily converted to 3-azido-5-amino-1,2,4-triazole. The total yield of compound **1** with two-step reaction is 40 %. Further, the target compound **2** was formed by coupling reaction of compound **1** with potassium permanganate at room temperature. A possible reaction process of **1** is shown in Scheme 1b. The intermediate of triazole-tetrazole fused ring (**1′**) could be formed by reacting 5-hydrazinotetrazolium chloride with cyanogen bromide. However, the formation of **1** resulted from a cleavage of N1–N2 bond of compound **1′**, the stable azido was formed. The cleavage is a simple process. Firstly, the C3–N1 bond became polarized, C3 atom possessed a positive charge and N1 atom possessed a negative charge. In addition, N2 atom also possessed a negative charge. Above of all could result in a repulsion upon N1–N2 bond. In the end, N1–N2 bond is interrupted.

According to our literature research, the representative methods for the synthesis of 3-azido-5-amino-1,2,4-triazole (**1**) has been reported in the literature [21]. The previous synthesis of 3-azido-5-amino-1,2,4-triazole (**1**) was synthe-
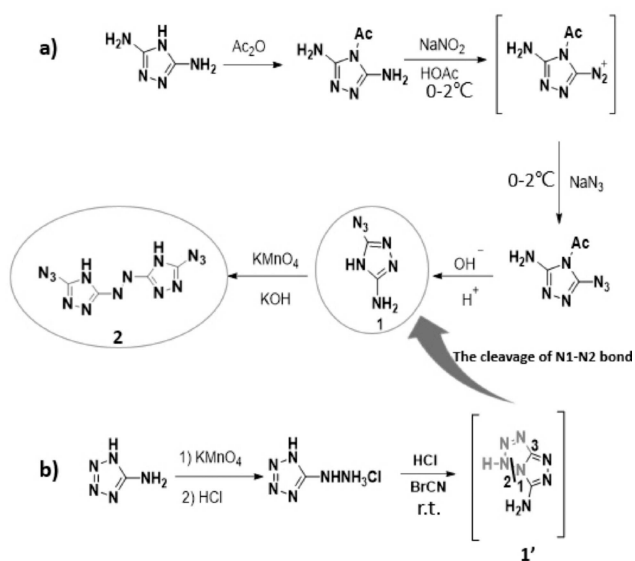
Scheme 1. a) The previous way to synthesize compound **1**. b) The new method to synthesize compounds **1** and **2**.

sized with diazotization-azidation (Scheme 1a). However, the synthesis suffered from some limitations such as the potential danger of diazotization and total synthesis of unsatisfactory yield (25%).

2.3.1 5-Hydrazinotetrazolium Chloride

5-Hydrazinotetrazolium chloride was prepared according the literature procedure [20].

2.3.2 Synthesis of 3-azido-5-amino-1,2,4-triazole(1)

Cyanogen bromide (2.12 g, 10.0 mmol) was added to a stirred solution of 5-hydrazinotetrazolium chloride (1.36 g, 10.0 mmol) in 1 mol L^{-1} HCl (30 mL). The solution was stirred at room temperature for 24 h. The reaction mixture was extracted with ethyl acetate and dried over sodium sulfate. The solvent was removed under reduced pressure and the products were dried as the dark red solid. Yield: 0.94 g, 75%. ^{1}H NMR (300 MHz, d$_6$-DMSO): $\delta = 6.28$ (s, 2H, NH2), 11.86 (s, 1H, NH). ^{13}C NMR (125 MHz, d$_6$-DMSO): $\delta = 140.03$, 156.49 ppm. IR (KBr): v =3399, 3162, 2438, 2146, 1662, 1603, 1542, 1457, 1404, 1363, 1218, 1101, 1016, 807,714 cm^{-1}. Elemental analysis for C$_2$H$_3$N$_7$ (125.04): calcd C 19.19%, H 2.41%, N 78.40%. Found: C 19.06%, H 2.52%, N 77.39%.

