

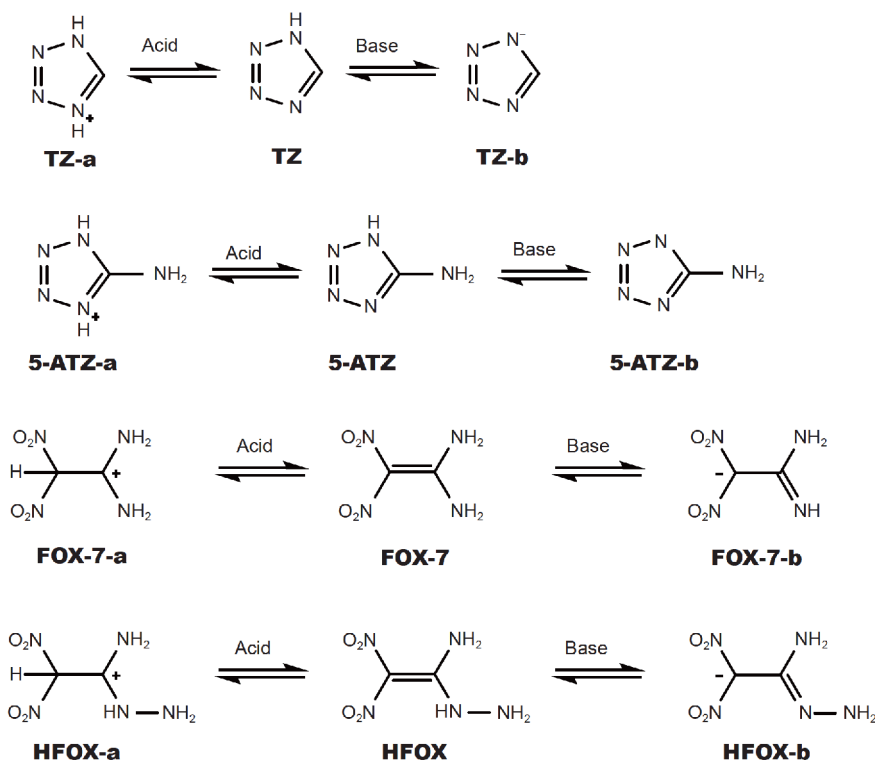


# Cationic and anionic energetic materials based on a new amphotère

Yuangang Xu<sup>1</sup>, Pengcheng Wang<sup>1</sup>, Qiuhan Lin<sup>1</sup>, Yao Du<sup>2</sup> and Ming Lu<sup>1\*</sup>

In general, amphotères can be divided into organic and inorganic amphoteric compounds. Oxides and hydroxides of aluminum, gallium, zinc, copper and chromium are inorganic amphoteric compounds [1], while organic amphoteric compounds, such as amino acids, peptides and proteins, usually include amino and carboxyl groups in one molecule [2]. In the field of energetic materials, some significant progresses have been made in recent years; however, amphoteric molecules are relatively rare [3–8]. As shown in Scheme 1, 1*H*-tetrazole (TZ) is an important core of energetic materials because of its

practical significance and diversity of properties. TZ can be deprotonated to an anionic TZ-b easily using common bases such as hydrazine, ammonia, or alkali and alkaline earth metal hydroxides or carbonates [9,10]. It can also be protonated to a cationic TZ-a under perchloric acid, but it is relatively difficult [11]. Similar to TZ, 5-aminotetrazole (5-ATZ), a weak acid ( $pK_a \sim 6$ ), nitrogen-rich (82%) compound, also presents an amphoteric characteristic and undergoes two acid-base equilibria, leading to three distinct states (neutral, cationic 5-ATZ-a, and anionic 5-ATZ-b), as depicted in Scheme 1 [12–14]. But it has most

