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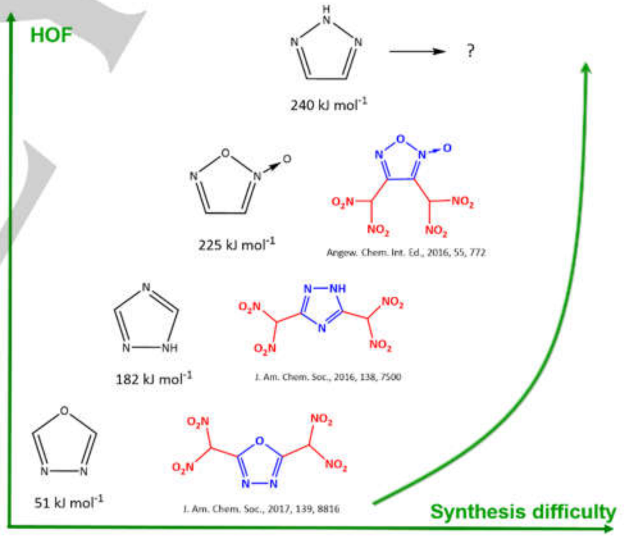
Gem-dinitromethyl substituted energetic metal-organic framework based on 1,2,3-triazole from *in-situ* controllable synthesis

Hao Gu, ‡[ab] Qing Ma, ‡[a] Shiliang Huang,[a] Zhenqi Zhang,[a] Qi Zhang,[a] Guangbin Cheng,[b] Hongwei Yang,*[b] and Guijuan Fan*[a]

Abstract: Synthesizing energetic metal-organic frameworks at ambient temperature and pressure has been always a challenge in the research area of energetic materials. In this work, through *in-situ* controllable synthesis, energetic metal-organic framework *gem*-dinitromethyl substituted dipotassium 4,5-bis(dinitromethyl)-1,2,3-triazole with "cage-like" crystal packing was obtained and characterized. Most importantly, for the first time we found that it could be successfully afforded with the catalytic effect of trifluoroacetic acid. This new compound exhibited its high density (2.04 g cm^{-3}) at ambient temperature, superior detonation velocity (8715 m s^{-1}) to that of lead azide (5877 m s^{-1}) and comparable to that of RDX (8748 m s^{-1}). Its detonation products are mainly N_2 (48.1 %), suggesting it is also a green energetic material. The above-mentioned performance indicates its potential applications in detonator devices as lead-free primary explosive.

Lead azide is a famous primary explosive, which has been widely used in civil and military detonator because of its cheap manufacture. However, in the applications of lead azide lead contamination is always an important issue which mainly destroys the human digestive, hematologic and nervous systems.[1] During the past decades, many "green" candidates have been discovered for the substitution of lead azide. Among them, the majority of reported candidates as green primary explosives have drawn much attention, such as potassium 1,1'-dinitramino-5,5'-bistetrazolate (K_2DNABT), potassium 4,5-bis(dinitromethyl)-furoxanate (K_2BDNMF) and potassium 4,4'-bis(dinitromethyl)-3,3'-azofurazanate (K_2BDNMAF).[2] A growing interest in new energetic materials featuring *gem*-dinitro- and fluorodinitro-explosophore groups emerged and also played a significant role in the design and construction of high energy density materials,[3,4] which also influenced greatly the development of energetic metal-organic frameworks.[5] After Shreeve et al synthesized the first potassium-based metal-organic framework featuring gem-dinitromethyl,[2c] Lu et al reported another similar structure *via* silver(I) ions coordinating with *gem*-dinitromethyl groups and their self-assembly characteristics.[6] As a N-N-N (N_3) backbone and attractive precursor, 1,2,3-triazole possesses the relatively high heat of formation (HOF) as well as multiple substituting positions among azole frameworks in comparison to tetrazole[7] and pentazole.[8] On the other hand, the correlation between *N*-heterocyclic frameworks with *gem*-dinitromethyl group and their corresponding synthesis difficulty was given in Scheme 1. So far, *gem*-dinitromethyl substituted mono-ring energetic frameworks with 1,3,4-oxadiazole, 1,2,4-triazole and furoxan have been released in rather recent years.[2b,9,10] In addition to the previously mentioned structures, *gem*-dinitromethyl substituted 1,2,3-triazole has not been synthesized yet. Considering the remarkably high HOF of 1,2,3-triazole (calculated by G2 *abinitio* method at 240 kJ mol^{-1}), it is necessarily worthy of overcoming its synthesis difficulty. Meanwhile, judicious combination of other energetic functionalized groups with 1,2,3-triazole is favorable for maintaining its high HOF in the whole molecule.