2.3.3 Synthesis of 3,3′-azo-5,5′-diazido-1,2,4-triazol (2)

To a suspension of 5-amino-3-azido-1,2,4triazol (0.62 g 5.0 mmol) in 5 mL of water was added a solution of potassium hydroxide (1.00 g, 8.0 mmol) in 5 mL of water. Potassium permanganate (0.80 g, 5.00 mmol) was added in portions for 0.5 h. The reaction mixture was stirred at room temperature for 2 h. The solid was removed by filtration, and the mother liquor was acidified to PH=2–3. The solid formed was filtered as the yellow solid. Yield: 0.43 g, 70%.^{1}H NMR (300 MHz, d$_6$-DMSO): No peak. ^{13}C NMR (125 MHz, d$_6$-DMSO): $\delta = 1458.60$, 163.50 ppm. IR (KBr): v = 2439, 2146, 1594, 1451, 1425, 1329, 1225, 1104, 1050, 991, 843, 759, 718 cm^{-1}. Elemental analysis for C$_4$H$_2$N$_{14}$ (246.16): calcd C 19.48%, H 0.84%, N 79.68%. Found: C 19.64%, H 0.93%, N 78.69%.

3 Results and Discussion

3.1 X-ray Crystallography

Single crystals of the compound **2** suitable for single-crystal X-ray diffraction were obtained by slow evaporation of methanol saturated solution at room temperature and ambient pressure. The single crystal X-ray structures is shown in Figure 2a. Compound **2** crystallizes in the triclinic space group *P*-1, with a cell volume of 679.24(7) Å^3 (Table S1). The presence of solvated H$_2$O gives rise to the low calculated density (1.556 g cm^{-3} at 100 K). Owing to electronic and chemical bond length of the conjugated system tends to be average, all C–N bond lengths of the triazole ring are in the range of 1.267–1.399 Å (Table S5). These extensive hydro-
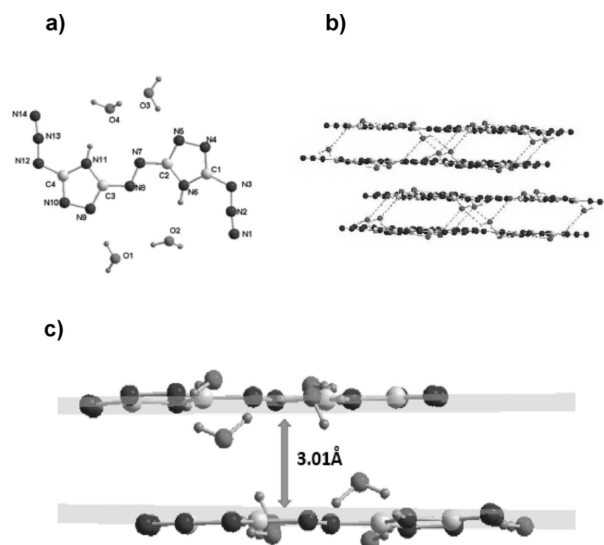
Figure 2. a) Molecular structure of **2**·4H$_2$O. b) Ball and stick packing diagram of compound **2**·4H$_2$O. Dotted lines represent hydrogen bonds. c) The distances between two layers of compound **2**.

gen bonds (N6—H6···O2 2.909(4) Å, N11—H11···O4 2.978(4) Å, O4—H4B···O3 2.859(4) Å, O4—H4 A···O4 2.848(4) Å) of **2** are presented in Table S3. All atoms are nearly coplanar (Figure 2b), which is supported by the dihedral angles: N8—N7—C2—N6 4.9(5)°, N2—N3—C1—N4 179.2(3)°, N2—N3—C1—N6 −1.9(5)°, N7—N8—C3—N9 −178.5(3)°, N7—N8—C3—N11 1.3(5)°, N13—N12—C4—N10 174.9(3)°, N13—N12—C4—N11 −5.3(6)°, as shown in Table S6. To notarize the tightness of the crystal packing, the distances between two azo centroids is 3.01 Å (Figure 2c), much shorter than typical geometrical parameters of aromatic π-π interactions (4.00 Å) [22].