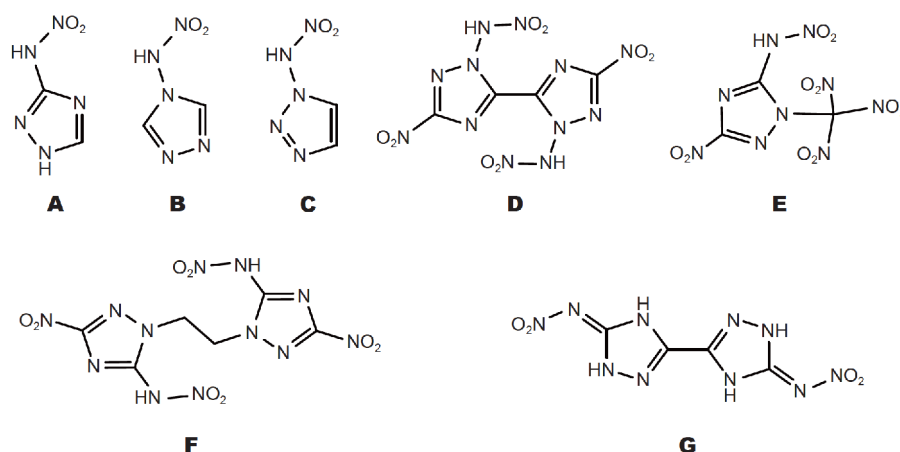


**Scheme 1** Different distinct states of TZ, 5-ATZ, FOX-7, and HFOX.

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**Figure 1** Energetic derivatives of triazole. 3-nitroamino-1,2,4-triazole (A), 4-nitroamino-1,2,4-triazole (B), 1-nitroamino-1,2,3-triazole (C), *N,N'*-(5,5'-dinitro-2*H*,2'*H*-3,3'-bi(1,2,4-triazole)-2,2'-diyl)dinitramide (D), *N*-(3-nitro-1-(trinitromethyl)-1*H*-1,2,4-triazol-5-yl)nitramide (E), *N,N'*-(1,1'-(ethane-1,2-diyl)bis(3-nitro-1*H*-1,2,4-triazole-5,1-diyl))dinitramide (F), and bis[3-(5-nitroamino-1,2,4-triazole)] (G).

often been employed as a cation precursor in energetic salts [15,16]. In addition to TZ and 5-ATZ, 1,1-diamino-2,2-dinitroethene (FOX-7) and 1-amino-1-hydrazino-2,2-dinitroethene (HFOX) also exhibit amphoteric properties (Scheme 1) [17–21].

Triazole derivatives have been used successfully to produce a large number of energetic materials. Nitro-amino-substituted monocyclic and bridged bicyclic triazoles are very important species (Fig. 1 A–G) [22–27]. By implementing nitroamino moieties, the oxygen balance and the energetic performance of the target molecule can be optimized. Simultaneously, the chemistry of A–G with bases to generate the corresponding anionic substrates was well established. But they have never been employed as cation precursors in energetic salts. 5,5'-diamino-4,4'-dinitramino-3,3'-bi-1,2,4-triazole (**1**) and its anionic salts based on **1-b** were synthesized by Klapötke *et al.* [28–30] in 2016. However, evidence for protonated **1** was not developed. The isolation of such species is of great interest to study a new form of nitroamino- and amino-substituted triazole and these molecules have potential as promising precursors that may enhance the properties of energetic salts. Herein we describe protonated **1** and coordination of **1-b** by the syntheses of salt containing the first cationic state of **1** and the potassium based 3D metal-organic framework (MOF) of **1-b**.