Scheme 1. Evolvement of *gem*-dinitromethyl substituted mono-ring *N*-heterocyclic frameworks with the increase of their individual HOF.

In addition to other azole-frameworks such 1,2,4-triazole and tetrazole, 1,2,3-triazole has relatively high regioselectivity, which has been revealed in its previous reactions of *N*-alkylation and *N*-amination.[11] In a continuing effort to seek more functionalized *gem*-dinitromethyl energetic materials, in this work we aimed to design and construct 1,2,3-triazole based *gem*-dinitromethyl specific molecules. To the best of our knowledge, no methods for the successful introduction of the *gem*-dinitromethyl group into carbon positions in 1,2,3-triazole mono-ring have been reported.

As shown in Scheme 2, 4,5-dicyano-2H-1,2,3-triazole (**1**) was prepared by cyclization of diaminomaleodinitrile and then 2H-

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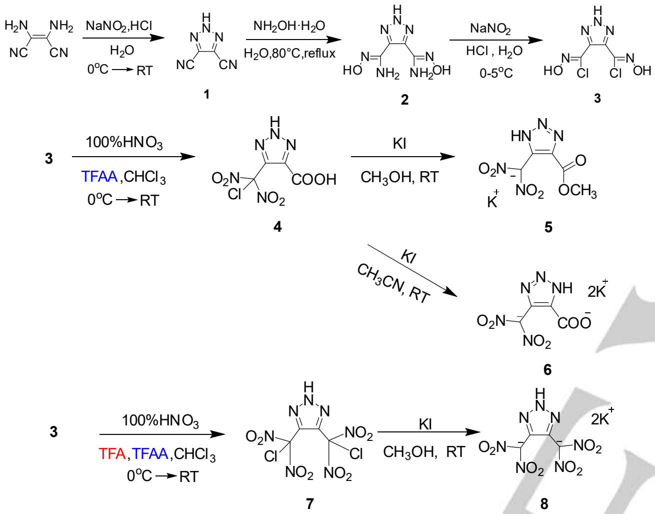
1,2,3-triazole-4,5-bis(carboxamidoxime) (**2**)[12] as well as 2H-1,2,3-triazole-4,5-bis(carboxoxim dichloride) (**3**)[13] were also synthesized as key intermediates being used in the next steps. Unlike the other synthesis of *gem*-dinitromethyl compounds,[2b,2c] in the initial attempt to get the target compound, nitration of **3** in 100% HNO_3/trifluoroacetic anhydride (TFAA) resulted in compound **4** as a colorless oil. Then reduction of **4** in the presence of potassium iodide and methanol led to potassium 4-dinitromethyl-5-methylformate-1,2,3-triazolate (**5**). To investigate the influence of aprotic solvent on the reduction reaction, we replaced anhydrous methanol (protic solvent) with anhydrous acetonitrile in the reduction of **4** and afforded another new compound dipotassium 4-dinitromethyl-5-carboxyl-1,2,3-triazolate (**6**). We hypothesize that compound **3** behaves different reactivity in its 4- and 5-position which thereby has remarkable influence on the formation of final nitration product.



Scheme 2. Synthesis of derivatives **4**–**8** based on **3** with or without trifluoroacetic acid as a catalyst and different solution effects in the reduction by iodine potassium.

Subsequently, we chose adding amount of trifluoroacetic acid (TFA) in the nitration system. To our surprise, major product **7** was obtained through gradient column chromatography (petroleum ether: ethyl acetate from 5:1 to 1:1), which implied that the role of TFA played as an efficient catalyst after the formation of **7**. It was also found that the reaction time and usage quantity of TFA (Comp.**3**: TFA: TFAA: 100%HNO_3=6: 8.8: 8.8: 5, in volume) were significant for affording considerable yield of dipotassium 4,5-bis(dinitromethyl)-1,2,3-triazolate (**8**) (detailed reaction conditions can be found in Table S1).