3.2 Physicochemical and Energetic Properties

Thermal stabilities of **2** was studied with DSC at a heating rate of $5\,°C\,min^{-1}$ under a nitrogen atmosphere range from 30 °C to 350 °C. It started to decompose at 193 °C (Figure 3) without melting. The decomposition temperature of **2** are higher than the criterion of 180 °C for green primary explosives.

The azido (-N$_3$) as a highly energetic group in the field of energetic materials is often used as an increase in nitrogen content. The enthalpy of formation of **2** is calculated using the Gaussian 09 program [23]. Compound **2** exhibits high positive heats of formation at $1345.1\,kJ\,mol^{-1}$, which owe to the two azido groups and large numbers of C—N and N—N bonds. The detonation properties of **2** are calculated with the EXPLO5 v6.01 [24,25]. Compound **2** shows its theoretical detonation velocity at $8345\,m\,s^{-1}$, which is superior to that of classical primary explosive Pb(N$_3$)$_2$ ($5920\,m\,s^{-1}$). And the detonation pressure is 26.7 GPa. The physical properties of **2** are summarized in Table 1. The measured density of compound **2** is $1.68\,g\,cm^{-3}$ at room temperature by gas pycnometer. The impact and friction sensitivities were determined by using a standard BAM Fall-hammer and a BAM Friction tester [26]. Its measured impact sensitivity (6 J), friction sensitivity (72 N) and electrostatic

Table 1. Energetic performance parameters of **2** and Pb(N$_3$)$_2$.

|	Pb(N$_3$)$_2$[m]	2
Formula	N$_6$Pb	C$_4$N$_{14}$H$_2$
M [g mol^{-1}]	291	246
IS [J][a]	0.6–4	6
FS [N][b]	0.3–0.5	72
ESD [J][c]	0.006–0.012	0.224
N [%][d]	28.9	63.4
Ω_{CO} [%][e]	−11.0	−32.5
Ω_{CO2} [%][f]	−11.0	−58.5
ρ [g cm^{-3}][g]	4.80	1.68
T_{dec} [°C][h]	315	193
$\Delta_f H_m$ [kJ mol^{-1}]/[kJ kg^{-1}][i]	450.1/1545.4	1345.1/5467.6
V_0 [L kg^{-1}][j]	230	736
D [m s^{-1}][k]	5877	8345
P [GPa][l]	33.4	26.7

[a] Impact sensitivity. [b] Friction sensitivity. [c] Electrostatic discharge sensitivity. [d] Nitrogen content. [e] Oxygen balance. For C$_a$H$_b$O$_c$N$_d$: 1600 (c-a-b/2)/M$_W$. [f] Oxygen balance. For C$_a$H$_b$O$_c$N$_d$: 1600 (c-2a-b/2)/M$_W$, M$_W$ = molecular weight. [g] Density measured by gas pycnometer (25 °C) [h] Temperature of decomposition according to DSC (5 °C min^{-1}). [i] Heat of formation. [j] Gas volume after detonation. [k] Calculated detonation velocities. [l] Calculated detonation pressure (m) Ref. [27]

discharge sensitivity (0.224 J) are superior to those of lead azide (IS: 1 J, FS: 4 N, EDS: 0.012 J).