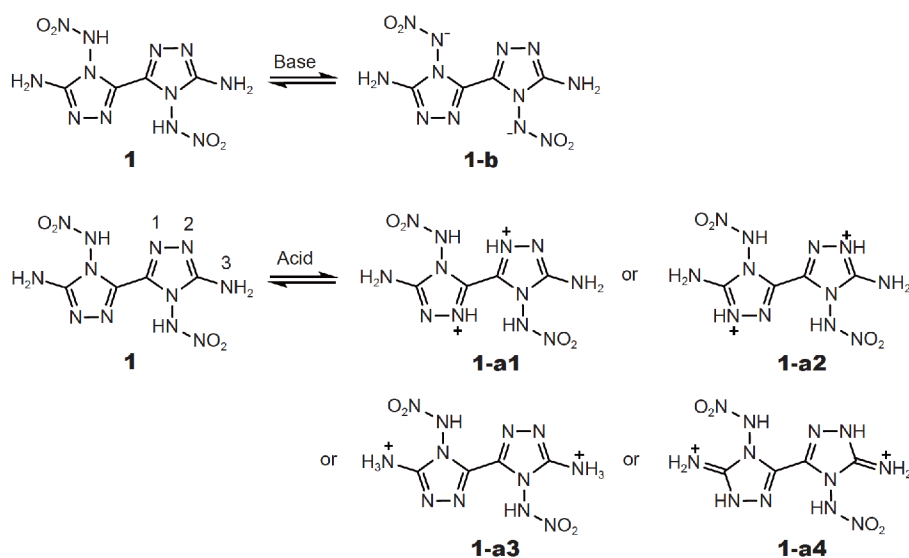
For the protonated products of **1**, there are four possible forms (**1-a1**–**1-a4**, see Scheme 2). Theoretically, except for the two nitroamino groups and the nitrogen atoms to which they are attached, other nitrogen atoms may be protonated with acids. Single-crystal X-ray analysis indicated that the proton was introduced at the N2

nitrogen and double bond transferred from C–N2 to C–N3, leading to the formation of **1-a4**.

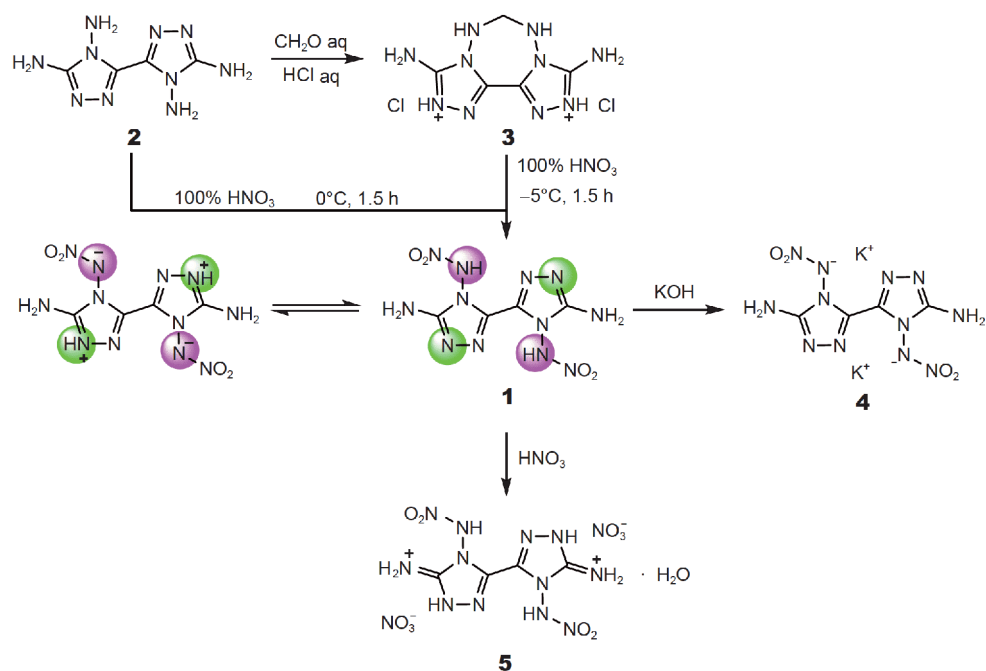
Compound **1** can be obtained by selective nitration of 4,4',5,5'-tetraamino-3,3'-bi-1,2,4-triazole (**2**) or a new synthetic route from 3,9-diamino-6,7-dihydro-5*H*-bis([1,2,4]triazolo)[4,3-*e*:3',4'-*g*][1,2,4,5]tetrazepine-2,10-dium chloride (**3**) [31,32]. Deprotonation of **1** with KOH gave the dipotassium salt **4**. Compound **1** was first treated with an excess of nitric acid (HNO<sub>3</sub>) at 25°C to yield nitrate monohydrate (crystals), **5** (Scheme 3).