Crystals of compounds **5**, **6** and **8** were obtained by slow evaporation from aqueous solutions of the corresponding compounds at room temperature, as pale yellow blocks or plates. All compounds have been fully characterized by X-ray crystallography. Their crystal structures and crystal packing were shown in Figure 1-2 and the crystallographic data and refinement details, selected bond lengths, angles are given in Table S2−12. Compound **5** crystallizes in the orthorhombic space group P nma with four molecular moieties in the unit cell and a density of 1.729 g cm^{-3} at 293K. Compound **6•H_2O** crystallizes in the monoclinic space group $P2_1/c$ with a density of 2.145 g cm^{-3} at 130K. Compound **8** crystallizes in the orthorhombic space group *P nnm* with eight molecular moieties in the unit cell and a density of 2.040 g cm^{-3} at 296K. During nitration or nucleophilic substitution reactions, H-proton usually transferred from 2-substituted position to 1- or 3- substituted positions, which have been reported recently.[14,15] In this work, H-proton transfers in compound **5** and **6** but settles in the 2-substituted position of compound **8**, which may attribute to the symmetry of two *gem*-dinitromethyl groups. In compound **5**, the methyl formate group is coplanar with the plane of 1,2,3-triazole (∠N1-C1-C4-O3=0°) while the *gem*-dinitromethyl group twisted out of the plane of 1,2,3-triazole with a large torsion angle (∠N3-C2-C3-N4=-93.53(18)°). Though formic-yl replaces methyl formate-yl in compound **6**, it shares the similar structural characteristics with compound **5** except that H-proton transfers from neighboring *gem*-dinitromethyl group to carboxyl group nearby. Because the existence of water molecule and anionic component in formic acid structure, compound **6** represents different intermolecular interaction. The strong and quite directed O7–H7A•••O5 (D•••A: 2.869(4) Å; D–H•••A: 161(4)°, symmetry code: -x+1, y-1/2, -z+3/2) and N1–H1•••O5' (D•••A: 2.639(4) Å; D–H•••A: 167(4)°, symmetry code: x, -y+3/2, z+1/2) hydrogen bond (H-bond) result in the formation of multiple H-bond chains. Meanwhile, the central ions K1 and K2 in **6** show different coordination features. In other words, K1 is coordinated with both O1 and O3 atoms in *gem*-dinitromethyl group while K2 is coordinated with O6 atom in formic-yl as well as O7 atom in water.

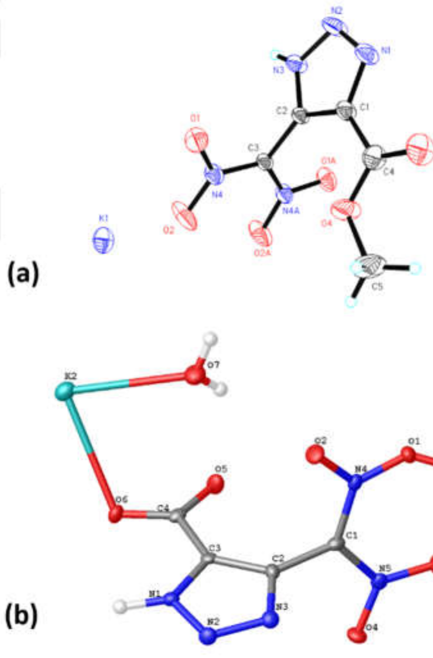


Figure 1. (a) Thermal ellipsoid plot (50%) and labelling scheme of **5**. (b) Thermal ellipsoid plot (50%) and labelling scheme of **6**•H_2O.

In comparison with complexes **5** and **6**, different coordination forms were seen in compound **8**. As illustrated in Figure 2a, *K* ions coordinate with *N* atoms in both sides of 1,2,3-triazole framework due to its high structural symmetry. Strong intermolecular H-bond interaction was found in Figure 2b with 2.15–2.45 Å length. Because the existence of *H*-bond interaction as well as O atoms and *N* atoms both coordinating with *K* ions, Figure 2c shows a 3D framework of compound **8** which represents a rarely seen "cage-

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like" crystal packing in 1,2,3-traizole except for the previously described beetle-like 3D network by S. Chen et al. [5b] Accordingly, two molecules could be assemble into a fused-ring like framework similar as benzo[1,2-d:4,5-d']bistriazole (Figure S1).