To obtain further information on inter- and intramolecular effects and comprehensively study their influence on crystal packing, the non-covalent interaction (NCI) plots of **2** are carried out. The results of NCI analysis are presented in Figure 4. The π-π interaction was intense and abundant in compound **2**, which could be easily observed as large isosurfaces. Because of the extensive π-π interaction, it could exhibit the close packing, acceptable impact sensitivity and acceptable friction sensitivity though the molecule exists two sensitive azido groups.
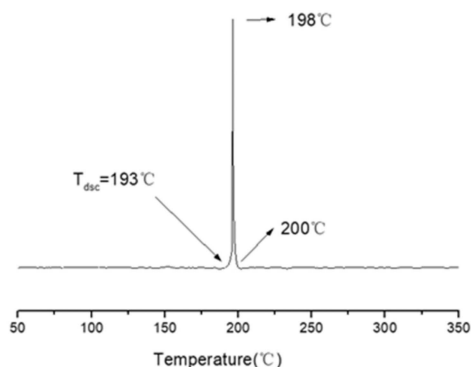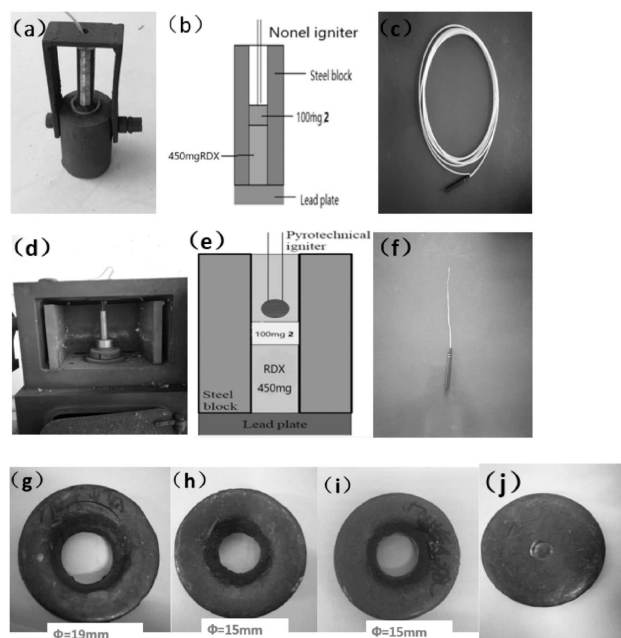

Figure 3. DSC curves of compound **2**.
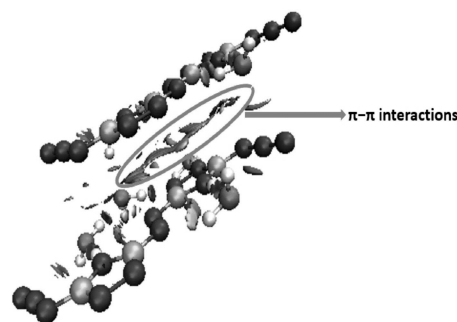
Figure 4. NCI analysis of π-π interactions for compound **2**. The isosurfaces in the ellipse indicating weak interaction, respectively.

3.3 Detonation Test

The feasibility of **2** as the primary explosive was confirmed by several detonation tests according to the military specification of PRC GJB 5891.19-2006. The detonation experiment against 5 mm lead block performed by using 100 mg of compound **2** to detonate 450 mg RDX with a nonel igniter. Surprisingly, the hole of 5 mm thickness lead plate crater diameter reached 15 mm (Figure 5h). A comparative test of lead azide with nonel igniter was carried out under same experimental conditions ($\Phi = 19$ mm) (Figure 5g). The result manifests that **2** can detonate RDX and the initiation capacity of **2** was closed to $Pb(N_3)_2$. In order to study the primary ability in practical application, we also try to use pyrotechnical igniter (Figure 5d–f). Comparing to nonel igniter under same experimental conditions, the same-sized hole of 5 mm thickness lead plate ($\Phi = 15$ mm) was obtained (Figure 5i). Furthermore, we evaluate the efficiency of **2** with nonel igniter by the minimum primary charge (MPC). The results demonstrate that 80 mg of **2** could be the threshold to detonate RDX to bore through the lead plate (Figure 5j).