Compound **1** (Fig. S1) crystallizes in the orthorhombic space group *Pbca* with four molecules in the unit cell with a calculated density of 1.783 g cm<sup>-3</sup> at 205 K (1.789 g cm<sup>-3</sup> at 173 K [28]). **1** has a zwitterionic resonance structure with a formal negative charge at the nitrogen atom N2 and a protonated nitrogen atom N5. A very strong intermolecular hydrogen bond is found between the atoms N5 and N2 [N5–H5⋯N2 2.803(3) Å]. The N5 atom proton forms two weak hydrogen bonds to the nitro group [N5–H5⋯O1 3.086(3) Å; N5–H5⋯N1 3.430(3) Å].

Suitable single crystals of **4** were grown in water solutions. Complex **4** crystallizes as a dihydrate in the monoclinic space group with a 3D porous framework. As depicted in Fig. 2, the central K ion displays a distorted quadrangular pyramid coordinated by three nitrogen atoms (N3, N6, and N6) from three different **1-b** ligands and two oxygen atoms (O3) from water molecules. Each **1-b** ligand exhibits a tetradentate coordination mode (see Fig. 2a), in which the N3 and N6 atoms adopt a bridging mode to connect to six different K ions. Every two adjacent amino groups (N6) of different ligands are bridged by two K ions to form a 1D chain. A 2D layer is formed