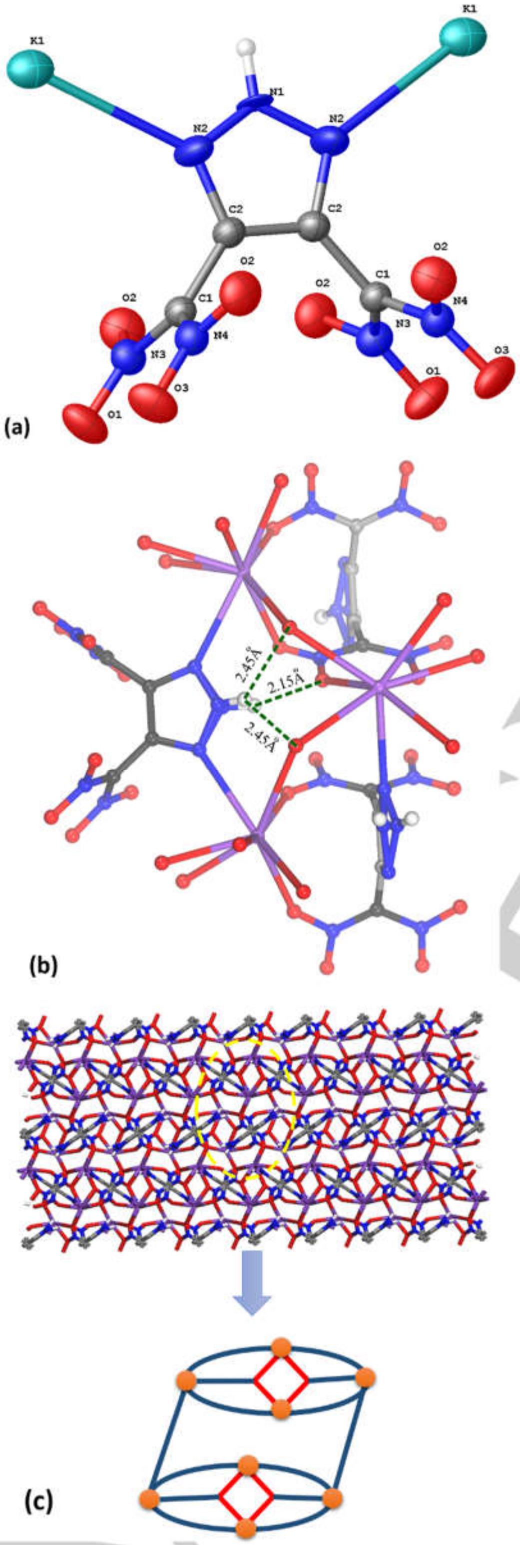

Figure 2. (a) Thermal ellipsoid plot (50%) and labelling scheme of **8**. (b) Intermolecular hydrogen bonding interaction of **8**. Dashed lines indicate strong hydrogen bond. (c) The "cage-like" 3D-framework diagram of **8**. Blue, orange and red color indicate organic framework, metal ion and K-O bond, respectively.

The molecule **8** has two possible orientations in its unit cell (Figure S1). Due to this disorder, the molecule **8** can arrange in a queue in two different ways along the *c*-axis and consequently the neighbouring queues can be parallel or antiparallel, as shown in Figure 3a and Figure 3c. Each K^+ cation was coordinated by three **8** molecules through seven O atoms and one *N* atom. By sharing two *O* atoms, a $K_2N_2O_{10}$ dimer was formed. Because of the different arrangement of 8 molecules, the $K_2N_2O_{10}$ dimer has two different configurations with the two K^+ centers symmetrically related by inverse center or 2-fold ration axis, as shown in Figure 3b.

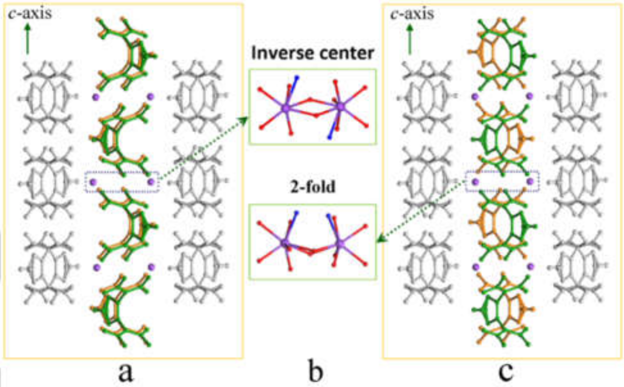

Figure 3. Two different arrangement of **8** molecules with neighbouring queues (a) parallel or (c) antiparallel, which results (b) two configuration s of $K_2N_2O_{10}$ dimer.