4 Conclusions

In summary, we introduced a unique synthesis of 3-azido-5-amino-1,2,4-triazole(**1**) and speculated the possible reaction process of **1**. The coupling compound **2** possessed high positive heats of formation (1345.1 kJ mol^{-1}/5.468 kJ g^{-1}), excellent thermal stability (193 °C) and remarkable detonation performance (P: 26.7 GPa, D: 8345 m s^{-1}). NCI analysis of π-π interactions explained the acceptable sensitivity (6 J, 72 N). Furthermore, the detonation tests confirmed compound **2** can detonate RDX through nonel igniter and pyrotechnical igniter successfully. The results indicated compound **2** could be used as a potential green metal-free primary explosive in practical application.

Acknowledgements

References

[1] Q. Zhang, D. Chen, D. Jing, G. Fan, H. Li, W. Wang, F. Nie, Access to green primary explosives via constructing coordination polymers based on bis-tetrazole oxide and non-lead metals, *Green Chem.* **2019**, *21*, 1947–1955.

[2] C. He, J. M. Shreeve, Potassium 4,5-bis (dinitromethyl) furoxanate: a green primary explosive with a positive oxygen balance, *Angew. Chem. Int. Ed.* **2016**, *55*, 772–775.

[3] T. Brinck, *Introduction to green energetic materials, Green Energetic Materials,* Wiley, Hoboken, **2014**.

[4] T. M. Klapötke, N. Mehta, Lead-free Primary Explosives, *Propellants Explos. Pyrotech.* **2014**, *39*, 7–8.

[5] N. Mehta, K. Oyler, G. Cheng, A. Shah, J. Marin, K. Yee, Primary explosives, *Z. Anorg. Allg. Chem.* **2014**, *640*, 1309–1313.

[6] M. H. V. Huynh, M. D. Coburn, T. J. Meyer, M. Wetzler, Green primary explosives: 5-Nitrotetrazolato-N2-ferrate hierarchies, *Proc. Mont. Acad. Sci.* **2006**, *103*, 10322–10327.

[7] D. Fischer, T. M. Klapötke, J. Stierstorfer, Potassium 1,1'-dinitramin-5,5'-bistetrazolate: A primary explosive with fast detonation and high initiation power, *Angew. Chem. Int. Ed.* **2014**, *53*, 8172–8175.

[8] J. W. Fronabarger, M. D. Williams, W. B. Sanborn, J. G. Bragg, D. A. Parrish, M. Bichayc, DBX-1-A lead free replacement for lead azide, *Propellants Explos. Pyrotech.* **2011**, *36*, 541–550.

[9] Y. Tang, C. He, L. A. Mitchell, D. A. Parrish, J. M. Shreeve, Potassium 4,4'-bis (dinitromethyl)-3,3'-azofurazanate: a highly energetic 3D metal-organic framework as a promising primary explosive, *Angew. Chem. Int. Ed.* **2016**, *55*, 5565–5567.

[10] D. Fischer, T. M. Klapötke, J. Stierstorfer, 1,5-Di (nitramino) tetrazole: high sensitivity and superior explosive performance, *Angew. Chem. Int. Ed.* **2015**, *54*, 10299–10302.

[11] D. Sheng, Y. Zhu, Y. Pu, Development of a new-generation primary explosives designing and synthesis, *Chin. J. Energet. Mater.* **2012**, *20*, 263–272.

[12] R. Matyáš, J. Pachman, *Primary explosives*, Springer-Verlag, Berlin, **2013**, p. 2–6.

Figure 5. (a–c) Picture of the test set up with nonel igniter to ignite; (d–f) Picture of the test set up with pyrotechnical igniter to ignite; (g) Perforated lead plate as the result of detonation test (100 mg Pb (N$_3$)$_2$ and 450 mg RDX); (h) Perforated lead plate as the result of detonation test (100 mg **2** and 450 mg RDX) with nonel igniter. (i) Perforated lead plate as the result of detonation test (100 mg **2** and 450 mg RDX) with pyrotechnical igniter. (j) One of lead plates that cannot be blasted out of the hole by using < 80 mg **2**.