**Scheme 2** Possible deprotonation and protonation sites of **1**.

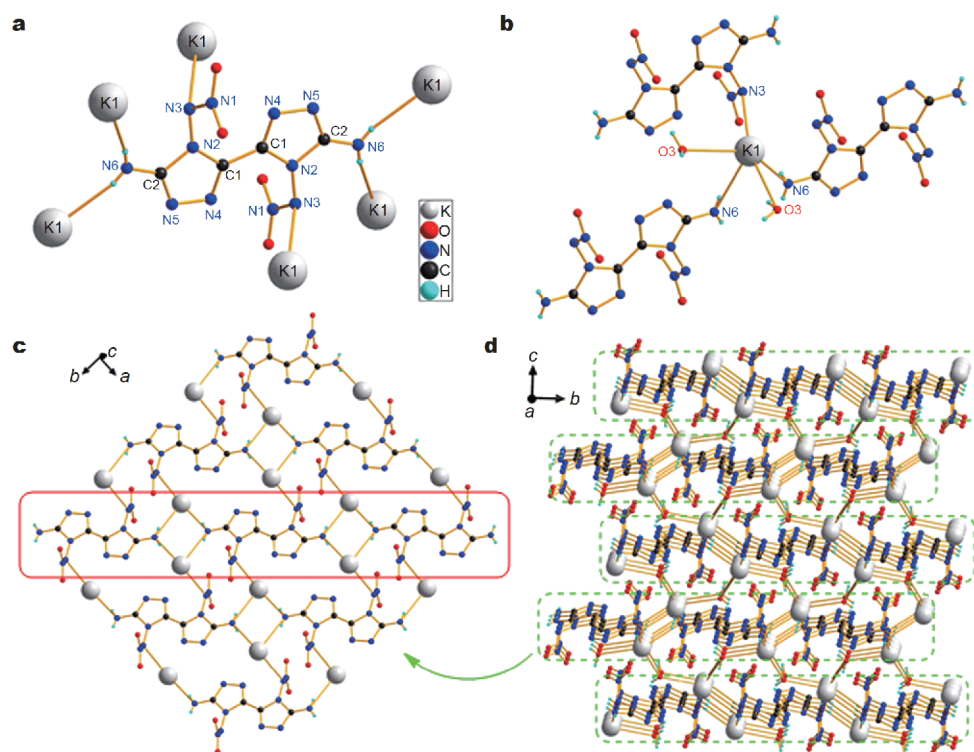


**Scheme 3** Synthesis of **1**, **4** and **5**.

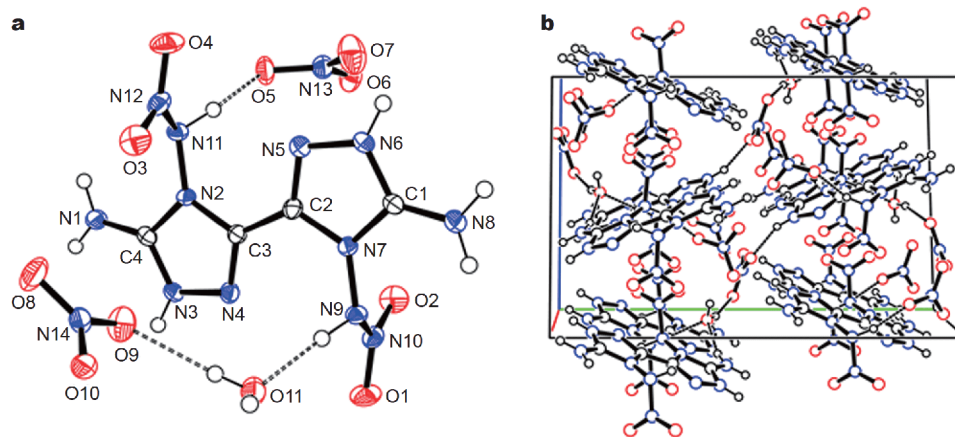
based on the coordination of N3 atoms with K ions (N3-K: 3.1024 Å) in the direction of *a* axis (Fig. 2c). The adjacent layers are linked by coordination of O3 from H<sub>2</sub>O molecules with K ions (O3-K: 3.2129 and 3.2295 Å), producing the stable 3D supramolecular network (see Fig. 2d). In terms of topology, the ligand can be viewed as an ensemble of eight-connected (8-c) node, with the K<sup>+</sup> serving as six-connected (6-c) node. Thus, the underlying

binodal (6,8-c) net with stoichiometry (6-c)<sub>2</sub>(8-c) presents a new topology (see Fig. S4).

Salt **5** crystallizes with one molecule of water in the monoclinic space group *P12<sub>1</sub>/c1* system (Fig. 3). It is composed of four molecules per unit cell with a crystal density of 1.878 g cm<sup>-3</sup> at 173 K. **5** has two protonated nitrogen atoms (N6 and N3) in the triazole moieties and two protonated nitrogen atoms (N9 and N11) in the



**Figure 2** (a) Coordination model of **1-b** in  $4 \cdot 2\text{H}_2\text{O}$ . (b) Coordination environment of  $\text{K}^+$  in  $4 \cdot 2\text{H}_2\text{O}$ . (c) The 2D layer in  $4 \cdot 2\text{H}_2\text{O}$ . (d) The 3D supramolecular framework in  $4 \cdot 2\text{H}_2\text{O}$  viewed down  $a$  axis.