The powdered samples of compound **8** displayed irregular flake morphology and the particle size were in the range of 20–50 *μm* with partially agglomeration (Figure S8). Different from twice decomposition in **5** (T_{p1}:131 °C, T_{p2}:181 °C) and **6** (T_{p1}:133 °C, T_{p2}: 223 °C) (Figure S9 and S10), **8** shows its onset decomposition temperature (T_d) at 120 °C and decomposition peak (T_p) at 131 °C with the heating rate of 5 °C min^{-1} (Figure S11). The detonation performance were evaluated by EXPLO5 V6.02.[16] Compound **8** shows its theoretical detonation velocity at 8715 m s^{-1}, which is superior to that of commercial primary explosive 2-diazonium-4,6-dinitrophenol (DDNP) (7651 m s^{-1}), $Pb(N_3)_2$ (5877 m s^{-1}) and comparable to that of RDX (8748 m s^{-1}). Its detonation pressure is 28.3 GPa, which is superior to that of DDNP (23.8 GPa), but slightly lower than that of $Pb(N_3)_2$ (33.4 Gpa).[1c,2b,2c] Its measured impact sensitivity (*IS*) is 1 J and friction sensitivity (*FS*) is 60 N by using standard BAM drop hammer as well as friction tester, which are superior to those of DDNP (*IS*: 1 J, *FS*: 5 N).[1c,2b,2c] Though its impact sensitivity is slightly sensitive comparing with that of $Pb(N_3)_2$ (2.5–4J), its friction sensitivity is more insensitive referred to that of $Pb(N_3)_2$ (0.1–1N). Its predicted detonation gasous products are mainly N_2 (g, 48.1%) which is higher than that of potassium 4,5-bis(dinitromethyl)furoxanate (less than 25%).[2b] Other products are O_2 (g, 17.1%), CO_2 (g, 13.8%), K_2CO_3 (s, 13.8%) and H_2O (g, 6.9%), suggesting as-synthesized energetic metal-organic framework is a green energetic material.

Table 2. Energetic and physical properties of **8**.

	8	DDNP	Pb(N$_3$)$_2$
ρ (g cm^{-3})[a]	2.04	1.73	4.80
Ω(%)[b]	+15.9	–60.9	–11.0
N (%)	27.8	26.7	28.9
N+O (%)	64.0	64.7	28.9
D (m s^{-1})[c]	8715	7651	5877
P (GPa)[d]	28.3	23.8	33.4
ΔH_f (kJ mol^{-1})[e]	-135	139	450.1
T_{dec} (°C)[f]	131	157	315
IS (J)[g]	1	1	2.5-4
FS (N)[h]	60	5	0.1-1

[a] Density measured by single-crystal X-ray diffraction and converted into room-temperature values; [b] Oxygen balance; [c] Calculated detonation velocity; [d] Calculated detonation pressure; [e] Heat of formation; [f] Decomposition temperature measured by DSC/DTA (β=5°C min^{-1}); [g] Impact sensitivity measured by BAM drop-hammer test; [h] Friction sensitivity measured by a BAM friction tester.

In summary, we developed a new *in-situ* controllable strategy for successfully synthesizing energetic metal-organic framework with mono-heterocyclic ring. These first reported frameworks in different reaction conditions were confirmed by single-crystal X-ray analysis. It is worth noting that, potassium 4,5-bis(dinitromethyl)-1,2,3-triazolate (**8**) has a high crystal density of 2.04 g cm^{-3} at the room temperature, calculated high detonation velocity (8715 m s^{-1}), which is superior to that of Pb(N$_3$)$_2$ (5877 m s^{-1}) and approach that of RDX (8748 m s^{-1}). The above-mentioned performance indicates its potential applications in lead-free primary explosives as high energy and green energetic material.

Acknowledgements

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Keywords: *gem*-dinitromethyl • energetic metal-organic framework • 1,2,3-triazole • high energy • green energetic material

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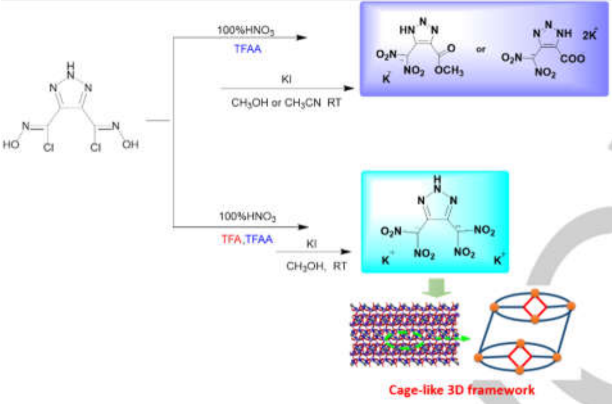
Energetic metal-organic framework featuring *gem*-dinitromethyl moiety and 1,2,3-triazole with a “cage-like” crystal packing was successfully prepared through *in-situ* controllable-synthesis strategy.



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