[13] X. Liu, W. Gao, P. Sun, Z. Su, S. Chen, Q. Wei, G. Xie, S. Gao, Environmentally friendly high-energy MOFs: crystal structures, thermostability, insensitivity and remarkable detonation performances, *Green Chem.* **2015**, *17*, 831–836.

[14] D. Trache, T. M. Klapötke, L. Maiz, M. Abd-Elghany, L. DeLuca, Recent advances in new oxidizers for solid rocket propulsion, *Green Chem.* **2017**, *19*, 4711–4736.

[15] H. He, J. Du, B. Wu, X. Duan, Y. Zhou, G. Ke, T. Huo, Q. Ren, L. Bian, F. Dong, Photoelectrochemical driving and clean synthesis of energetic salts of 5, 5'-azotetrazolate at room temperature, *Green Chem.* **2018**, *20*, 3722–3726.

[16] J Tang, D. Chen, G. Zhang, H. Yang, G. Cheng, A "green" primary explosive: design, synthesis, and testing, *Synlett* **2019**, *30*, 885–892.

[17] D. Chen, H. Yang, Z. Yi, H. Xiong, L. Zhang, S. Zhu, G. Cheng, C8 N26H4: An environmentally friendly primary explosive with high heat of formation, *Angew. Chem. Int. Ed.* **2018**, *57*, 2081–2084.

[18] M. Deng, Y. Feng, W. Zhang, X. Qi, Q. Zhang, A green metal-free fused-ring initiating substance, *Nat. Commun.* **2019**, *10*, 1339.

[19] D. Chand, D. A. Parrish, J. M. Shreeve, Di (1H-tetrazol-5-yl) methanone oxime and 5,5'-(hydrazonomethylene) bis (1H-tetrazole) and their salts: a family of highly useful new tetrazoles and energetic materials, *J. Mater. Chem. A.* **2013**, *1*, 15383–15389.

[20] Y. Liu, G. Zhao, Y. Tang, J. Zhang, L. Hu, G. H. Imler, D. A. Parrish, J. M. Shreeve, Multipurpose [1,2,4] triazolo [4,3-b][1,2,4,5] tetrazine-based energetic materials, *J. Mater. Chem. A.* **2019**, *7*, 7875–7884.

[21] T. P. Kofman, V. I. Namestnikov, Synthesis of 3-azido-5-amino-1, 2, 4-triazole, *Russ. J. Org. Chem.* **2003**, *39*, 579–584.

[22] J. Zhang, J. Zhang, D. A. Parrish, J. M. Shreeve, Desensitization of the dinitromethyl group: molecular/crystalline factors that affect the sensitivities of energetic materials, *J. Mater. Chem. A.* **2018**, *6*, 22705–22712.

[23] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, Gaussian 09, Revision a. 02, Gaussian, Inc.: Wallingford CT **2009**.

[24] M. Sućeska, *EXPLO5, Version6.02*, Zagreb, Croatia, **2013**.

[25] M. Sućeska, Calculation of the detonation properties of CHNO explosives, *Propellants Explos. Pyrotech.* **1991**, *16*, 197–202.

[26] Test methods according to the UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, United Nations Publication, New York, 4th edn, **2003**; (b) 13.4.2 Test 3 (a) (ii) BAM Fallhammer, pp. 75–82; (c) 13.5.1 Test 3 (b) (i): BAM friction apparatus, pp. 104–107.

[27] B. Khasainov, M. Comet, B. Veyssiere, D. Spitzer, On the mechanism of efficiency of lead azide, *Propellants Explos. Pyrotech.* **2017**, *42*, 547–557.