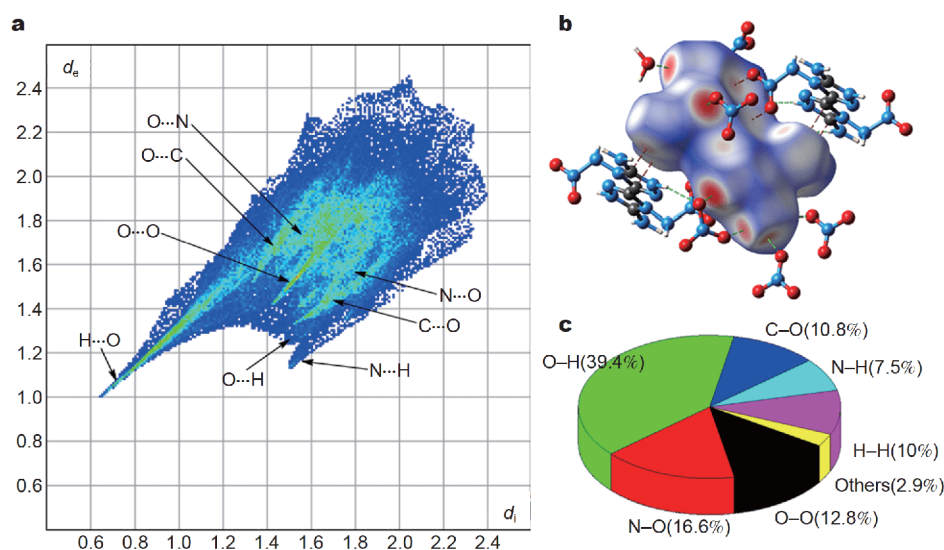


**Figure 3** (a) Crystal structure of **5**; thermal ellipsoids are drawn at the 50% probability level. (b) Packing diagram of **5** viewed down the  $a$  axis. Unit cell indicated and dashed lines represent hydrogen bonding.

nitramino moieties. To obtain a better understanding of interactions between **1-a4** and nitrate ions, the two-dimensional (2D) fingerprint plot of **1-a4** in the crystal stacking of **5** and the associated Hirshfeld surface were calculated [33] (see Fig. 4). Only one remarkable spike on the bottom left ( $\text{H} \cdots \text{O}$  interactions constitute 31.2% of the total weak interactions) in the Fig. 4a denotes the

hydrogen bonds (blue dashed lines in Fig. 4b) from **1-a4** to nitrate ions and water molecules, while weaker  $\text{O} \cdots \text{O}$ ,  $\text{O} \cdots \text{N}$ , and  $\text{O} \cdots \text{C}$  interactions were found among neighboring **1-a4** cations.

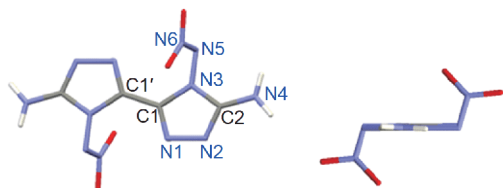
By comparison, we specify the atomic labels of **1**, **1-b** in  $4 \cdot 2\text{H}_2\text{O}$ , and **1-a4** in **5** as shown in Table 1. The C1–C1' and the C2–N4 bonds in **1-a4** are shorter than those in **1**



**Figure 4** (a) 2D fingerprint plot of **1-a4** in the crystal stacking of **5**. (b) Hirshfeld surface for **1-a4**. (c) The individual atomic contact percentage contribution to the Hirshfeld surface.

**Table 1** Selected bond lengths (Å), angles (°) and torsion angles (°) of **1**, **1-b** in  $4 \cdot 2\text{H}_2\text{O}$ , and **1-a4** in **5**

	<b>1</b>	<b>1-b</b> in $4 \cdot 2\text{H}_2\text{O}$	<b>1-a4</b> in <b>5</b>
<b>Bond lengths</b>			
C1–C1'	1.559(4)	1.447(5)	1.443(3)
C1–N1	1.284(3)	1.288(3)	1.288(3)
C2–N2	1.405(3)	1.332(3)	1.335(3)
C1–N3	1.359(3)	1.392(3)	1.388(3)
C2–N3	1.405(3)	1.367(3)	1.365(3)
C2–N4	1.459(3)	1.299(3)	1.301(3)
N1–N2	1.527(3)	1.378(3)	1.378(3)
N3–N5	1.384(2)	1.370(3)	1.368(3)
N5–N6	1.235(2)	1.427(3)	1.417(3)
<b>Bond angles</b>			
N6–N5–N3	101.72(16)	113.66(19)	112.94(17)
<b>Torsion angles</b>			
N3–C1–C1'–N3'	180.00	180.00	179.50
N1–N2–C2–N4	178.60	178.65	178.60



and similar to those in **1-b**. The observed bond lengths of N3–N5 and N5–N6 in the three compounds are between the values of a N–N single bond and a N=N double bond

due to electron delocalization in the triazole ring. The N3–C1–C1'–N3 and N1–N2–C2–N4 torsion angles are nearly 180°, which means both ring systems and the amino groups are located in plane. The two nitramino groups are tilted out of the plane by 78° (**1**), 66° (**1-b**), and 67° (**1-a4**), respectively.

The physicochemical energetic properties for **1**, **4**, **5** and standard energetic properties for comparison are reported in **Table 2**. The thermal stability (onset temperature) of **4** and **5** were evaluated by thermal gravimetric analysis (TGA, see Fig. S5). **4** has good thermal stability with an onset decomposition temperature ( $T_{\text{dec}}$ ) of 220.4°C, which is comparable to that of the reported potassium based primary explosives, such as potassium 4,4'-bis(dinitromethyl)-3,3'-azofurazanate (229°C) [34] and potassium 4,5-bis(dinitromethyl)furoxanate (218°C) [35], and slightly lower than that of the dilithium 3,3'-diamino-4,4'-dinitramino-5,5'-bi-1,2,4-triazolate trihydrate (240°C) [29]. The weight loss (4.3%) at 108.3°C for protonated compound **5** was related to dehydration; however it was found to be more thermally stable ( $T_{\text{dec}} = 262.2^\circ\text{C}$ ) than deprotonated product **4**, while they have better thermal stabilities than RDX (1,3,5-trinitro-1,3,5-triazacyclohexane, 204°C).

Experimental densities measured at 25°C show that the protonated compound **5** has a higher density ( $1.84 \text{ g cm}^{-3}$ ) than RDX and **1**. The density of **4** is  $1.98 \text{ g cm}^{-3}$  and it is equal to that of the potassium based 3D MOF, potassium 4-(5-amino-3-nitro-1*H*-1,2,4-triazol-1-yl)-3,5-dinitropyrazole [36].

**Table 2** Physiochemical properties and energetic performances of **1**, **4**, **5**, and comparison with traditional energetic materials

	<b>1</b> <sup>a</sup>	<b>4</b>	Pb(N <sub>3</sub> ) <sub>2</sub>	<b>5</b>	RDX
$\rho^b$ (g cm <sup>-3</sup> )	1.76/1.78	1.98	4.8	1.84/1.88	1.8
$T_{\text{dec}}^c$ (°C)	259	220.4	315	262.2	204
OB <sup>d</sup> (%)	-16.8	-13.2	-11.0	7.4	0.0
N <sup>e</sup> (%)	58.73	46.38	28.9	45.58	37.84
N+O <sup>f</sup> (%)	81.10	64.05	28.9	86.49	81.05
$\Delta H_f^g$ (kJ mol <sup>-1</sup> )	691.9	531.6	450.1	70.9	70.3
$T_{\text{det}}^h$ (K)	3,771	3,451	3,353	3,747	3,810
$D^i$ (m s <sup>-1</sup> )	8,846	7,827	5,877	9,076	8,795
$P^j$ (GPa)	31.2	25.8	33.4	35.7	34.9
IS <sup>k</sup> (J)	9	4	2.5–4	8	7.5
FS <sup>l</sup> (N)	120	40	0.1–1	200	120

a) Ref. [28]. b) Density measured by a gas pycnometer at 25°C. Values after slashes were crystal densities. c) Decomposition temperature from TGA (5°C min<sup>-1</sup>). d) Oxygen balance (based on CO). e) Nitrogen content. f) Nitrogen and oxygen content. g) Calculated heat of formation in solid state. h) Detonation temperature. i) Calculated detonation velocity. j) Calculated detonation pressure. k) Impact sensitivity. l) Friction sensitivity.

The heats of formation of **4** and **5** were calculated by using the Gaussian 09 suite of programs [37] (see the Supplementary information). Using the densities and calculated heats of formation, the energetic properties of **4** and **5** were calculated using Explo5 program [38]. **4** was predicted to have a detonation velocity ( $D$ ) of 7,872 m s<sup>-1</sup> and detonation pressure ( $P$ ) of 25.8 GPa which are superior to those of the traditional primary explosives Pb(N<sub>3</sub>)<sub>2</sub> ( $D = 5,877$  m s<sup>-1</sup>,  $P = 33.4$  GPa). And the detonation temperature of **4** (3,451 K) is comparable to that of the Pb(N<sub>3</sub>)<sub>2</sub> (3,353 K). The  $D$  of **5** is 9,076 m s<sup>-1</sup>, which is slightly lower than that of HMX (1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane, 9,221 m s<sup>-1</sup>).

The impact and friction sensitivities of **4** and **5** were determined using a standard BAM fall hammer and a BAM friction tester, respectively [39]. **5** has an acceptable impact sensitivity (IS) of 8 J and friction sensitivity (FS) of 200 N compared to those of RDX and HMX (IS = 7.4 J, FS = 120 N). However, it exists as the monohydrate which would lower its measured sensitivities. **4** exhibits sensitivity to external stimuli with an IS of 4 J and FS of 40 N.

In summary, the exciting discovery of the first isolated cationic 5,5'-diamino-4,4'-dinitramino-3,3'-bi-1,2,4-triazole salt (**5**) that has been synthesized and fully characterized by single-crystal X-ray analysis. **5** is a secondary explosive with high decomposition temperature (262.2°C), enhanced detonation parameters in comparison to those of RDX, and lower sensitivity to HMX. Coordination of the anionic 5,5'-diamino-4,4'-dinitramino-3,3'-bi-1,2,4-triazole yielded the primary explosive **4**, the higher performance and larger nitrogen and oxygen content of which relative to Pb(N<sub>3</sub>)<sub>2</sub> make this

compound a competitive candidate as a green primary explosive. The deprotonated and protonated approach resulted in two new compounds which not only fall into different classes of explosives but also show improved or comparable properties to those of the standard compounds.

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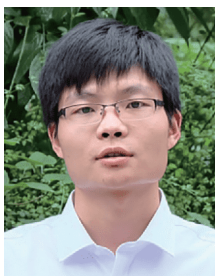
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**Author contributions** Xu Y and Lu M designed and engineered the experiments; Xu Y performed the experiments, analyzed the data and wrote the paper with support from Wang P, Lin Q, and Du Y. Du Y contributed to the Explo5 calculation. All authors contributed to the general discussion.

**Conflict of interest** The authors declare that they have no conflict of interest.

**Supplementary information** Experimental details and supporting data are available in the online version of the paper.



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## 基于一个新两性化合物的阳离子和阴离子含能材料

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**摘要** 本文报道了5,5'-二氨基-4,4'-二硝氨基-3,3'-双-1,2,4-三唑(**1**)的第一种阳离子形式及其合成和表征. 化合物**1**与硝酸反应生成了**5**, 与RDX相比, 这是一种具有更高的分解温度和更好爆轰性能的炸药, 与HMX相比其敏感度更低. **1**的阴离子作为配体和钾离子的自组装合成了起爆药**4**, 与目前广泛使用的 $\text{Pb}(\text{N}_3)_2$ 相比较, 它的性能更加优异. 两性化合物**1**的两个衍生物分离具有重要意义: (1) 说明了化合物**1**的两性性质; (2) 开启了它们作为有前景的含能前体的研究, 为更多含能离子盐的合成提供参考.